

Durham E-Theses

The effect of substrate temperature on the structure and properties of vacuum deposited films

Geoffrey Owen

How to cite:

Owen, Geoffrey (1982) The effect of substrate temperature on the structure and properties of vacuum deposited films. Doctoral thesis, Durham University.

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a <https://etheses.durham.ac.uk/id/eprint/7510/> is made to the metadata record in Durham E-Theses
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full Durham E-Theses policy](#) for further details.

THE EFFECT OF SUBSTRATE TEMPERATURE ON
THE STRUCTURE AND PROPERTIES OF VACUUM
DEPOSITED FILMS

by

Geoffrey Owen

Thesis presented in application for the degree of
Doctor of Philosophy to the University of Durham,
Department of Applied Physics and Electronics

The copyright of this thesis rests with the author.
No quotation from it should be published without
his prior written consent and information derived
from it should be acknowledged.



ABSTRACT

A study of vacuum deposited films of the charge transfer complex (TTF)(TCNQ) and several polycyclic aromatic hydrocarbons is described. Fluorescence techniques have been used to investigate the annealing behaviour of low temperature deposits of anthracene, pyrene, perylene and tetracene, in order to establish the cause of the structural optimum, or singularity which is known to occur when films of some of these materials are deposited onto substrates maintained at one third their normal boiling points ($0.33 T_B$). Evidence is presented for the formation of a metastable state in the vicinity of $0.33 T_B$ in the case of anthracene, pyrene and perylene.

A detailed study of the topography of (TTF)(TCNQ) films has revealed a pronounced structural singularity at a deposition temperature of 213K which was accompanied by an apparent reduction in the activation energy for conduction. However, it was shown that this apparent optimisation of electrical properties was associated with crystallite orientation effects rather than a reduction in the influence of grain boundaries.

In-situ infrared absorption spectroscopy has confirmed that films of (TTF)(TCNQ), either deposited at, or annealed to 213K adopt a neutral lattice structure with no evidence of charge transfer between donors and acceptors. Annealing experiments have established that this neutral lattice possesses short range order and has a metastable, glass-like, structure. Furthermore, conclusive evidence is presented for the formation of a disordered phase of (TTF)(TCNQ) below $0.33 T_B$ which exhibits anomalous infrared activity of the totally symmetric vibrational modes of both (TTF) and (TCNQ). This observation is considered to be analogous to the formation of excimers in disordered films of the aromatic hydrocarbons, prepared below $0.33 T_B$. On the

basis of this evidence a model is discussed in which the observation of an optimum substrate temperature effect in evaporated films of molecular solids is attributed to the formation of a dense metastable state which has a thermodynamic stability intermediate between the crystalline and disordered state of materials.

TO

ANN, MARK AND SUZANNE

ACKNOWLEDGEMENTS

I wish to extend my sincere thanks to my Academic Supervisor, Gareth Roberts, and his Staff and Students, for the time and effort they have devoted, and the advice and encouragement he, in particular, has given during the course of the project. I also wish to thank my Employers, Imperial Chemical Industries PLC, who have provided financial support and the necessary facilities for carrying out the work described within. I owe a special debt of gratitude to my Industrial Supervisor, Bill Barlow, for his constant support and interest, and acknowledge that without his help and encouragement this project could not have been undertaken.

The work was, for the most part, carried out at ICI Corporate Laboratory, at Runcorn, and I wish to extend my appreciation to Ann Sibbett and Bob Murray (Electron Microscopy), Bernard Cook (Infrared), Geoff Booth (X-Ray Diffraction) and to other members of the Structural Chemistry Group, who have contributed significantly to its success. I thank Hugo Steven and his staff for their help in the synthesis of (TTF)(TCNQ) and other members of the Physical Sciences Group with whom I have been associated throughout this period for their help and cooperation. In particular, I thank Colin Hawkes, Dai Williams, Debbie Lloyd, Nigel Perry, Ian Gibb, David Roughley and Graham Merrington for their practical help and advice. Finally, I wish to make special mention of Christine Steven, both for her help and support and for typing the manuscript, and my wife Ann for her patience and constant encouragement during the time it has taken to produce this thesis.

CONTENTS

CHAPTER 1Page No

1.1	The Optimum Substrate Temperature Effect in Vacuum Deposited Films	4
1.2	Nucleation of Vacuum Deposited Films	11
1.2.1	Films deposited at low substrate temperatures	13
1.2.2	Film growth at higher substrate temperatures	14

CHAPTER 2

2.1	Vacuum Deposition - Equipment and Techniques	23
2.1.1	The Birvac evaporator	23
2.1.2	Low temperature substrate holders	26
2.1.3	Water condensation in vacuo at low temperatures	31
2.1.4	The electron beam reactive evaporator	35
2.1.5	Film thickness measurement	39
2.2	Electrical Conductivity Measurements	43
2.2.1	Resistance measuring circuit for TTFTCNQ films	43
2.2.2	Electrical measurements on discontinuous metal films	47
2.3	Spectroscopic Studies of Organic Thin Film Deposits	50
2.3.1	Film deposition onto low temperature substrates	50
2.3.2	The vibrational spectra of TTFTCNQ films	52
2.3.3	Determination of the fluorescence spectra of aromatic hydrocarbon films	53
2.3.4	The ultra violet/visible absorption spectrophotometer	54
2.4	Structural Analysis Techniques	55
2.4.1	Scanning electron microscopy	55
2.4.2	Transmission electron microscopy	56

CHAPTER 3

3.1	Introduction	59
3.1.1	Structure and properties of polycyclic aromatic compounds	60
3.1.2	Fluorescence spectra of polycyclic aromatic compounds ⁽⁷⁾	61
3.1.3	Previous studies of the electronic spectra of thin films of (PCA) compounds	63
	(i) The use of fluorescence to study disorder in films deposited at low temperatures	63
	(ii) The effects of annealing	67
	(iii) Absorption studies of PCA films	68
3.2	Result of the Fluorescence Study of (PCA) Compounds	69
3.2.1	Films of Anthracene	69
3.2.2	Films of Pyrene	71
3.2.3	Films of Perylene	73
3.2.4	Films of Tetracene	74
3.3	Discussion	75
3.3.1	The OST effect in films of polycyclic aromatic compounds	75

CHAPTER 4

4.1	Introduction	95
4.1.1	The crystal structure of (TTF) (TCNQ)	95
4.1.2	Periodic bond chain theory	97
4.1.3	Parameters which influence the topography of films	99
4.1.4	Earlier studies of (TTF) (TCNQ) films	100
4.2	Experimental	107
4.2.1	Film preparation	107
4.2.2	The surface replication technique	108

4.3	Results	109
4.3.1	Film topography using SEM	109
4.3.2	The influence of deposition rate on film topography	110
4.3.3	The influence of substrate temperature upon film topography	111
4.3.4	X-ray diffraction of TTF TCNQ films	118
4.3.5	Electron diffraction of (TTF) (TCNQ) films	119
4.4	Discussion	121
4.4.1	Films deposited below 240K	123
4.4.2	Films deposited at substrate temperatures above 235K	135

CHAPTER 5

5.1	Introduction	149
5.1.1	Band assignments in TTF and TCNQ	151
5.1.2	Vibronic effects	154
5.2	Experimental Results	161
5.2.1	The spectra of films in the as-deposited state	161
5.2.2	Annealing studies	171
5.2.3	Annealing in the high temperature region	174
5.3	Discussion	177
5.3.1	Electronic transitions in TTF TCNQ	178
5.3.2	The origin of anomalous infrared activity in films deposited below 190K	180
5.3.3	The formation of a neutral lattice between 190 and 230K	187
5.3.4	The disorder - SRO transformation in (TTF) (TCNQ) films	193
5.3.5	The SRO $\rightarrow$ crystalline transformation	199

CHAPTER 6

6.1	Introduction	209
6.1.1	Electrical conductivity in (TTF) (TCNQ) single crystals	209
6.1.2	Electrical properties of (TTF) (TCNQ) films	212
6.2	Results of Electrical Resistivity Measurements on (TTF) (TCNQ) Films	216
6.2.1	Annealing behaviour	218
6.2.2	Tempering experiments	219
6.2.3	Stepwise annealing	221
6.2.4	Determination of the activation energy of the annealing process	223
6.2.5	The temperature dependence of the resistivity of annealed films	227
6.3	Discussion	232
6.3.1	The annealing behaviour of films	232
6.3.2	The electrical properties of annealed samples	252

CHAPTER 7

7.1	The Optimum Substrate Temperature Effect and the Formation of a Metastable State	275
7.2	Future Work	280
7.2.1	Introduction	280
7.2.2	The preparation of films for TEM and electrical conductivity measurements	282
7.2.3	TEM of discontinuous metal films	283
7.2.4	Electrical conductivity measurement on discontinuous metal films	284
7.2.5	Discussion of the results obtained from the study of discontinuous metal films	285

APPENDIX 1

APPENDIX 2

APPENDIX 3

CHAPTER 1

INTRODUCTION

Vacuum evaporation and related techniques, such as sputtering⁽¹⁾ and chemical vapour deposition⁽²⁾ are used extensively both by Industry and Academia for the preparation of supported thin films and surface coatings. They make an important contribution to many areas of material research and technology and have applications ranging from the preparation of new materials⁽³⁾, dispersion hardening of metals⁽⁴⁾, coating of machine tools and turbine parts⁽⁵⁾, decorative coating⁽⁶⁾, solar control film⁽⁷⁾, and so on. The list is already long and over the last ten years has grown steadily, so that vacuum deposition techniques now form the basis of a large and rapidly expanding industry.

The main advantages of vacuum deposition as compared to other methods of preparing thin films are that they are able to provide a high purity product with reproducible properties, and equally important in the case of solid state electronics applications, are fully compatible with modern methods of producing solid state devices and microelectronic circuits. However, like all thin film techniques they suffer from one important disadvantage which often precludes their use in certain applications, for example, the preparation of primary semiconductor substrates for microprocessors. Because of the nature of the growth process, films prepared by vacuum deposition are polycrystalline and consist of small crystallites, separated by grain boundary regions within which the normal lattice of the crystalline phase is disrupted. Consequently, in most respects the properties of evaporated films are inferior to those of bulk single crystals. Electrical properties, for example, which involve charge carrier transport between grains are strongly influenced by film topography, often to the point where carrier scattering at grain



boundaries dominates the conduction process⁽⁸⁾ and reduces electrical conductivity by orders of magnitude compared to that of bulk single crystals. Much of the technology of thin film growth, particularly in the area of solid state electronics is, therefore, devoted to minimising grain boundary effects so as to achieve levels of performance approaching that of bulk material.

A procedure often employed for growing high quality films involves epitaxial growth under conditions of low supersaturation, approaching thermodynamic equilibrium. The method of Hot Wall Epitaxy⁽⁹⁾ has been used, for example, to grow films of PbTe which have carrier mobilities as high as good quality single crystals. Such techniques are, however, only suitable for coating areas of a few cm². A more practical approach must be adopted in depositing film for applications involving the use of large area supports, such as photovoltaic cells for solar energy conversion⁽¹⁰⁾, or electroluminescent panels⁽¹¹⁾ for illumination purposes. For applications such as these, grain boundary scattering of carriers plays a crucial role in reducing the overall efficiency of vacuum deposited thin film devices, and in preventing them competing successfully with more conventional technology. In order to achieve adequate processing rates for large area applications it is usually necessary to work at higher supersaturations, at the expense of film quality, but to carry out a process of optimisation which involves changing experimental parameters in a systematic way. The two most important parameters for a single component material are the effective pressure of the evaporant, or deposition rate, and in particular the temperature of the substrate onto which a film is grown. Clearly a process of optimisation covering a wide range of deposition rates and substrate temperatures is both time consuming and costly, and one that could be telescoped if a

microscopic theory of film growth were available to enable the influence of both parameters on film topography and properties to be quantitatively predicted.

In the absence of a quantitative microscopic theory a number of so called empirical rules have been established which relate film topography to certain physical properties such as melting point (T_m). Perhaps the best known of these empirical structure/property relationships, is that developed by Movchan and Demchishin⁽¹²⁾ which for thick films of metals and oxides predicts the existence of three zones as a function of reduced temperature T_s/T_m where T_s is the substrate temperature during growth and T_m the melting point of the substance. Each of these zones has its own characteristic structure and physical properties, ranging from tapered crystals with domed tops separated by void boundaries at $T_s/T_m < 0.3$, to columnar grains with dense well defined boundaries between ($0.3 < T_s/T_m < 0.5$) and equiaxed grains for $T_s/T_m > 0.5$. The Movchan-Demchishin model is based upon a considerable body of work carried out in Russia over twenty years prior to 1974. It has been reviewed in a recent paper by Thorton⁽¹³⁾.

A more recent study has established the existence of an empirical relationship between substrate temperature and the normal boiling point (T_B) of a material. Thus, Vincett, Barlow and Roberts (VBR), in a series of papers⁽¹⁴⁻¹⁶⁾, have shown that when a range of materials are deposited under vacuum onto a surface maintained at a temperature equal to one third of their normal boiling point ($0.33 T_B$), certain properties are optimised. Furthermore, this optimum coincides with a structural singularity which manifests itself as a minimum in surface roughness. T_s is perhaps the most critical and easily

controllable parameter responsible for determining the structure and properties of vacuum deposited films, and because this observation enables the optimum substrate temperature for growth to be accurately located with reference to an easily measurable microscopic property of materials, it is clearly of importance, both scientifically and technically, to establish the cause of the effect. This is the main objective of the present study.

(VBR) have proposed that the optimum substrate temperature (OST) effect is associated with re-evaporation from disordered regions of condensed films. Because of its obvious relevance to the present work their proposal will now be considered in more detail.

1.1 The Optimum Substrate Temperature Effect in Vacuum Deposited Films

(VBR)⁽¹⁶⁾ were able to identify sharply optimised properties in films of a number of materials deposited in a narrow range at 0.33 of their respective boiling points. Films of anthracene, for example, exhibited a pronounced minimum in surface roughness at the OST. Their list of materials and the corresponding optimised property of each are reproduced in Table (1.1). Remarkably, the OST effect applies to materials with very different properties, from organic hydrocarbons such as anthracene and pyrene, which crystallise with molecular lattices, to materials with ionic lattices such as ZnO and CdS. Furthermore, the former retain their molecular identity on evaporation whereas the latter dissociate in the vapour phase and must, therefore, recombine on the substrate after impingement. On the basis of these and other observations, for example, the insensitivity of the OST to deposition rate, VBR concluded that surface diffusion of adsorbed species was not responsible for the OST effect, but that

Table 1.1^a Summary of the OST effect for a variety of vacuum-deposited materials
 T_{OST} is the substrate temperature at which the property listed in column 2 was optimised.
The OST is expressed as a fraction of the normal boiling point T_B in column 4

Material	Optimised Property	Optimum Temperature T_{OST} (K)	$(T_{OST}/T_B)^b_{corrected}$
Phthalocyanine	Smoothness	285	0.33
Anthracene	Smoothness	213	0.35
Pyrene	Smoothness	187	0.31
Se	Electrophotographic performance, homogeneity	335	0.32
ZnO	Smoothness, light scattering	768-793	?
ZnSe	Epitaxial order	566	0.31
ZnTe	Electrical Conductivity optical absorption	643	0.33
CdS	Photovoltaic effect ultrasonic generation	473	0.30
CdTe	Photo-emf	540	0.34
PbS	Charge mobility	495	0.32
PbTe	Charge mobility	496	0.31
SnTe	Charge mobility	518	0.32
PbSe	Charge mobility	553	0.34

(a) See reference (16) for full details, including references to the original papers

(b) Corrected for deposition rate according to the VBR theory

re-evaporation probably was.

An examination of Table (1.1) reveals that all of the properties which are optimised are likely to be structure sensitive and should therefore be strongly influenced by the grain boundary distribution within condensed films. Because the extrapolated vapour pressure data of the crystalline phase of materials at their respective OST's, are many orders of magnitude below the effective pressure exerted by the incoming evaporant flux, (VBR) concluded that re-evaporation takes place from disordered or 'liquid-like' regions of condensed films. The location of the OST is then the point at which the effective vapour pressure of the incoming flux is equal to the vapour pressure exerted by this 'liquid-like' phase.

(VBR) estimated the vapour pressure of this liquid-like phase from the Clausius-Clapeyron ⁽¹⁷⁾ equation (1.1)

$$\log_{10} \frac{P_B}{P_{OST}} = \frac{-\Delta H_{v/l}}{2.3RT_B} \left(\frac{T_B}{T_{OST}} - 1 \right) \quad (1.1)$$

Where P_B is the vapour pressure (1 N.M^{-2} ; 760 torr) at T_B and P_{OST} that at the OST ($0.33 T_B$). $\Delta H_{v/l}$ is the molar latent heat accompanying the liquid/vapour phase change. If $\Delta H_{v/l}$ is assumed to remain constant, then invoking Trouton's Rule ⁽¹⁸⁾ ($\frac{\Delta H_{v/l}}{T_B}$ a constant $\sim 88 \text{ kJ mole}^{-1}$) and putting $T_{OST} = \frac{1}{3} T_B$, the vapour pressure at the OST is estimated to be about 10^{-9} N.M^{-2} ($\sim 10^{-5} \text{ Torr}$).

Assuming ideal gas behaviour, the effective pressure (P_{eff}) of the impinging flux can be calculated from the Hertz-Knudsen ⁽¹⁹⁾ equation (1.2)

$$R = 3.5 \times 10^{22} (\text{MT}_s)^{-\frac{1}{2}} P_{eff} \text{ cm}^{-2} \text{ sec}^{-1} \quad (1.2)$$

For typical impingement rates of between $10^{14} - 10^{15} \text{ molecules cm}^2 \cdot \text{sec}^{-1}$,

a (P_{eff}) for anthracene ($M = 178$; $T_{\text{source}} = 400\text{K}$) of $10^{-6} - 10^{-5}$ Torr is estimated. (VBR) noted that for the materials listed in Table 1 the rates of deposition used corresponded to effective pressures of between 5×10^{-7} Torr and 5×10^{-4} Torr, which would cause T_{OST} to vary between $0.33 T_B$ and $0.4 T_B$, respectively and does, of course, explain the weak dependence of the OST on deposition rate.

These estimates serve to emphasise the point that at the OST the rate of re-evaporation from a disordered phase, which is assumed to have the same thermodynamic properties as the liquid phase, is of the same order as the rates of deposition typically used to prepare films by vacuum evaporation. In other words films deposited at the OST are grown under quasi-equilibrium conditions. However, a substrate temperature of $0.33 T_B$ will, in general, be much lower than the melting point of a material so that the OST falls in a region of the phase diagram where the solid is thermodynamically the most stable state. Thus, in order to explain the OST effect, VBR proposed that during deposition small disordered regions form within the film when a number of molecules become trapped in non-crystalline configurations, for times at least as long as the time taken to deposit a monolayer. They considered that this disordered material might be concentrated in grain boundary regions between crystallites and should interfere with the proper growth of crystals within the film. Since this would result in a decrease in the perfection and size of crystallites and an increase in the concentration of disordered material it clearly would have an effect on those properties, such as carrier mobility, which are markedly effected by scattering centres within a film.

VBR envisaged that the optimum substrate temperature, in non-dissociable compounds, is that at which a balance between molecular diffusion, which is necessary to promote crystal growth, and re-evaporation from disordered regions, is established so that material in the disordered regions can just crystallise. They postulated that an increase in free volume occurred within disordered regions near the OST, which enabled sufficient diffusion to allow crystallisation and was, therefore, responsible for the abrupt improvement in film properties observed at the OST. Vincett⁽²⁰⁾ has since shown that Trouton's Rule can be generalised to include materials which evaporate associatively or dissociatively, so that the above proposals should also apply to this class of materials.

Amorphous Condensates

If (VBR's) proposals are correct then the formation of amorphous condensates on substrates cooled below $0.33 T_g$ should be a general phenomena, at least for those materials which are known to undergo a transition to give the glassy⁽²¹⁾ state. In fact, because of the high cooling rates⁽²²⁾ achieved during vacuum deposition onto cooled substrates, this method has been used to prepare a very wide range of materials in the amorphous state. However, there have been very few systematic attempts to examine the effect of substrate temperature during deposition upon the 'amorphicity' of films produced in this way. Gutzow and Avramov⁽²³⁾ have derived a mechanism for the formation of amorphous condensates from the vapour phase and were able to show that amorphous state is produced by condensation onto substrates below the glass transition temperature T_g . They identified the conditions for direct formation of the amorphous phase as being related to the

melting point T_m , such that $T_g = \frac{2}{3} T_m$. In support of this mechanism they were able subsequently⁽²⁴⁾ to show that glassy thymol is produced at condensation temperatures lower than -65°C ($\sim \frac{2}{3} T_m$). However, Haida et.al.⁽²⁵⁾, have shown that for chloroform condensed from the vapour phase at 20K, $T_g/T_m = 0.4$, which is outside the range ($\frac{1}{2} - \frac{2}{3}$) normally observed for glasses prepared by rapid cooling of liquids. They found⁽²⁶⁾ that a better correlation exists between T_g and normal boiling point T_b . With few exceptions they were able to show that T_g/T_b had a value between ($\frac{1}{4} - \frac{1}{3}$) T_b for a range of organic compounds including methanol, methylene chloride and cyclohexene. Turnbull and Cohen⁽²⁷⁾ have also pointed out that a good correlation exists between T_g and T_b in agreement with the result of Haida et.al.⁽²⁶⁾.

A number of studies⁽²⁷⁻²⁹⁾ have shown that amorphous condensates are produced when water is deposited onto low temperature substrates. The temperature at which crystallisation of these amorphous condensates began was found to be dependent upon the temperature of the substrate and varied between 113K⁽²⁷⁾ and 153K⁽²⁸⁾ ($0.3 - 0.41 T_b$). Condensation temperatures of 50K⁽²⁹⁾, or lower, were needed to ensure that the film produced was entirely amorphous. Koverda⁽³⁰⁾ et.al. have determined the effect of condensation temperature upon the rate of crystallisation of amorphous films of; water, dichloroethane and chloroform, prepared by vapour deposition. From this work they conclude that the concentration of crystalline nuclei decreases with decreasing condensation temperature and that on annealing these act as ready-made centres for crystallisation. At the lowest condensation temperature (80K) films did not crystallise significantly until they were annealed to 165K, when the number of nuclei increased by a factor of 10^4 in less than one degree. This phenomena is referred

to as 'shock' crystallisation⁽³⁰⁾ and is discussed in more detail in Chapter 6.

Similar behaviour has been reported for amorphous films of other materials such as germanium⁽³¹⁾ and its alloys⁽³²⁾, selenium⁽³³⁾, antimony⁽³⁴⁾, SnTe⁽³⁵⁾, Cd₃As₂⁽³⁶⁾ and InSb⁽³⁷⁾. In each of these materials electrical conductivity has been used to monitor the annealing process. On annealing above some critical transition temperature they all exhibited a large irreversible decrease in resistance. Although in certain cases e.g. germanium and SnTe, the resistance decrease was associated with the onset of crystallisation, in others, such as Cd₃As₂ and InSb, crystallisation did not occur until higher temperatures. In the case of selenium films the decrease in resistance was accompanied by continuous growth of trigonal crystallites. DTA experiments⁽³⁸⁾ on selenium show that in addition to an endothermic change in the vicinity of T_g (320 - 330K) a second exothermic anomaly also occurs between 390K and 420K, depending upon annealing rate, which may also be associated with crystallisation. Haida also reported an endothermic anomaly followed by an exothermic peak which they ascribed to a glass transition and crystallisation respectively.

Zdanowicz⁽³⁹⁾ et.al. have proposed that the mechanism of crystallisation of amorphous Cd₃As₂ films involves two steps; the first gives a metastable state which is then able to crystallise at higher temperatures. A similar mechanism has been proposed by Burton and Ray for Pd-Si alloys⁽⁴⁰⁾. Moreover, VBR⁽¹⁵⁾⁽¹⁶⁾ have shown, with the aid of electroabsorbance measurement on anthracene films, that films deposited below the OST contain a significant proportion of disordered material even after annealing to room temperature, while those

deposited above the OST do not. Since Perkampus et.al.⁽⁴¹⁾ have also shown that disordered films of anthracene deposited at 77K undergo a transition in the vicinity of 200K ($T_{opt} \sim 213K$), it is possible that a two step mechanism of crystallisation is of general applicability. The absence of an endothermic glass transition anomaly in amorphous films of materials like germanium and antimony may be due to continuous crystallisation on nuclei which are precipitated during film growth, or as proposed by Haida et.al. for some organic glasses to their small configurational heat capacities⁽²⁶⁾.

It would appear that other work on amorphous or glassy condensates prepared by vapour deposition, supports the main hypothesis of VBR that the OST effect is associated with the formation of the disordered phase. However, it also raises questions about the nature of this disordered phase and suggests rather than being a disordered amorphous phase, it may in fact be a metastable state with glass-like properties; unlike a disordered phase which is thermodynamically unstable, a glass is a solid in internal equilibrium, in which there exists a definite set of equilibrium positions and about which each molecule or atom oscillates, but it lacks the translational symmetry of the solid state. It is a reasonable assumption that in many of its properties this metastable state would behave like a liquid. In fact, it has been suggested⁽⁴²⁾ that a glass and its supercooled liquid could form a single, metastable thermodynamic phase that is in local equilibrium. Thus, the formation of a metastable glassy state with liquid-like properties could provide a natural explanation for the relationship between the OST effect and T_B .

The work of Koverda et.al.⁽³⁰⁾ and others provides a strong indication that in order to obtain the disorder phase of a material free of

incipient nuclei of the crystalline phase, it is necessary to deposit films at substrate temperatures much lower than T_g . If, as suggested, T_g and the OST are identical, any study of the OST effect must, therefore, take growth of the crystalline phase, both during deposition and subsequent annealing, into consideration. VBR, moreover, proposed that films deposited at the OST are comprised of crystalline nuclei separated by small disordered regions. An adequate description of the formation of the growth of crystallites from the vapour phase must, therefore, be incorporated into an explanation of the OST effect. A semi-quantitative description of film growth is contained within the Theory of Nucleation. Since this forms the basis of much of the work described in the main body of the thesis, a brief account of heterogeneous nucleation on surfaces will now be given.

1.2 Nucleation of Vacuum Deposited Films

The various unit processes involved in the growth of films from the vapour phase are represented schematically in Figure (1.1). The first stage in the growth process involves adsorption of molecules onto a surface and these then diffuse together to form nuclei of the condensed phase. This formative or 'nucleation' stage has a major influence upon topography and the properties of vacuum deposited films because it determines both the number density and size of crystallites and, therefore, ultimately controls the grain boundary distribution within condensates. Where the formation of more than one phase is thermodynamically possible their respective rates of nucleation also determine the relative proportion of each phase within the condensate.

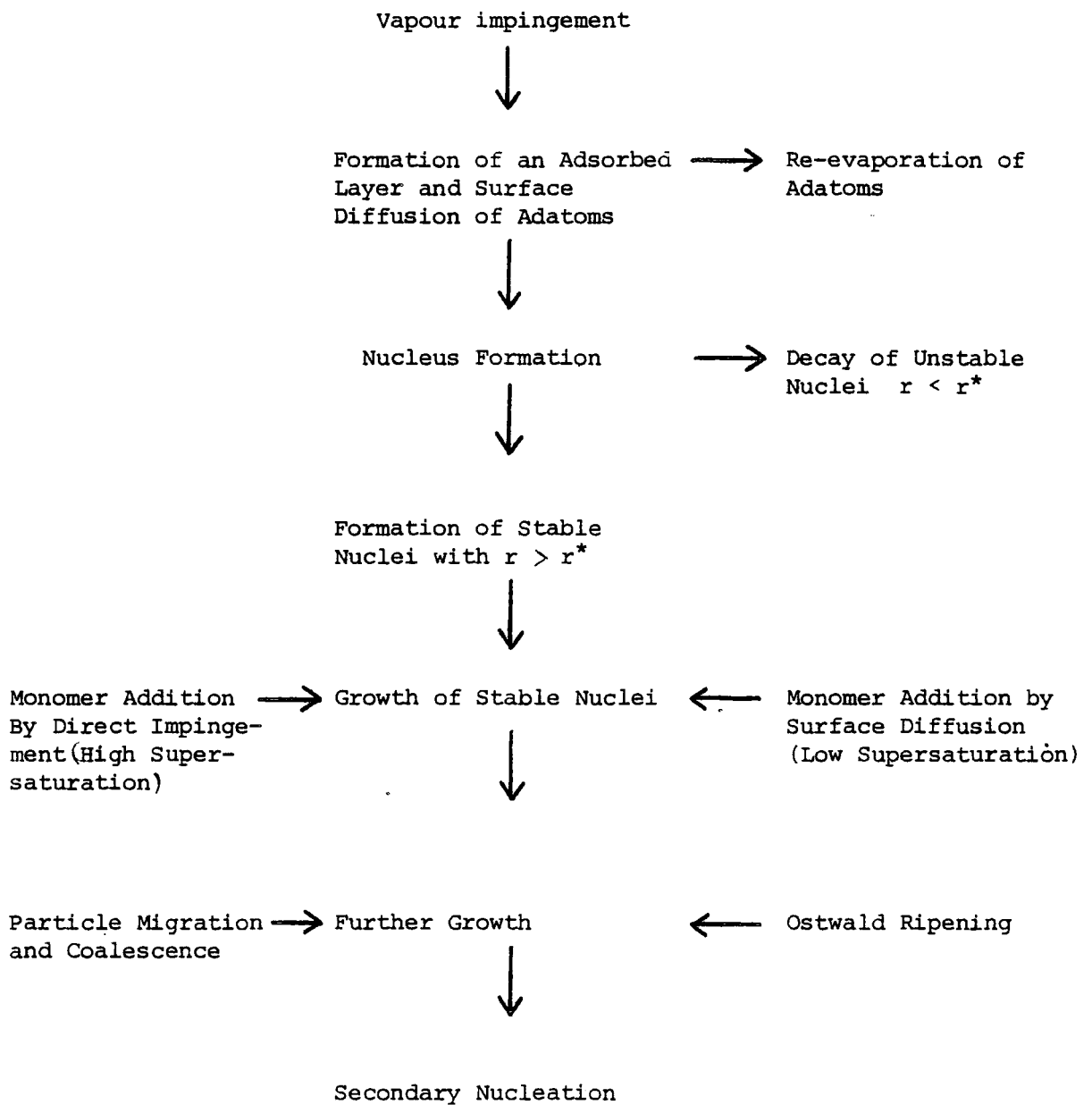


Figure 1.1 The various unit processes involved in heterogeneous nucleation and growth of films from the vapour phase

Theoretical models of heterogeneous nucleation and thin film growth have been reviewed on numerous occasions. An excellent bibliography of the subject is provided by Neugebauer⁽⁴³⁾ in The Handbook of Thin Film Technology and the interested reader is referred to this article for further information and references. Both the Classical⁽⁴⁴⁾ and the Atomistic⁽⁴⁵⁾ models of nucleation make use of the concept of a nucleus of critical size r^* , above which a particle is stable and is able to grow, and below which it is unstable and dissociates. The idea of a critical nucleus arises because, as shown in Figure (1.2), the free energy of formation ΔG goes through a maximum (ΔG^*) for a nucleus of size r^* . This corresponds to a minimum in aggregate stability and for a spherical nucleus,

$$\Delta G^* = \frac{4}{3} \pi r^{*3} \sigma \quad (1.3)$$

where σ is the surface energy of the critical nucleus.

If a metastable equilibrium is established between adsorbed monomers and aggregates of various sizes, the concentration (n^*) of critical nuclei is, in the Classical model, given by,

$$n^* = n_1 \exp \left(\frac{-\Delta G^*}{kT} \right) \quad (1.4)$$

where n_1 is the concentration of adsorbed monomers. The rate j at which adsorbed monomers are incorporated into the growing nuclei depends on the surface concentration of adsorbed monomers, their jump frequency ν_0 and their jump distance:

$$j = C n_1 \nu_0 \exp \left(\frac{-\Delta G_{sd}}{kT} \right) \quad (1.5)$$

C is a constant which contains the size of the critical nucleus and other geometric factors, and ΔG_{sd} is the activation free energy for

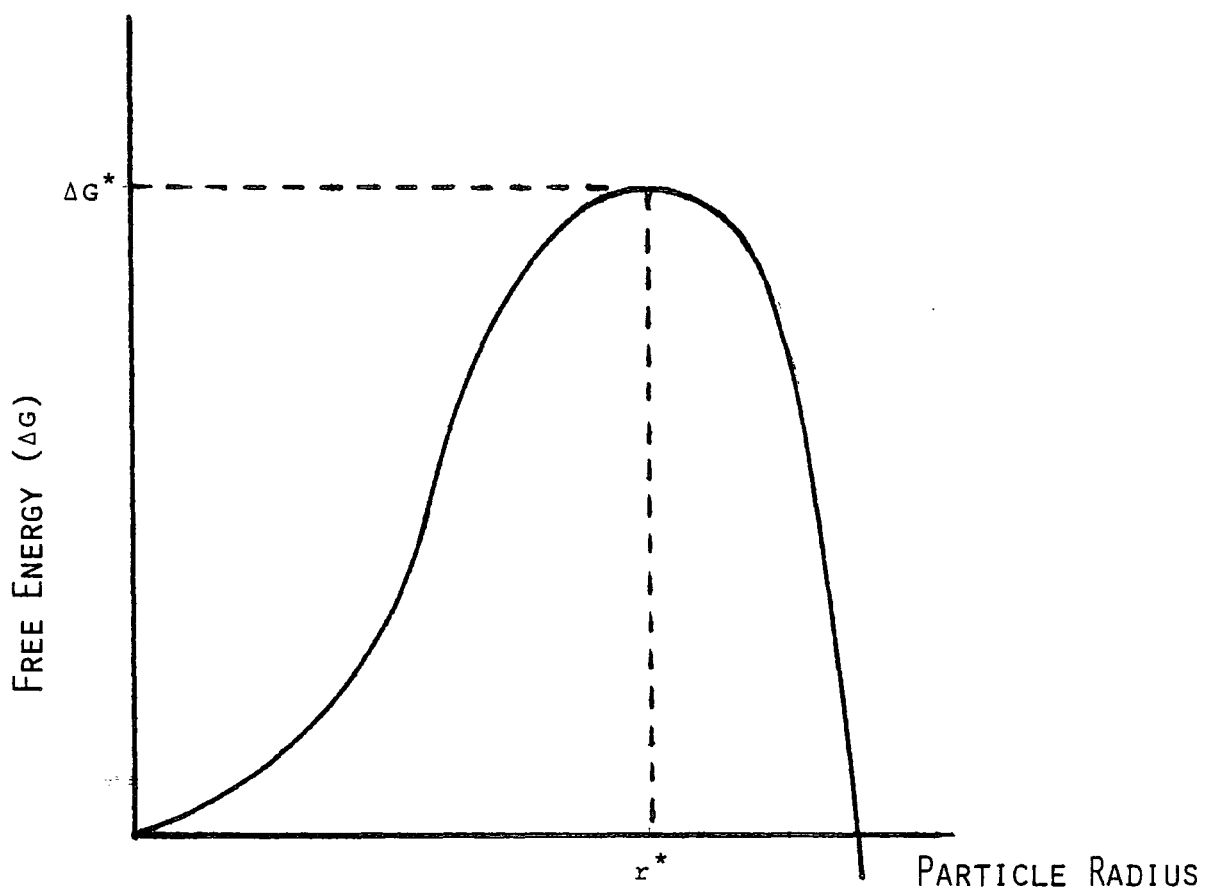


Figure 1.2. The free energy of formation of a particle as a function of radius (r). The stability of the particle is a minimum at a critical radius r^* .

surface diffusion.

The concentration (n) of surface adsorbed monomers is given by

$$n = \tau_a = \frac{R}{v_o} \exp (\Delta G_{des}/kT) \quad (1.6)$$

$$n = R \tau_a \quad (1.6a)$$

ΔG_{des} is the free energy change accompanying the desorption of monomers from the surface, τ_a is the residence time of an adsorbed monomer on the surface and R is given by equation (1.2). Combining equations (1.4) (1.5) and (1.6) gives the frequency of formation of critical nuclei (I^*).

$$I^* = jn^* = CR \exp (\Delta G_{des} - \Delta G_{sd} - \Delta G^*)/kT \quad (1.7)$$

Using the equations given in this section it is possible to make certain qualitative predictions about the influence of substrate temperature upon the topography of vacuum deposited films.

1.2.1 Films deposited at low substrate temperatures

At low substrate temperatures ($\Delta G_{sd} \gg kT$) equation (1.5) predicts that rate of diffusion of adsorbed monomers on the surface will be very much reduced, and according to equation (1.7) this should also decrease the rate of nucleation. Within the atomistic theory of nucleation the critical nucleus may, in fact, be a single atom, at low substrate temperatures or very high supersaturations. Thus, a supercritical nuclei is formed when two atoms (or molecules) form a pair, whose stability is determined by a single bond. This occurs at a substrate temperature given by

$$T_{1-2} = \frac{-E_{sd} + E_2}{k \ln(R/v_1 N_o)} \quad (1.8)$$

where E_{sd} is the activation energy for surface diffusion. E_2 the

dissociation energy of the pair, v_1 the desorption energy of the monomer and N_0 the density of monomer adsorption sites. Below T_{1-2} adsorbed monomers are stable entities and need not be incorporated into nuclei to remain on the substrate. In this event the film will have a disordered structure.

At slightly higher substrate temperatures ($\Delta G_{sd} \sim kT < \Delta G^*$) it is possible for films to contain both disordered material and nuclei of the crystalline phase as proposed by VBR. Now at a constant rate of impingement,

$$\left(\frac{\partial \Delta G^*}{\partial T} \right)_R > 0$$

and from equation (1.7) the rate at which critical nuclei are created will decrease very rapidly with increasing temperature. Therefore, as surface diffusion increases, allowing nucleation to take place, the rate of nucleation will increase to a maximum and then decrease again at ($kT \approx \Delta G^*$). On the basis of VBR's model this would be the region of the OST effect.

1.2.2 Film growth at higher substrate temperatures

If nucleation is assumed then the size of a crystal face in the high temperature (low supersaturation) regime is, according to the theories of Burton, Cabrera and Frank⁽⁴⁶⁾, determined by the rate of advance of steps upon the face. This latter rate is proportional to the mean displacement ($\bar{X}$) of molecules on the face, which is given by the Einstein equation (1.9)

$$\bar{X} = (2 D_{sd} \tau_a)^{1/2} \quad (1.9)$$

$\bar{X}$ is the distance an adsorbed monomer diffuses on the surface of a crystal prior to desorption. The temperature dependence of the

surface diffusion coefficient D_{sd} is given by,

$$D_{sd} = a^2 v_{sd} \exp(-\Delta G_{sd}/kT) \quad (1.10)$$

where a^2 is the jump distance between adsorption sites and v_{sd} is the speed with which adsorbed monomers migrate. τ_a is given by equation (1.6). Combining equations (1.6), (1.9) and (1.10) and putting $v_{sd} = v_o^{(47)}$ gives;

$$(\bar{X}) = 2^{\frac{1}{2}} a \exp \left((\Delta G_{des} - \Delta G_{sd})/2kT \right) \quad (1.11)$$

At high substrate temperatures ($\Delta G_{des} \sim 2kT$) the rate of desorption according to equation (1.6) becomes appreciable, causing a reduction in $(\bar{X})$ and therefore in the average size of crystallites. Surface roughness should also increase at this point. At lower substrate temperatures ($\Delta G_{sd} \sim 2kT$) surface diffusion rate is reduced according to equation (1.5) and both $(\bar{X})$ and crystallite size are again reduced. Thus, equation (1.11) predicts a maximum in crystallite size between $\Delta G_{des} < kT > \Delta G_{sd}$. Furthermore, since a decrease in surface diffusion should also cause increased surface roughness, films deposited at substrate temperatures within the temperature range defined above, might be expected to exhibit a smoothness optimum with large well formed crystallites growing in the plane of the film. However, this structural optimum will definitely occur well within the region of the phase diagram where the crystalline phase is thermodynamically the most stable. It is not associated with the formation of the disordered phase, but could be mistaken for the OST effect if film topography were investigated at only a few substrate temperatures.

On the basis of nucleation and surface diffusion theory structural optima are expected to occur in films deposited at least two substrate temperatures. The predicted high temperature optimum is, according to equation (1.11), caused by a maximum in $(\bar{X})$ and should lead to a reduction in grain boundary effects, but there is no reason, a-priori, why this should be associated with the formation of a disordered phase or, indeed, why it should be related to T_B . On the other hand the low temperature structural optimum predicted at maximum nucleation rate (equation (1.7)), also corresponds to the point at which reduced surface mobility is expected to result in the formation of the disordered phase, and appears to provide the best fit to (VBR's) criteria for the OST effect. However, in this case, it is difficult to understand why those properties which are most influenced by grain boundary scattering, such as carrier mobility, should be optimised at the OST; the effect of scattering would, under normal circumstances, be directly proportional to the number of crystallites per unit surface area, because, as the average crystallite dimension decreases the boundary concentration will automatically increase. In an attempt to resolve this issue, an in-depth study has been carried out of both the topography and electrical conductivity of vacuum deposited films of the charge transfer complex tetrathiafulvalene-tetracyanoquinodimethane (TTF)(TCNQ). The results of this study are described in Chapters 4 and 6 respectively.

The choice of (TTF)(TCNQ) for this study was largely dictated by the pronounced anisotropy which it displays in both its structure and many of its electrical properties. As discussed in the introduction to Chapter 6 it was hoped that this would facilitate an investigation of the structure/property relationship. A full account of the

structure and electrical properties of this unusual material can be found at the beginning of Chapters 4 and 6, respectively.

An alternative explanation for the OST effect and one which is supported by previous work on amorphous condensates, is that it coincides with the glass transition temperature of a material and is, therefore, associated with the formation of a metastable rather than unstable disordered structure. Since neither phase possess long range order, diffraction techniques, with the possible exception of Radial Distribution Function Analysis⁽⁴⁸⁾, are unable to differentiate between these two alternatives. Optical phenomena on the other hand, and in particular those associated with vibronic effects⁽⁴⁹⁾, often provide detailed information about molecular interactions; in favourable circumstances they can be used to make quantitative determinations of molecular interaction potentials⁽⁵⁰⁾. Fluorescence techniques, for example, have been used extensively⁽⁵¹⁾ to monitor changes in the local environment of molecules in the excited state and polycyclic aromatic compounds which are generally intensely fluorescent, are frequently used as probes for this purpose. Since VBR have already established the existence of a structural optima in the case of anthracene and pyrene, fluorescence techniques have been used to investigate the possibility that the OST in these materials is associated with a metastable state. This work is described in Chapter 3, which also contains the results of a study of the other aromatic hydrocarbons, perylene and tetracene. A résumé of previous, related work on the fluorescence properties of vacuum deposited aromatic hydrocarbons is given in the introduction to Chapter 3.

Vibronic effects have also been shown to be important in

charge transfer complexes⁽⁵²⁾ in general and (TTF)(TCNQ)⁽⁵²⁾ in particular. Since charge transfer occurs in the ground state, absorption spectroscopy and more specifically infrared vibrational spectroscopy have been used to study vibronic effects in these materials. Changes in the local environment of molecules which modify the degree of charge transfer are detected by their effect upon the vibrational properties of both the donor and acceptor. Since electron transfer in (TTF)(TCNQ) is known⁽⁵⁴⁾ to be extremely sensitive to molecular interactions, infrared spectroscopy was used to investigate changes in the local structure of films both in the as-deposited state and during the annealing process. The results of this study are described in Chapter 5 which also contains an account of vibronic effects in charge transfer complexes.

A summary of the main conclusions arising out of the work discussed in Chapters 3 to 6, inclusive, is given in Chapter 7. This final Chapter also contains a section devoted to a preliminary study of substrate temperature effects in oxide supported metal films. This section is included to indicate potential applications of the techniques described in the main body of the thesis, to the study of sintering in heterogeneous catalysts.

Vacuum equipment and thin film deposition techniques are described in Chapter 2, which also includes a description of the instrumental techniques used to study the properties of films. Materials preparation and purification are discussed in the Appendix.

References for Chapter 1

1. Wehner, G.K., and Anderson, G.S., in Handbook of Thin Film Technology, Chapter 3, Ed., Maissel, L.I. and Glang, R., Publ., McGraw-Hill 1970.
2. Amick, J.A., Schnable, G.L. and Vossen, J.L., J. Vac. Sci. Technol., 14, 1053 (1977).
3. Polk, D.E., Giessen, B.C. and Gardner, F.S. Mat. Sci. Eng. 23, 309 (1976).
4. Majumder, K.S., Thin Sol. Films, 42, 327 (1977).
5. Buhl, R., Pulker, H.K. and Moll, E., Thin Sol. Films, 80, 265 (1981).
6. Igasaki, Y. and Mitsuhashi, H., Thin Solid Films, 70, 117 (1980).
7. Howson, R.F., Ridge, M.I. and Bishop, C.A., Thin Sol. Films, 80, 137 (1981).
8. Anderson, J.C., Thin Sol. Films, 18, 239 (1973).
9. Lopez-Otero, A., Thin Sol. Films, 49, 3 (1978).
10. Carlson, D.E. and Wronski, C.R., Appl. Phys. Lett., 28, 671 (1976).
11. Theta, R. and Braguier, T., Thin Sol. Films, 80, 143 (1981).
12. Movchan, B.A. and Demchishin, A.V., Phys. Met. Metallogr. 28, 83 (1969).
13. Thornton, J.A., Ann. Rev. Mater. Sci., 7, 239 (1977).
14. Vincett, P.S., Barlow, W.A. and Roberts, G.G., Nature, 255, 542 (1975).
15. Roberts, G.G., Keating, B.S., Vincett, P.S. and Barlow, W.A., J. Phys. C. 11, 3847 (1978).
16. Vincett, P.S., Barlow, W.A. and Roberts, G.G., J. Appl. Phys. 48, 3800 (1977).
17. Glasstone, S., Thermodynamics for Chemists, p.227, Publ. Van Norstrand, 1964.
18. ibid., p.232.
19. Glang, R., in reference 1, Chapter 1.

20. Vincett, P.S., J. Phys. Chem., 82, 2797 (1978).
21. Turnbull, D., Trans., A.I.M.E., 221, 422 (1961).
22. Ewart, S., Comberg, A. and Wihl, H., Mat. Sci. Eng., 23, 275 (1976).
23. Gutzow, I. and Avramov, I., J. Non-Cryst. Sol., 16, 128 (1974).
24. Avramov, I., Gutzow, I. and Alyakov, S.P., Thin Sol. Films, 34, 35 (1976).
25. Haida, O., Suga, H. and Seki, S., Thermochim. Acta, 3, 177 (1972).
26. Haida, O., Suga, H. and Seki, S., J. Non-Cryst. Sol., 22, 219 (1976).
27. Beaumont, R.H., Chihara, H. and Morrison, J.A., J. Chem. Phys., 34, 1456 (1961).
28. Pryde, J.A. and Jones, G.O., Nature, 170, 685 (1952).
29. Olander, D.S., Rice, S.A., Proc. Nat. Acad. Sci. USA, 69, 98 (1972).
30. Koverda, V.P., Skripov, V.P. and Bogdanov, N.M., Sov. Phys. Crystallogr., 19, 379 (1974).
31. Chik, K.P. and Lim, P-K., Thin Sol. Films, 35, 45 (1976).
32. Chopra, K.L., Randhawa, H.S. and Malhotra, L.K., Thin Sol. Films, 47, 203 (1977).
33. Larmagnac, J.P., Carles, D. and Lefrancois, G., Thin Sol. Films, 69, 237 (1980).
34. Kinbara, A., Ohmura, M. and Kikuchi, A., Thin Sol. Films, 34, 37 (1976).
35. Brown, R.W., Millner, A.R., Allgaier, R.S., Thin Sol. Films, 5, 157 (1970).
36. Zdanowicz, L., Poczowski, G., Weclawicz, C., Niedzwiedz, N., and Kwiecien, T., Thin Sol. Films, 34, 161 (1976).
37. Ekenbach, W., Fuhs, W., Stuke, J., J. Non-Cryst. Solids, 5, 264 (1971).

38. Grenet, J., Larmagnac, J.P. and Michon, P., Thin Sol. Films, 67, 617 (1980).
39. Zdanowicz, L., Miotkowska, S. and Niedzwiedz, N., Thin Sol. Films, 34, 41 (1976).
40. Burton, J.J., Ray, R.P., J. Non-Cryst. Solids, 6, 393 (1971).
41. Haller, W., Stichtenoth, H. and Perkampus, H.-H., Chem. Ber., 78, 1221 (1974).
42. Angell, C.A., Clarke, J.H.R. and Woodcock, L.V., in 'Adv. in Chem. Phys.', 48, 397 (1981), Ed. Prigogine, I. and Rice, S.A.
43. Neugebauer, C.A., in reference (1) Chapter 8.
44. Hirth, J.P. and Pound, G.M., "Condensation and Evaporation" Macmillan, N.Y., (1963).
45. Walton, D., J. Chem. Phys., 37, 2182 (1962).
46. Burton, W.K., Cabrera, N. and Frank, F.C., Phil. Trans. Roy. Soc. London, A234, 299 (1951).
47. Chopra, K.L., "Thin Film Phenomena", p.140, Publ. McGraw-Hill.
48. Chen, H.S., Proc. Symp., "The Structure of Non-Crystalline Materials Soc. of Glass Tech., Cambridge 1976, Taylor and Francis, London, 1977, p.79.
49. Zuzuki, H., "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press Publ., (1967) p.59.
50. Birks, J.B., and Kazzaz, A.A., Proc. Roy. Soc., A304, 291 (1968).
51. Bradley, R.A., in "Modern Fluorescence Spectroscopy", 2, Ch.3., 91, Ed. E.R. Wehry.
52. Ferguson, E.E. and Matsen, F.A., J. Chem. Phys., 29, 105 (1958).
53. Duke, C.B., Ann. New York Acad. Sci., 313, 166 (1978).
54. Metzger, R.N. and Bloch, A.N., J. Chem. Phys., 63, 5098 (1975).

CHAPTER 2

VACUUM EQUIPMENT AND INSTRUMENTATION

Thin films examined in the present study were deposited under so called high vacuum conditions at pressures less than 10^{-5} torr ($\sim 10^{-3}$ Pa). They were characterized using a combination of structural, electrical and spectroscopic techniques. The purpose of this chapter is to provide a description of the equipment used for their preparation and characterization. The conditions used for the growth of films of specific materials are dealt with at the beginning of the appropriate chapter, that is 3, 4, 5 and 6.

Section 2.1.1 contains a description of the Birvac vacuum system used for the growth of TTF TCNQ and discontinuous metal films on cooled substrates. Films prepared with this equipment were characterized by structural and electrical measurements. Low temperature spectroscopic studies on organic films were carried out on films deposited inside a continuous flow cryostat which is described in section 2.1.2. Since residual water condensation occurs on cooled surfaces under high vacuum conditions it was important to establish the temperature at which this occurred for the pressure range used in the present study. This was done using infrared spectroscopy and the results are presented in section 2.1.3. This first section also contains a description of the reactive electron beam evaporator, which was constructed for the preparation of oxide films used as substrates in the study of discontinuous metal deposits, described in ch. 7.

Techniques used for the characterization of films are organised into three separate sections dealing with electrical, spectroscopic and microscopic or structural methods, respectively. Section 2.2 contains details of the four and two probe circuits used for in-situ measurement of the electrical resistivity of TTF TCNQ and, discontinuous

metal films. Vibrational spectroscopy, that is, infrared was used to examine thin films of TTFTCNQ, whilst aromatic hydrocarbon films were studied with the aid of spectrofluorometric and fluorescence lifetime measurements. A brief description of the operation of these spectrometers is given in section 2.3. Morphology and structural studies were carried out using scanning and transmission electron microscopy. X-Ray diffraction was also used to examine the effect of substrate temperature on the structure of annealed films of TTFTCNQ. A description of the image analyser used in the treatment of transmission electron microscope data is included in this final section on structure determination.

2.1 Vacuum Deposition - Equipment and Techniques

2.1.1 The Birvac evaporator

Evaporation of organic solids and pure metals was carried out inside a 30 cm. cylindrical glass chamber which was evacuated to a base pressure of 10^{-6} torr, using a liquid nitrogen trapped, 10 cm. oil vapour diffusion pump, backed by a single stage mechanical pump. The main frame, base plate and liquid nitrogen trap were part of the original system, built by Birvac Ltd., but the remaining accessories were purchased from Edwards Vacuum or were purpose built. All valves were manually operated. A sorption trap was installed between the backing pump and the remainder of the vacuum system, to prevent back diffusion of oil vapour below 10 torr. A by-pass was used for pumping at pressures above 10 Torr to prevent saturation of the absorbant with atmospheric moisture. A backing pressure of 5×10^{-2} torr was routinely obtained with an Edwards ES200 ($11 \text{ M}^3 \cdot \text{h}^{-1}$.) pump. The diffusion pump was an Edwards type EO4 which had a pumping speed of 600 l.s.^{-1} at the throat. This was reduced to about 200 l.s.^{-1} by the liquid nitrogen

trap and baffle valve (Edwards type H74B), which was used to isolate the work chamber from the diffusion pump. All 'O' rings were Viton, including the two 30 cm. seals on the sample preparation chamber. Substrate holders, rotary feed throughs, were installed in interchangeable work chamber lids constructed from DURAL. System pressure was monitored using Penning and Pirani gauges. A Centronics AIG50 quadrupole mass spectrometer, capable of measuring to 60 a.m.u. was used for monitoring the partial pressure of residual gases.

Resistance heated evaporation sources

Metals were evaporated from resistance heated foil and wire sources constructed, from either molybdenum or tungsten. Foil sources were used for evaporating copper, silver and gold and a coil of tungsten wire for aluminium. Evaporation of metals for nucleation studies, which are described in Chapter 7, was also carried out in a unit similar to that described above but used exclusively for this purpose. This reduced the extent of surface contamination by organic materials, but for all practical purposes results were identical to those obtained using the Birvac evaporator. Organic materials were evaporated from fused silica or stainless steel crucibles using a Da Silva⁽¹⁾ type tubular source made from molybdenum foil. A rotating turret source was used for sequential evaporation of different materials during the same pump down cycle. This is shown in Figure 2.2. It was suitable for three types of source described above. It was rotated manually by a chain drive, operated from outside the vacuum system, bringing each source into the evaporating position in sequence, and allowing the evaporation of up to four different materials to be carried out without letting the system up to atmospheric pressure.

Figure 2.1. The Birvac Evaporator with the CF104 Cryostat installed,
and associated equipment for in-situ electrical
conductivity measurements.

- a) Chessel x-t recorder
- b) Keithley 610C electrometer
- c) Vacuum gauges
- d) PAR 135 electrometer
- e) Keithley microvoltmeter
- f) Oxford Instruments DTC-2 temperature controller
- g) Edwards film thickness monitor and rate meter
- h) Keithley 227 constant current source
- i) Keithley high voltage power supply
- j) Bryan's x-y recorder



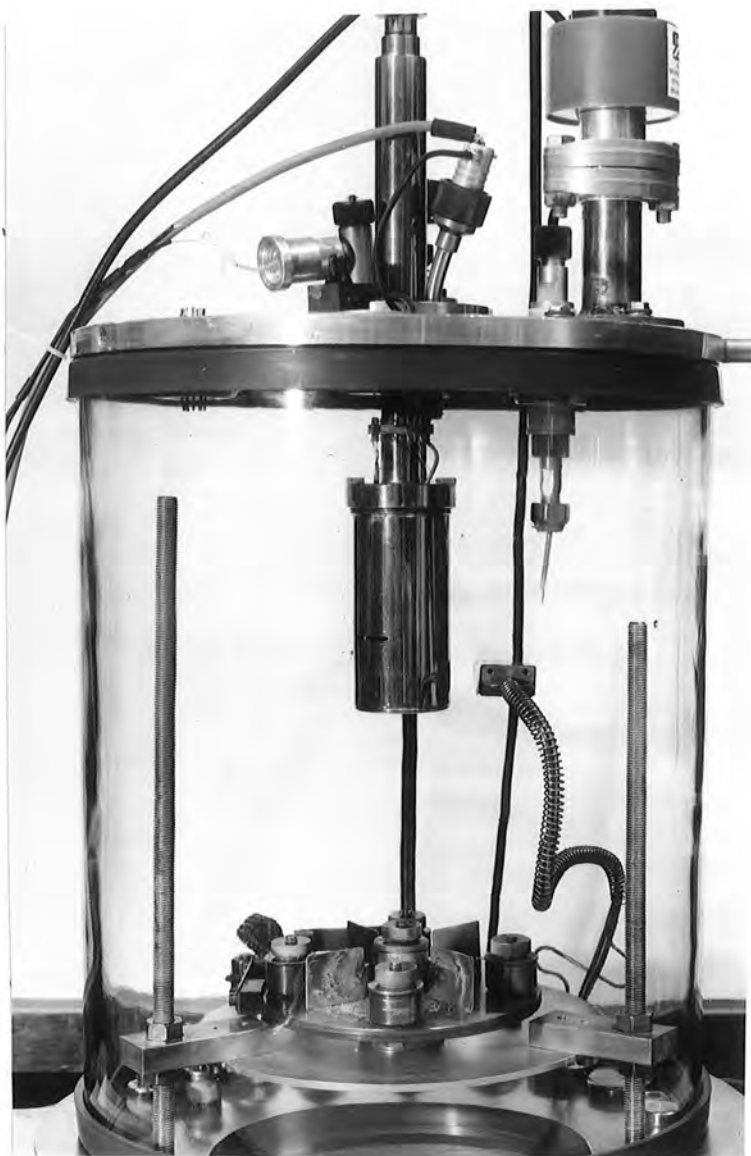


Figure 2.2. The work chamber of the Birvac evaporator with the
turret source (A) and Oxford Instruments CF 104 cryostat

Power to the evaporation source was provided by a thyristor controlled 1 K.VA (100A, 10v) transformer with maximum current input regulated by a Variac control. Evaporation of metals was normally carried out using manual control of the current output of the transformer, since the temperature of the source was not monitored. When evaporating organic solids the temperature of the crucible was monitored using a Chromel/Alumel thermocouple, referenced to room temperature (25°C), and cemented into the base of the crucible in close proximity to the sample. The signal from this thermocouple was fed to a three term Eurotherm temperature controller. Power output was regulated via the thyristor, which was connected to the secondary of the transformer. Controlling power to the crucible in this way prevented surges as the controller switched on and off and caused less interference to electrical measurements. With this arrangement it was possible to control the temperature of the crucible to within 1°C at temperatures in the range 100°C to 300°C. There was a tendency for the temperature to overshoot if the initial heating rate was too high due to a thermal lag between the heater and the crucible. Heating rate was proportional to the difference between the set temperature and the measured temperature of the crucible. To avoid overshooting the desired temperature the normal heating procedure involved setting the temperature on the Eurotherm controller approximately 20°C below that required. After this lower setting had been reached the temperature was then increased to the desired value over a period of 5 mins. A setting of 30 to 40% maximum power at the variac gave satisfactory control for crucible temperatures between 100°C and 300°C.

2.1.2 Low temperature substrate holders

Two methods of cooling substrates were used for the growth of films at low temperatures. Experiments requiring accurate control of temperature, for example, in studying the effect of substrate temperature on the electrical properties of films, were carried out using a continuous flow cryostat (CFC) modified for use in the Birvac evaporator. This cryostat was used for in-situ spectroscopic measurements. In addition films were prepared for morphology studies by deposition onto a substrate with a temperature gradient along its length. This latter substrate holder provided a convenient method of studying changes in film morphology over a wide range of temperatures in a single run.

The continuous flow cryostat

The CF104 continuous flow cryostat is a commercial instrument manufactured by Oxford Instruments (O.I.) for use between 2.5K and room temperature. The temperature range can be extended to 500°K by the use of gold seals. In the present work it was used in conjunction with an (O.I.) DTC 2 three term digital temperature controller, which has a four digit display accurate to 0.1 K. The temperature of the cryostat sample block was measured using an (O.I.) cryogenic linear temperature sensor (CLTS). This is a surface thermometer consisting of three thin alloy sensing grids laminated into an epoxy resin matrix and connected in series in the form of a printed circuit.

The two alloys are special grades of nickel and manganin processed for equal and opposite non-linearities in their temperature dependent resistance. The printed circuit is bonded to a copper base, bolted in position on the heat exchanger block, which is shown in Fig. 2.9. Because it has a low thermal mass and large surface in

contact with the block it responded rapidly and accurately to temperature changes. The sensor resistance was measured by the temperature controller using a 4 probe measuring circuit, it was then linearized, and converted into a digital readout. The CLTS was factory calibrated at 4.2K, 77K and 273K but periodic checks of the circuit output were carried out at 77K and 273K.

Sample block temperature was controlled to an accuracy of $\pm 0.1\text{K}$, using a 39Ω resistance heater, located on the heat exchanger, to balance out the heat lost to the coolant. The output from the heater was controlled by the DTC-2. In addition to providing a controlled temperature the DTC-2 output could also be manually set to give a constant heating rate. Fine control of temperature was achieved by altering the coolant flow rate, which was either liquid nitrogen or helium, pumped from a 17ℓ. dewar, via an (O.I.) CFS300 evacuated transfer tube. Although designed specifically for use with helium, the CFS 300, was also used for transferring nitrogen. When used for nitrogen, it was necessary to evacuate the transfer tube to a pressure of $<10^{-5}$ torr., using a take-off line from the Birvac work chamber and also to pump the gas to the cryostat with a small vacuum pump ($100\ell.\text{min}^{-1}$, Edwards Speedivac 2) capable of reaching a base pressure of 10^{-1} torr. The majority of experiments were in fact carried out using liquid nitrogen as coolant because of the expense and inconvenience of using liquid helium. The greater thermal capacity of liquid nitrogen, coupled with the fact that the cryostat was designed for operating with liquid helium, meant it was only possible to control the sample temperature to within $\pm 0.2\text{K}$, which was regularly achieved. With the pumping pressure of the coolant as low as 10^{-1} torr, a base temperature of about 70°K was possible when using liquid nitrogen, which is some way below its normal boiling point of 77.4K .

When liquid helium was used as a coolant, the flow rate through the cryostat was controlled using a needle valve in conjunction with a flow meter, which was included as part of the temperature controller unit. Because the flow rate of nitrogen through the transfer tube was much lower than that of helium it was not possible to regulate it in this way. In this event course control of nitrogen flow rate was achieved by altering the valve located at the point where the transfer tube enters the cryostat.

The cryostat was located centrally in the lid of the Birvac evaporator, directly above the evaporant source. A 10 cm. flange, fitted during manufacture to the top of the cryostat, was seated on an 'O' ring seal in the lid of the evaporator and held in position by three brackets. The body of the cryostat was electrically earthed via the lid to the evaporator base plate except when carrying out certain types of electrical measurement (see chapter 6.2). The source to substrate distance was 10 cm. in the case of the organic evaporation source and 15 cm. when depositing metals. Rotary feed throughs in the lid operated masks which were used to interrupt the evaporant flux and also to define the area of film deposition. A photograph of the complete system, with the cryostat installed in the work chamber of the Birvac evaporator is shown in Figures 2.1 and 2.2.

All electrical leads entered the cryostat via two ten pin feed-throughs. Internally, all leads were bonded to the body of the cryostat with GE varnish, type 7032, in order to minimize conduction of heat from external sources to the sample. The sample holder was surrounded by a gold plated cylindrical radiation shield which was connected to the centre tube through a copper thermal link flange and cooled by the out-going refrigerant. When used for preparing films for structural and

electrical measurements, the radiation shield had a single hole 2 cm in diameter, in the bottom, with two slits (2 cm x 0.2 cm) in the side, to take a sliding evaporation mask which was located 0.1 cm from the front surface of the sample substrate.

When used for spectroscopic measurements a radiation shield, with four, 2 cm. optical windows, was used. The cryostat was installed in an outer vacuum jacket which had five optical ports. This outer jacket was evacuated either through a valve in the top flange of the cryostat or for higher pumping speeds through one of its unused optical ports. A base pressure of 5×10^{-6} torr was achieved by a 5 cm air cooled diffusion pump (EO2) backed by a sorption trapped rotary pump. The pumping system was mobile allowing it to be used with a number of spectrometers. The method of film deposition when using the cryostat for spectroscopic measurements is described in section 2.3.1. This mobile pumping station was also used for purifying TTF TCNQ and hydrocarbons by sublimation as described in Appendix 1.

The Temperature Gradient Substrate

Deposition onto a substrate with a temperature gradient maintained along the length was found to be a very effective way of examining film structure across the whole range of substrate temperatures in a single evaporation experiment. Temperature gradient experiments were carried out using the Birvac evaporator. A photograph of the apparatus installed on an evaporator lid is shown in Figure 4.4.

It consists of a strip of stainless steel (8 cm x 2.5 cm x 0.2 cm) clamped to a copper cold finger, with a Minco strip heater bonded in position at the other end. The cold finger was located off centre in the lid of the evaporator at a vertical distance of 17 cm from the source. The minimum temperature obtainable with liquid nitrogen in the cold finger was about -100°C . The Minco strip heater was self adhesive and

consisted of a metal foil heater sandwiched between two strips of polymer films (6 cm x 2.5 cm). A 1A, 25V mains operated power supply (Weir, Minireg) was used to provide current to the heater. The temperature gradient was controlled by altering the current to the heater and was monitored by 10 chromel/alumel thermocouples spot welded to the stainless steel strip, located at intervals of approximately 0.5 cm along its length. Flat thermocouple wires about 1 mm wide were spot welded one on top of the other. Their position on the stainless steel strip could be determined to within 0.1 cm. For ease of dismantling the thermocouple wires were fed to a terminal strip screwed onto the lid of the evaporator, all the chromel leads being fed to a common terminal. Whilst it was recognized that differential heating of these terminals during the course of an evaporation was a possible source of error in measuring temperature, junctions generally registered a variation of only 1 or 2°C during an evaporation. This was considered to be acceptable, since the resolution of a thermocouple was of the same order, that is 1 to 2°C/m.m. for a temperature gradient of 70°C from end to end. Thermocouple signals were taken out through a multipin feed through in the lid of the evaporator to a ten position switching box and were referenced to ice (0°C). Each thermocouple e.m.f. could be referenced in turn using a digital voltmeter. With this apparatus it was possible to establish a temperature gradient which was stable to within $\pm 2^\circ\text{C}$, during the course of an evaporation lasting 1 to 2 hrs. The temperature sensed by each thermocouple was measured repeatedly during an evaporation. There was a small deviation from linearity at the high temperature end.

When studying visible changes in film structure as a function of substrate temperature it was sufficient to deposit materials directly onto the metal strip and determine their position using a ruler. In the case of films of TTFTCNQ (Chapter 4) changes in structure were quite marked and could easily be determined to within 0.1 cm, but for electron microscopy experiments, film thickness measurements etc, material was deposited onto a glass microscope slide (7.5 x 2.5 x 0.2 cm), or onto freshly cleaved carbon coated mica. During deposition the glass slide was held in position against the metal strip used for producing the temperature gradient, by two strips of glass filled PTFE. Apiezon T vacuum grease was used to provide thermal contact between the slide and the metal strip. It was shown that good thermal contact was established by covering only part of the metal strip with a glass slide and evaporating TTFTCNQ onto both simultaneously. The characteristic change in visible properties, which were observed for TTFTCNQ films, occurred at precisely the same position, and therefore the same temperature, on both the glass slide and stainless steel substrate.

2.1.3 Water Condensation in Vacuo at Low Temperatures

The condensation of water vapour is an important consideration when depositing films at low temperatures under high vacuum conditions. According to Washburn⁽²⁾ the equilibrium vapour pressure of ice is described by the following equation

$$\log_{10} p \text{ (torr)} = \frac{A}{T} + B \log_{10} T + CT + DT^2 + E \quad 2.1$$

where T is absolute temperature, A = -2445.57, B = 8.2312, C = -1677 x 10⁻⁵, D = 120514 x 10⁻¹⁰, E = -6.7572.

The major constituent of the residual gas in an unbaked vacuum system is water vapour⁽³⁾. At a partial pressure of 10⁻⁶ Torr of water equation 2.1, shows that condensation of ice will

commence at about 160K, because at this temperature the vapour is supersaturated with respect to the solid phase. The sticking coefficient of water vapour is likely to be extremely low in the vicinity of the equilibrium vapour pressure consequently the rate of deposition will be small. However, it is calculated (equation 2.1) that a temperature of only 20K lower, that is about 140K, corresponds to a vapour pressure of approximately 10^{-9} torr. Consequently in a vacuum chamber operating with a base pressure in the region of 10^{-6} torr, significant amounts of water vapour are expected to condense out on any surface cooled below about 150K. A pressure of 10^{-6} torr of H_2O at 300K corresponds to⁽⁴⁾ an impingement rate of approximately 5×10^{14} molecules $cm^{-2} sec^{-1}$. For a sticking coefficient of unity this corresponds to a deposition rate of about 12 monolayers per minute, assuming 2.5×10^{15} molecules of water is equivalent to monolayer coverage. These figures are only very approximate since condensation rate will depend upon sticking coefficient. They are intended to illustrate the point that co-condensation of water vapour is almost certain to occur in films deposited at low temperatures. It is also of interest that at a temperature of 100K the vapour pressure of water has fallen to about 10^{-16} torr, consequently the use of near U.H.V. (ca. 10^{-8} torr) conditions, without bake-out, to deposit films at liquid nitrogen temperature will not necessarily prevent water from being deposited with the material of interest, albeit at a much lower rate. Clearly it is necessary to ensure that water vapour is absent from films deposited at low temperatures if a study of their annealing behaviour is to be at all meaningful.

When using the CF104 cryostat to study the spectroscopic properties of organic films, as described in Chapter 5, the condensation of water vapour was monitored by observing the increase in intensity of the O-H stretching vibration, which is located at 3240 cm^{-1} , as a function of time and temperature. Above a substrate temperature 150K no band was observed at 3240 cm^{-1} after a period of 1 hr at a pressure of 10^{-5} torr. On cooling below this temperature, however, a band was observed to grow rapidly at the O-H stretching frequency. When the sample was cooled rapidly to 120K and the intensity of the O-H band recorded as a function of time, the data shown in Fig. 2.3 were obtained. Because of the approximate nature of the experiment no significance is attached to the fact that the graph in Fig. 2.3 appears to have two straight line portions. However, it is clear that at this temperature water is condensing at a high rate onto the cooled NaCl substrate.

When depositing TTFTCNQ films for infrared studies (Chapter 4), a further complication arose. At 150K and a total pressure of 10^{-5} torr in the cryostat, there was no evidence of water vapour condensing onto the substrate for a period of an hour prior to deposition of TTFTCNQ. However, films deposited at this temperature contained considerable amounts of water, which was removed by heating above 180K. The inference being that water vapour was effectively trapped by the TTFTCNQ as it was deposited onto the cooled substrate. The results of experiments carried out much below 150K, even at pressures in the region of 10^{-8} torr in unbaked vacuum systems must therefore be interpreted with caution. Films deposited above 160K did not contain detectable amounts of water vapour.

Once water has condensed, even onto a clean substrate, it was found to be necessary to increase the substrate temperature to about

Figure 2.4. Decrease in intensity of the O-H vibration of water, due to evaporation from a substrate at 180K in a vacuum of 5×10^{-6} Torr.

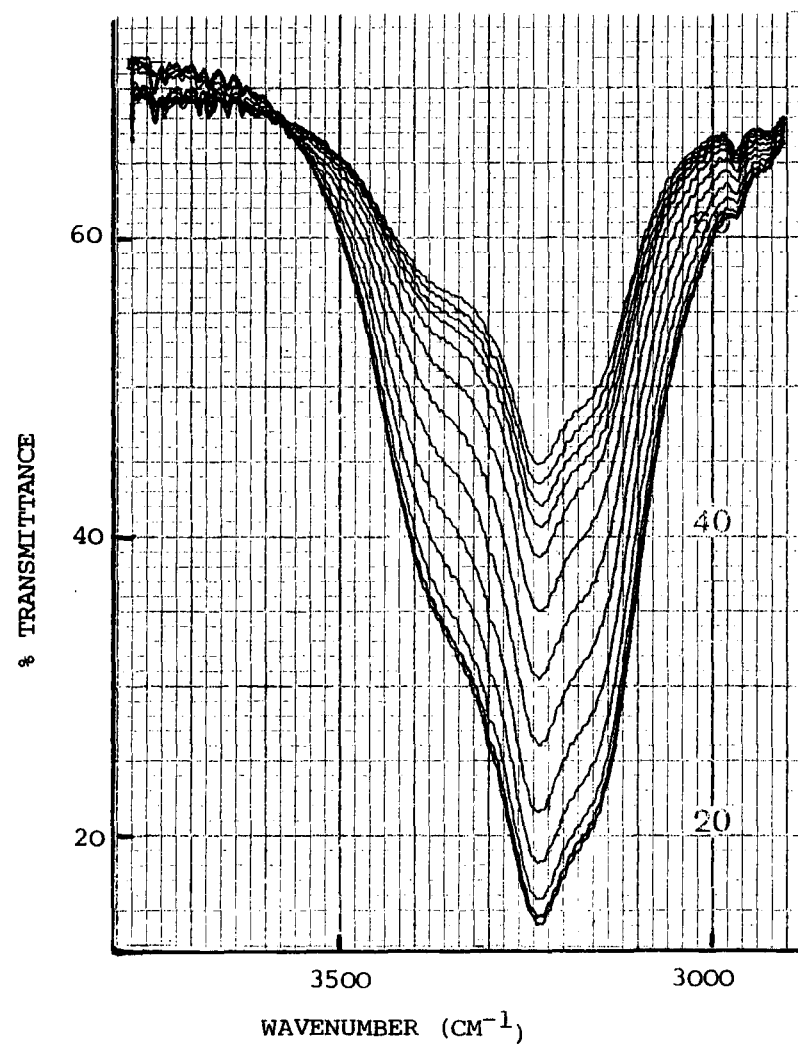
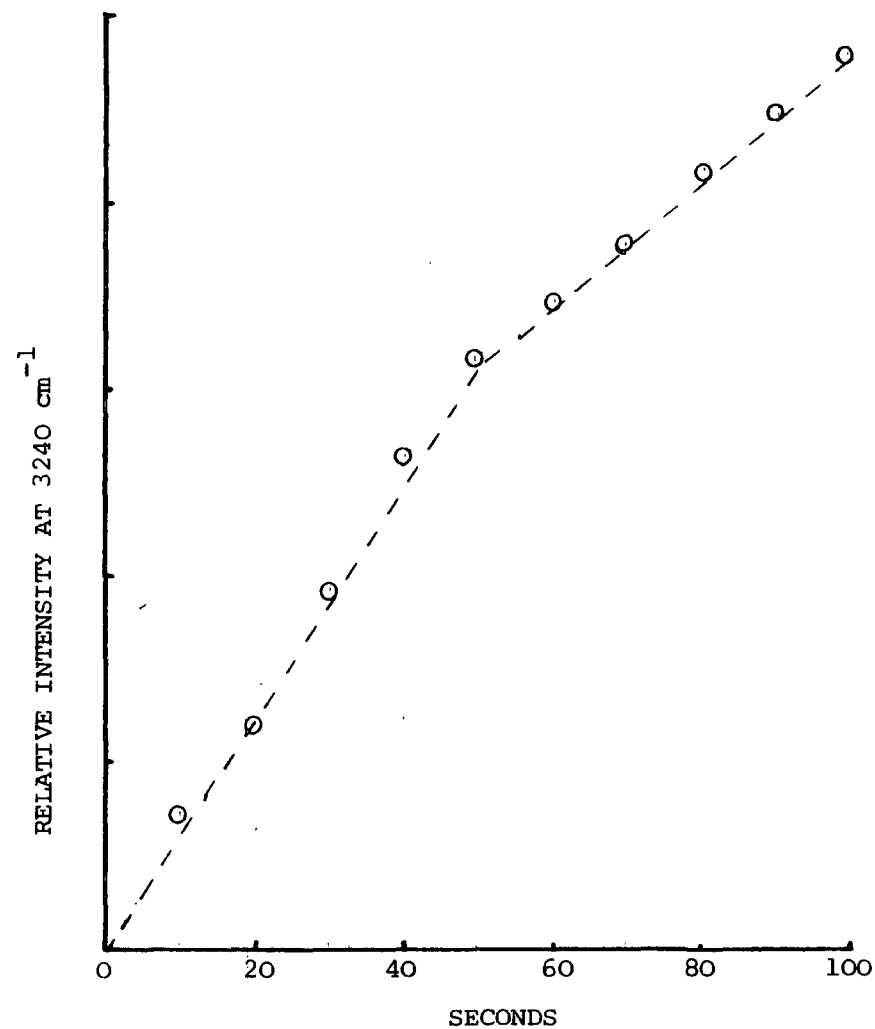


Figure 2.3. Deposition of water vapour onto a substrate cooled to 120K in a vacuum of 5×10^{-6} Torr.



180K in order to remove it. The decrease in intensity of the O-H band (3240 cm^{-1}) at 180K, is plotted against time in Fig. 2.3b. Clearly any intrinsic change in the structure of films, occurring in this temperature region may be distorted by a simultaneous loss of water by evaporation. If, for example, this were to result in a film with a larger internal volume it might cause an increase in molecular diffusion within the film, possibly starting the transformation.

The above observations indicate the advisability of carrying out film deposition experiments onto low temperature substrates inside baked UHV chamber at background pressures of 10^{-9} torr or less. At this pressure the impingement rate is equivalent to monolayer coverage occurring in 10 hours. Such equipment was unfortunately not available for the present study, therefore it was necessary to minimize the rate of water deposition onto substrates in other ways. When carrying out spectroscopic and electrical measurements on films using the CF104 cryostat the sample was almost totally enclosed within a cooled radiation shield as described earlier, in section 2.1.2, which intercepted impinging water molecules and reduced the number reaching the substrate surface. When the CF104 cryostat was used in conjunction with the Birvac evaporator films were deposited through a hole 2 cm in diameter located in the bottom of the radiation shield. This hole was closed off by a spring loaded copper disc, in thermal contact with the radiation shield, which was only removed to deposit the film and then immediately replaced. In addition, the vast majority of films were deposited above 160K, but when films were deposited below this temperature it was automatically assumed that they contained occluded water and due consideration of this fact was given when discussing the results.

2.1.4 The electron beam reactive evaporator

The preliminary TEM study of supported metal films described in Chapter 7 involved the preparation of thin oxide films which required the development of an electron beam reactive evaporator. This technique has been described in detail by Bunshah^(4a). Briefly it consists of high power electron beam (e.b.) source inside a differentially pumped vacuum system, which allows a high pressure of reactive gas to be introduced into the evaporation chamber, whilst maintaining a low operating pressure (c.a. 10^{-5} Torr), essential for its operation, inside the e.b. generator. When evaporating oxides, such as alumina (Al_2O_3), they dissociate in the vapour phase, which results in the formation of oxygen deficient deposits. The presence of oxygen in the evaporation chamber (c.a. 10^{-3} to 10^{-4} Torr) suppresses this dissociation so that stoichiometric deposits are obtained. A schematic diagram of the evaporator showing its more important features is given in Figure 2.5. The conditions employed to grow films of Al_2O_3 used in the present study are described in Chapter 7.

The electron beam gun

The e.b. source was manufactured by Leybold-Hereaus. It is a self accelerated Peirce type source, operating at a nominal negative voltage of 12 kV, with a maximum cathode emission current of 500 mA. The filament cathode was heated by a current of 200A. The source was operated with the anode at ground potential, and located very close to the filament cathode. Electrons emitted from the cathode were accelerated by the field through a hole in the anode, 0.4 cm in diameter. The electron beam was focussed and bent through an angle of 90° , using a system of magnetic lenses, and impinged on the evaporant,

contained in a water cooled copper crucible. The minimum beam spot size was about 0.4 cm. at the sample. The copper crucible was supported on two electromagnetic pole pieces which allowed the beam to be scanned over the sample. This facility also enabled the beam to be magnetically deflected between two positions on the crucible at a rate of between 1-100 Hz, which was continuously variable. The evaporation of two materials could therefore be carried out simultaneously. The relative rates of evaporation of both materials was controlled by varying the time spent by the electron beam and hence the heat supplied at each of the two positions. This dwell time ratio was also continuously variable, between 0-100%, using a ten turn potentiometer.

Differential pumping

As discussed earlier, reactive evaporation is normally carried out at pressures in excess of 10^{-4} torr. This pressure is too high for e.b. guns of the present design, operating in the normal mode, because of the occurrence of voltage discharge. In order to overcome this problem the gun was operated in the differentially pumped mode, that is by pumping the gun and vacuum chamber separately. The pressure differential between the chamber and the e.b. generator was maintained by the low conductance of the anode hole, which provided the only connection between them.

The conductance of gas through an orifice in the molecular flow regime is given by equation (2.1)⁽⁶⁾

$$F = \frac{1}{4} v_A A \quad \text{where } v_A = \frac{8RT}{\pi M}^{\frac{1}{2}} \quad (2.1)$$

A is the cross sectional area of the orifice and v_A is the mean molecular speed. The other symbols have their usual meaning. With A measured in cm^2 , T in degrees K and M in g.mole^{-1} .

$$F = 3.64 A \left(\frac{T}{M} \right)^{\frac{1}{2}} \text{ l.s}^{-1} \quad (2.2)$$

At 300K, a 0.4 cm diameter anode hole has a conductance of approximately 1.5 l.s^{-1} for air. Therefore, in order to maintain a pressure of 10^{-5} torr inside the e.b. generator, while operating at 10^{-3} torr in the main chamber requires a pumping speed (S_{total}) at the anode of 150 l.s^{-1} . The e.b. generator was evacuated through a 10 cm right angled valve (VG type) of conductance (F valve 400 l.s^{-1}) using an Edwards EO4 diffusion pump (10 cm diameter) with a pumping speed (S_{pump}) of 600 l.s^{-1} . The combined pumping speed of the pump, plus valve was calculated, using equation (2.3) ⁽⁷⁾, to be 200 l.s^{-1}

$$\frac{1}{S_{\text{total}}} = \frac{1}{F_{\text{valve}}} + \frac{1}{S_{\text{pump}}} \quad (2.3)$$

assuming molecular flow conditions. Table (2.1) shows the pressure observed in the beam generator compartment at various pressures of oxygen inside the main chamber, measured under static conditions with the electron beam gun switched off. Table 2.1 demonstrates that the beam generator can be operated satisfactorily at a pressure as high as 10^{-2} torr with this pumping arrangement.

The base pressure inside the e.b. generator was 10^{-7} torr, when using Edwards type 704 diffusion pump fluid. Although a liquid nitrogen trap interspersed between the gun and the diffusion pump would have reduced contamination, by eliminating back diffusion of oil vapour, it was not possible to fit one with the present arrangement. The diffusion pump was backed by a sorption trapped ED200 two stage rotary pump, at a pressure of 5×10^{-2} torr.

Table 2.1

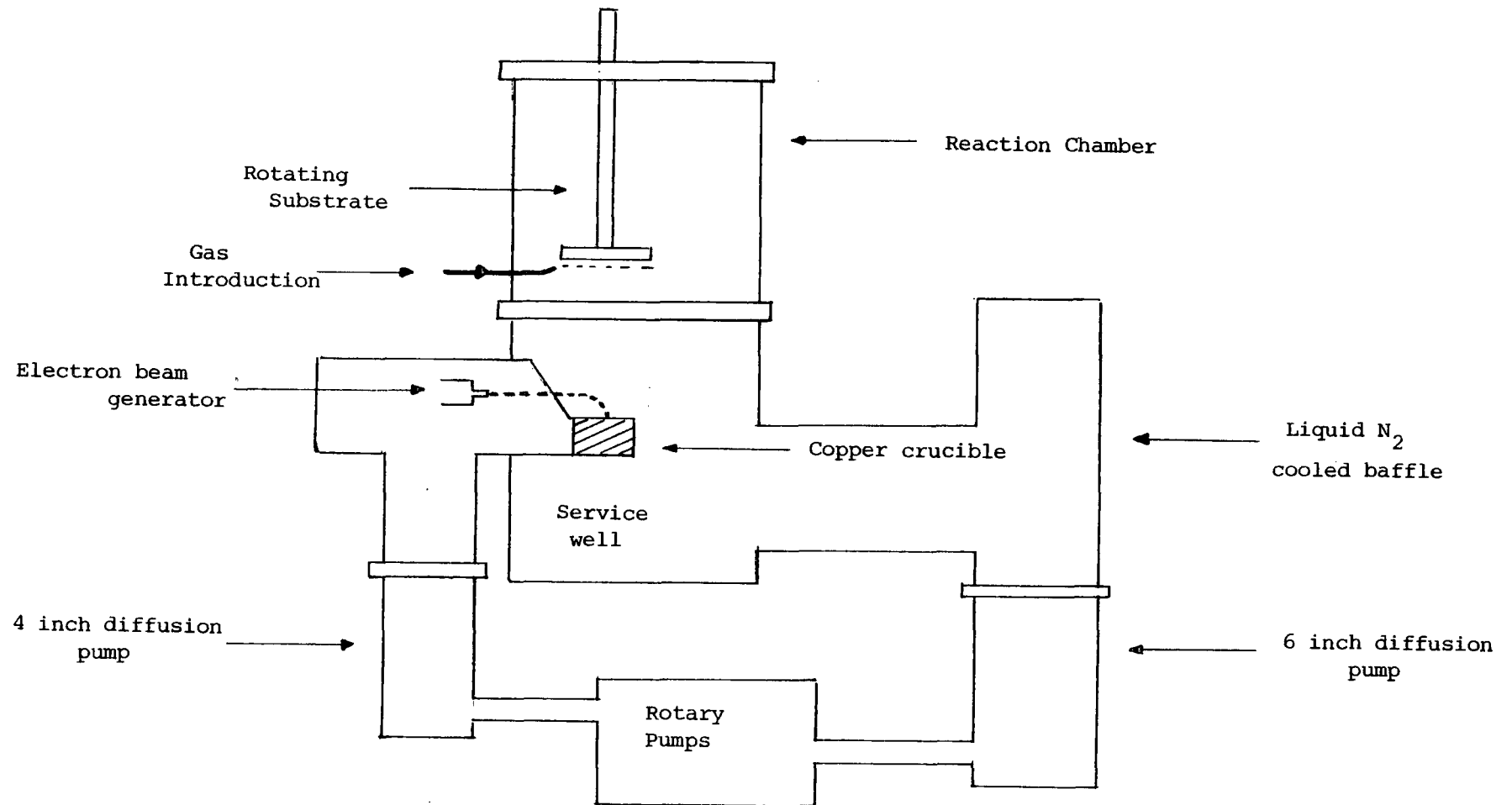
Measured Pressures (torr)	
Beam Generator	Main Chamber
8×10^{-6}	10^{-4}
3×10^{-6}	4×10^{-4}
6×10^{-5}	5×10^{-3}
1×10^{-4}	10^{-2}

Vacuum system and evaporation chamber

The main vacuum system was manufactured by Vacuum Generators (V.G.). Both the main chamber and services well were 30 cm in diameter, made from stainless steel and were water cooled. Although the system was built to U.H.V. specification, demountable Viton seals were fitted to the two main chamber flanges because of the need for frequent sample changes. The electron beam gun flanges were also fitted with Viton seals. All other flanges on the system were fitted with copper gaskets compressed between stainless steel knife edges. The copper evaporation crucible was cooled during evaporation with a water flow of 6 l.min^{-1} . The e.b. generator was fitted onto a 14 cm flange in the service well. A resistance heated molybdenum foil source was also located in the services well, adjacent to the copper crucible (not shown in Fig. 2.5), supported on two 500 Amp feed throughs. Power to this source was provided by a 3 phase, 5 kVA transformer which was controlled by a Zenith variable transformer. Because of high voltage pick-up from the electron beam gun it was necessary for safety reasons, to earth or encase all exposed vacuum feed-throughs.

Gases (oxygen, nitrogen or argon) were fed into the system from a flange on the service well via a V.G. MD7 UHV leak valve. Pressure in the main chamber was measured with a V.G. TCS8 ion gauge. Background pressure was measured at intervals with a quadrupole mass spectrometer (V.G. type QX.200). Water was the main residual gas at a total pressure of 10^{-6} Torr and there was little evidence of hydrocarbon contamination at this pressure. A Pirani gauge was used for measuring pressures in excess of 10^{-3} Torr, during reactive

Figure 2.5. Differentially Pumped Electron Beam Reactive Evaporator



evaporation. The chamber and service well were pumped by a 15 cm (1300 l.s⁻¹) oil (Santovac-5) vapour diffusion pump (Edwards EO6) through a V.G. liquid nitrogen trap (type CCT 150) mounted on a 24 cm flange in the side of the services well. A titanium sublimation (V.G. TS2) pump powered by a 7V, 50A power supply (SPS4) was also fitted inside the services well for increased pumping speed at pressures below 10⁻⁵ Torr. A liquid nitrogen baffle was fitted above the sublimation pump. The diffusion pump was backed at 10⁻³ torr by a 20M³ hr⁻¹, two stage ED330 rotary pump and was protected from back-streaming by a bakeable foreline (VG RT2) sorption trap. When operating at high chamber pressures (>10⁻³ Torr) during an evaporation, the sorption trap was by-passed using a high conductance line in order to increase its pumping speed. The base pressure in the main chamber, was less than 5 x 10⁻⁹ Torr, without bake-out and with the gun flange sealed, using both the diffusion and titanium sublimation pumps. With the gun in position the system base pressure was 10⁻⁷ Torr.

A number of accessories were fitted into the chamber and lid on UHV flanges including; a motorised rotary feedthrough (VG type for a rotating substrate holder, high current (200 Amps) electrodes for substrate heating and a water cooled quartz crystal oscillator for monitoring deposition rates. The use of quartz crystal film thickness monitors is discussed in 2.1.5. A large observation port 15 cm in diameter was installed in the chamber for monitoring the position of electron on the evaporant source during deposition.

2.1.5 Film thickness measurement

Quartz crystal micro-balances were used to measure film thickness during deposition in both the Birvac and electron beam evaporators described in section 2.1. In the case of TTFTCNQ (Chapter 4)

independent measurements of thickness were also made, using either thin film interference techniques or by UV/visible absorption spectroscopy.

Quartz crystal film thickness monitors

A detailed account of the application of quartz crystal microbalances to the study of thin film deposition is given in the Handbook of Thin Film Physics⁽⁸⁾. The unit used to follow deposition in the Birvac evaporator (section 2.1) was an Edwards FTM 2 film thickness monitor and rate meter. The FTM 2 makes use of an AT cut quartz crystal, oscillating in the shear mode at 6 M.Hz. The drive circuit for the monitoring crystal was located under the base plate outside the vacuum chamber and its output compared to a reference crystal oscillating at a fixed frequency of 6.5 M.Hz inside the main unit. A difference frequency is generated from the monitoring and reference crystals which is then mixed with a signal from a variable frequency generator to produce a final difference frequency of between 0 and 150 kHz. The mass of material deposited causes a reduction of the natural resonance frequency (f_0) of the monitoring crystal, which for AT cut crystals operating in the shear mode is given by⁽⁸⁾

$$f_0 = \frac{N}{d_q}$$

where N is 1.67×10^6 Hz mm and d_q the crystal thickness.

For a mass ΔM of material deposited the change in frequency of the crystal is given by

$$\Delta f = \frac{-K f_0 \Delta M}{N \rho_q A_m}$$

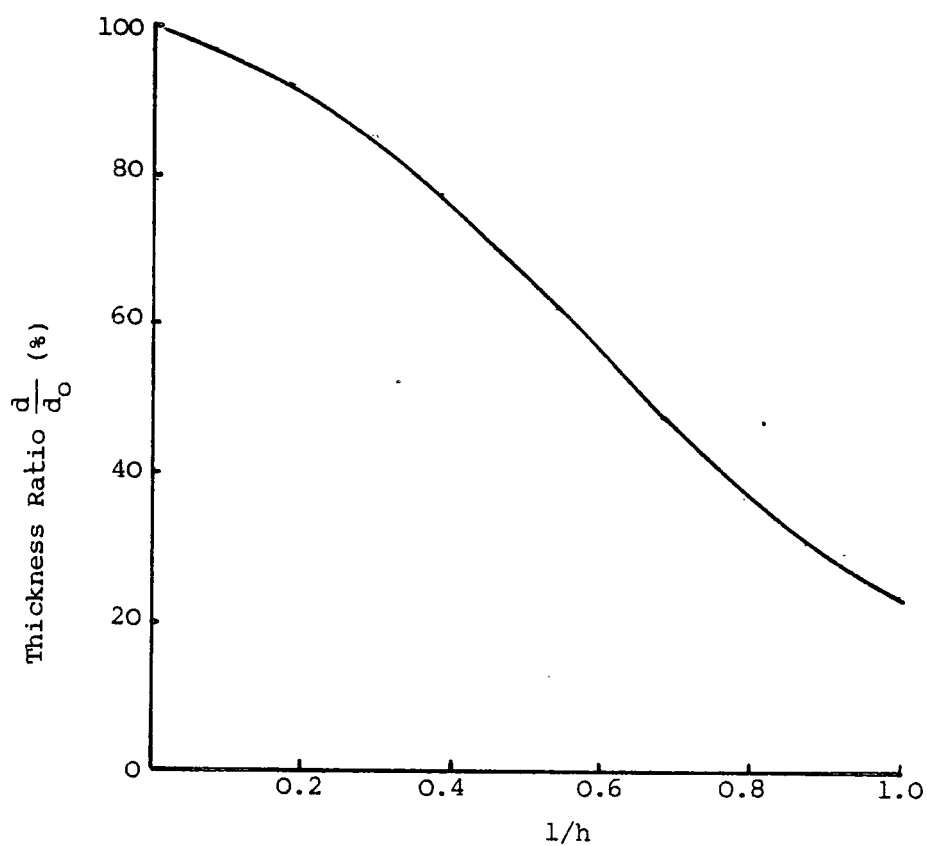
where $K \approx 1$ ρ_q is the density of quartz (2.65 g cm^{-3}) and A_m is area of the electrode used to drive the crystal. For TTFTCNQ with a

density of 1.6 g cm^{-3} and an electrode area of 0.25 cm^2 , Δf is $\approx 0.1 \text{ Hz. } \text{\AA}^{-1}$. For a metal deposit such as silver which has a density of 10.9 g/cm^3 this increases to $\approx 1 \text{ Hz } \text{\AA}^{-1}$.

A dc signal proportional to the final difference frequency actuates a frequency shift meter, which could be read to an accuracy of 1 Hz. Since the dc signal could be attenuated by an amount which was proportional to the density of the material being deposited, the film thickness was determined directly from the meter.

Because the stray feeds generated by the electron beam source, used in the evaporator described in section 2, interfered with deposition monitoring, a different type of crystal oscillator was used. In this case a unit manufactured by M. Rhodes & Company Limited was used, which employs a specially shaped plane convex circular crystal oscillating at 5 M.Hz. The only important difference between this unit and the FTM 2 is that the crystal was encased in a water cooled stainless steel housing. The receiving face of the crystal made contact with the case which was maintained at ground potential. A spring loaded second contact held the crystal in position against the case. This type of housing was found to be unaffected by the electron beam gun, and to provide much more efficient cooling which was essential due to the intense heat from the evaporant source.

There are a number of reasons why the mass of material deposited onto the monitoring crystal is in general different from that laid down onto the support. In the present work the temperature of the substrate during film deposition was different from that of the crystal oscillator. Since the sticking coefficient is dependent on substrate temperature, and in the case of TTFTCNQ was found to be less than one in the region of room temperature (see Chapter 4), an additional



Calculated from $\frac{d}{d_0} = 1 + \frac{1}{h^2}$

Figure 2.6. Film thickness distribution for a small surface source

method involving the use of UV/VIS absorption for thickness determination was used. The positioning of the monitoring crystal with respect to the substrate was also an important consideration.

Angular distribution of the evaporant source

The angular distribution of evaporant flux depends upon the geometry of the source used. For example the spatial distribution of material from a Knudsen cell obeys a cosine law⁽⁹⁾. The source used for evaporating organic solids in the present work was a small silica cylinder, 0.5 cm in diameter. The theoretical angular distribution from this source is to a good approximation⁽¹⁰⁾ (<1% error) the same as that for a single-surface element source, which is plotted in Fig. 2.6⁽¹¹⁾. The thickness ratio, d/d_0 , is the thickness of film deposited at a distance l from the centre of a plane surface, parallel to the surface of the source and whose centres fall upon the same straight line, divided by the thickness at $l = 0$, that is the centre thickness; h is the distance between centres of the source and receiving surface. It is clear from Fig. 2.6 that at a ratio of $\frac{l}{h} = 0.3$, the mass of material deposited begins to decrease rapidly. In the present case $h = 10-20$ cm, therefore a substantial difference between the amount of material deposited on the crystal monitor and the substrate, is expected, if the distance between them is greater than 3 to 6 cm. When carrying out the evaporation of materials every effort was made, either to locate the crystal as close to the sample as possible, or place it in a position which, with reference to the source, was spatially equivalent to that of the substrate. When a series of similar evaporations were carried out the crystal was always placed in the same position for each run, therefore, results were comparable.

UV/visible absorption spectroscopy

This method was used to make accurate determinations of TTFTCNQ film thickness and is discussed in Appendix 2. A description of the spectrophotometer used for this purpose is given in section 2.3.4.

2.2 Electrical Conductivity Measurements

2.2.1 Resistance measuring circuit for TTFTCNQ films

The electrical conductivity of TTFTCNQ films was measured in the plane of the film, using a four point probe technique. The measuring circuit is shown schematically in Fig. 2.7 while the equipment used to make the measurements is shown in the photograph, Fig. 2.6. A constant current was supplied to probes 1 and 4 with a Keithley Constant Current Source, type 227, and was monitored by a battery driven Phillips multimeter type PM 2503, capable of measuring a current of 1 micro amp, full scale deflection, to an accuracy of $\pm 1\%$. The current source output was constant with an accuracy of $\pm 1\%$, for a current of 10^{-5} amps. Continuous monitoring of sample conductance was normally carried out using a constant current of 10 μ A or less, in order to avoid effects due to Joule heating. The voltage generated at probes 2 and 3 by the passage of a current through the sample, was measured with a battery operated electrometer (Princeton Applied Research, Model 135) which was used in the floating mode. That is, the voltage difference between probes 2 and 3 was measured with respect to earth, using the triaxial facility which this electrometer provides. Operation in the floating mode avoided the introduction of earth loops, since there was a single earthing point in the circuit, which occurred at the constant current source. The cryostat containing the sample was also grounded at this point, which effectively placed the sample inside an earthed shield. Circuit low was connected to

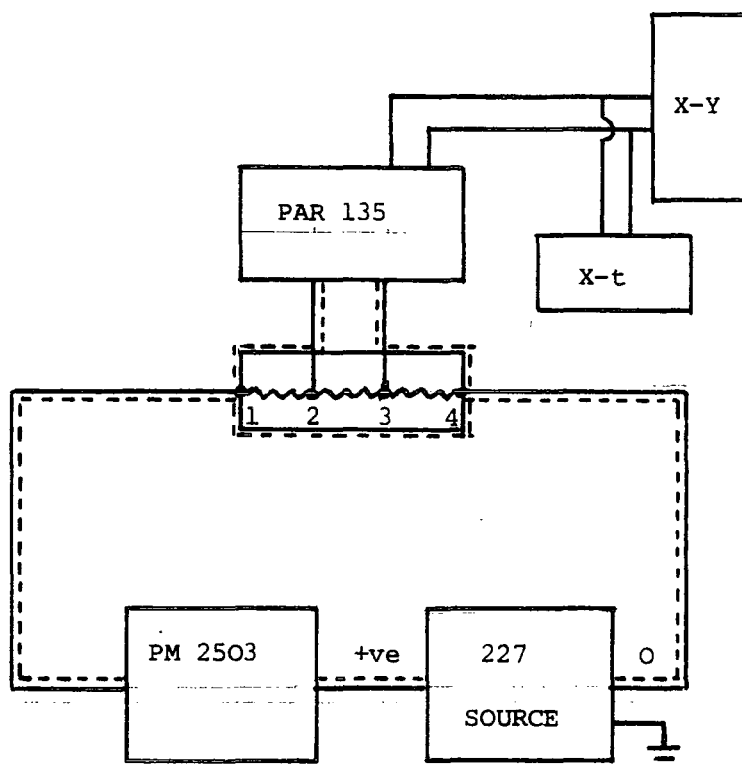


Figure 2.7. Circuit for four probe conductivity measurements

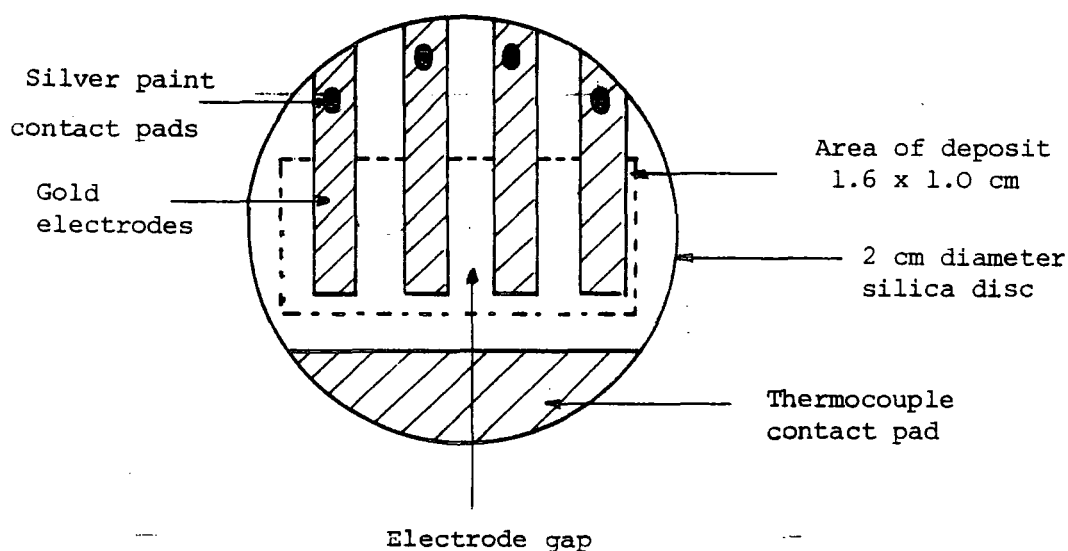


Figure 2.8. Four probe electrode configuration

ground at the constant current source.

Electrical leads to the sample inside the CF104 cryostat which is described in section 2.1.2 were made from enamel insulated copper wire, terminated at a ten pin feed through (see section for cryostat details). Shielded multicore cable (Radiospares) was used to carry the current and voltage leads to a grounded terminal box which was connected to the current supply and electrometer instruments using 50 ohm screened coaxial cable (polythene insulated). The voltage measured by the PAR electrometer could, when required, be monitored continuously using both a Bryans X-Y recorder to plot voltage against sample temperature, and a two pen X-t recorder for plotting voltage as a function of time (Chessel Instruments). A connection between the electrometer case and the earth terminal on both of the above instruments was not included, to eliminate earth loops. In the 4 probe configuration the circuit was used to measure resistances as high as 10^7 ohms. For higher resistances it was necessary to carry out two terminal measurements, using the electrometer in the ohmmeter mode. In this event the resistance of the film between terminals 2 and 3 was measured and the two outer terminals 1 and 4 were shorted through the constant current source, which was operated in the grounded position. This ensured the two outer electrodes were at earth potential and helped to prevent the build up of charge on the surface of the film.

Electrode configuration for 4 probe conductivity measurements

Conductivity measurements were carried out on TTFTCNQ films deposited onto fused silica discs, located on the bottom of the cold finger of the CF104 cryostat which is described in section 2.1.2. Film deposition is discussed in Chapter 6. The fused silica discs

were supplied by Heraus Quartz and were 1.5 mm thick and 2 cm in diameter. They were subjected to a thorough cleaning procedure which is described at the end of this section, prior to deposition of the evaporated metal thin film electrodes. A diagram of the four probe electrode configuration is given in Fig. 2.8. Evaporated gold electrodes ($500\text{\AA}$ thick) were used to make contact to the TTFTCNQ film. Gold has been shown to provide satisfactory ohmic contacts to TTFTCNQ⁽¹²⁾. However, its adhesion to fused silica is poor, and so a keying layer of aluminium ($100\text{\AA}$ thick) was deposited first. Both metals were deposited sequentially through a mask in the same pump down cycle at $<10^{-5}$ torr, using a rotatable turret source which is described in section 2.1,

Using the mask arrangement described in section 2.1.2, it was possible to deposit TTFTCNQ films in the same pump down cycle as the electrodes, so avoiding atmospheric contamination of the gold film. However, exposure of the electrodes to air prior to deposition of the TTFTCNQ did not have a significant effect on the measured film conductivity, substrates were prepared in batches of six and stored in separate sealed plastic containers until required. A number of difficulties were encountered when trying to put top electrodes onto TTFTCNQ. Under certain deposition conditions the surface roughness of the film resulted in the formation of non-conducting layers of metal at the film thicknesses used. Furthermore, electrodes deposited on top of TTFTCNQ films prepared at low temperature, were frequently disrupted presumably as a result of stresses introduced when annealing. Because of the difficulty in obtaining consistent results, four probe measurements on TTFTCNQ films were carried out using bottom electrodes,

that is, by depositing the TTFTCNQ on top of the gold electrodes.

The temperature of the disc was monitored using a gold, 0.05% Iron; Chromel P thermocouple bonded with silver paint to an aluminium/gold contact pad deposited onto the substrate at the same time as the electrodes. Spots of conductive silver paint (Dotite) were also placed at the contact end of each electrode near to the edge of the disc. Phosphor bronze wires were used as springs to make contact with the thin film electrodes, and the silver blobs served as pressure pads to prevent mechanical damage to the metal films. Prior to use, each substrate with electrodes deposited was inspected for damage using a low power optical microscope (x10 magnification).

Sample mounting procedure

The substrate was cemented in place on the heat exchanger flange of the CF104 cryostat using Dotite silver paint. In order to improve the drying characteristics of the Dotite most of the solvent was removed by evaporation and replaced with tertiary butyl methyl ether. The substrate was located on the base of the cryostat heat exchanger by a glass filled PTFE annulus which carried the phosphor bronze wires used to make electrical contact with the film. The assembled arrangement is shown in Fig. 2.9. A shallow recess, the same diameter as the silica slide was cut out of the sample retaining block to a depth of 1 mm to aid in locating the contacts on the silver pads and to centralize the disc. The phosphor bronze springs were located in channels cut into the filled PTFE block and were held in position by the heads of four 6 BA screws, in holes drilled out of the block. Thin walls between these channels prevented electrical shorting of adjacent probes. The current and voltage leads were soldered onto tabs on the end of the 6 BA screws. Electrical continuity between the thin film electrodes and the leads



Figure 2.9. The CF 104 cryostat heat exchanger with a substrate installed for four probe conductivity measurement.

and the absence of electrical shorts between probes and the body of the cryostat was established prior to installing the cryostat inside the vacuum system. The thermocouple was cemented in place at this stage. The junction was positioned well clear of the filled PTFE block to ensure that the surface temperature of the slide and not that of the block was measured. A channel cut into the block helped locate the thermocouple on the slide.

Finally, a copper foil mask was positioned on the front surface of the block to define the area (2 cm x 1 cm) of TTFTCNQ film deposited onto the slide and also prevent material from being deposited between the electrical contacts on top of the block. The whole assembly was attached to the cryostat cold finger with four 6 BA screws.

2.2.2 Electrical measurements on discontinuous metal films Resistance measuring circuit

The conductivity of discontinuous metal films was measured using a conventional two electrode technique. Similar to that described by Negabauer and Webb⁽¹³⁾ and as recommended in the Keithley 610C Electrometer Handbook. The measuring circuit and a photograph of the equipment that was used are shown in Figs. 2.10 and 2.1, respectively. A Keithley high voltage power supply was used to provide up to 1200 volts to the sample. The current passing through the sample to earth was monitored using a Keithley 610C Electrometer which had an internal impedance of $>10^{13} \Omega$. The output from the electrometer was fed to one channel of a two pen recorder. The electrometer was used in the fast feedback mode when measuring resistances above $10^{10} \Omega$, but samples generally responded sufficiently fast to enable the normal

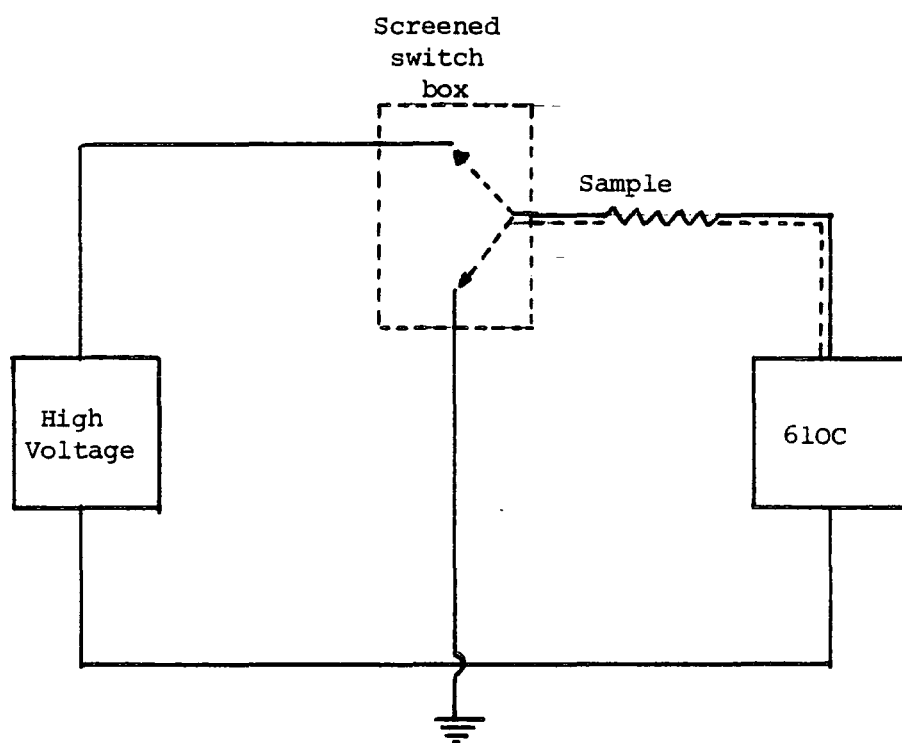


Figure 2.10. Circuit for two probe conductivity measurements

mode to be used at lower resistances. All leads used were 50 Ω copper shielded co-axial cable.

The voltage was applied to the sample via a lead from a multi-pen feed through in the evaporator lid. The current monitoring lead to the electrometer was taken out through a separate, specially adapted, vacuum feed-through which provided for a continuous length of co-axial cable between the sample and the electrometer. The screen from the current lead was connected to the body of the cryostat, which was in turn connected to earth via the evaporator lid. An earth lead was connected between the low binding post on the electrometer and the evaporator lid. This arrangement was found to be satisfactory for measuring conductances as low as $10^{-14}\Omega$, since it was limited only by the conductance of the current monitoring co-axial lead which has a leakage current of 10^{-16} A. A switch, housed in a screened box, was included in the circuit to enable the power supply to be disconnected from the sample, whilst at the same time connecting the high tension side of the sample directly to earth. This was originally included for the purpose of measuring very low conductances but in the event was not required. However, it was left in the circuit as a convenient method of ensuring that both electrodes of the sample were grounded during film deposition, and to facilitate discharge of high resistance samples which were often observed to accumulate charge at high applied voltage.

Substrate mounting and electrode configuration

Two silver electrodes 1 cm wide were deposited on top of a thin layer of a metal oxide supported on either fused silica or pyrex discs (2 cm x 0.15 cm). The preparation of the oxide layer and deposition of discontinuous metal films is discussed in Chapter 7. The electrodes were approximately $1000\text{\AA}$ thick and were deposited from the resistance

heated source inside the electron beam evaporator described in section 2.1.4, at a pressure of 10^{-6} torr. A rotating substrate holder operating at 10 rpm was used to coat six substrates simultaneously. An electrode gap of 1 mm was used for the electrical measurements described in Chapter 6. This was produced by soldering 1 mm thick wires to the copper mask used to define the electrode deposition area. Samples with a 0.1 mm electrode gap were studied initially and although these gave similar results it was decided that the larger 1 mm gap should be used to reduce any influence that the electrode might have during subsequent growth of the discontinuous metal film.

Samples were bonded with Dotite to the heat exchanger flange of the CF104 cryostat, as already described Fig. 2.20. The current sensing and high voltage leads were located in holes in the base of the cryostat. Contact to the electrodes was made by two thin copper wires soldered to these leads. The wires were bonded to the thin film electrodes with Dotite. Samples prepared in this way had resistances in excess of $10^{14} \Omega$ prior to deposition of a discontinuous metal film. The sample was enclosed by a radiation shield as described in section 2.1.2.

A gold, 0.05% iron; chromel P thermocouple referenced to liquid nitrogen and bonded to the surface of the slide with Dotite was used to measure sample temperature. The output from the thermocouple was monitored on the second channel of the two pen recorder used for displaying sample current.

Substrate cleaning procedure

Initially an exhaustive fifteen stage cleaning procedure was employed for both glass and silica slides. The procedure was developed originally for cleaning slides for Langmuir-Blodgett multi-layer studies⁽¹⁴⁾ which require extremely clean and grease-free surfaces. However, it was inconvenient and a much shorter cleaning procedure was eventually used which gave satisfactory results. Slides were submitted to ultrasonic cleaning for 15 minute periods in 'Analar' methylene chloride, methanol, distilled water and finally rinsed in methanol and polished with a glass cloth until free of surface debris. Microscopic examination of cleaned slides, using top illumination and viewed against a dark background showed that slides not subjected to the final polishing stage, after either the exhaustive cleaning process or the shortened one, had a particulate deposit on the surface. This was removed by polishing. Good adhesion of evaporated metals and organics was obtained on slides cleaned in this way and there were very few pinholes when observed in an optical microscope.

2.3 Spectroscopic Studies of Organic Thin Film Deposits

2.3.1 Film deposition onto low temperature substrates

The CF104 cryostat described in section 2.1.2. was used to carry out in-situ fluorescence and infrared studies of organic films. The substrate, which was either a fused silica or sodium chloride single crystal disc (1 cm diameter) was cemented into position in a hole in the gold plated copper, sample holder, using Dotite conducting silver paint. The sample holder was fixed in place onto the bottom flange of the cryostat heat exchanger with six screws. A thin indium wire seal was compressed between the flanges to improve thermal contact between sample holder and heat exchanger. The

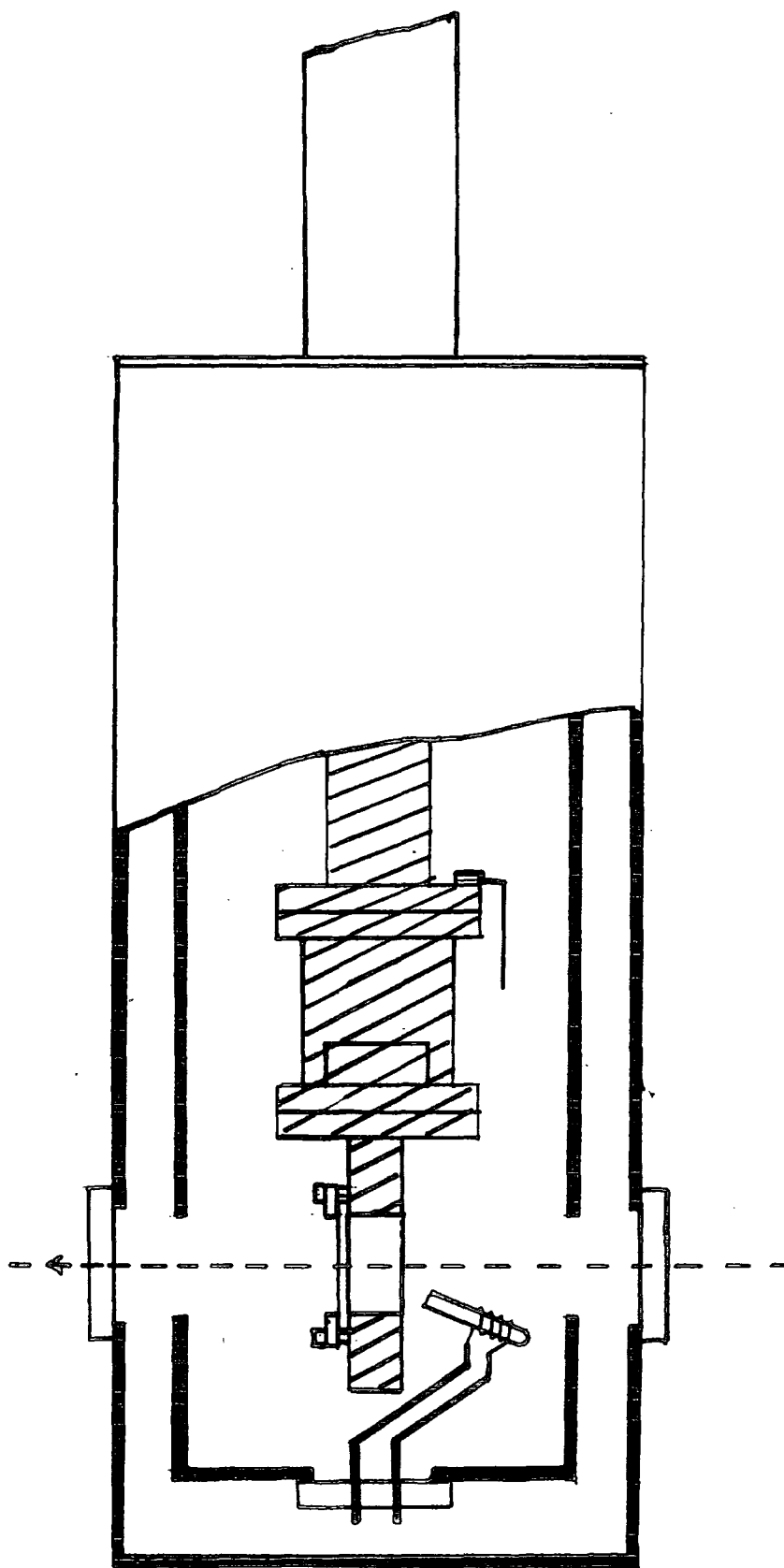


Figure 2.11. Schematic of the CF104 cryostat as used for in-situ infrared and fluorescence spectroscopy of evaporated film.

temperature of the sodium chloride disc was monitored directly by a Gold/O.05% Iron, Chromel P thermocouple located in a small hole drilled into the disc. The temperature of the silica disc was not monitored directly but was taken to be the same as the CLTS.

Thin films of the organic solids studied were deposited from a small silica capillary tube which was positioned inside the cryostat radiation shield, out of line of the optical path. The open end of the capillary tube was located at a distance of about 1 cm from the substrate surface as shown schematically in Fig. 2.11. It was supported in a small coil of nichrome heater wire which had a resistance of 6 ohms/metre. The wire was attached to screw contacts on thick copper wires, which were cemented into a glass disc located in the bottom port of the radiation shield and served as current feed throughs. Thinner wires were soldered to each feed through and taken up the outside of the radiation shield to a second multipin connector in the lid of the cryostat. Current to the heater was provided by a Weir Minireg power supply which had a variable output up to 1A.

Using this arrangement it was possible to monitor the progress of thin film deposition although it wasn't possible to measure the source temperature. The substrate temperature increase, as a result of radiated heat from the source was observed to be less than 1°C. A plug of silica wool was inserted into the neck of the capillary tube to prevent spitting of the contents and to improve the uniformity of the deposit.

2.3.2 The vibrational spectra of TTFTCNQ films

Infrared Spectrometers

Most of the infrared data presented in Chapter 4 was obtained using a Perkin Elmer 580 ratio recording spectrometer, over the wavelength range $4000\text{--}180\text{ cm}^{-1}$. Two important features of this spectrometer, as far as the present work was concerned were: its suitability for making quantitative measurements, and its repeated scan facility. With these facilities it was possible to accurately monitor changes in the relative concentration of a particular species during the annealing process. Unlike more conventional optical null spectrometers, ratio recording also provides for accurate location of the 0% transmission line in highly absorbing sample. This is particularly appropriate for studies of TTFTCNQ, because of its high reflectivity in the infrared region. Spectra were normally recorded using mode 2 operating conditions, which gave a scan time of 10 minutes for the full spectral range at a resolution of 2.8 microns and a relative noise level of 0.3. The spectrometer sample compartment was connected to a re-circulating pump through a molecular sieve trap to reduce interference from the presence of water vapour in the sample beam.

Spectra were also obtained using a Perkin Elmer Grating Infrared spectrometer, which is an optical null machine covering the frequency region $4000\text{--}600\text{ cm}^{-1}$. Because of the difficulties encountered with high absorbance samples only limited use was made of this spectrometer. Because the model 580 provides for greater accuracy, all infrared band frequencies quoted were obtained with this spectrometer which was calibrated against the C=O stretch of CO_2 located at 2335 cm^{-1} .

2.3.3 Determination of the fluorescence spectra of aromatic hydrocarbon films

The Farrand Spectrofluorometer

The fluorescence spectra of thin films of aromatic hydrocarbons were examined using a Farrand Mk 1, double grating spectrofluorometer in the spectral region 300-700m μ . Both monochromators were accurate to 2m μ and slits corresponding to bandwidths of 10m μ and 1m μ were normally employed in the exciting and analysing monochromators, respectively, unless otherwise states. This combination was found to give good resolution at minimum sacrifice of sensitivity in most cases. Appropriate filters were positioned as per the handbook in order to prevent unwanted radiation from entering the analysing monochromator. A type 7-54 filter transmitting below about 400 nm was normally employed between the exciting monochromator and the lamp. The choice of filter between the sample and the analysing monochromator was determined to some extent by the sample being studied and will be referred against the appropriate material in Chapter 3.

In order to avoid possible re-adsorption of the emitted signal in the bulk of a deposited film, the fluorescence signal was taken from the front surface of the substrate, i.e. from the top surface of the film.

Measurement of fluorescence decay times

The fluorescence decay time of evaporated films of aromatic hydrocarbons, which are discussed in Chapter 3, was measured with a TRW Instruments Model 75A Decay Time Fluorometer⁽¹⁵⁾. The exciting signal was provided by a TRW model 35A Nanosecond Spectral Source which produces short duration light pulses (<10ns) using either a nitrogen or dueterium discharge lamp, capable of operating at

frequencies of up to 5000 Hz. Excitation pulses from the source, and the resulting fluorescent signal from the sample were monitored simultaneously, using two photomultiplier tubes (RCA type 931A), which were connected to the two inputs of a type C/A plug-in of a Tekronix 555 30 MHz bandwidth, dual beam, independent dual time base oscilloscope. Signals from the source and sample were displayed simultaneously on the oscilloscope screen using the same time base. A TRW model 32A Decay Time Computer was used to produce electronically simulated excitation and decay pulses. These were displayed on the other time base of the oscilloscope, using a second type C/A plug-in.

To measure the fluorescence decay time of a sample, the 32A Computer was used to change the shape of the simulated excitation pulse so that it exactly matched that of the actual light pulse. Although the real time duration of the electronically simulated pulse was of the order of 50 to 400 μ s, because of the dual time base facility it was possible to superimpose it upon the actual sample pulse, which has a width of less than 10 ns. This allowed exact matching of both signals. Having set up the computer in this way, the fluorescence signal from the sample was then matched with the simulated decay curve from the computer using only the amplitude and decay time controls. The decay time was read directly from the digital display on the computer.

Full details of the equipment and its applications are given in the manufacturers handbook and in the open literature⁽¹⁵⁾.

2.3.4 The Ultra Violet/Visible Absorption Spectrophotometer

A Beckmann Model 25 double beam spectrophotometer was used to measure UV/visible absorption Spectra of films and solutions. The model 25 used, has an extended photocathode and was capable of

measuring light at wavelengths from 190 to 900 nm. A tungsten lamp was used in the visible range and a deuterium source in the ultra-violet region of the spectrum. A mirror bridge vibrating in the horizontal plane at a set frequency directs a monochromatic beam into both the sample and reference cells at the displacement frequency of the bridge, and allows for increased signal to noise ratio with a base line drift less than 0.009A over the whole range. A single grating-monochromator, with 1200 lines per mm, blazed at 250 nm gave a resolution of 0.2 nm with a slit width of 0.02 mm. Output from the photomultiplier was linearized to give a direct reading in absorbance units and was recorded on a Beckmann x-t single pen recorder with full scale sensitivity between 0.1A and 2A. Further information about the use of the model 25 is given in Appendix 2.

2.4 Structural Analysis Techniques

2.4.1 Scanning electron microscopy

The bulk of the work was carried out using a Jeol JSM 35 microscope. It had a standard configuration, with a low resolution stage and a working distance of 3.9 cm from lens to sample. This allowed large area samples (2.5 x 2.5 cm) to be examined. A tungsten filament source was used for studies on TTFTCNQ, since the higher intensity lanthanum hexaboride source normally used appeared to be sensitive to contamination by TTFTCNQ, which resulted in a considerable reduction in image quality. An accelerating voltage of 35 kV was used, unless otherwise stated. On occasion films of TTFTCNQ were observed to suffer significant beam damage, however, this appeared to be limited to only a small number of samples and for the bulk of films studied there was no apparent change under the beam. In most cases, films of TTFTCNQ had sufficiently high conductivity to prevent

charge build up by the electron beam, and there was no need to deposit a thin layer of metal on the top surface. When studying films deposited at low temperatures, however, a metal film replication technique was used which is described in Chapter 4. Because of their low conductivity it was necessary to coat films of aromatic hydrocarbons with a surface layer of either aluminium or gold to prevent charging effects. Substrates were bonded to the microscope sample stage with Dotite which was also used to provide electrical contact between the stage and the front surface of samples. A tilting microscope stage was used which enabled the orientation of the sample to be changed with respect to the electron beam. The sample holder was also rotatable through a full 360° in the horizontal plane, providing a different perspective of selected areas of a sample.

The vacuum inside the microscope, which was liquid nitrogen trapped was approximately 10^{-6} Torr.

2.4.2 Transmission electron microscopy

A Phillips EM 300 Transmission Electron Microscope operated at 100 KV was used to examine films of TTFTCNQ and to study ultra thin metal films prepared by vacuum deposition. The microscope was calibrated against an epitaxial film of gold, with a $[100]$ orientation, grown by vacuum deposition onto air cleaved rock salt at 100°C , and was operated in the selected area diffraction mode. Studies of TTFTCNQ films were carried out on a low resolution goniometer stage, whilst a high resolution goniometer stage was used for work on thin metal films. A liquid nitrogen cold finger surrounded the sample in order to reduce contamination by adsorbed gases. A very large aperture setting was used in the case of TTFTCNQ.

Analysis of micrographs, of discontinuous metal film, that is the determination of particle size distribution, particle density etc., was carried out using a Joyce Loebel microprocessor based, Magiscan Image Analyser. The Magiscan had previously been programmed⁽¹⁶⁾ using either Fortran or MAGIC the latter being a specially adapted form of BASIC. Hardware consisted of a television camera, visual display unit (VDU), teletype and microprocessor. The television camera was used to display an image of the micrograph on the visual display unit. The Magiscan processed that part of the image with an optical density greater than a minimum level, which was pre-calibrated visually prior to analysis, to allow for differences in contrast between micrographs. An image of those areas of the micrograph selected for analysis by the microprocessor was then displayed on the VDU. Further editing was carried out at this stage using a light pen to add to or subtract from the displayed image. The results obtained were displayed in the form of a histogram on the VDU and printed out as hard copy at the teletype.

References for Chapter 2

1. Da Silva, E.M., Rev. Sci. Instr., 31, 959 (1960).
2. see Eisenberg, D., and Kauzmann, W., 'The Structure and Properties of Water', Oxford Univ. Press (1969), p.60.
3. Casewell, H.L., IBM J. Res. Develop., 4, 130 (1960).
4. Glang, R., in 'Handbook of Thin Film Technology', p.1-82, Ed. Massel, L.I. and Glang, R., Publ., McGraw-Hill (1970).
5. Bunshah, R.F. and Raghuram, A.C., J. Vac. Sci. Technol., 9, 1385 (1972); Bunshah, R.F., in 'Science and Technology of Surface Coatings', Ed., Chapman, B. and Anderson, J.C., Academic Press, (1974).
6. Dushman, S. and Lafferty, J.M., in Scientific Foundations of Vacuum Technique', 2nd Edition, p.90. John Wiley & Sons, (1962).
7. In reference (6) p.91.
8. In reference (4) p.1-107.
9. In reference (4) p.1-55.
10. In reference (4) p.1-59.
11. In reference (4) p.1-58.
12. Chen, T.H. and Schechtmann, B.H., Thin Solid Films, 30, 173 (1975).
13. Nengebauer, C.A. and Webb, M.B., J. Appl. Phys., 33, 74 (1962).
14. Blodgett, K.B., J.A.C.S., 57, 1007 (1935); Langmuir, I., Proc. Roy. Soc., 110A, 423 (1926).
15. Reprints of a number of technical papers are available from TRW Instruments, 139 Illinois St., El Segundo, California 90245.
16. Williams, D.T. and Wylie, I.C., Private Communication.

CHAPTER 3

A FLUORESCENCE STUDY OF EVAPORATED FILMS OF POLYCYCLIC AROMATIC HYDROCARBONS

3.1 Introduction

Among the various substances found by VBR⁽¹⁾ to conform to the optimum substrate temperature (OST) rule, anthracene was, as mentioned in Chapter 1, particularly notable for the pronounced structural singularity Table (111) observed in films deposited at substrate temperatures in the vicinity of 213K. Furthermore, electroabsorbance measurements^{(2), (3)} carried out on films of anthracene deposited between 173K and 253K detected the presence of a new absorption band located at 403 nm. The magnitude of this band for a constant electric field was shown to be a sensitive function of the substrate temperature employed during deposition. It underwent a rapid decrease in intensity between 203K and 223K, which is the region of the OST of anthracene. VBR assigned the band at 403 nm to a non-crystalline or 'disordered' phase, consisting of randomly oriented molecules of anthracene and considered that the rapid change in its intensity at the OST provided strong indirect evidence that a molecular re-arrangement was occurring at this temperature. This observation was in part responsible for the proposal that the OST effect is associated with re-evaporation from disordered or glassy regions of vacuum deposited films. However, the above mentioned electro-absorbance measurements were carried out on films which had been annealed at room temperature, after deposition, and as such the band at 403 nm was presumably caused by residual disorder located within grain boundary regions between crystallites. While it appears reasonable to assume that the residual disorder remaining after annealing should be proportional to initial degree of disorder incorporated during the deposition stage, an investigation of films in the as-deposited state could provide direct confirmation of the existence of a disordered phase at temperatures below the OST and lend additional support to the view that the OST effect is

associated with the phase boundary between the disordered and crystalline states of a material. This is the main purpose behind the study of evaporated films of polycyclic aromatic compounds.

3.1.1 Structure and Properties of Polycyclic Aromatic Compounds

Polycyclic or polynuclear aromatics (PCA) constitute a large group of chemically and physically related molecules, which are characterised by their high thermal stability. They readily undergo sublimation or evaporation at reduced pressure, without decomposition and exhibit an additivity in their molar heats of sublimation⁽⁴⁾ (ΔH_{sub}). Inokuchi et.al.⁽⁵⁾ have determined the so called inner heats of sublimation (ΔU_{sub}), which is defined as ($H_{\text{sub}} - RT$), for a number of (PCA's) from which they established that each carbon atom contributes a value of $1.51 \text{ kcal.mole}^{-1}$ to ΔU_{sub} . ΔH_{sub} is the enthalpy of sublimation. They concluded that this additivity is due to the fact that (PCA's) typically crystallise in the form of a molecular lattice and that within such a lattice intermolecular forces are derived almost entirely from dispersion effects. Now, because intermolecular forces in (PCA's) are predominantly van der Waals in nature, and the so called empirical relationships, such as Troutons rule, are known to provide a reasonably good approximation for such molecules, as outlined in Chapter 1, their OST's should according to VBR be located close to $0.33 T_B$. As shown by VBR this is certainly true of anthracene ($\text{OST} = 0.35 T_B$), and should therefore be true of other (PCA's), since they form a closely related molecular series. The OST of (PCA's) may, therefore, be located with reasonable accuracy without the necessity of carrying out a detailed study of film topography as a function of substrate temperature.

Four (PCA's) were examined in the course of this work and their molecular structures are given in Table (3.1). Their normal boiling

Table 3.1 Physical and structural data of selected aromatic hydrocarbons. Their predicted OST's are listed in column 6.

Physical Data

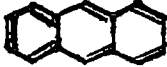
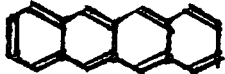
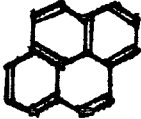
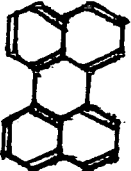
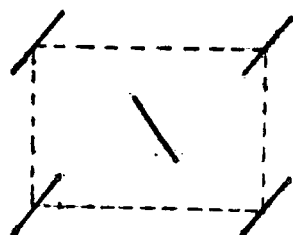
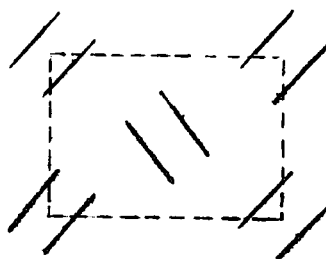
<u>Compound</u>	<u>Formula</u>	<u>Molecular Structure</u>	<u>Lattice Type</u> (See Fig 3.(I))	<u>Normal</u> ⁸ <u>Boiling Point</u> (°K)	0.33 x b.p. (°K)
Anthracene	C ₁₄ H ₁₀		A	613	202.3
Tetracene	C ₁₈ H ₁₂		A	720 ⁽⁴²⁾	240
Pyrene	C ₁₆ H ₁₀		B ₁	479	158
Perylene	C ₂₀ H ₁₂		B ₁	~673	222.1

Figure 3.1 Aromatic hydrocarbon lattices viewed parallel to the molecular planes



TYPE A



TYPE B

points are listed in column 5 while the predicted OST ($= 0.33 T_B$) is given in column 6. Robertson⁽⁶⁾ has classified (PCA) crystals according to the lattice types given in column (4) of Table (3.1). He pointed out⁽⁷⁾ that planar aromatic hydrocarbons generally crystallise with one of two distinct lattice types according to their in-plane molecular dimensions. Thus, molecules like anthracene and naphthacene which possess both long and short axes, adopt the lattice structure shown as type A in Figure (3.1). Disc shaped molecules, such as pyrene/perylene on the other hand, prefer the lattice structures designated as type B, in Figure (3.1). Both diagrams represent views down the C axis parallel to the molecular plane. This difference in lattice structure has important consequences for the fluorescence spectra of (PCA's), as will now be discussed.

3.1.2 Fluorescence Spectra of Polycyclic Aromatic Compounds⁽⁷⁾

Because the b-axis periodicity of the A type lattice in Figure (3.1) is of the order of $6\text{\AA}$ and the angle of inclination of the molecular planes to the symmetry plane of the crystal is large, π orbital overlap between adjacent parallel molecules is severely restricted. As a consequence coupling between molecules in the lowest excited singlet state is small compared to the intramolecular energy, which results in a fluorescence spectrum similar to that of the isolated molecule (monomer) in solution. However, when a type B lattice structure is adopted, the lattice unit is a pair of almost completely overlapping parallel molecules with an interplanar spacing of the order of $3.5\text{\AA}$ and a reduced angle of inclination, approaching 45° , with respect to the symmetry plane of the molecule. This has the effect of increasing π orbital overlap between molecules within each pair or dimer, and enables an electronically excited molecule

in the lowest excited singlet state to interact with an unexcited molecule in the singlet ground state⁽⁹⁾. As a result of this increased interaction, the normal monomer fluorescence spectrum is replaced by a broad structureless emission which is shifted to considerably longer wavelengths than the corresponding molecular fluorescence. This type of emission is normally referred to as 'excimer' fluorescence⁽⁹⁾ and provides evidence of an increased intermolecular interaction in the excited state. An enthalpy of dissociation of 10 K cal mole⁻¹ has been found for the pyrene excimer, for example, although Stevens and Ban⁽¹⁰⁾ have shown that the ground state of an excimer is unstable.

In addition to the spectral changes referred to above, excimer formation also leads to an increase in the radiative lifetime of the excited state. As the radiative, or fluorescence lifetime (τ_F) is exponentially dependent upon the difference ΔE in energy between the ground and excited states⁽¹¹⁾, if the net effect of an increased intermolecular interaction is to reduce ΔE ⁽¹²⁾, as it is in the case of excimer formation, this leads to an increase in τ_F . On the other hand, excimers which are unable, for steric reasons, to attain an equilibrium state with D_{2h} symmetry emit at higher frequency, and because of their disturbed symmetry, possess a higher transition moment, which causes a reduction in decay time⁽¹³⁾. Both the fluorescence spectrum and lifetime are, therefore, able to provide detailed information about molecular interaction potentials and should in principle serve as probes of the local or short range structural order within films of aromatic hydrocarbons. There are, in fact, a number of previous studies described in the literature in

which fluorescence and other optical techniques have been used to examine the structure of low temperature deposits (PCA's). Because of their relevance to the present study these will now be discussed.

3.1.3 Previous Studies of the Electronic Spectra of Thin Films of (PCA) Compounds

(i) The use of Fluorescence to study disorder in films deposited at low temperatures

Perkampus⁽¹⁴⁻¹⁶⁾, with Pohl⁽¹⁷⁻¹⁹⁾, Stichtenoth^(13,20), and Haller and Stichtenoth⁽²¹⁾ carried out what was probably the earliest systematic spectroscopic study of evaporated hydrocarbon films, between 1957 and 1974. The methods they used to prepare these films were the same as those employed in the present study and involved deposition onto substrate temperatures as low as 77K at pressure of $\sim 10^{-6}$ Torr. They were able to show that the degree of disorder incorporated into films of anthracene and perylene during growth was dependent upon the temperature of the substrate during deposition and upon subsequent annealing, both of which had a marked effect upon their fluorescence spectra and lifetimes. At low deposition temperatures (77K) the spectrum of an anthracene film is quite unlike that of single crystal anthracene. It consists of a single broad unstructured emission which is red shifted in comparison to the crystal spectrum⁽¹⁷⁾. A similar spectrum was also observed in films deposited at 203K⁽¹⁸⁾. On annealing to room temperature this broad fluorescence band is replaced by the structured fluorescence of the crystalline form.

An X-ray structure determination⁽²²⁾ of similarly prepared anthracene films showed that an amorphous, glass-like structure was

obtained at low deposition temperatures and that this transformed into a polycrystalline structure on annealing. Thus, it was inferred that the broad structureless emission observed in as-deposited films of anthracene at low substrate temperatures, originated from amorphous or glass-like regions. Many observations suggest that excimer fluorescence is emitted preferentially by lattice defects⁽¹⁵⁻²¹⁾, because at such defects, molecules may be prevented from adopting normal lattice positions, and are for steric reasons forced into a configuration similar to that observed for pyrene or perylene lattices, Figure (3.1). Thus, in 'glassy' films of anthracene, which normally crystallises with a type A lattice, the introduction of disorder is thought to result in the formation of dimeric species in the ground state in which the molecular planes are situated parallel to each other at a distance of about $3.5\text{\AA}$, which leads to a perturbation of the first excited singlet state, as it does in excimers of pyrene and perylene.

Although anthracene excimers have not been detected in solution, so called sandwich dimers of anthracene have been prepared by photolytic dissociation of dianthracene⁽²³⁾ in a matrix at 77K. Excimeric emission is observed from this dimer which corresponds to that of an anthracene film sublimed at low temperatures. However, the decay time of the excimeric emission from sandwich dimer is reported⁽³⁸⁾ to be approximately 220 nanoseconds which is about an order of magnitude longer than that observed for low temperature deposits of anthracene. Furthermore, decay time was found to be frequency dependent, which contrasts with the behaviour of monomer fluorescence from single crystal anthracene. This was taken⁽¹³⁾ as evidence that the potential energy of defect centres is distributed in disordered films,

which causes them to have different decay times. The major contribution to the total fluorescence spectrum of low temperature deposits of anthracene was thought to derive from strongly disturbed emission centres rather than from excimers of the type produced by dianthracene dissociation. Confirmation of this view was provided by a time resolved fluorescence study⁽²¹⁾ of low temperature deposits of anthracene.

A similar conclusion was derived by Müller, Bässler and Vaubel⁽²⁴⁾ in respect of tetracene films deposited at low substrate temperature. Tetracene, like anthracene, does not exhibit excimer fluorescence when in single crystal form, however, like anthracene a broad excimer-like emission was observed from tetracene films deposited at 77K. They suggested that 'the emission spectrum of tetracene films deposited at low substrate temperatures is a superposition of a large number of relatively narrow spectra, emitted by excited sandwich pairs whose molecular coordinates are subject to a statistical variation, yielding a gaussian distribution of pair binding energies in the excited state'. From the average half width of the tetracene emission (1200 cm^{-1}) they calculated that a variation of only $0.12\text{\AA}$ in the intermolecular pair distance is sufficient to account for the observed emission spectrum. However, their results did not allow them to distinguish between emission of a genuine excimer type or that originating from excited sandwich pairs forced by the surround matrix to adopt an excimer-like configuration even in the ground state. Because the rate constant for excited pair formation was low Müller et.al.⁽²⁴⁾ interpreted their results on the basis that only a certain fraction of lattice sites have a conformation allowing excimer or excited dimer formation. Energy transfer from originally

excited monomers singlet states may then be the rate determining step for excited pair formation. Maruyama et.al.⁽²⁵⁾ arrived at a similar conclusion based on the results of their absorbance and fluorescence studies on low temperature deposits of tetracene films.

Since both pyrene and perylene crystallise with a type B lattice, Figure (3.1), they exhibit excimeric emission even when deposited onto room temperature substrates. Like materials with type A crystal lattices both perylene and pyrene form glassy amorphous films when deposited at low temperatures and as expected they also exhibit excimer fluorescence. However, since the introduction of disorder causes disruption of the lattice, and introduces traps for excitons, in contrast to anthracene and tetracene, deposition of films at low temperatures should reduce the likelihood of excimer formation in type B materials rather than enhance it. Haller et.al.⁽²¹⁾ have shown in the case of pyrene that this leads to a shift of the fluorescence spectrum to lower frequencies, compared to the single crystal spectrum. Time resolved measurements established an increased intensity on the low frequency side of the instantaneous spectra. Since the decay time of monomeric pyrene emission is about 400 to 500 nanoseconds⁽²⁶⁾ and that of pyrene excimers 110-180 nanoseconds⁽²⁷⁾ the long-lasting decay processes were attributed by Haller et.al. to emission from deformed levels. Kamura et.al.⁽²⁸⁾ and Maruyama and Iwasaki⁽²⁹⁾ also observed a single broad emission band in the spectrum of perylene films deposited at 77K, which like that of pyrene was also shifted to higher frequency compared to the single crystal spectrum. Although neither group carried out a detailed study of the emission spectrum, Maruyama and Iwasaki reported weak bands on the

high frequency side of the excimer emission band which they associated with monomer fluorescence.

Low temperature deposits of pyrene and perylene thus appear similar in that disorder causes a decrease in the excimer contribution. In general, however, molecules like pyrene and perylene which exhibit excimer emission in the crystalline form are less sensitive to their immediate environment than are anthracene and tetracene. The reason being that the pair of molecules which make up an excimer are so strongly bound in the excited state that the interaction with their immediate environment provides a relatively weak perturbation⁽³⁰⁾. Despite this, fluorescence experiments do appear to provide a convenient and sensitive method of monitoring the ordering process which occurs when films deposited at low temperatures are annealed.

(ii) The effects of annealing

On annealing at room temperature, low temperature deposits of all four compounds undergo crystallisation, which is accompanied by changes in the fluorescence spectrum. The form which these changes take is determined by the type of lattice structure (A or B) adopted on crystallisation. Thus, anthracene and tetracene adopt the type A lattice; consequently on annealing the excimer-like emission observed at low temperature is replaced by the structured monomer emission of the crystalline phase. In the case of anthracene first visible signs of crystallisation begin to appear as monomer-like vibrational structure on the high frequency side of the broad excimer-like emission band, at temperatures in the vicinity of 200K⁽¹³⁾. Haller et.al.⁽²¹⁾ for example, first observed a small shoulder at $24,500\text{ cm}^{-1}$ on annealing a film of anthracene deposited at 77 K, to 193K. Changes in the time resolved spectrum, however,

only became significant on annealing to 233K, while at room temperature the total spectrum was the same as that of crystalline anthracene. Similarly, when low temperature deposits of tetracene are annealed in the vicinity of room temperature crystallisation becomes noticeable after several hours⁽²¹⁾. This is accompanied by an irreversible decrease in excimer emission intensity and the appearance of monomer emission bands. The fluorescence decay time of tetracene films was, however, found to be independent of temperature⁽²⁴⁾.

The effect of annealing on the fluorescence of low temperature deposits of both pyrene⁽²¹⁾ and perylene⁽²⁸⁾ has also been examined. Since both compounds prefer to adopt a type B lattice, changes were not as marked as for anthracene and excimer emission predominated even at room temperature. In the case of pyrene⁽²¹⁾ annealing caused a shift to higher frequency and excimer fluorescence intensity increased, which was taken as evidence for removal of lattice defects.

(iii) Absorption studies of PCA films

Electronic absorption spectroscopy has also been used to monitor the annealing process in (PCA's) deposited onto low temperature substrates^{(29), (31)}. In general, annealing causes an increase in the Davydov splitting contribution⁽²⁵⁾, which is very much reduced in films prepared at low deposition temperatures because of the effects of disorder. Since Davydov splitting is associated with the crystalline phase of materials this observation confirms the conclusions derived from fluorescence measurements, that annealing causes disordered films, obtained at low deposition temperatures, to crystallise. In the case of anthracene, a recent study⁽³²⁾ of the absorption spectra of very thin films deposited onto low temperature substrates has confirmed that the transformation from the disordered

to crystalline phase begins in the region of 190K, which agrees with the results of the fluorescence study⁽²¹⁾ mentioned earlier. A detailed investigation of the location of the onset of the transformation from the disordered to the crystalline phase, does not appear to have been carried out for tetracene, pyrene or perylene.

This brief review of earlier work clearly shows that fluorescence techniques can be used to monitor the disorder → order transformation in vacuum deposited films of (PCA) compounds. Since VBR suggested that the OST effect is associated with just such a transformation, confirmation that it occurs in the vicinity of the OST would provide strong support for their proposal. Annealing experiments have, therefore, been carried out on low temperature deposits of the four compounds mentioned, viz. anthracene, tetracene, pyrene and perylene, by monitoring changes in their fluorescent properties as a function of temperature. The results of this study will now be described.

3.2 Result of the Fluorescence Study of (PCA) Compounds

Methods of material purification are described in Appendix 1. The absence of major impurities was established by fluorescence and absorption measurements on solutions of all four compounds. Thin films were prepared inside the Oxford Instruments cryostat, as described in Section (2.3.1). Film thickness was measured by absorbance, following removal of the film by dissolution and was in most cases found to be approximately 50,000Å. Instrumental techniques are described in section (2.3.3).

3.2.1 Films of Anthracene

The fluorescence spectrum of an anthracene film deposited and measured at 77K is shown in Figure 3.2, curve (A). It consists of a single broad excimeric emission band with a peak maximum located

at 470 nm. The spectrum, changed on annealing so that by 265K, curve (B), a shoulder was observed on the high frequency side of the excimeric band, located at approximately 425 nm. Annealing to 305K produced further changes as shown by curve (C). Thus, the intensity of the 470 nm band was greatly reduced while the shoulder at 425 nm had increased in intensity and was resolved to give a peak with a maximum at 420 nm. A new peak was also observed at 442 nm in the spectrum of the film annealed at 305K. On cooling the film to 200K there was a small increase in band intensities, otherwise the spectrum was identical to curve (C). This latter spectrum resembles that of the crystalline form of anthracene, except that the shoulder at 402 nm in curve (C) was of much lower intensity than is normally observed⁽³³⁾.

The spectrum of a film deposited at a substrate temperature of 235K is shown in Figure (3.3). Curve (A) is the spectrum of the film in the as deposited state while curve (B) is a spectrum of the same film taken after annealing to 285K. Apart from a small increase in the relative intensity of the band located at 402 nm and a blue shift of 2-4 nm, both spectra are identical and moreover are very similar to that obtained for crystalline anthracene.

Changes in the relative peak intensities of the 425 nm and 470 nm bands were monitored during the annealing process, between 77K and 305K. The results are shown in Figure (3.4). Changes in the peak intensity of the 470 nm band was monitored at two different annealing rates of 2K min^{-1} (Curve (A)) and 4K min^{-1} , (curve (B)) respectively. Relative intensities are plotted in arbitrary units. In both cases the 470 nm band, exhibited similar behaviour, decreasing

Anthracene Films

Figure 3.2. Changes in the fluorescence spectrum of an anthracene film deposited at 77K (Curve A), annealed to 265K and measured (Curve B) and then annealed to 305K and measured (Curve C).

Figure 3.3. The spectrum of a film deposited at 235K and measured (Curve A) then subsequently annealed at 285K (Curve B).

Figure 3.4. Changes in the fluorescence intensity of films deposited at 77K as a function of annealing temperature.

Curve (A) and (B). The intensity at peak maximum for the band initially located at 470 nm. Annealing rate 2K min^{-1} and 4K min^{-1} , respectively.

Curves (C) and (D) The intensity at the peak maximum for the band initially located at 425 nm and then annealed at 2K min^{-1} and 4K min^{-1} , respectively.

Figure 3.5. The effect of annealing upon the fluorescence lifetime (nanoseconds) of a film deposited at 10K.

FIGURE 3.2

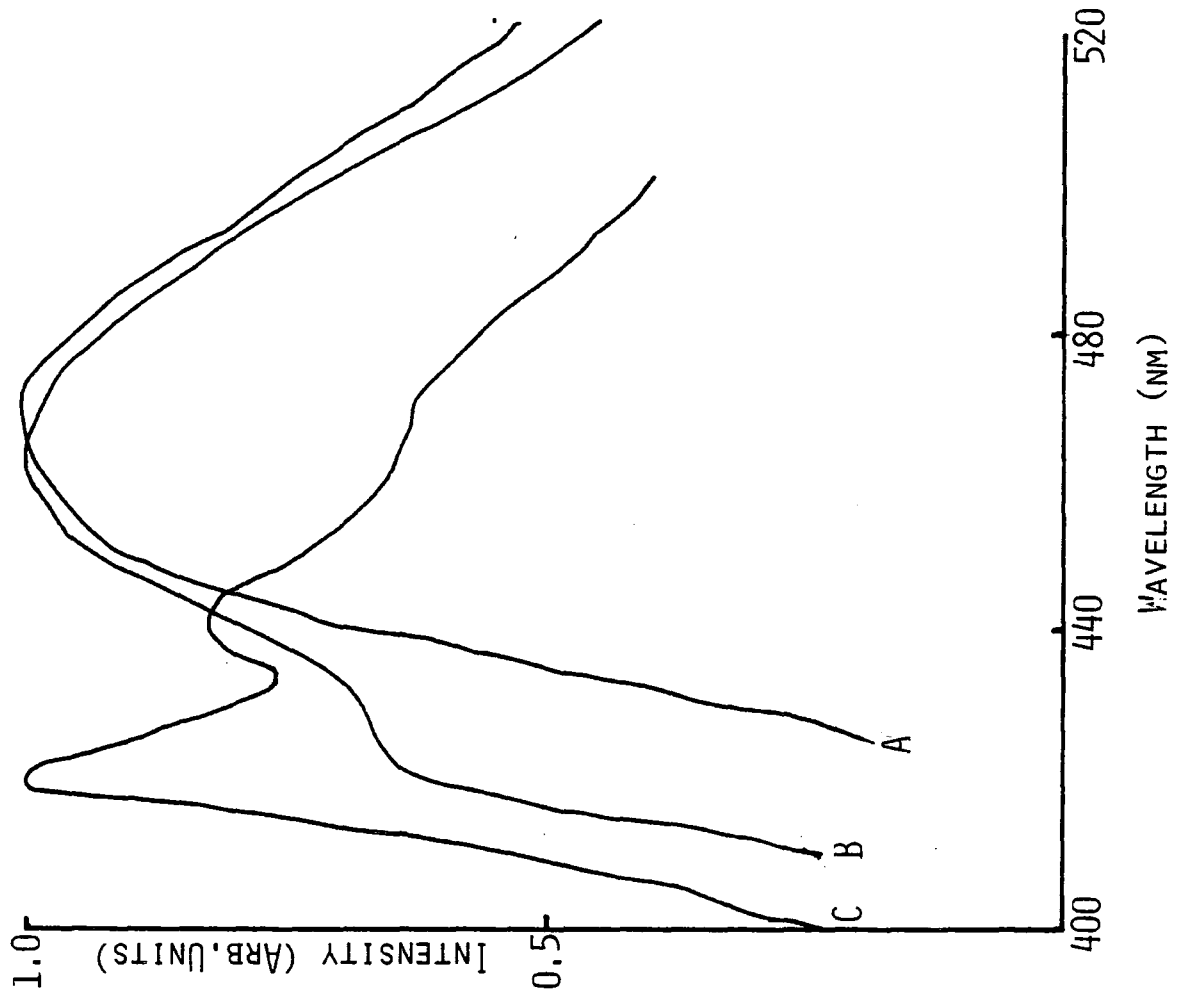


FIGURE 3.3

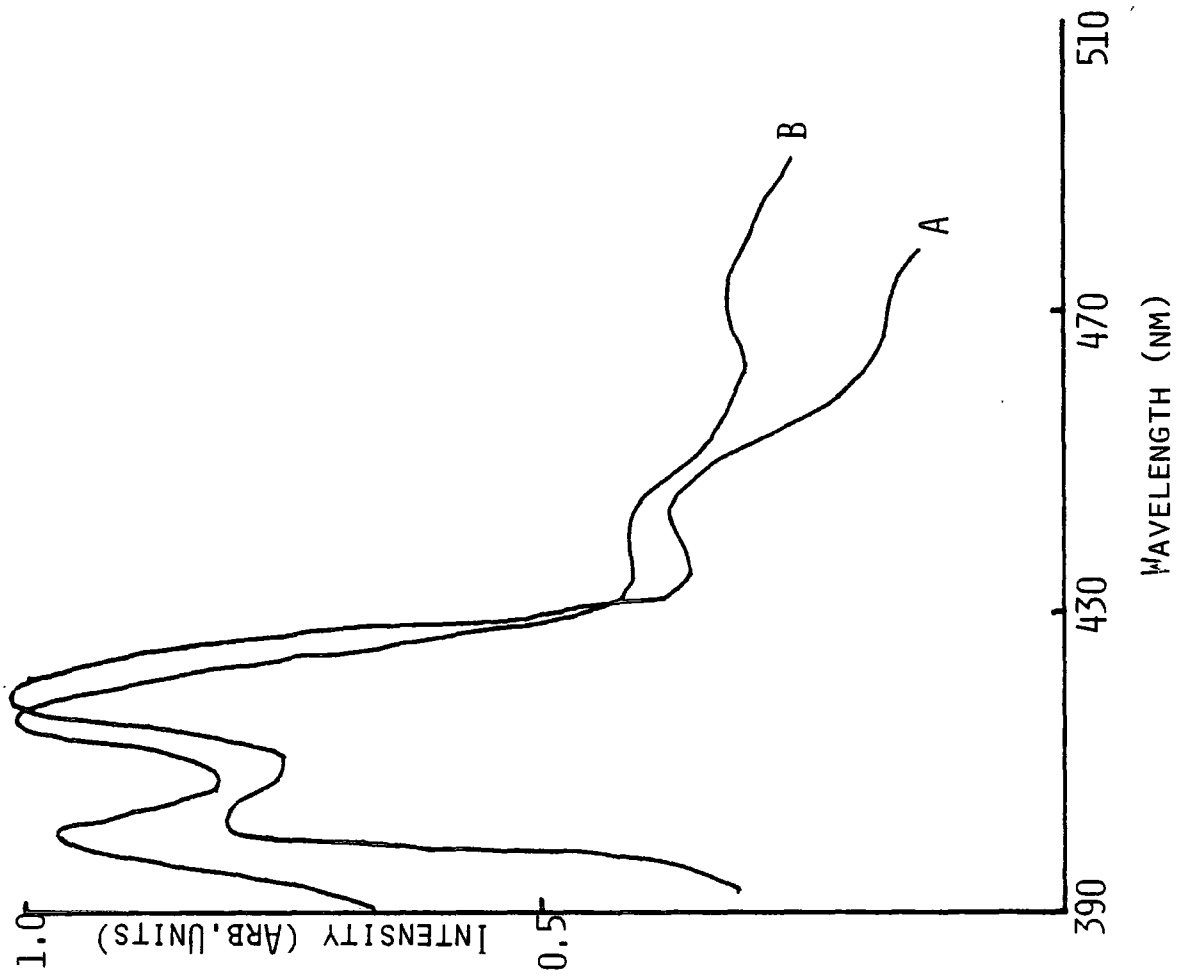


FIGURE 3.4

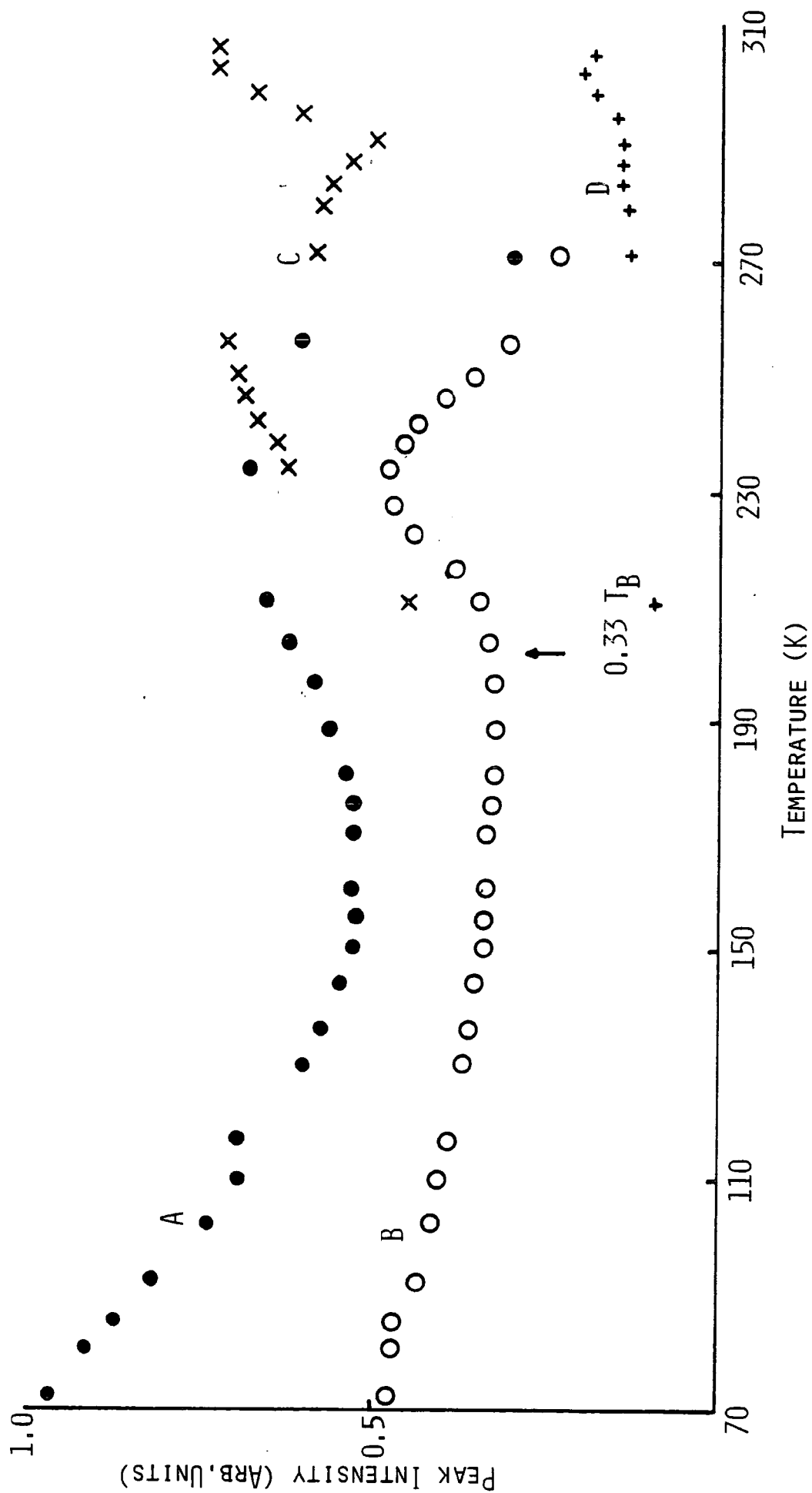
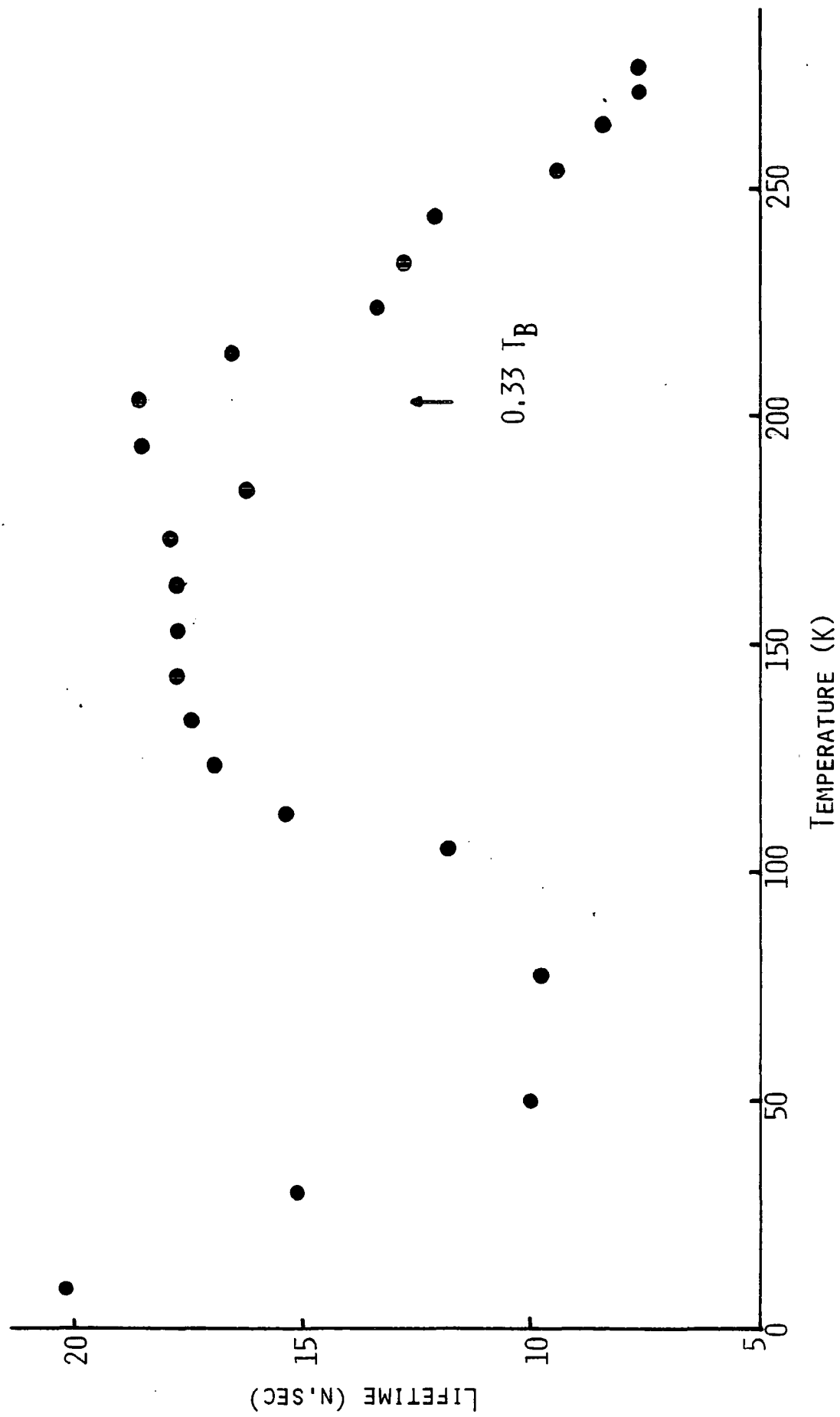


FIGURE 3.5



at low temperatures and then increasing to a maximum in the vicinity of 230K, before decreasing again between 230K and 270K. Annealing at the lower rate (2K min^{-1}) resulted in a much broader intensity maximum than was the case for the film annealed at 4K min^{-1} . The intensity of the 425 nm band only became significant above 200K. In the case of the film heated at 2K min^{-1} two maxima were observed at 255K and 305K. The intensity of the 425 nm band was not monitored between 210K and 270K in the case of the film annealed at 4K min^{-1} , although a small peak in intensity was observed at 302K, curve (D).

The annealing process was also monitored by measuring the change in fluorescence lifetime (τ_F) as a function of temperature. The results shown in Figure (3.5) were obtained from a film of anthracene deposited at a substrate temperature of 10K. Between 10K and 50K τ_F fell by a factor of two and then increased again to a broad maximum between 125K and 175K. A small decrease in τ_F above 175K was followed by a second maximum at 200K. Above 200K τ_F dropped sharply to a value of 5.5 n.secs, which is close to that of crystalline anthracene. The decrease in τ_F above 200K coincided with the increase in intensity of the 470 nm band which was mentioned earlier.

3.2.2 Films of Pyrene

As with anthracene, the spectrum of pyrene films deposited at low temperatures (77K) consisted of a single broad excimeric emission located at approximately 475 nm. The spectrum of a film deposited at 77K is shown in Figure (3.6). Curve (A) is the spectrum of the film in the as-deposited state and curve (B) that obtained after annealing to 245K. The band maximum was blue shifted to 460 nm on

annealing. Figure (3.7) shows the spectrum of a film deposited at 200K, curve (A) and then annealed to 280K, curve (B). Although the emission is still excimeric in character a shoulder had developed at 420 nm and a further blue shift of the peak maximum to 446 nm was apparent when compared to the 77K deposit, although the band intensity remained almost unchanged between 200K and 280K as shown by curve (C) in Figure (3.8).

Figure (3.8) contains annealing data for three films deposited at 10K, curve (A), 77K, curve (B) and 200K (curve (C)). The decrease in intensity between 20K and 50K which was observed when the film deposited at 10K was annealed was irreversible. Only a small intensity change was recorded on cooling the sample down again after annealing to 50K. Between 80K and 175K the relative intensity remained approximately constant for both the 10K and 77K deposits. Above 175K, however, the fluorescence intensity of former dropped away rapidly while that of the latter showed a marked increase, reaching a maximum at about 200K and then decreasing smoothly to room temperature. As mentioned above the intensity of fluorescence from the 200K deposit changed very little on annealing.

The apparent difference between the annealing curves of the 10K and 77K deposits above 175K was partly resolved by plotting the total area under the excimeric emission band as a function of temperature for both films. The results are shown in Figure (3.9). In both cases intensity decreases rapidly above 200K although the position of the high temperature peak maxima differ by about 25K. It is possible that this difference was due to the fact that the 10K deposit was

Pyrene Films

Figure 3.6. The effect of annealing upon the emission spectrum of a pyrene film deposited at 77K (Curve A). Curve (B) is the spectrum of the same film after annealing to 245K and recorded at this temperature.

Figure 3.7. The effect of annealing upon the emission spectrum of a pyrene film deposited at 200K (Curve A). Curve (B) is the spectrum of the same film recorded after annealing to 280K.

Figure 3.8. The change in intensity at the peak maximum as a function of annealing temperature for three films deposited at: 10K (Curve A), 77K (Curve B), and 200K (Curve C), respectively.

Figure 3.9. The change in total emission intensity as a function of annealing temperature for two films deposited at 10K (Curve A) and 77K (Curve B).

Figure 3.10. Simultaneous measurement of the change in fluorescence intensity (Curve A) and lifetime (Curve B) during annealing of a film deposited at 10K.

FIGURE 3.6

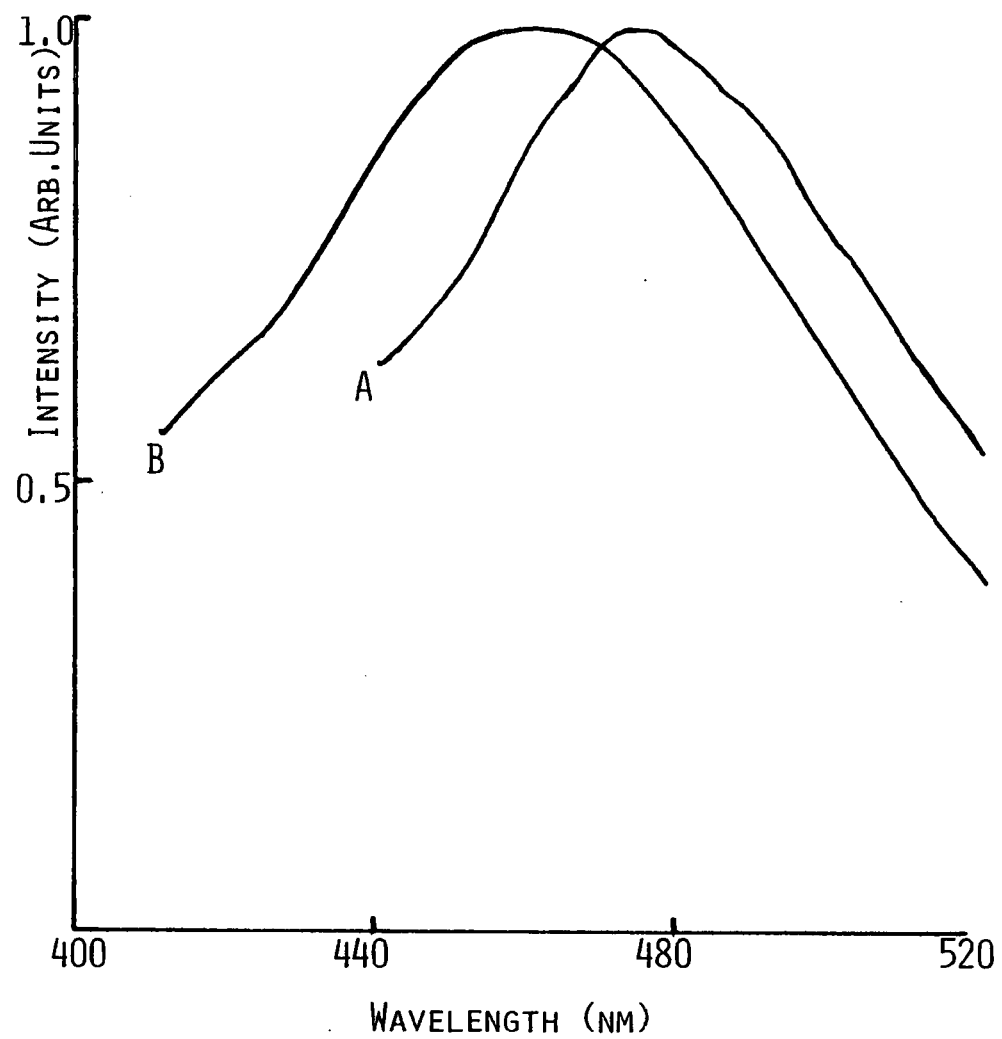


FIGURE 3.7

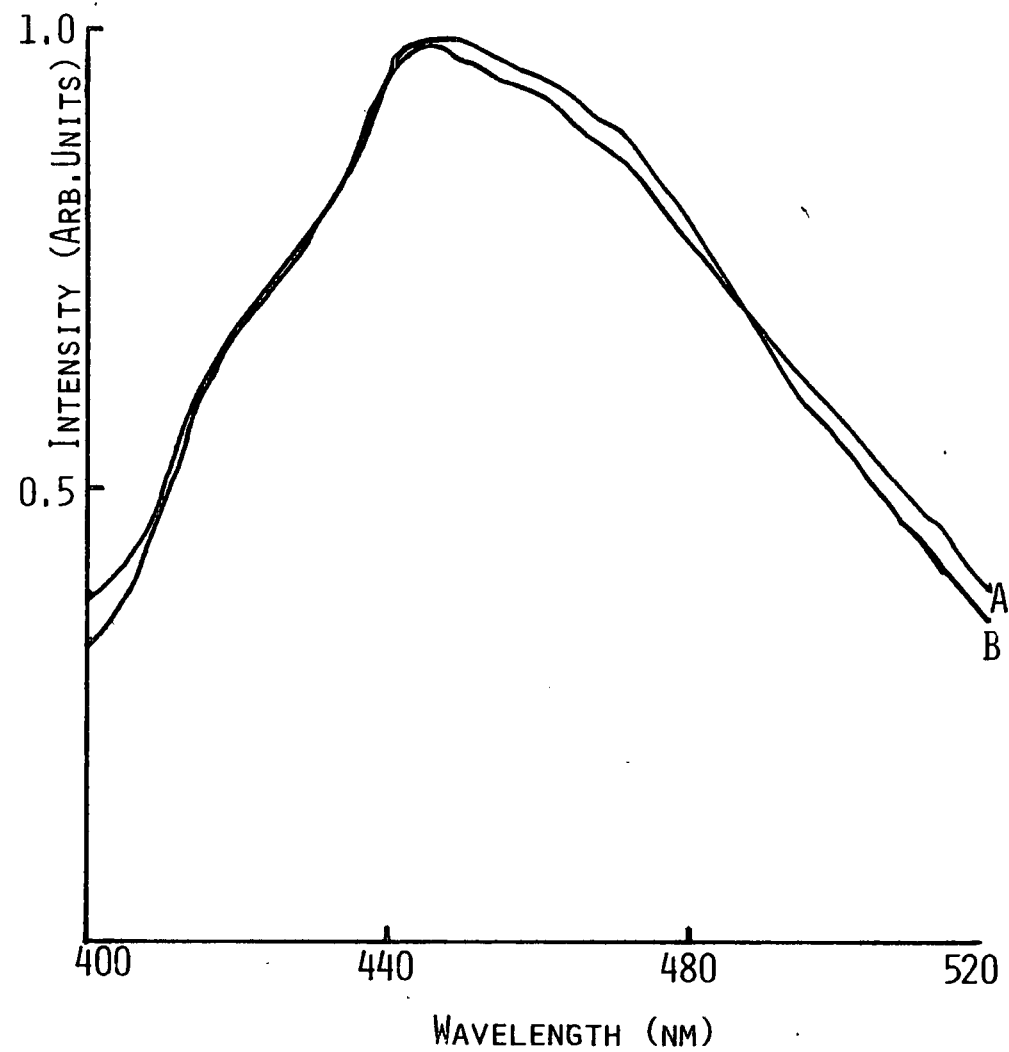


FIGURE 3.8

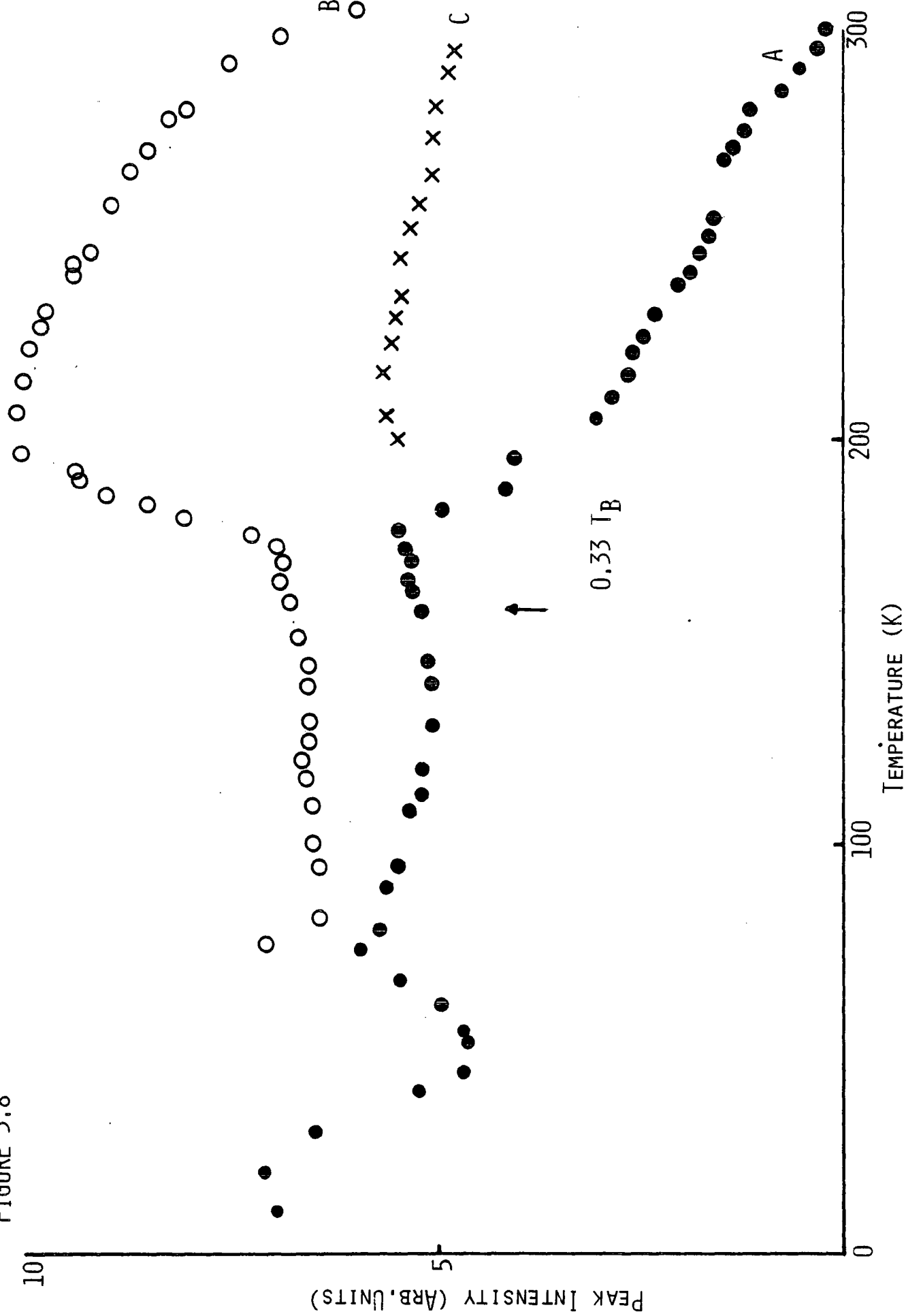


FIGURE 3.9

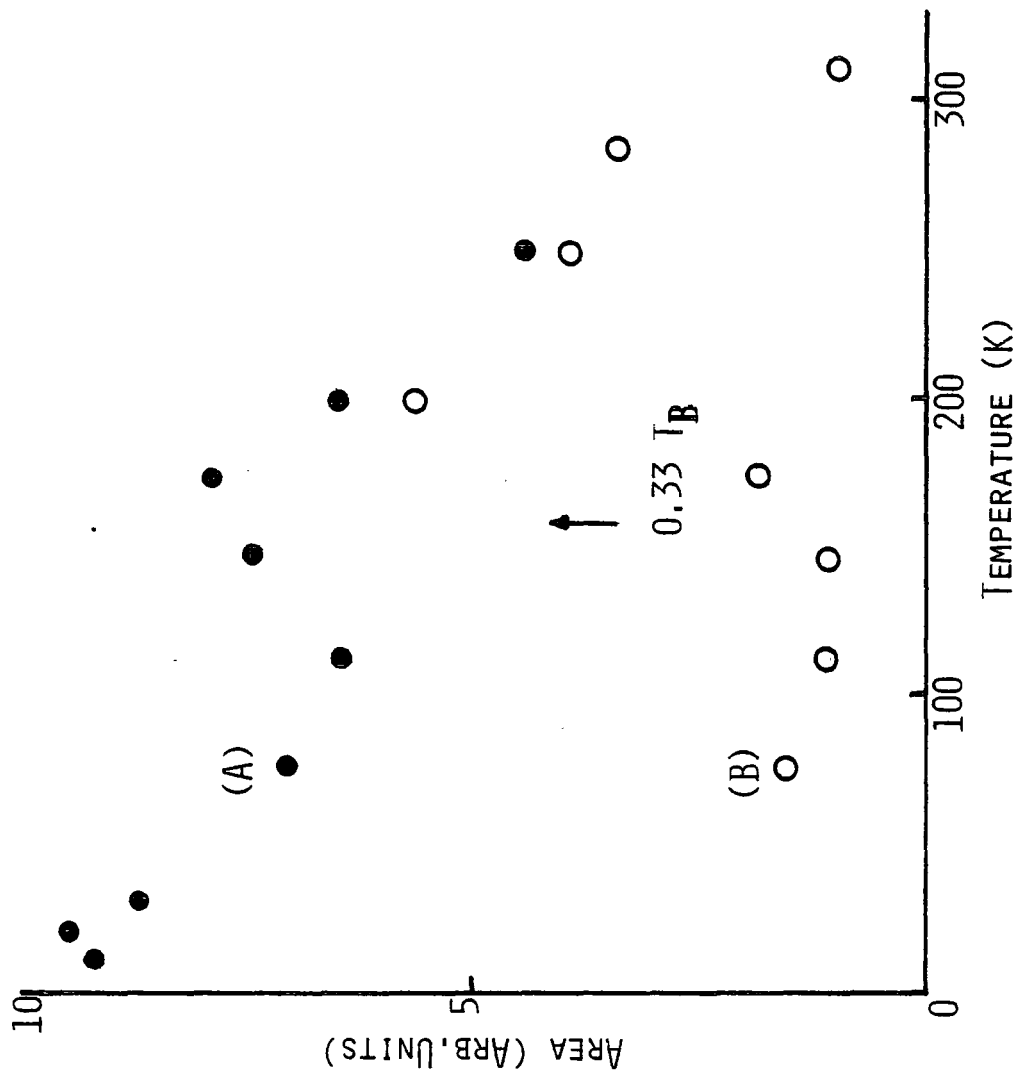
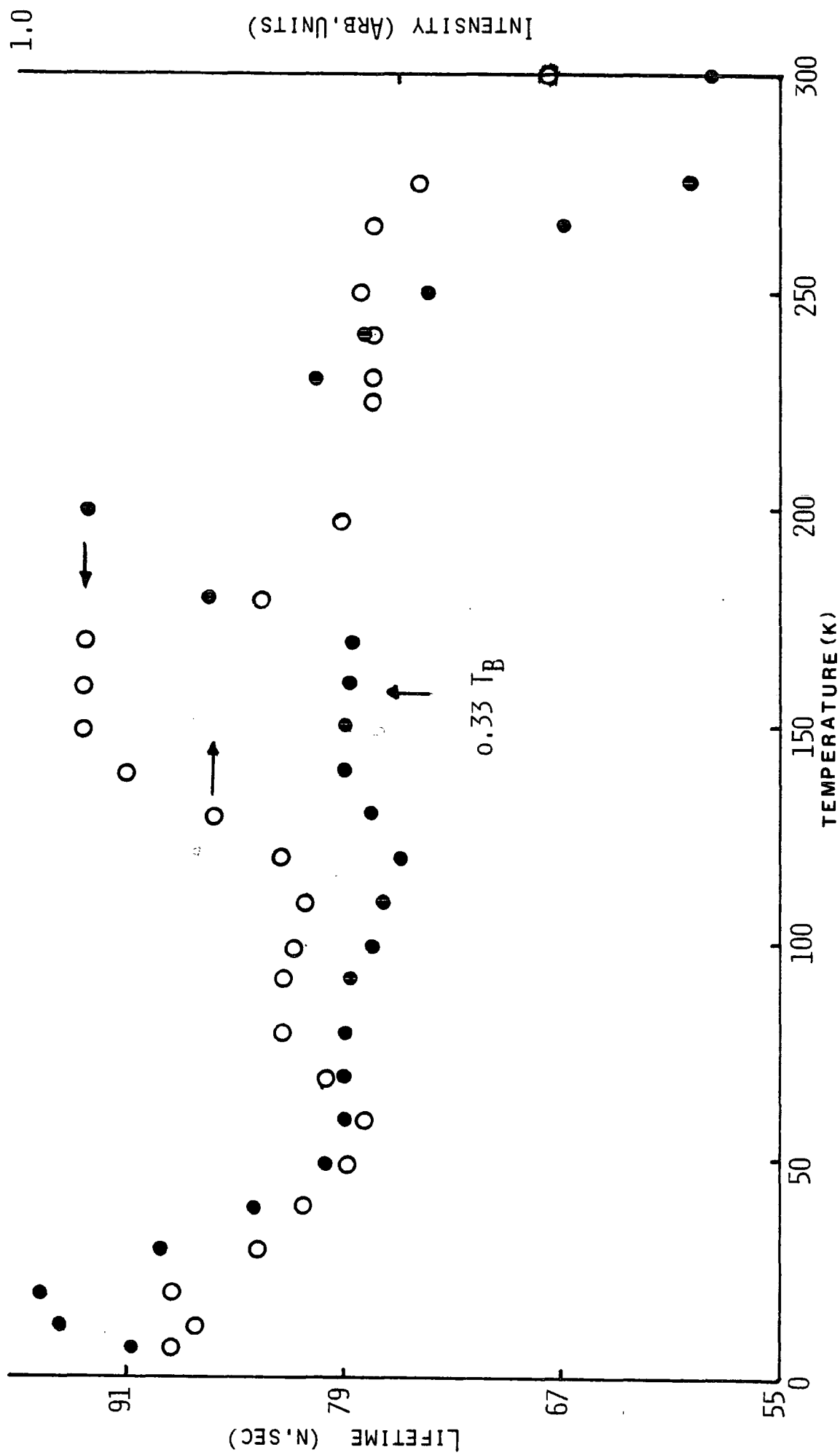


FIGURE 3.10



annealed at 2K.min^{-1} , compared to 4K.min^{-1} for the 77K deposit. However, measurements of fluorescence intensity carried out using the TRW decay time fluorometer suggest this is not the case.

Since the maximum of the time dependent fluorescence decay curve is proportional to the measured intensity for a given excitation frequency it also was used to monitor changes in intensity which occurred on annealing, while simultaneously measuring fluorescence lifetime. The results are shown in Figure (3.10) curves (a) and (b), respectively. As before the measured intensity is a maximum between 150K and 175K and decreases, although not monotonically, above this temperature. At each point on the curve the intensity was measured at constant temperature, thus, it appears that heating rate is not responsible for the difference in location of the two maxima in Figure (38).

As with anthracene the position of the high temperature maxima of the intensity and lifetime curves are located at different temperatures, the latter occurring at 200K and the former at about 160K. A second maximum was observed in the fluorescence lifetime curve at 25K with weaker ones located at 85K and 150K, both of which coincided approximately with maxima in the intensity curve.

3.2.3 Films of Perylene

As with pyrene the fluorescence spectrum of perylene films deposited at 77K consisted of a single broad excimeric band located at 557 nm, as shown in Figure (3.11), curve (A). A small red shift (6 nm) was observed on annealing to 260K, curve (B) and fine structure was apparent in the vicinity of the peak maximum. Otherwise both spectra were very similar. As Figure (3.12), curve (A) shows, the broad excimer emission also dominates the spectrum of a film deposited at 240K, although the peak maximum was located at

Perylene Films

Figure 3.11. Changes in the fluorescence spectrum of a film of perylene deposited at 77K (Curve A) and subsequently annealed and measured at 260K (Curve B).

Figure 3.12. Changes in the fluorescence spectrum of a film deposited at 240K (Curve A), annealed to 300K and recorded (Curve B) and then cooled to 77K and recorded.

Figure 3.13. The effect of annealing upon the peak intensity of the excimer emission band for three films of perylene. Curves A and B; Deposited at 77K and annealed at 2K and 4K min⁻¹, respectively. Curve C; Deposited at 240K.

Tetracene Films

Figure 3.14. The effect of annealing upon the fluorescence spectrum of a tetracene film deposited and recorded at 77K (Curve B), after annealing and recording at 298K (Curve B) after recooling and recording at 77K (Curve C).

Figure 3.15. The shift in frequency (at the peak maximum) of the excimer emission from a film deposited at 77K, as a function of annealing temperature.

Figure 3.16. The change in peak intensity of excimer emission from two films of tetracene deposited at 77K and annealed at 2K min⁻¹ (Curve A) and 4K min⁻¹ (Curve B), respectively.

FIGURE 3.11

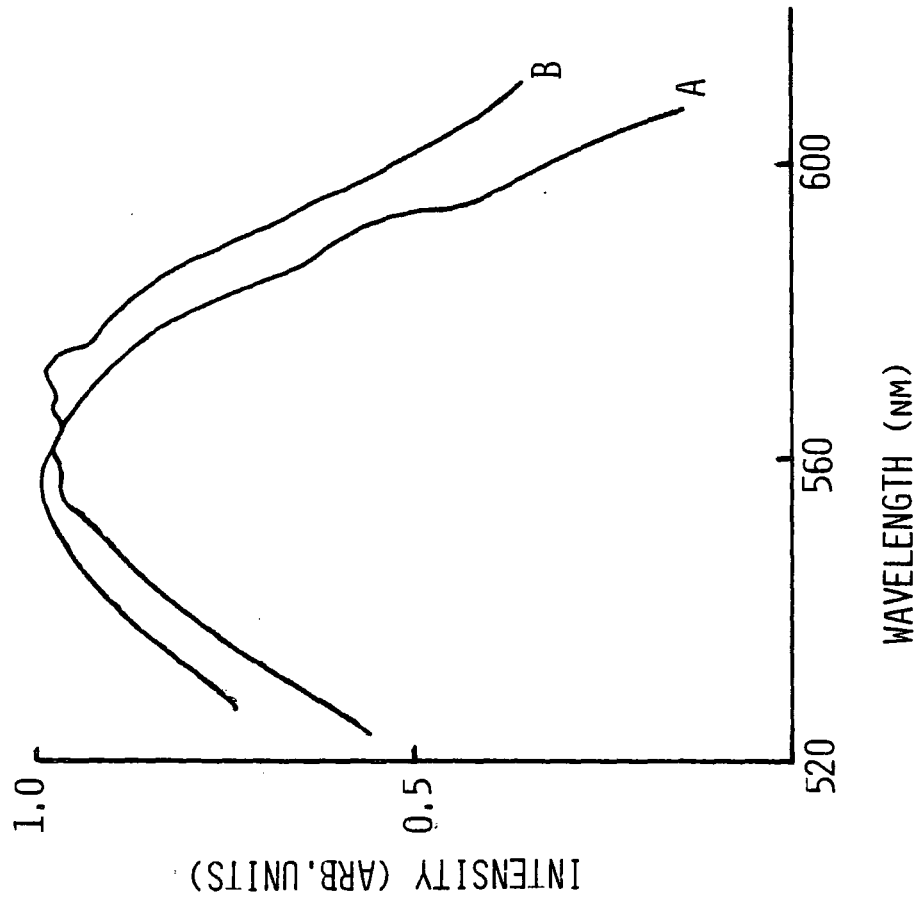


FIGURE 3.12

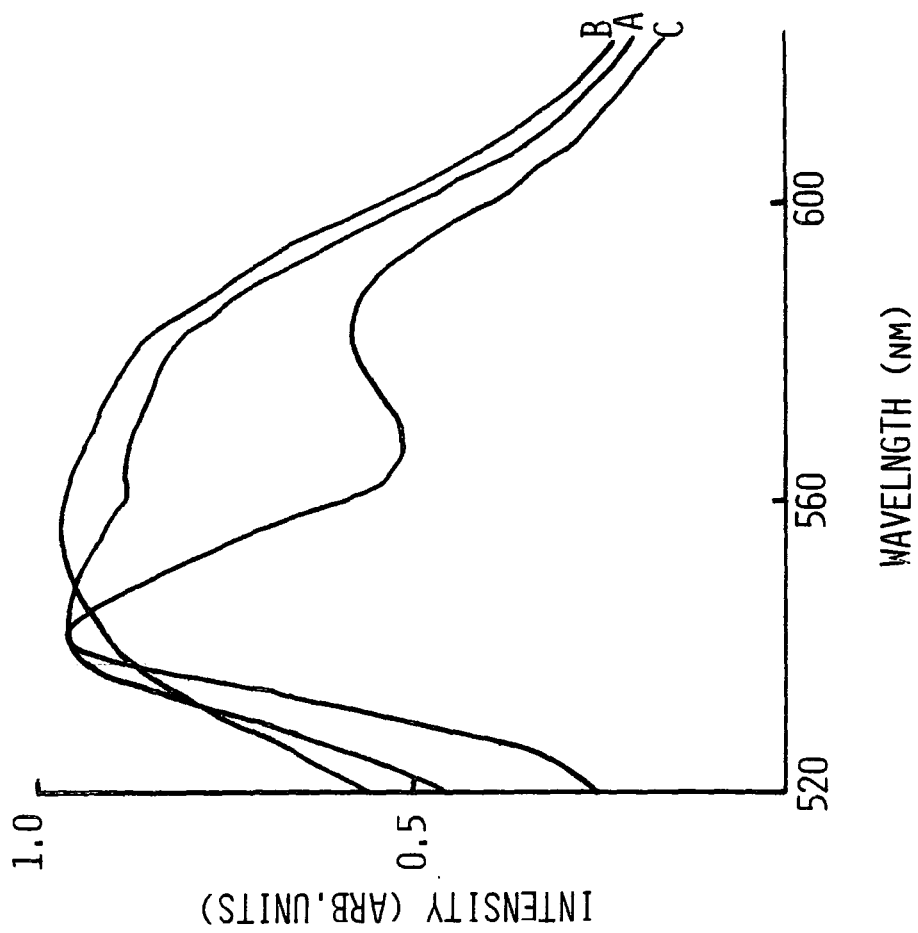
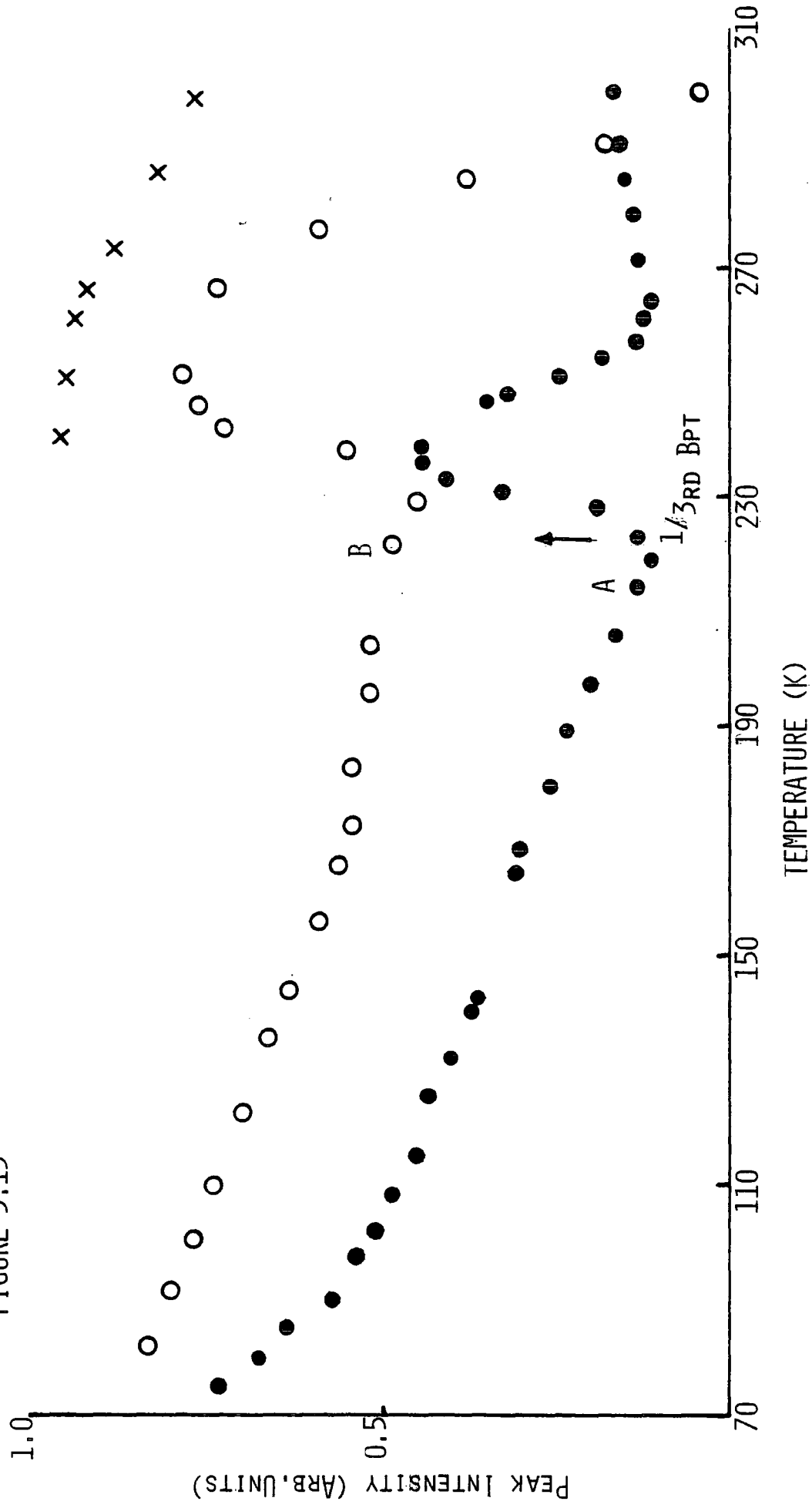


FIGURE 3.13



540 nm with a shoulder visible at about 570 nm. On annealing to 300K the shoulder increased in intensity which resulted in the formation of a single broad band and the peak maximum was shifted to 552K as shown in curve (B). This was accompanied by a small increase in band width. However, as curve (C) shows, on cooling the annealed film to 77K the single broad emission previously observed was resolved into two peaks located at 540 nm and 580 nm, with the intensity of the latter decreasing relative to the former with decreasing temperature. A threefold increase in intensity of the 540 nm band was observed on cooling between 300K and 77K.

Changes in peak intensity of the excimer band which occurred as a result of annealing are recorded in Figure (3.13). Curves (A) and (B) were obtained from films deposited at 77K and annealed at 2K and 4K per minute, respectively. Curve (C) is the annealing curve for the 240K deposit. Both films deposited at 77K exhibited similar annealing behaviour, i.e. a monotonic decrease in intensity between 77K and 200K, followed by a pronounced increase in intensity to a peak at 236K (2K min⁻¹) and 250K (4K min⁻¹). The intensity then fell sharply, although in the former case it increased again slightly above 270K. In the case of the 240K deposit the peak intensity of the excimer band had decreased to about $\frac{3}{4}$ of its original value by room temperature.

3.2.4 Films of Tetracene

The spectrum of tetracene films deposited at 77K also consisted of a single broad featureless excimeric emission band centred at 590 nm and shown as curve (A) in Figure (3.14). On heating to room temperature the intensity change recorded in Figure (3.16) was observed for two films annealed at 2K min⁻¹, curve (A) and 4K min⁻¹,

FIGURE 3.14

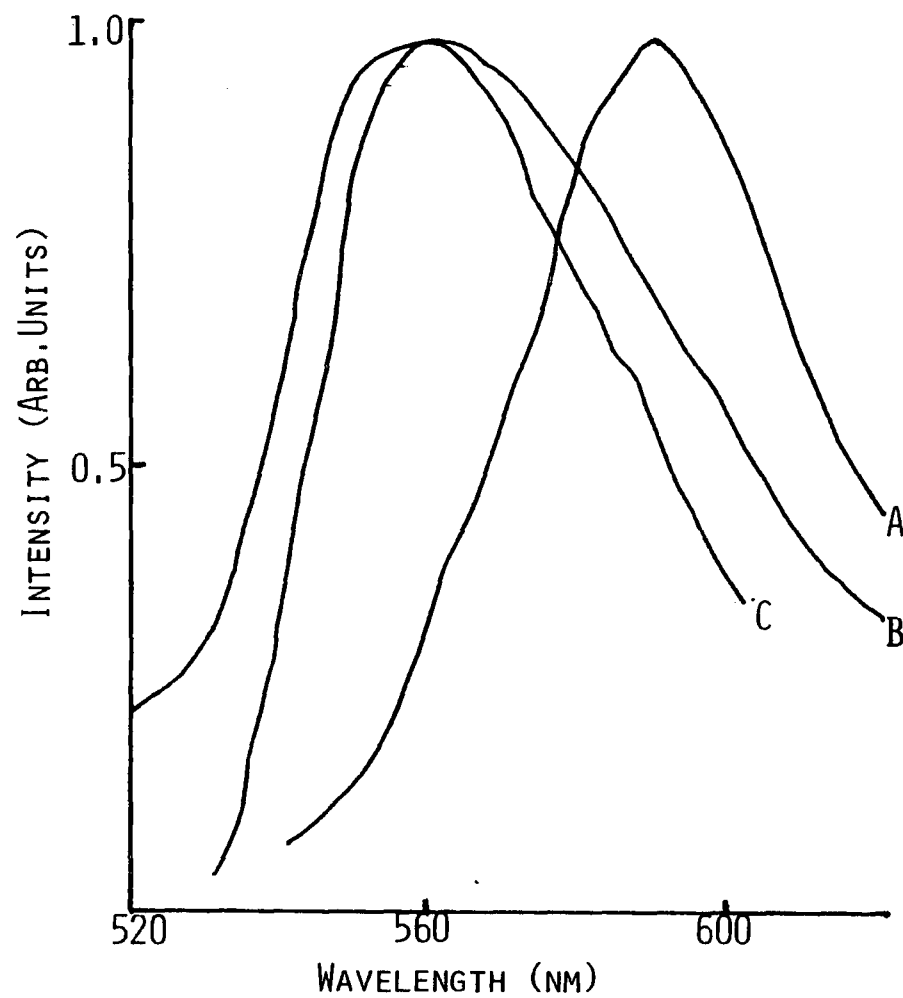
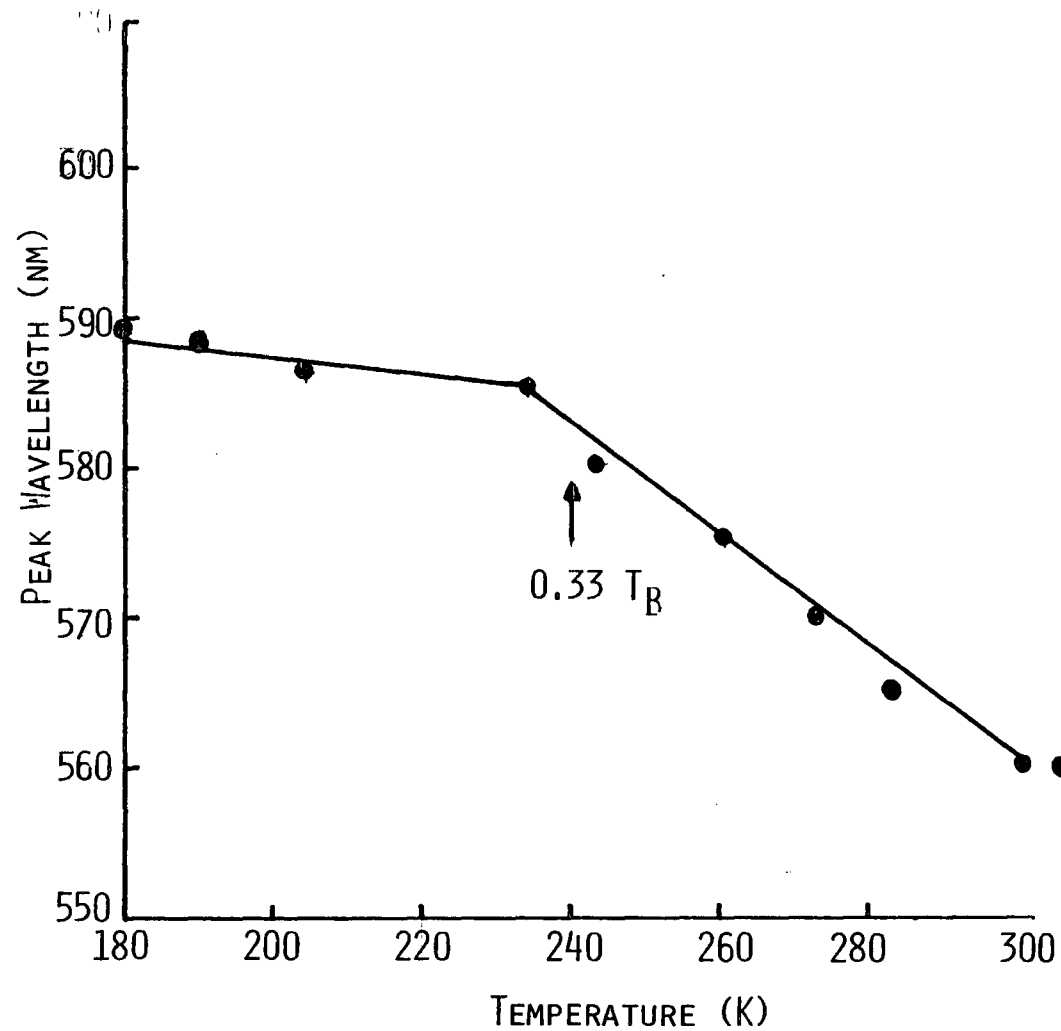
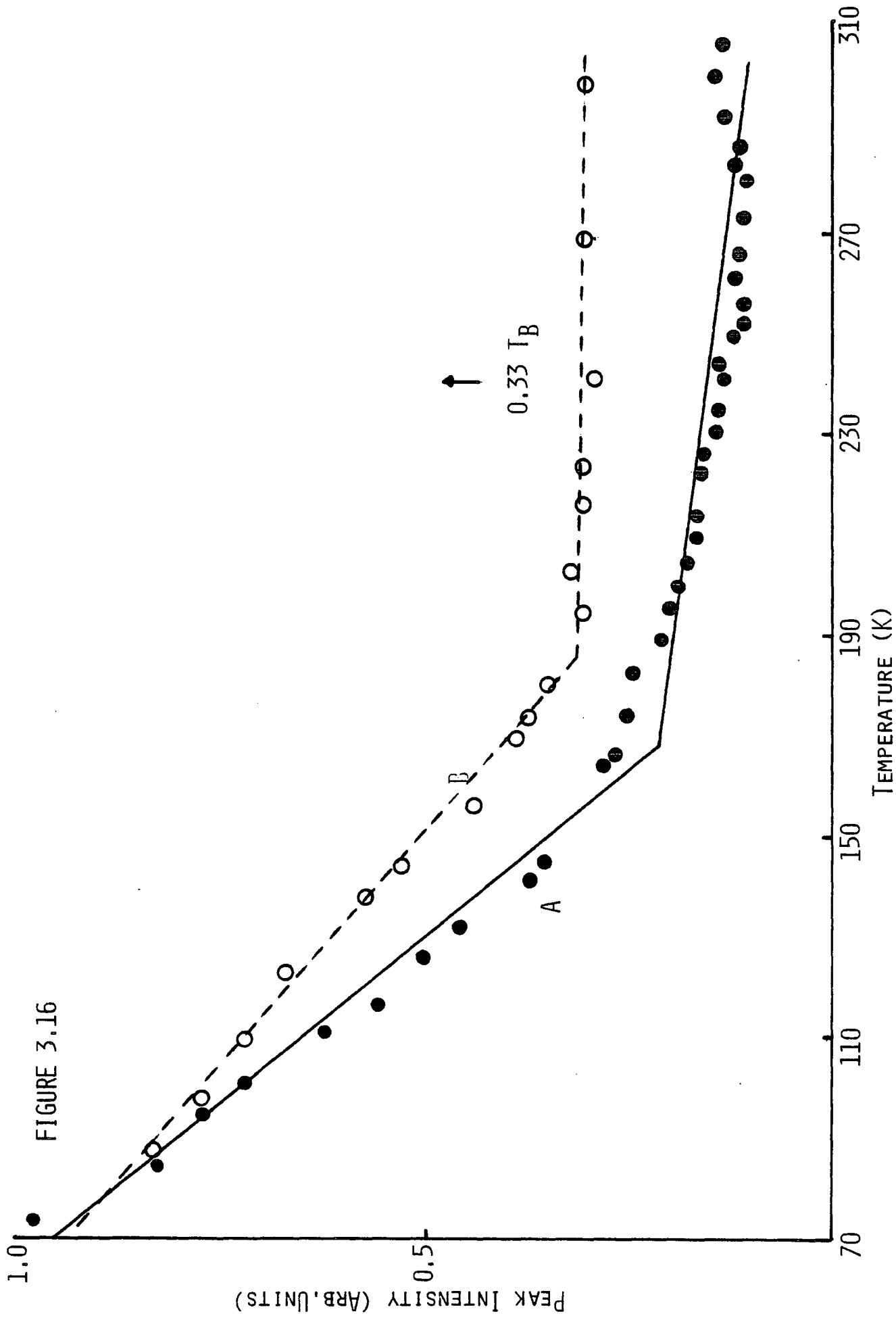


FIGURE 3.15





curve (B). This change in intensity was accompanied by a shift in the peak maximum to the blue which first began to occur at about 190K and then accelerated above 234K as shown by the data in Figure (3.15). At 298K the peak maximum had blue shifted to 560 nm as shown by spectrum (B) in Figure (3.14). On cooling the annealed film to 77K the original intensity was restored, however, the shift in band frequency observed on annealing was irreversible as shown by spectrum (C) in Figure (3.14), which although much narrower than spectrum (b) still has a maximum located at 560 nm. The solid lines drawn through the experimental points in Figures (3.15) and (3.16) are included simply to indicate that a change in rate has occurred.

3.3 Discussion

3.3.1 The OST effect in films of Polycyclic Aromatic Compounds

The observation of a peak in the emission intensity from excimer-like centres, during the annealing of low temperature deposits of; anthracene, perylene and pyrene, has important implications for the optimum substrate temperature effect. On comparing the curves in Figures (3.4), (3.8) and (3.13) with the physical data listed in Table 1, column 6, it is clear that for all three compounds the excimer emission intensity first began to increase at temperatures that correspond closely to their respective OST's ($0.33 T_B$). This apparent correlation between excimer emission intensity and annealing temperature is remarkable because as will now be discussed, it provides strong evidence for the existence of a metastable state, intermediate in stability between the disordered and crystalline state in the vicinity of the OST, for these three materials. In

order to understand why it is that fluorescence intensity goes through a maximum on annealing, it is necessary to consider how disorder is introduced into films during deposition at low temperatures.

(i) The Formation of Disordered Films at Low Deposition Temperatures

In the gas phase, molecules are able to rotate freely about all three of their principle axes at all reasonable temperatures. However, when a large anisotropic molecule such as anthracene impinges onto a surface, or is incorporated as part of a condensed phase, interaction with the surface or surrounding molecules causes a decrease in its rate of rotation. In general the rate of rotation about each of its three principle axes is different and varies with temperature, according to an equation of the form

$$r_{\text{rot}} = \frac{1}{\tau_{\text{rot}}} = \nu_0 \exp \frac{-E_{\text{rot}}}{kT}$$

Where E_{rot} is an activation energy associated with rotation about one of the molecular axis, ν_0 is the rotation frequency of the molecule in the condensed phase as $\frac{1}{T} \rightarrow 0$ and τ_{rot} is a relaxation time for rotation.

Molecules impinging onto a surface from the gas phase, unless reflected, are known⁽³⁴⁾ to lose their excess kinetic very rapidly and equilibrate within the timescale of a few lattice vibrations. ($\sim 10^{-13}$ sec). Thus, after impingement the rotation rate of molecules about each of their three principle axes is a function of substrate temperature, rather than their kinetic energy prior to impingement.

As in the crystal the activation energy for rotation about each axis will, in general, be different even for an isolated anisotropic

ad-molecule because its potential energy is determined by its orientation relative to the surface. Numerous studies have shown that large planar aromatic molecules adopt an orientation in which their plane is parallel to the surface when deposited at low substrate temperatures. Seki and Itoh⁽³²⁾, for example, have demonstrated that this type of orientation is adopted by anthracene molecules even when deposited onto substrate temperatures at 7K. Quateryllene⁽³⁶⁾ and phthalocyanines⁽³⁷⁾ give a parallel orientation at room temperature. At higher substrate temperatures even large molecules, for example quateryllene (300°C), are able to adopt a perpendicular orientation which usually results in a parallel alignment of the ab plane of crystallites relative to the surface. The substrate temperature at which the transition from an in-plane to out-of-plane orientation occurs, will of course depend upon the magnitude of the anisotropic molecule/surface interaction potential relative to kT . The influence of substrate temperature on crystallite orientation in vacuum deposited films is discussed in more detail in Chapter 4.

Since our study of PCA's is primarily concerned with the annealing behaviour of films deposited at 77K or less, on the basis of what has been said, it is reasonable to assume that such films initially contain a large proportion of molecules oriented parallel to the surface, in the as-deposited state. Furthermore, molecules which subsequently impinge onto a layer oriented in this way should also preferentially adopt a parallel configuration; so that deposition at low temperatures facilitates an out-of-plane interaction between adjacent layers of molecules, which is, of course, the main requirement for excimeric emission in the excited state. Thus, it is possible to understand why even in the absence of molecular rotation films of

molecules such as anthracene and tetracene, which prefer to adopt an A-type crystalline lattice, should exhibit excimer emission when prepared at low deposition temperatures. Pyrene and perylene, of course, stack as dimers in single crystals so that it is hardly surprising that they prefer to stack in this way in films formed at low temperatures. Clearly not all molecules will lie flat on the surface after impingement, some will be forced to adopt out-of-plane orientations. Fryer's⁽³⁷⁾ high resolution electron microscopy studies of phthalocyanines and the work by Seki and Itoh⁽³²⁾ on low temperature deposits of anthracene does, however, confirm that a large proportion of molecules have a parallel orientation.

Transforming a film in which molecules are initially lying flat on the surface, to give one of the two structure types shown in Figure (3.1) requires considerable molecular re-organisation, particularly for type A and B, lattices. Although, as discussed in Chapter 6, the axis perpendicular to the molecular plane is normally the easy axis of rotation in crystalline (PCA's), the fact that there is a good correlation between the predicted OST and the temperature at which excimer emission intensity increases, implies a redistribution of the bonding between molecules and not just re-orientation about a single axis. Molecular rotation is of course a necessary prerequisite for such a re-organisation and the lack of rotation in condensates produced at low deposition temperatures is undoubtedly the main cause of disorder. However, the present annealing experiments and those of others indicate that despite evidence for substantial molecular motion in PCA deposits, crystallisation does not begin to occur in earnest until near room temperature, which raises the question;

if molecular diffusion is possible why is it that nucleation of the crystalline phase does not occur at low temperatures? In answering this question it is important to realise that in addition to the kinetic barrier associated with molecular motion, the ordering process requires a change in the molecular configuration, which may involve an increase in the repulsive part of the interaction potential and lead to the formation of a metastable state.

(ii) The Metastable State in (PCA) Condensates

As discussed in Chapter 6, if a film deposited at low substrate temperatures is initially disordered or amorphous, and contains no nuclei of the crystalline phase then the disorder $\rightarrow$ crystalline transformation must proceed via states of intermediate thermodynamic stability⁽³⁹⁾; short range order must be established before crystallisation can proceed. The disorder $\rightarrow$ crystalline transformation is, therefore, envisaged as proceeding via a two step mechanism involving:-

- a) the establishment of short range order over a relatively small distance about the size of the unit cell.
- b) Nucleation of the crystalline phase within this intermediate phase.

In the absence of nucleation the intermediate phase is thermodynamically metastable and, as will be shown in Chapter 6, is able to exist over a surprisingly wide temperature range. It is proposed that the transient increase in excimer emission which occurred in the vicinity of the OST in pyrene, perylene and anthracene is associated with the formation of this metastable state. Evidence consistent with this proposal will now be reviewed in respect of each of the five aromatic hydrocarbons studied.

Anthracene Films

Although no attempt was made to locate precisely the maximum substrate temperature at which the disordered phase of anthracene is first observed in as-deposited films, this should be possible in principle since the observation of excimer fluorescence apparently provides a sensitive indicator of the onset of disorder. However, on comparing the present results with the electroabsorbance measurements^{(2), (3)} of VBR a link between the disorder $\rightarrow$ order transformation, as monitored by changes in the fluorescence spectra of films, and the OST effect in anthracene is readily established. Thus, the pronounced decrease in the intensity of the electroabsorbance band (403 nm) which VBR assigned to the disordered phase of anthracene was in the present case paralleled by a change from an excimer-like to monomer-like fluorescence specimen for two films deposited at 190K and 235K, respectively.

The spectra in Figure (3.2) show that anthracene films deposited at 77K, curve (A), are still highly disordered even after annealing to 265K, curve (b), and that the broad excimeric emission characteristic of the disordered state of anthracene is not reduced significantly until annealing is carried out in the vicinity of room temperature. It is suggested, therefore, that the rate of crystallisation remains low even after annealing to temperatures appreciably higher than those needed to produce the crystalline phase during deposition i.e. 235K (see Figure (3.3)).

The 'sandwich dimer' of anthracene is inherently unstable in the ground state and if permitted by the surrounding matrix to undergo relaxation⁽⁴⁰⁾, it loses its 'sandwich' configuration. In

fact, Morris⁽⁴¹⁾ has shown that atom-atom potential calculations incorrectly predict that the 'sandwich' configuration is the most stable form of the anthracene dimer. The repulsive interaction, which is dominated by the quadrupole-quadrupole term, determines the structure of the dimer. The most stable configuration appears to be one in which the long axes of a pair of anthracene molecules are approximately parallel but the in-plane short axes are inclined at an angle of 55° to each other, hence the term 55° dimer (or stable dimer).

It is suggested that films deposited at 77K contain a substantial proportion of dimers which do not have a sandwich configuration and may, therefore, be 55° dimers. As Figure (3.2) shows, only a small blueshift occurred on annealing the 77K deposit to 265K, whereas, intensity Figure (3.4) and lifetime Figure (3.5), measurements provide evidence of marked irreversible changes occurring within the film during annealing. Furthermore, the excimer-like band peaked at 470 nm in the 77K deposit, which represents a blue shift of ~ 100 nm compared to the emission from anthracene sandwich dimers produced by photolysis of dianthracene. This and the short lifetime suggests that sandwich dimers, if present at 77K, are strongly perturbed.

If the initial decrease in fluorescence lifetime observed on annealing a film deposited at 10K, Figure (3.5), is associated with dissociation of sandwich dimers into monomers then it is possible to account for the increase in lifetime between 75K and 150K as being due to the formation of stable dimers, as proposed by Seki and Itoh⁽³²⁾. However, the rapid decrease in lifetime above 200K coincides with an increase in the intensity of the band at 425 nm previously assigned

to the 55° dimer, which peaks at about 256K. Since a further increase in 55° dimer concentration should have resulted, in either no change, or an increase in fluorescence lifetime, these results do not appear to be consistent.

A reasonable explanation of these results is provided if the band at 470 nm is assigned to the 55° dimer and that at 425 nm to the metastable state of anthracene. In the spectrum of the 235K deposit, Figure (3.4) a band located at 416 nm is apparent. This may simply be the 425 nm band shifted to higher frequency, since a strong band was also observed at 420 nm on annealing the 77K deposit to room temperature, curve (C), Figure (3.3). A continuous blue shift of this band would be consistent with a gradual increase of long range order via a metastable state, with a structure intermediate between the 55° dimer and the crystalline phase. This would also explain why the intensity of the 470 nm band (55° dimer) increased to a maximum at 230K and then decreased again and would suggest that 230K is the upper limit for the formation of metastable films of anthracene during deposition.

Tetracene Films

Like anthracene, single crystals of tetracene have an A-type lattice structure. However, unlike anthracene, excimer fluorescence still dominated the spectrum of films even after annealing at 298K for several hours, which suggests that crystallisation of low temperature deposits, which is known to⁽²⁴⁾ occur at room temperature, does so at a slow rate. Although, as Figure (3.15), curve (A), shows, the fluorescence intensity decreased by about an order of magnitude when films deposited at 77K were annealed, the intensity was fully

restored on re-cooling to 77K, Figure (3.14), curve (C) indicating that the change was reversible, and that crystallisation had not occurred. However, the shift in band frequency recorded in Figure (3.15), was not reversed on cooling which suggests that even in the absence of crystallisation an irreversible change had occurred on warming the film. The shift in band frequency increased sharply above 234K, but a change was first observed at about 180K, which coincides approximately with the temperature at which the rate of change of intensity decreased, as shown by curves (A) and (B). Bässler et.al.⁽²⁴⁾ also observed a change in slope of the excimer emission intensity vs temperature curve in the vicinity of 200K for tetracene films deposited at liquid nitrogen temperatures. Their initial interpretation of this behaviour, which was given in the Introduction (3.1.4), was that it is associated with a change in the rate of an energy transfer process rather than a change in the structure of the film. However, in a subsequent paper Bässler et.al.^(41a) found with the aid of thermally stimulated current measurements, that on annealing, charge carriers are released from traps within tetracene films. For films deposited below 130K the measured thermally stimulated current increased to a maximum in the vicinity of 180K and then decreased at higher temperatures. According to Bässler et.al.^(41a) a distribution of localised states exist in low temperature deposits ($T \leq 130\text{K}$) and for films deposited at 180K the centre of the trap distribution is located at 0.07 eV above the valence band. If the fluorescence process corresponds to a transition between the conduction band of tetracene and this distribution of traps, and annealing causes these traps to be removed, this should lead to an

irreversible shift in excimer emission to higher frequency, as was actually observed, Figures (3.14) and (3.15). The magnitude of the shift, as measured at the peak maximum, was ~ 30 nm (1090 cm^{-1}), which is about twice that expected for traps located 0.07 eV (570 cm^{-1}) above the valence band, and is therefore in reasonable agreement with the results of Bässler et.al. Frequency shift measurements were made on a film deposited at 77K .

Since removal of traps which are responsible for non-radiative decay is unlikely to change the number of emission centres, only their energy, it is possible to understand why the change in fluorescence intensity was reversible while the shift in band frequency was not. Although Bässler et.al. interpreted their results on the basis of an optimum quasi-amorphous structure formed at deposition temperatures of 180K and possessing short range order there was no evidence of a maximum in fluorescence intensity of the type observed for anthracene, from either of the 77K deposits on annealing, Figure (3.15). It is possible that the removal of traps responsible for the frequency shift observed on annealing tetracene films, was caused by restricted rotation of molecules, since Vaubel and Bässler⁽⁴²⁾ have presented evidence for some molecular re-arrangement within the unit cell above 180K in crystalline tetracene. Turlet and Philpott⁽⁴³⁾ have also reported the observation of a discontinuous change in the Davydov splitting near 186K , which they associate with the occurrence of a first order phase transition. In view of these earlier observations and since 180K corresponds to $0.25 T_b$ rather than $0.33 T_b$ it is concluded that the changes observed in the fluorescence intensity of

tetracene films were not associated the OST effect or with the formation of a metastable precursor of the crystalline phase of the type observed for anthracene.

Perylene Films

Low temperature (77K) deposits of perylene exhibited the broad structureless excimer emission which is characteristic of α -perylene. However, this emission was blue shifted by about 60 nm to 556 nm, as compared to excimer emission from single crystal perylene, at the same temperature. On the other hand the observed emission coincides almost exactly with that from crystalline β -perylene⁽⁴⁴⁾, which at 293K is located at 550 nm. The β -crystal has a structure similar to that of anthracene (A-type) and is monomeric rather than dimeric, but exhibits a broad excimeric emission at high temperatures. On cooling, the emission spectrum of the β -form develops monomer-like structure at temperatures above 77K. When the crystal examined was grown from material which had not been zone refined Von Freydorf et.al.⁽⁴⁴⁾ observed an intense band at 540 nm, with a shoulder at 570 nm. Now, for the film deposited at 240K the spectrum Figure (3.12) was excimer like after annealing to 299K, although a small amount of structure was discernible at the deposition temperature. Furthermore, on cooling the annealed film to 77K two peaks were observed at 540 nm and 580 nm which coincide with those observed in the β -form at low temperatures. The low temperature emission spectrum from the non-zone refined β -form is very similar to the Y type⁽⁴⁴⁾ of fluorescence observed when α -perylene is cooled to low temperatures. However, Y-type emission is only observed in crystals

cooled below about 50K, unlike the film deposited at 240K. It is concluded, therefore, that the β -form of perylene (type A lattice) is obtained at deposition temperatures $\geq 240\text{K}$.

The lack of structure in the spectrum of the 77K deposit Figure (3.11) suggests that dimeric rather than monomeric species predominate in low temperature deposits, although the fact that the spectrum is blue shifted by $60\text{\AA}$ compared to that of α -peryene crystals infers that the excimer emission centres are strongly perturbed. As discussed for pyrene, the origin of the blue shift may be an increase in the intermolecular distance, or alternatively the molecular centres may be shifted laterally with respect to each other. Michel-Beyerle and Vakhot⁽³⁰⁾ and Cohen et.al.⁽⁴⁵⁾ have shown that both types of perturbation combine to decrease the binding energy of the perylene excimer, relative to the completely overlapped configuration, which leads to an increase in the excimer emission frequency and eventually to Y-type emission at low enough temperatures.

The β -phase of perylene undergoes a transformation to the α -phase above 430K ⁽⁴⁴⁾. Crystallisation of disordered low temperature deposits should, therefore, proceed via the β -phase, which, having an A-type lattice, implies that the annealing behaviour of perylene will be similar to that of anthracene. Thus the pronounced peak in fluorescence intensity observed on annealing a 77K deposit in the vicinity of the predicted OST, is thought to be due to the formation of a precursor state similar to that of the 55° dimer of anthracene, although without further experiments it is not possible to be more specific about the structure of this precursor state. Furthermore, a substrate temperature of 240K appears to be the upper limit for the formation of the metastable state of perylene.

Pyrene Films

Pyrene has a much stronger tendency toward dimer formation in both the crystalline state and in solution, than does anthracene or even perylene. It crystallises with the type B lattice and single crystals are known to exhibit excimer fluorescence at all temperatures between 1K and 400K. Since the bonding between pairs of molecules in the excited state is strong⁽¹⁰⁾ the pyrene excimer is only weakly effected by perturbations, such as might occur as a result of a change in its immediate environment. It is therefore, hardly surprising that the broad featureless excimer band characteristic of pyrene was observed from films deposited at both 77K and 200K, Figures (3.6) and (3.7). For single crystal pyrene a shift from 476 nm to 471 nm is observed⁽¹²⁾ between 77K and 250K, respectively. A blue shift of 14 nm was observed on annealing the 77K deposit to 245K, Figure (3.6) which suggests a slightly larger relaxation of the molecular interaction has occurred than that normally observed for single crystals. A much larger blue shift of 30 nm (compared to single crystal pyrene) was observed for the film deposited at 200K, Figure (3.7), curve (A). The spectrum of this film changed very little on annealing to 280K, curve (b), which suggests that whatever the internal structure it was relatively stable.

One explanation of the larger blue shift observed for the 200K deposit is the possibility that molecules interact less strongly in the ground state in films deposited at this substrate temperature. This would have the effect of increasing the intermolecular spacing of the dimer in the ground state relative to the excited state, which would result in a blue shifted emission. An increase in the intermolecular spacing of only $0.05\text{\AA}$ would be sufficient to account for

a shift of ~ 30 nm⁽¹²⁾. The unsymmetrical shape of the emission from the 200K deposit, with the shoulder at 420 nm, also suggests that the excimer emission centre is strongly perturbed in this film; pyrene monomer⁽⁴⁵⁾ exhibits a band at 420 nm.

Excimer emission from pyrene single crystals has a lifetime of 180 ns at 77K, falling to 70 ns at 293K⁽⁴⁷⁾. Thus it appears, that the results of Figure (3.10), curve (A), where the maximum lifetime observed, even at the deposition temperature (10K), was only of the order of 90 ns, falling to 60 ns at room temperature, support the above proposal, that the dimer binding energy in low temperature deposits is less than in the crystal; as argued in Section (3.1.3) an increase in the energy difference between the ground and excited state should lead to a decrease in the radiative lifetime⁽¹¹⁾. A particularly interesting feature of the annealing curve in Figure (3.10), curve (A), is the pronounced maximum in fluorescence lifetime at 200K. The lifetime began to increase at 170K, which is just 10K above the predicted OST for pyrene and provides strong evidence of an increase^{(11) (12)} in the intermolecular binding energy, within dimers, as discussed for anthracene. Curve (B) in Figure (3.10) depicts the change in fluorescence intensity of the same 10K deposit, as determined from the maximum height of the fluorescence decay curve. It is notable that the emission intensity peaked between 150K and 170K, some 30K to 50K below the lifetime maximum located at 200K. Furthermore, the decrease in emission intensity above 170K coincided with the sharp increase in lifetime.

Since the increase in emission intensity between 125K and 150K was accompanied by a small change in lifetime it is proposed that

annealing causes the removal of traps which act as centres for non-radiative decay; quantum yield (ϕ_F) (fluorescence intensity) is determined by the relative rates of radiative (k_F) and non-radiative (k_{NR}) processes⁽⁴⁸⁾, according to

$$\phi_F = \frac{k_F}{k_F + k_{NR}} \quad \text{and} \quad \tau_F = \frac{1}{k_F + k_{NR}}$$

However, the decrease in emission above 170K cannot be associated with an increase in k_{NR} because this would lead to a decrease in τ_F rather than an increase. The increase in lifetime (τ_F) implies, therefore, an increase in the repulsive interaction between molecules. In the vicinity of the OST, followed by a decrease in this interaction above 200K.

The results given in Figure (3.8) provide support for the above proposal. The effects of annealing on the intensity of emission from the 10K deposit are similar although less pronounced than the changes recorded in Figure (3.10), Curve (B). An improved coincidence between the two sets of data was obtained when the integrated intensity, Figure (3.9) curve (a), was plotted rather than the peak intensity. In the case of the film deposited at 77K (curve (B)), Figure (3.8) the emission intensity did not begin increasing until 175K and peaked at 200K suggesting that the precise location of the transition temperature is dependent on substrate temperature during deposition.

Summary of Fluorescence Properties of PCA's Films

Annealing experiments with evaporated films of PCA compounds have established that an increase in fluorescence intensity occurs in the vicinity of the predicted OST (0.33N B pt) for anthracene, pyrene and perylene. This observation is consistent with the proposal that the OST effect is associated with the formation of a metastable

state, possessing only short range order. An increase in fluorescence lifetime was observed during the annealing of anthracene and pyrene films, prior to the increase in excimer emission intensity, which is thought to indicate an increased repulsion between molecules in the ground state at the OST. It is proposed that this increased repulsive interaction is responsible for the observation of the metastable state, since it constitutes an energy barrier to crystallisation of the amorphous or disordered phase produced at low substrate temperatures. Although the activation barrier to rotation within disordered films is thought not to be responsible for preventing crystallisation, in the case of anthracene, pyrene and perylene, it may be important in the case of tetracene, which did not exhibit increased fluorescence in the vicinity of its predicted OST ($\sim 240\text{K}$).

A more exhaustive study of the changes which occur in both the fluorescence lifetime and the total fluorescence spectrum, in the vicinity of the predicted OST, is necessary in order to verify the above proposals. In particular, an experimental estimate of the relative magnitude of repulsive interaction potentials between molecules could be provided by observing changes in both the frequency and the lifetime of excimer emission in a series of pyrene and perylene films deposited close to the predicted OST; detailed calculations, relating to excited and ground state potentials to intermolecular distance which are available for both pyrene and perylene dimers would facilitate such a study. Experimentally determined interaction potentials are of interest in connection with the mechanism of glass formation and the role of the pair potential

in stabilising metastable states⁽⁴⁹⁾.

Emission often occurs preferentially from trapping centres or defect sites and if exciton migration or energy transfer takes place after excitation, traps can have a disproportionately large effect upon the fluorescence properties of films. Since films produced at low temperatures have a high concentration of such traps the observed excimer-like emission characterises disordered regions. It is difficult therefore to distinguish between films which are homogeneously disordered and those in which disorder occurs at the boundary between microcrystals on the basis of fluorescence measurement although the disappearance of the Davydov splitting in low temperature deposits does support the former. Furthermore, because fluorescence emission is characteristic of the excited state population it serves only as an indirect probe of the ground state which may have a different configuration and almost certainly has a reduced binding energy compared to the former, as Stevens and Ben⁽¹⁰⁾ have shown for excimers. Absorption techniques, however, characterise the ground state population and should, therefore, provide a means of distinguishing between homogeneous and heterogeneous disorder within films and of probing directly the interaction between molecules within low temperature condensates. This was the object of the infrared study of (TTF)(TCNQ) described in Chapter 6.

References for Chapter 3

1. Vincett, P.S., Barlow, W.A., and Roberts, G.G., J. Appl. Phys., 48, 3800 (1977).
2. Roberts, G.G. and Keating, B.S., J. Phys. C., 7, 1595 (1974).
3. Vincett, P.S., Barlow, W.A. and Roberts, G.G., Nature, 255, 542 (1975).
4. Wolf, K.L. and Weghofer, J., Z. Physik. Chem., B, 39, 194 (1938).
5. Inokuchi, H., Shiba, S., Handa, T. and Akamatu, H., Bull. Chem. Soc. Japan, 25, 299 (1952).
6. Robertson, J.M., Proc. Roy. Soc., (London) A207, 101 (1951).
7. Stevens, B., Spectrochimica Acta, 18, 439 (1962).
8. Handbook of Chemistry and Physics, 58th Edition, 1977-78, CRC., Press.
9. Förster, Th., Angew. Chem. Internat. Edit., 8, 333 (1969).
10. Stevens, B. and Ban, M.I., Trans. Faraday Soc., 60, 1515 (1964).
11. Ross, R.T., Photochem. and Photobiol., 21, 401 (1975).
12. Birks, J.B. and Kazzaz, A.A., Proc. Roy. Soc., (London) A304, 291 (1968).
13. Perkampus, H.H. and Stichtenoth, H., Z. Physik. Chem., 76, 18 (1971).
14. Perkampus, H.H., ibid, NF 13, 278 (1957).
15. Perkampus, H.H., ibid, NF, 19, 206 (1959).
16. Perkampus, H.H., ibid, NF, 24, 1 (1960).
17. Perkampus, H.H. and Pohl, L., ibid, NF, 39, 397 (1963).
18. Perkampus, H.H. and Pohl, L., ibid, NF, 40, 162 (1964).
19. Perkampus, H.H. and Pohl, L., Theoret. Chim. Acta, 1, 116 (1964).
20. Perkampus, H.H. and Stichtenoth, H., Z. Physik. Chem., NF, 74, 72 (1971).

21. Haller, W., Stichtenoth, H. and Perkampus, H.H., Chem. Ber., 78, 1221 (1974).
22. Bönsch, G., Kleinert, G., Flamersfeld, A., Z. Physik., 222 363 (1969).
23. Tomlinson, W.J., Chandross, E.E., Fork, B.L., Pryde, C.A. and Lamola, A.A., Appl. Optics, 11, 533 (1972).
24. Müller, H., Bässler, H., Vaubel, G., Chem. Phys. Lett. 29, 102, 1974.
25. Maruyama, Y., Machida, K., Iwasaki, N., Iwashima, S., Chem. Lett., 911 (1975).
26. Birks, J.B., Photophysics of Aromatic Molecules, London (1970) referred to in (21).
27. Kramer, K., Z. Naturforsch., 22a, 1108 (1967).
28. Kamura, Y., Shirotani, I., Ohno, K., Seki, K. and Inokuchi, H., Bull. Chem. Soc. Jap. 49, 418 (1976).
29. Maruyama, Y. and Iwasaki, N., Chem. Phys. Lett., 24, 26 (1973).
30. Michel, M.E. and Yakhot, V., *ibid*, 49, 463 (1977).
31. Kamura, Y., Seki, K. and Inokuchi, H., Chem. Phys. Lett., 30, (35) 1975.
32. Seki, H. and Itoh, U., J. Chem. Phys., 72, 2166 (1980).
33. Crystalline anthracene
34. Lennard-Jones, J.E., Proc. Roy. Soc. London, A163, 127 (1937).
36. Maruyama, Y., Iwaki, T., Kajiwara, T., Shirotani, I. and Inokuchi, H., Bull. Chem. Soc. Jap., 43, 1259 (1970).
37. Fryer, J.R., Ninth Int. Congr. Elect. Microscopy, Toronto, 1978, 1, 256 (1978).
38. Fielding, P.E. and Janargin, R.C., J. Chem. Phys., 47, 247 (1967).
39. Avramov, I. and Gutzow, I., J. Non-Cryst. Solids, 16, 128 (1974).

40. Chandross, E.A. and Ferguson, J., J. Chem. Phys., 45, 3554 (1966).
41. Morris, J.M., Molecular Physics, 28, 1167 (1974).
- 41a. Eiermann, R., Hoffberger, W., Bässler, H., J. Non-Cryst. Solids, 28, 415 (1978).
42. Vaubel, G. and Baessler, H., Mol. Cryst. Liq. Cryst., 12, 39 (1970).
43. Turlet, J.M. and Philpott, M.R., J. Chem. Phys. 62, 4260 (1975).
44. Von Freydorf, E., Kinder, J. and Michel-Beyerle, M.E., Chem. Phys., 27, 199 (1978).
45. Cohen, M.D., Haberkorn, R., Huler, E., Ludmer, Z., Michel-Beyerle, M.E., Rabinovich, D., Shanon, R., Warshel, A. and Yakhot, V., Chem. Phys. 27, 211 (1978).
46. Mansour, S., and Weinreb, A., Mol. Cryst. Liq. Cryst., 27, 111 (1974).
47. Inoue, A., Yoshihara, K., Kasuya, T. and Nagakura, S., Bull. Chem. Soc. Jap., 45, 720 (1972).
48. Bradley, R.A., in Modern Fluorescence Spectroscopy, 2, Ch 3., 91, Ed. E.R. Wherry.
49. Angell, C.A., Clarke, J.H.R. and Woodcock, L.V., in Adv. in Chem. Phys. Vol XLVIII, 397 (1981), Ed. Prigogine, I., and Rice, S.A.

CHAPTER 4

THE TOPOGRAPHY OF (TTF) (TCNQ) FILMS

4.1 Introduction

4.1.1 The Crystal Structure of (TTF)(TCNQ)

(TTF)(TCNQ) is a (1:1) charge transfer complex of the donor 2,2'-bis 1,3-dithiole, commonly referred to as tetrathiafulvalene (TTF), and the acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ). It has the molecular structure given in Figure (4.1). The crystal structure of the complex has been determined by several groups⁽¹⁾ and is shown in Figure (4.2), which is taken from the paper by Kistenmacher et al. Figure (4.2a) is a view down the (010) direction of the crystal, normal to the ac plane whilst Figure (4.2b) is an alternative view down (100) normal to the ab plane. Crystals of (TTF)(TCNQ) are monoclinic with space group $P2_1/C$, their most notable feature being the way in which molecules of TTF and TCNQ are arranged in the form of homologous, or segregated 1-dimensional (1-d) stacks, parallel to the crystallographic b-axis. Within these stacks there is considerable overlap between the π orbitals of adjacent molecules, so much so that the interplanar spacings are, (TTF); $3.47\text{\AA}$ and (TCNQ); $3.17\text{\AA}$, which are somewhat less than the expected van der Waals distance of $3.6\text{\AA}$ ⁽²⁾.

The amount of charge transferred from TTF to TCNQ in the ground state has been determined by a number of techniques⁽³⁾ to be less than unity. The generally accepted value is 0.59 ± 0.02 , which was estimated from neutron⁽⁴⁾ and elastic X-ray scattering measurements⁽⁵⁾. As a result of this charge transfer, the (1-d) donor and acceptor stacks contain open shell radical cation and anions, respectively. Because of the strong interaction between the π electron orbitals on

Figure 4.1. Molecular structure of (TTF) (TCNQ)

Figure 4.2a. A view normal to the ac plane of the crystal packing in (TTF) (TCNQ). The shaded molecules have their centroids at $y = \frac{1}{2}$.

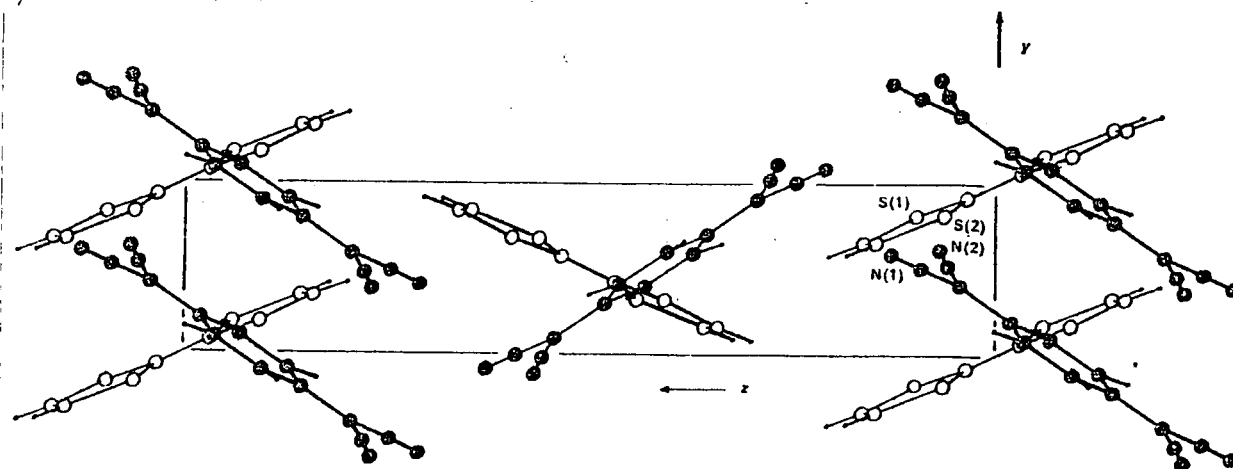
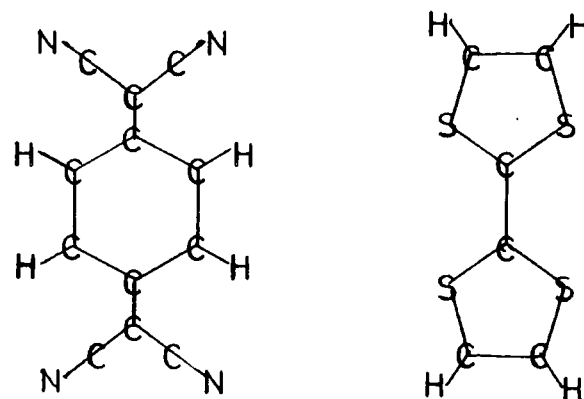
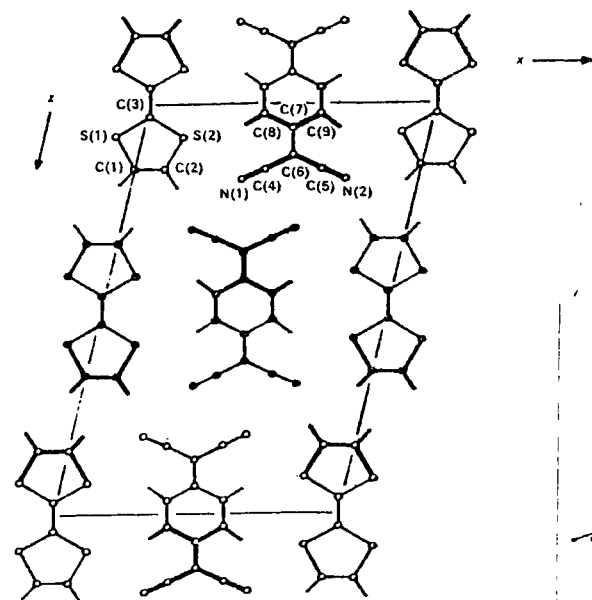


Figure 4.2b. A view down $[100]$ of the crystal packing in (TTF) (TCNQ). The shaded molecules have their centroids at $x = \frac{1}{2}$.

adjacent molecules, these extra 'electrons' and 'holes' are delocalised within a given stack forming partially filled 1-d bands. (TTF) (TCNQ) is therefore a highly anisotropic or 'quasi 1-d metal'⁽⁶⁾, with a high electrical conductivity along the b-axis of the crystal and much lower values of conductivity in the a and c directions. As a consequence the complex exhibits unique electrical and optical properties which have been the subject of intense theoretical and experimental investigation since its discovery in 1972⁽⁷⁾. The electrical properties of (TTF) (TCNQ) are discussed in more detail in Chapter 6.

VBR's⁽⁸⁾ study of vacuum deposited anthracene films revealed a structural optimum which manifested itself as a definite but barely perceptible minimum in surface roughness in the vicinity of 213K. A similar investigation of perylene⁽⁹⁾ failed to reveal any structural optimum, although it appears from the results of the previous chapter that an OST effect is expected for this substance. Since an investigation of the OST effect was a main aim of the work described in this and subsequent chapters, the observation of a structural optimum was considered to be of primary importance in determining the choice of a suitable material for this in depth study. Evaporated films of (TTF) (TCNQ), with its highly anisotropic properties would, it was reasoned, exhibit marked topographical and morphological changes as a function of growth conditions and so increase the probability of observing and accurately locating an OST effect.

It was concluded from the study of aromatic hydrocarbon films, presented in the previous chapter, that short range or nearest neighbour interactions play a crucial role in the observation of an OST effect in these materials. As will now be discussed these

same forces are important in determining the morphology of molecular crystals. In the case of (TTF)(TCNQ) these intermolecular forces are dominated by the out-of-plane interaction i.e. they are 1-dimensional. As will now be shown this leads to a particularly simple picture of crystal growth which is readily applied to the preparation of polycrystalline films from the vapour phase.

4.1.2 Periodic Bond Chain Theory

The morphology of a crystal can be considered to be the result of a growth process involving the formation of bonds between atoms or molecules which go to make up the lattice. A 'Periodic Bond Chain' (PBC) theory of crystal growth was developed some years ago by Hartmann and Perdok⁽¹⁰⁾ which emphasised the importance of the interaction potential, or bonding strength between molecules, in determining morphology. Central to their theory is the assumption that strong bonds form more readily than weak bonds. The growth rate of a crystal in a given direction is, therefore, proportional to the bonding strength between molecules in that same direction. Hence, to a good approximation, PBC theory predicts that when a crystal is grown under equilibrium conditions, its morphology is determined by the anisotropy of the molecular interaction potential.

Planar aromatic compounds and (TTF)(TCNQ) in particular with its 1-dimensional lattice, provides a particularly striking example of the essential correctness of the above statement. As already mentioned, in the case of (TTF)(TCNQ), molecules interact most strongly in a direction perpendicular to the molecular plane, consequently the crystallographic b-axis is the direction of most rapid growth, and under equilibrium conditions the most prominent

crystal faces are those containing the b-axis. Furthermore, from the unit cell dimensions⁽¹⁾ the bonding strength between molecules along the three principal axis' scale as $b > a > c$ and the relative rates of growth of the corresponding faces are:- $ab > bc > ac$. This prediction is borne out by experiments⁽¹¹⁾ with evaporated thin films, as will shortly be discussed, and by the solution growth results of Sherwood et al⁽¹²⁾. The latter have made a systematic examination of the conditions of supersaturation and growth rate which are required in order to produce crystals of (TTF)(TCNQ) of extremely high perfection.

In the present study, growth of films was carried out by vapour phase deposition onto low temperature substrates, which corresponds to conditions of high supersaturation. Now, Coleman⁽¹³⁾ has shown from his extensive study of solution grown crystals of (TTF)(TCNQ), that at low supersaturations growth along the a axis dominates, which results in the formation of a transverse habit crystal. At higher supersaturations, however, the growth rate along the b-axis accelerates, in line with the predictions of PBC theory, and the normal crystal habit, i.e. elongated in the b-direction, results. Growth in the c direction was found to be slow and uniform under different conditions of supersaturation. Similar considerations should extend to growth from the vapour phase, thus at low substrate temperatures (high supersaturation) b-axis growth should be the predominant feature, with the contribution from growth in the a direction increasing at higher substrate temperatures (lower supersaturation). Armed with this information it should be possible in the case of (TTF)(TCNQ) to establish the existence of a correlation between the morphology of crystallites contained within a film and the OST effect far more readily than could be achieved for less anisotropic

molecules.

4.1.3 Parameters which Influence the Topography of Films

Crystal morphology is only one of a number of parameters which determine the topography of vapour deposited thin films. Other parameters of equal or greater relevance include; the size and number density of crystallites, and the orientation of their crystallographic axis, relative to the substrate surface. The latter is a particularly important factor in determining the properties of films of highly anisotropic molecules, like (TTF) (TCNQ), in a given measurement direction. The influence of substrate temperature on these various topographical features must, therefore, be incorporated into any model of film growth from the vapour phase.

All three parameters, i.e. crystallite size, density and orientation are a function of;

- a) the rate of nucleation (J') of the crystalline phase during film deposition, and
- b) the average distance ($\bar{X}$) which a molecule travels on the surface prior to desorption.

These are in their turn determined by the activation free energies associated with; surface diffusion (ΔG_{sd}), desorption (ΔG_{des}) and nucleation (ΔG^*) processes, as outlined in the section on nucleation in Chapter 1.

It would appear, therefore, that a qualitative picture of the influence of deposition temperature on film topography may be developed within the framework of the theories of nucleation and the periodic bond chain. Such an approach, while satisfactory at higher

substrate temperatures and low supersaturation, requires modification when applied to the deposition of films at substrate temperatures low enough to prevent nucleation of the crystalline phase. Under these conditions, although the considerations of the PBC theory still apply, in that nearest neighbour interactions play a vital role in determining short range order (SRO) within films, it is necessary also to take into account that in the absence of the stabilising influence of LRO there is the possibility that intermolecular interactions may be repulsive, rather than attractive which would lead to thermodynamic instability. Furthermore, molecular relaxation rate, particularly of large planar aromatic molecules is known⁽¹⁴⁾ to be reduced significantly at low temperatures. Thus, if an ad-molecule is prevented by a kinetic barrier from undergoing relaxation to give a minimum energy configuration relative to nearest neighbours this will result in the formation of films with disordered structures as discussed in Chapter 3. It will be shown that both SRO and molecular relaxation rate have an important bearing upon the OST effect.

In previous work on evaporated films of (TTF) (TCNQ) the emphasis has been placed on studying the electrical properties of samples deposited at room temperature and above. However, because of its relevance to the present study, a brief resume of the structural aspects of previously published work will now be given.

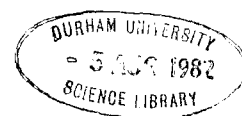
4.1.4 Earlier Studies of (TTF) (TCNQ) Films

(i) Film morphology

Several groups have carried out structural studies of vacuum grown TTF/TCNQ films. In the original work by Chaudhari et.al.⁽¹⁵⁾ the complex was deposited onto the (100) and (112) faces of NaCl. Films deposited at a substrate temperature of 70°C had an

epitaxial relationship $(010)_{FO} \parallel (110)_S$, where the subscripts refer to the complex and substrate respectively. Because of the equivalence of the $(110)_S$ and $(\bar{1}10)_S$ substrate directions, their films exhibited double positioning, i.e. 'a mosaic' of $(010)_{FO} \parallel (110)_S$ and $(010)_{FO} \parallel (\bar{1}10)_S$ when deposited on the (100) face of NaCl. When deposited onto the (112) face a singly positioned film was obtained, since this face of the crystal contains only the $(1\bar{1}0)$ direction. The (010) direction of $(\text{TFE})\text{TCNQ}$ corresponds to the crystallographic b-axis, i.e. the films were oriented with the ab plane of crystallites parallel, and the c-axis perpendicular, to the substrate. In a subsequent paper Simonyi et al ⁽¹⁶⁾ produced singly positioned films on (100) NaCl substrates subjected to compressive stress, along (110), as well as on polar (010) faces of ferroelectric triglycine sulphate. They determined that the best conditions for growth of epitaxial films were; a substrate temperature of around 70°C, and a high deposition rate, of the order of 10^8 Å s^{-1} , and observed that the b-axis' of crystallites were parallel to the film plane. Above a film thickness of 1500 Å , even under the best conditions for epitaxial growth, random overgrowths were observed, which were thought to be associated with the lattice mismatch between $(\text{TFE})\text{TCNQ}$ and the substrate.

Chen and Schectman ⁽¹⁷⁾ and more recently Reinhardt et al ⁽¹⁸⁾ have deposited films onto substrates maintained near room temperature. Using X-ray diffraction, Chen and Schectman observed that the preferred crystallite orientation was one in which the ab plane was parallel to the film surface, when deposited onto fused silica substrates. Reinhardt et al made the same observation using transmission electron microscopy for films deposited onto both NaCl (100) and glass. Chen



and Schectman found that films deposited at 195K and 77K showed only two anomalous assymmetric peaks in the X-ray diffraction pattern, at $2\theta = 24$ and 25.6° . On removing the film from the substrate the diffraction pattern obtained on the powder gave lines which could all be attributed to TTF⁺TCNQ⁻, except for the anomalous peaks at $2\theta = 24$ and 25.6° , which remained. These authors also noted that films deposited at 195K had a different growth habit, with the direction of most rapid growth, which they assumed to be the b-axis, perpendicular, rather than parallel to the substrate.

(ii) Vapourisation of (TTF) (TCNQ)

In general TCNQ charge transfer complexes are sensitive to thermal decomposition and most decompose before melting. However, there are a number of TCNQ complexes, particularly those involving organic donors, such as the quinolines and N-methyl[phenazinium]⁽¹⁹⁾ salts which have been observed to sublime in vacuo. (TTF) (TCNQ) was, for example, observed⁽¹⁵⁾ to sublime unchanged at temperatures above 350K and pressures less than 10^{-3} torr to give (1:1) stoichiometric deposits. This conclusion was based upon measurements of the optical and infrared spectra and transmission electron diffraction patterns of thin films⁽¹⁵⁾. Chen and Schectman also concluded that (TTF) (TCNQ) sublimed unchanged, primarily as the associated complex rather than as individual neutral components, on the basis of optical absorption measurements obtained by dissolving films in acetonitrile. The infrared data of Wozniak et al⁽²⁰⁾ and the UPS measurements of Lin et al⁽²¹⁾, however, indicated that the complex dissociated to some extent on vapourisation since both TTF⁺ and TCNQ⁻ as well as complex were observed in their films deposited at low temperatures.

This latter observation is supported by the mass spectroscopy study of $(\text{TTF})(\text{TCNQ})$ carried out by Siedle and Hertz⁽²²⁾. They found only $(\text{M}+\text{H})^+$ species in the methane chemical ionization mass spectrum with no evidence of higher molecular weight aggregates and concluded that the complex dissociates on volatilization into TTF and TCNQ. Because of this conflicting evidence it was considered important to re-establish that $(\text{TTF})(\text{TCNQ})$ does in fact sublime intact in vacuo.

The procedures used to prepare and purify the $(\text{TTF})(\text{TCNQ})$ used in this work are described in Appendix 1. Purification involved repeated sublimation of the complex and the results of analysis carried after each purification step are listed in table (A.1.1). It is clear from the table that within the error of the analytical technique the composition is essentially unchanged after three sublimations, which supports the earlier observations. This conclusion is somewhat surprising in view of the large difference between the vapour pressures of the two neutral precursors, TTF^0 ⁽²³⁾ and TCNQ^0 ⁽²⁴⁾, at the temperatures used to vapourise $(\text{TTF})(\text{TCNQ})$. The formation of associated species in the vapour phase as proposed by Chen and Schectman would thus appear to be a strong possibility. However, in a very recent paper, de Kruif and Govers⁽²⁵⁾ have measured the enthalpies of sublimation of TTF^0 , TCNQ^0 and the (1:1) complex, using mass loss and applied torsion effusion techniques. Simultaneous measurement of the vapour pressure (p) of the complex, using both techniques, gave values for p(t) (torsion) and p(w) (mass loss). These authors have argued that p(w) depends upon the mean molecular mass (M) of the vapour and it can be shown that

$$\frac{p(w)}{p(t)} = \left(\frac{M}{M_1}\right)^{\frac{1}{2}}$$

where M_1 is the molecular formula mass, taken to be 204.3, i.e. the

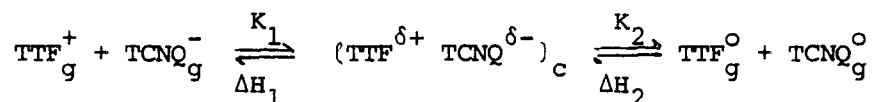
molecular weight of the complex divided by two. When M is different from M_1 the ratio $p(w)/p(t)$ will not equal unity. Since the torsion effusion experiment gives the total pressure, while the mass loss experiment provides a weighted mean molecular mass of the vapour, association of molecules in the vapour phase should give a value of $p(w)/p(t)$ greater than unity. The results of de Kruif and Govers⁽²⁵⁾ demonstrated very convincingly that $p(w)/p(t)$ was unity for TTF° , TCNQ° and $(\text{TTF})(\text{TCNQ})$ and on the basis of their data it must be concluded that the vapour above all three compounds consists almost entirely of monomeric species.

They further showed, with the aid of a quadrupole mass spectrometer, that the complex evaporates stoichiometrically and obtained a value of 130 kJ mole^{-1} for its sublimation enthalpy. Their experimental value for heat of sublimation of TTF ($95.3 \text{ kJ mole}^{-1}$) agrees with the result of Sandeman et al⁽²³⁾ (92 kJ mole^{-1}), but that of TCNQ ($126.1 \text{ kJ mole}^{-1}$) was somewhat higher than obtained by Boyd⁽²⁴⁾ ($104.8 \text{ kJ mole}^{-1}$).

It should be remembered that de Kruif and Govers define the enthalpy of sublimation of the complex (1:1) as "the enthalpy difference per 204.3g between the vapour and crystalline phases in which the vapour phase consists of 0.5 mol TTF and 0.5 mole TCNQ". For 1 g.mole of complex, i.e. 408.6g therefore, the value is 260 kJ mole^{-1} . It is possible on the basis of their measurements to speculate about the species present in the vapour phase.

Using data from the paper by Metzger⁽²⁶⁾ combined with that obtained by de Kruif and Govers, a Born-Haber⁽²⁷⁾ cycle was constructed for TFTCNQ and this is shown in Figure (4.3). Since de Kruif and Govers showed that only monomeric species were formed on evaporation, the two possible modes of dissociation of the complex at equilibrium,

which need to be considered are:-



The partial vapour pressures of the four monomeric species depends upon the two heats of dissociation ΔH_1 and ΔH_2 which are given in Figure (4.3) and are $658.4 \text{ kJ mole}^{-1}$ and $258.4 \text{ kJ mole}^{-1}$, respectively. Integration of the van't Hoff equation⁽²⁹⁾ gives

$$\ln K_1 = - \frac{\Delta H_1}{RT} + I' \quad (4.1)$$

and

$$\ln K_2 = - \frac{\Delta H_2}{RT} + I'' \quad (4.2)$$

also $K_1 = \rho \text{TTF}^+ \cdot \rho \text{TCNQ}^-$

$$K_2 = \rho \text{TTF}^0 \cdot \rho \text{TCNQ}^0$$

ρ is partial pressure; ideal gas behaviour is assumed

Assuming the constants of integration are equal ($I' = I''$) and

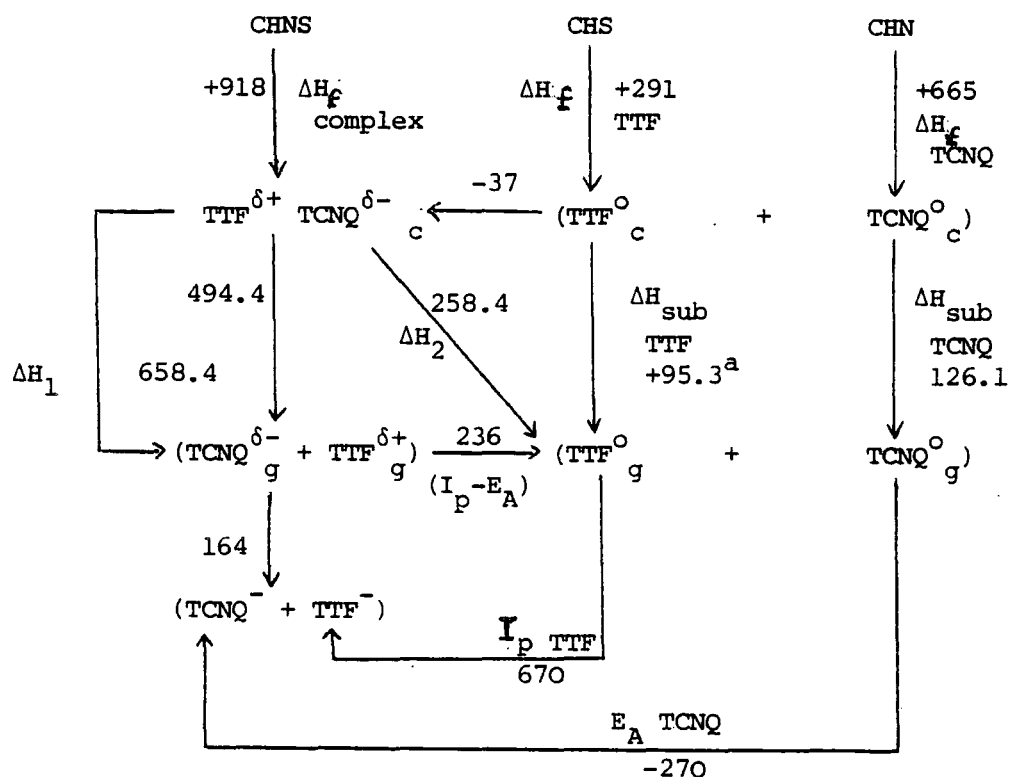
combining equations (4.1) and (4.2) gives

$$\log. \left(\frac{\rho \cdot \text{TTF}^0}{\rho \cdot \text{TCNQ}^+} \right)^2 = \frac{\Delta H_2 - \Delta H_1}{2.303 RT} = 51.9 \quad (4.3)$$

where $\rho \text{TTF}^0 = \rho \text{TCNQ}^0$ and $\rho \text{TTF}^+ = \rho \text{TCNQ}^+$.

Substitution for ΔH_2 and ΔH_1 in equation (4.3), with T equal to 400K demonstrates that the partial pressure of ionic species in the vapour phase, above the TTFTCNQ complex, is many orders of magnitude less than the partial pressure of neutral species. This conclusion is borne out by the sublimation enthalpy of 260 kJ mole^{-1} of TTFTCNQ obtained de Kruif and Govers which is almost exactly that calculated

Figure 4.3. Born-Haber Cycle for (TTF)(TCNQ)



a) From the result of de Kruif and Gover⁽²⁵⁾

ΔH_f is the heat of formation and ΔH_{sub} that of sublimation; I_p is the ionization potential of TTF and E_A the electron affinity of TCNQ; the subscripts c and g refer to the crystalline and gas phase respectively; the quantities quoted are measured in kJ mole⁻¹ and δ is the degree of charge transfer in the complex.

for ΔH_2 (258.4 kJ mole⁻¹) from Figure (4.3). On the basis of this simple analysis it would appear that the vapour phase above TTFTCNQ complex is composed entirely of the neutral molecules TTF^0 and TCNQ^0 .

Two important conclusions can be drawn from previously published work which have implications for the results of the present structural study of thin films of TTFTCNQ.

- a) Film morphology is sensitive to deposition parameters, and in particular substrate temperature during growth. The orientation of the b-axis with respect to the film plane is dependent on substrate temperature in line with the predictions of PBC theory.
- b) The available thermal and vapour pressure data confirm that the complex dissociates in the vapour phase to give almost exclusively TTF^0 and TCNQ^0 . Since molecular associates are not present in the vapour phase, formation of the complex can only take place if the diffusion of adsorbed precursor molecules occurs after impingement onto a surface.

Both conclusions are also relevant to an analysis of the results obtained from infrared and conductivity measurements, which are described in Chapters (5) and (6), respectively.

The results of the structural study, which will now be described, were obtained using X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Because of the highly disordered nature of films deposited at low temperature it was not possible to carry out a systematic study of film structure over the whole temperature range, using XRD or TEM and the results presented in sections (4.3.2) and (4.3.3), respectively, were largely confined to samples prepared above 250K. SEM was, however, employed for films deposited over the entire substrate

temperature range from about 10K to 300K and the results are presented in section (4.3.1). The results section is preceded by a short experimental section devoted to film preparation and surface replication techniques.

4.2 Experimental

4.2.1 Film Preparation

Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) were carried out on samples prepared either by deposition onto fused silica slides at constant substrate temperature, using the CF104 cryostat, or by the temperature gradient substrate (TGS) method described in section 2.1.2. Transmission Electron Microscopy (TEM) was also carried out on films prepared by the TGS method, although in this case the substrate was cleaved mica sheets coated with a thin (100-200Å) carbon release layer. For TEM, films were removed from the mica substrate by immersion in distilled water and then picked up onto copper grids from the water surface. The uppermost layers of mica supporting the (TTF)(TCNQ) film were removed by cleaving, prior to immersion in water, to prevent contamination by the grease used to improve thermal contact to the cryostat. Films were not removed from the substrate for SEM and XRD studies.

Film thicknesses of up to 10,000Å were deposited for SEM and XRD studies, at rates of between 1Å/second and 10Å/second although most of the present work was carried out on films deposited at the lower rate. For TEM studies a layer 300Å thick was deposited at 1Å/sec. Films were examined down to a thickness of 50Å and although it was possible to observe crystallites of (TTF)(TCNQ) in these thinner films, diffraction patterns obtained using TEM were too weak

to allow an analysis of the early stages of growth.

4.2.2 The Surface replication technique

SEM of films deposited below room temperature could not be carried out in-situ because a cold stage was not available. However, a study of films in the as-deposited state was possible with the aid of a surface replication technique. This consisted simply of the evaporation of a thin layer of metal, approximately $300\text{\AA}$ thick, onto the surface of the TTF TCNQ film after deposition, prior to annealing. The metal, either gold or aluminium, was evaporated onto the deposit of TTF TCNQ at high rate ($300\text{\AA min}^{-1}$), to reduce the exposure time to the evaporant source. Samples were cooled about 20K below their deposition temperature to minimise thermal damage and avoid surface annealing during the evaporation of the metal.

The purpose of the metal layer was to prevent the loss of material from the TTF TCNQ film on warming, and to stop surface and grain boundary migration, which might otherwise lead to crystallisation and growth, on annealing to room temperature. Because of this protective metal layer films retained their as deposited structure even after annealing for several weeks at room temperature. Experimental verification of the efficacy of the technique is given in Figure (4.15). Plates c and d, are micrographs (mg's) of the same film of TTF TCNQ deposited at 120K onto a silica substrate. Plate (c) is a micrograph of a region of the film coated with a layer of gold prior to annealing. Plate (d) is a different area of the same film which was not coated prior to annealing. Crystallite growth is clearly apparent in the micrograph of uncoated film, but was entirely absent in the gold coated region. Similar observations were made on

numerous other films deposited between 10K and 230K which testify to the effectiveness of the replication technique in preserving the as-deposited structure of films. Other examples are also given in Figure (4.15), for films deposited at 13K (plates (a) and (b)) and 160K, (plates (e) and (f)). In both cases the micrograph on the left is the metal coated area of the film. Further discussion of these micrographs is left until the section dealing with the SEM of low temperature deposits.

4.3 Results

4.3.1 Film Topography using SEM

It was possible, using the TGS technique, to examine a substrate temperature interval of approximately 90K in a single evaporation experiment. Differences in topography were easily discernible with the naked eye, due to marked changes in visible appearance, particularly to reflected light, along its length. These changes are very apparent in Figure (4.4) which is a photograph of a film evaporated directly onto a (TGS) at a deposition rate of 70Å/min. A schematic drawing of this sample is given in Figure (4.5). The temperatures at which changes in the visible appearance of the film occurred are indicated. The characteristic feature of each region is described in the diagram. No deposit was observed above a substrate temperature of 276K for this particular example.

The characteristic descriptions given in Figure (4.5) refer to the sample after annealing at room temperature for several hours. Immediately after deposition and prior to annealing, films had a somewhat different appearance. The most interesting region of the sample was that corresponding to a substrate temperature of between 207K and 220K which is indicated in Figure (4.4). Prior to annealing it was canary yellow and transparent, and remained so for about one

Figure 4.4. A photograph of the temperature gradient substrate apparatus, with a film of (TTF)(TCNQ) deposited along its length, showing the marked changes which occur in the visible appearance of films as a function of substrate temperature. The yellow band marked with an arrow is the region of the OST.



Figure 4.5. Schematic drawing showing the change in visible appearance of a film of (TTF)(TCNQ) deposited onto a TGS as a function of substrate temperature

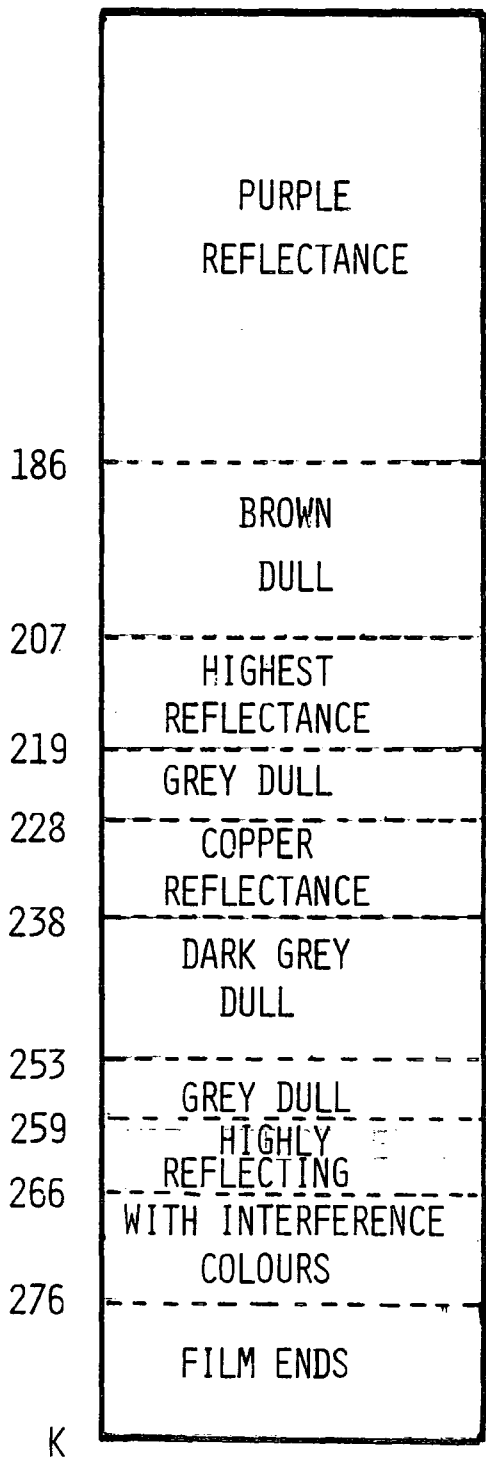
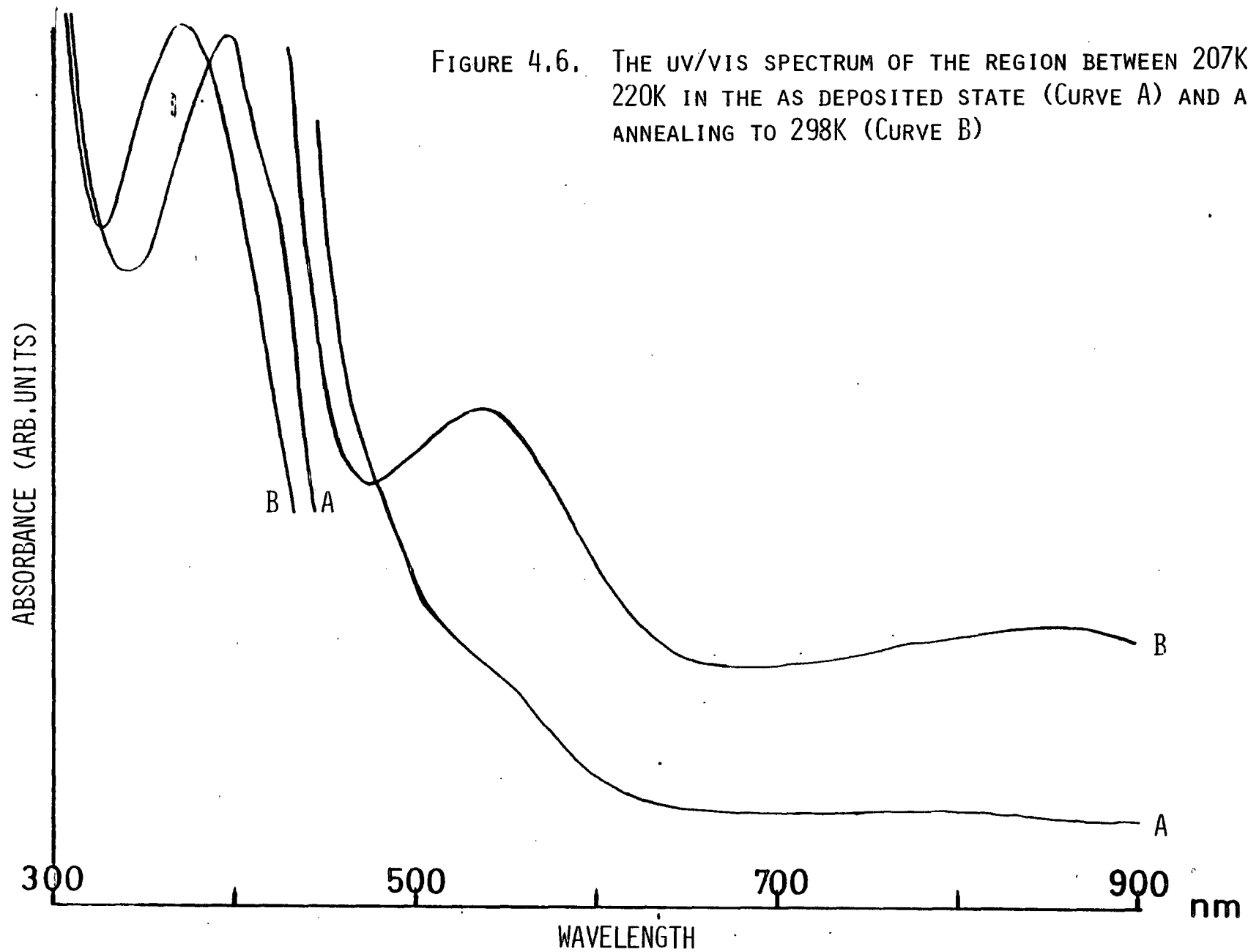


FIGURE 4.6. THE UV/VIS SPECTRUM OF THE REGION BETWEEN 207K AND 220K IN THE AS DEPOSITED STATE (CURVE A) AND AFTER ANNEALING TO 298K (CURVE B)



hour at room temperature, before becoming greeny blue. The change, when it began, spread from the colder end to cover the whole region between 207 and 220K in about 30 mins. It was monitored using the Beckmann 25 UV/visible spectrometer and the corresponding change in the UV/vis spectrum is given in Figure (4.6). After 24 hrs this same region of the film had a metallic glance and was highly reflecting. Less pronounced changes were observed up to about 240K, but beyond this deposition temperature the film did not appear to change upon annealing. Further discussion of the significance of these changes is deferred until Chapter 5.

4.3.2 The Influence of Deposition Rate on Film Topography

From the discussion in Chapter 1 the effective pressure, or deposition rate, if the evaporant was expected to influence the growth of films, although as pointed out earlier, its effect is likely to be much less pronounced than that produced by a change in substrate temperature. The TGS technique was used to examine the influence of deposition rate on film topography in the range $0.3\text{\AA sec}^{-1}$ to $10\text{\AA sec}^{-1}$. Since the change in the visible appearance of films, in going from one topographical type to another, was so marked, it was hoped that it would be possible to determine the influence of deposition rate by observing the substrate temperature at which these changes occurred. In general, an increase in the rate of deposition did, in fact, cause a shift in the position of the various regions shown in Figures (4.4) and (4.5), to higher substrate temperatures, although the pattern of changes in the visible appearance of films remained the same. Unfortunately, the technique was not sufficiently sensitive, or reproducible, to enable a quantitative assessment of the effect of deposition rate to be carried out. It was observed, however, that the region of film which remained yellow for the longest period

of time, after annealing to room temperature, corresponded to a substrate temperature of between 215K and 220K which was apparently relatively insensitive to changes in the rate of deposition.

SEM revealed some differences in the topography of films prepared at higher deposition rates. In particular there was a tendency for needle-like crystals to form at low substrate temperatures as shown in Figure (4.7) m.g (a). At higher substrate temperatures (268K) there was evidence of needle-like dendritic growth such as that shown m.g(b) in Figure (4.7). Both micrographs were obtained from a film deposited at the highest rate employed, i.e. $10\text{\AA sec}^{-1}$. These dendrites consist of fine needle-like crystals, indicated by  in m.g.(b), growing from large flat surfaces of crystallites, which are themselves oriented out of the film plane. At the slightly higher temperature of 274K, for the same film, dendritic growth was not immediately apparent, although secondary growth centres were observed as shown in m.g.(e) of Figure (4.7). All three micrographs were obtained from a part of the film which had not been coated with metal prior to annealing. Needle-like growth was not observed at the corresponding substrate temperature for those parts of the film which had been coated with metal prior to annealing as demonstrated by the three micrographs given on the R.H.S. of Figure (4.7).

4.3.3 The Influence of Substrate Temperature upon Film Topography

To avoid the complications of needle-like growth at higher deposition rate the topographical studies and the electrical conductivity measurements of Chapter 6 were normally carried out on films deposited at $1\text{\AA sec}^{-1}$. Topographical changes are, therefore, for

most part described with particular reference to samples prepared under these same conditions. Where a different deposition rate was used it is referred to in the appropriate plate. Micrographs included in this section are all representative of the various substrate temperature regions indicated in Figure (4.5), although many were specially selected because they provide a good illustration of a particular topographical feature. It is emphasised, however, that these examples were chosen from many hundreds of micrographs which were taken of (TTF)(TCNQ) films. For example, when carrying out SEM on a sample prepared by the TGS method the film was normally examined every 2 mm along its length. Therefore, the interpretation of the SEM results is based upon a very much larger body of data than it was possible to present here.

The micrographs included in Figures (4.8) to (4.15) which follow were considered to be representative of the substrate temperatures indicated on the page immediately preceding each plate. The magnification used is also indicated. Unless otherwise stated a voltage of 35 KV was employed. Characteristic topographical features of films deposited within various substrate temperature zones will now be described.

(i) Films deposited above 265K

This region was highly reflecting to visible light and exhibited interference colours. M.g.(d) in Figure (4.10) was taken of a film deposited at about 261K, and shows a pronounced tendency toward growth in the plane of the film. Crystallites were very thin in the perpendicular direction. At higher deposition temperatures the average size of crystallites decreased as can be seen in m.g.(f) of Figure (4.10), however, at this temperature growth was still largely confined

to two dimensions. As discussed in the following sections this region corresponds to that which gave the $0,0,n$ reflections in X-Ray diffraction i.e., the ab plane of the crystallites is parallel to the substrate.

In films deposited at higher deposition rates it was possible to observe the growth of crystallites out of the film plane at substrate temperatures above 270K as shown, for example, in a film deposited at $5\text{\AA sec}^{-1}$ in Figure (4.8). Although in plane growth is still very much in evidence in all the micrographs of Figure (4.8) the number of crystals growing out of the film plane increased with increasing temperature, reaching a maximum at 282K (m.g(b)). At this point crystals growing out of the plane were large with a high degree of perfection and had an ab plane aspect ratio approaching unity and were very thin in the c direction. To one side of each of these crystallites the underlying film was depleted. This effect is more easily observed in m.g.(d) which is a lower magnification shot of m.g(c).

Figure (4.9) which is a low magnification ($\times 2000$) study of a film deposited at $10\text{\AA sec}^{-1}$, between 260K and 274 provides striking evidence for the rapid increase in the concentration of crystals growing out of the film above about 265K.

(ii) Films deposited between 265 and 240K

Below 260K films which were highly reflecting at higher temperatures, began to exhibit surface roughness and to the naked eye appeared very dull and grey. At the high temperature end of this region, in the vicinity of 265K, in-plane '2-d' growth still predominated, as for example in m.g's(e) and (f), Figure (4.10), but

SEM micrographs of (TTF)(TCNQ) films

Figure 4.7. Films deposited at higher deposition rates (10^8 Å sec^{-1})

(a) & (c) Deposited at 228K x 20,000

(b) & (a) Deposited at 268K x 40,000

(e) & (f) Deposited at 274K x 40,000

Micrographs (a), (b) and (e) were not coated with metal prior to annealing while (c), (d) and (f) were coated with metal prior to annealing voltage: 35 KV

Figure 4.8. Film deposited at 5^8 Å sec^{-1} , at substrate temperature above 270K

(a) 272K x 10,000 (b) 282 x 10,000

(c) 286 x 10,000 (d) 286 x 4,800

(e) 289 x 10,000 (e) 291 x 10,000

Figure 4.9. Film deposited at 10^8 Å sec^{-1} , at substrate temperature between 260K and 274K

(a) 260K (b) 262K

(c) 264K (d) 268K

(e) 271K (f) 274K

Magnification: x 2,000 (1 cm = $50,000^8 \text{ Å}$)

Figure 4.10. Film deposited at 1^8 Å sec^{-1} , at substrate temperatures between 255K and 270K

(a) 255 (b) 257K

(c) 258 (d) 261K

(e) 264 (f) 268K

Magnification: x 20,000 (1 cm = $5,000^8 \text{ Å}$); voltage 30KV

crystallites began to exhibit roughness below this temperature as in m.g(c). By 255K the pattern of growth had changed again to one of out-of-plane growth m.g's(a) and (b). However, unlike films obtained in the region above 260K the underlying '2-d' growth was disrupted and the surface of the films became very irregular and poorly reflecting. As the substrate temperature decreased further this irregular pattern of growth was maintained, but crystallites decreased in size, as shown in m.g(e) of Figure (4.11) of a 240K deposit.

(iii) Films deposited between 240K and 220K

The disordered structure apparent in m.g(e) of Figure (4.11) for the film deposited at 240K gave way to a pronounced out-of-plane alignment of crystallites, which was a characteristic feature of films deposited in the vicinity of 235K, and is also shown in Figure (4.11) m.g's(c) and (d). The surface density of crystallites was also a maximum for films deposited at 235K. Below 235K, the concentration of crystallites with an out-of-plane orientation decreased with decreasing substrate temperature. When compared to the above mentioned micrographs it is clear from m.g's(d) and (b) that gaps have developed between the vertically oriented crystallites, the latter having taken on a stalagmite-like appearance growing out of an underlying fine grained disordered film.

The series of micrographs referred to above were taken of a film which had not been coated with metal prior to annealing. This unusual pattern of growth was examined in more detail by the replication technique referred to earlier which was used to establish if the structure was formed during deposition or as a result of annealing.

The micrographs shown in Figure (4.12) were obtained from the same film between 229K and 239K using the TGS technique. M.g's (b) (d) and (f) in Figure (4.11) were obtained from the film coated with metal prior to annealing and therefore corresponds to the film in the as-deposited state, while m.g's(a), (c) and (e) were taken of the uncoated film at the same substrate temperatures, (b) (d) and (f), respectively, after annealing at room temperature. Despite the difference in the magnification factor for the two sets of micrographs it is obvious that a pronounced change in the structure of the film occurred on annealing. The as-deposited film had a fine grained disordered structure with what appears to be small crystalline regions dispersed within it, in the form of small clumps. The number density of these crystallites first increased with temperature to a maximum at 233K (micrograph 3) and then decreased, until they had all but disappeared by 240K. The annealed film on the other hand contains thin lath-like crystals and has a very much more open grained structure than those of Figure (4.11). It is also apparent that, like the film in Figure (4.7), material has either been lost from the film on annealing or extensive restructuring has occurred. Micrographs (a) and (b) in Figure (4.11) also suggest that re-evaporation has taken place from film deposited at temperatures down to 220K.

Further support for re-evaporation from films deposited between 240K and 220K comes from micrographs (a) and (b) of Figure (4.7). Micrograph (a) was taken from a film deposited at high rate (10^8 sec^{-1}) 229K and then annealed, while (b) is the same film coated with metal prior to annealing. Again considerable restructuring of the former is evident in the form of needle-like growth and larger neonatal

crystallites⁽¹³⁾ which can only have occurred as a result of annealing. By 245K the topography of the annealed and unannealed portions of the film were practically identical.

(iv) Films deposited between 220 and 190K

The region between 220K and 190K is believed to include the OST and consequently was studied in some detail, in an attempt to establish the existence of a structural optimum. Samples were prepared by deposition onto a constant temperature, rather than a gradient temperature substrate. The micrographs in Figure (4.13) (a) to (f) were obtained from deposits prepared at 197, 210, 213, 215, 217 and 222K, respectively. All samples were prepared at a deposition rate of $1\text{\AA sec}^{-1}$. With the exception of (a) ($\times 10,000$) all micrographs have a magnification factor of $\times 20,000$.

It is apparent from the micrographs that there is a trend away from the randomly oriented crystallites of the 222K (micrograph f a) sample toward a film with oriented crystallites at 197K (m.g (a)). Films deposited between 197K and 210K (m.g (b)) and a very similar structure with what is presumably the b-axis of well formed prisms oriented out of the film plane, particularly at 197K. By 210K the crystallite grain boundaries were becoming less well defined and had all but disappeared at 213K. In the region between 213-217K (Figures c to e) films, when viewed from the top, had very little structure and crystallites were poorly defined. Figures 14a and 14b are micrographs of a thicker ($30,000\text{\AA}$) film deposited at 213K, showing a view from the top and a section through the film, respectively. It is obvious from these micrographs that films deposited in the region of

SEM micrographs of (TTF)(TCNQ) films (continued)

Figure 4.11. Films deposited at $1\text{\AA sec}^{-1}$, at substrate temperatures between 240K and 220K

(a) 222K	(b) 226K
(c) 232K	(d) 235K
(e) 240K	(f) 245K

Magnification: $\times 20,000$ ($1\text{ cm} = 5,000\text{\AA}$); voltage: 30KV

Figure 4.12. Films deposited at $1\text{\AA sec}^{-1}$, at substrate temperatures between 229K and 239K

m.g's (a) & (b) deposited at 229K

m.g's (c) & (d) deposited at 233K

m.g's (e) & (f) deposited at 239K

(b), (d) and (f) are of films coated with metal prior to annealing,
Magnification: $\times 10,000$. Voltage: 35 KV.

(a), (c) and (e) are of uncoated film. Magnification: $\times 40,000$.

Figure 4.13. Films deposited at $1\text{\AA sec}^{-1}$, at substrate temperatures between 197K and 222K

m.g. (a) 197	$\times 10,000$	(b) 210K	$\times 20,000$
(c) 213	$\times 20,000$	(d) 215K	$\times 20,000$
(e) 217	$\times 20,000$	(f) 222K	$\times 20,000$

Voltage: 35 KV.

Figure 4.14. Film deposited at $5\text{\AA min}^{-1}$, at a substrate temperature of 213K

(a) section through the film at 45° tilt

(b) top view of the film

Magnification: $\times 2,000$ Voltage: 30 KV

Figure 4.15. Films deposited below a substrate temperature of 190K

m.g's (a) & (b) deposited at 10K

(c) & (d) " " 120K

(e) & (f) " " 160K

(b), (c) and (e) were taken of films coated with metal prior to annealing

(a), (d) and (f) were taken from the uncoated film

Magnification: $\times 2,000$, except for (b) ($\times 5000$)

Figure 4.11

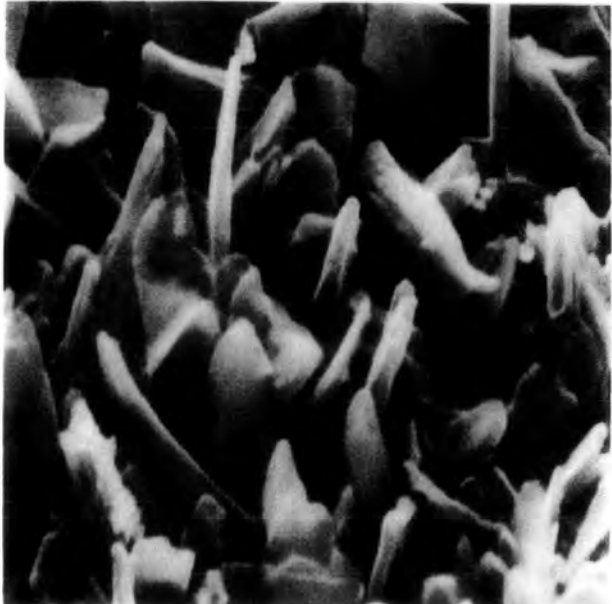
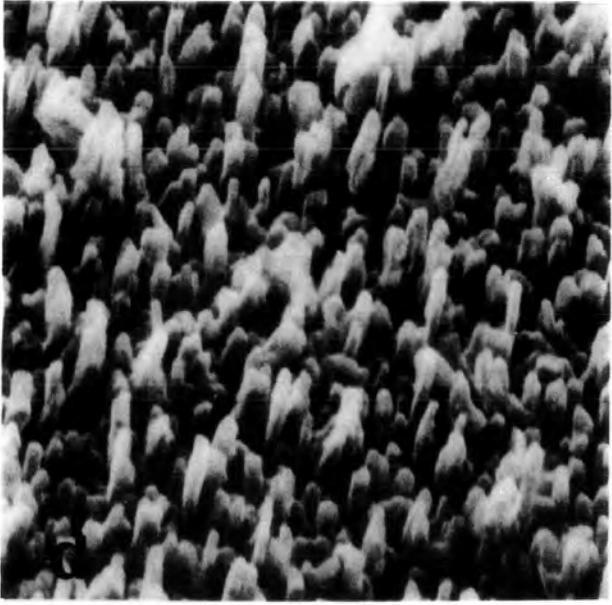
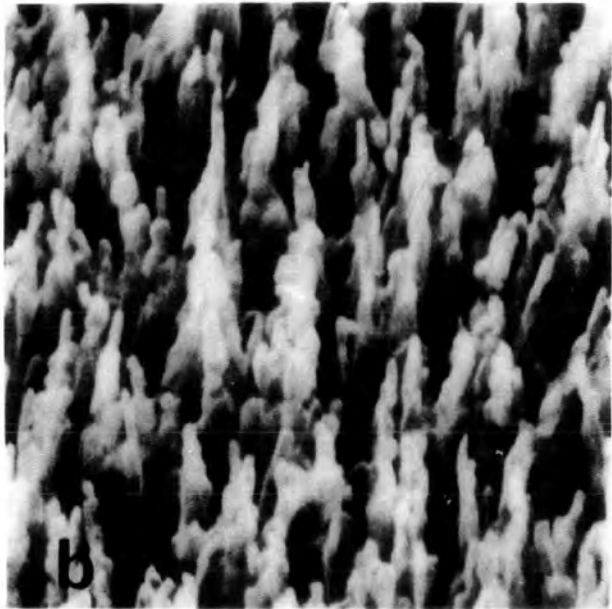
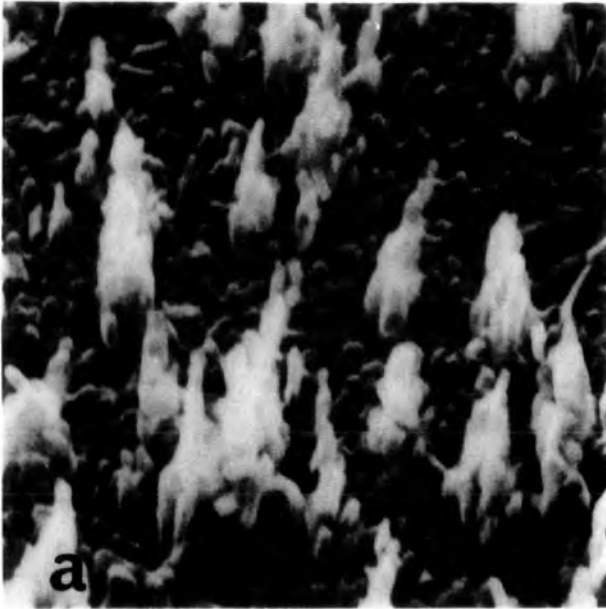


Figure 4.12.

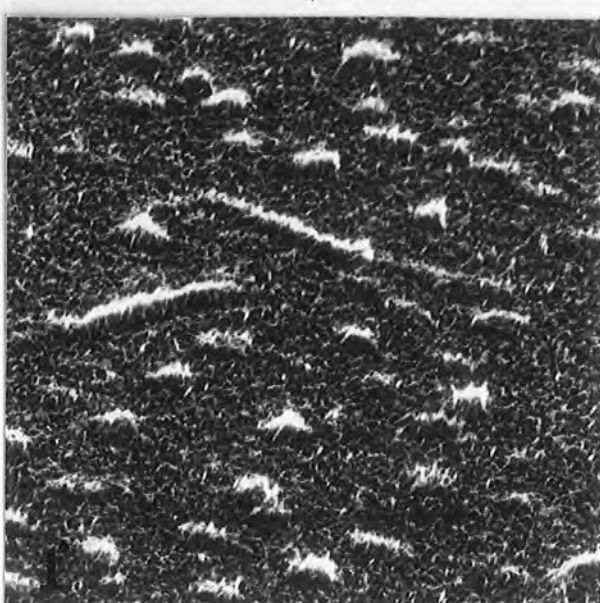
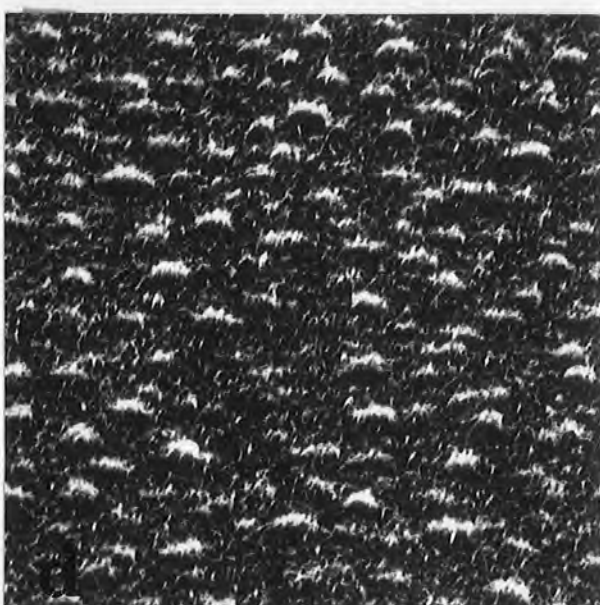
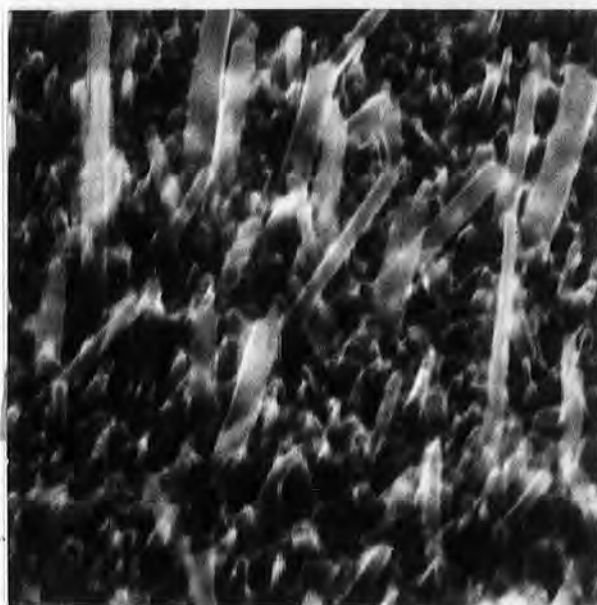
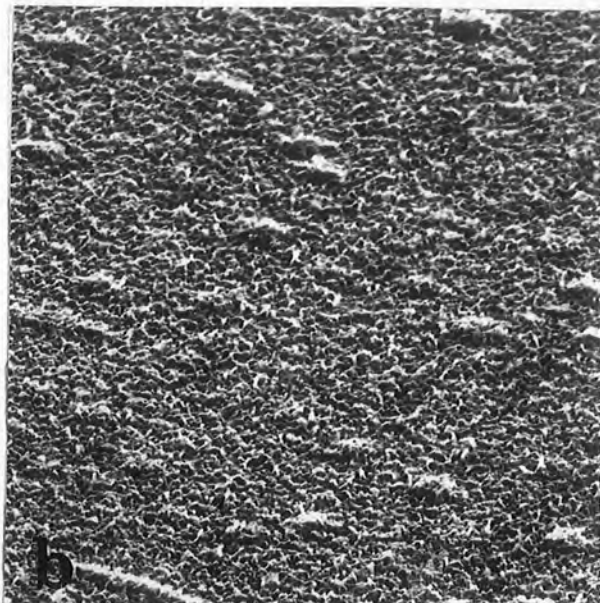


Figure 4.13

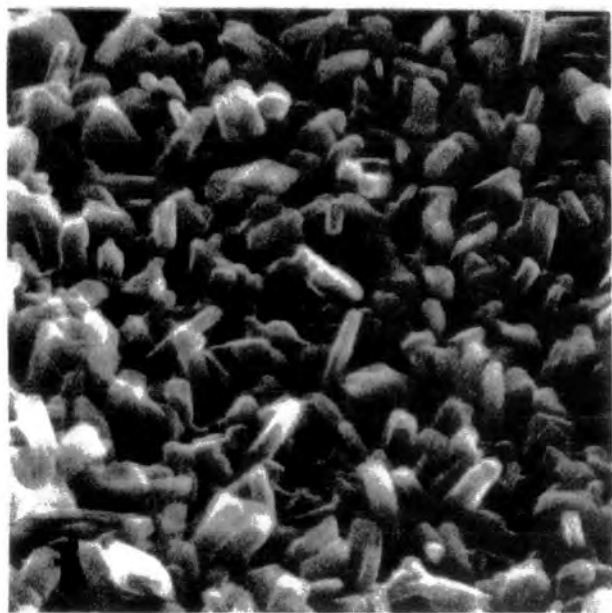
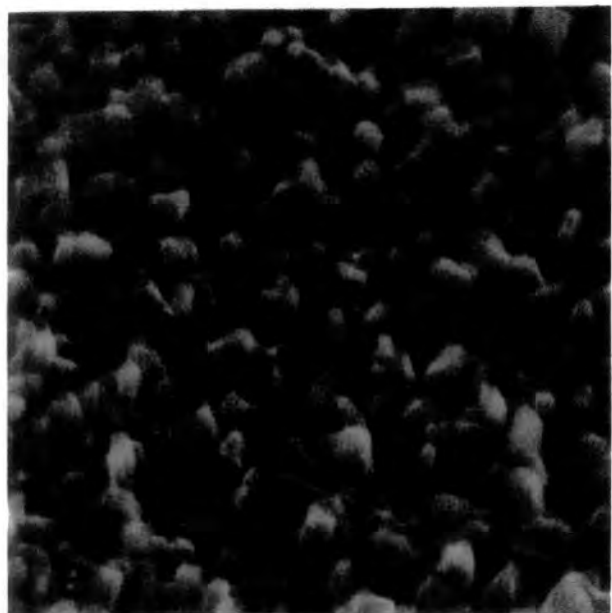
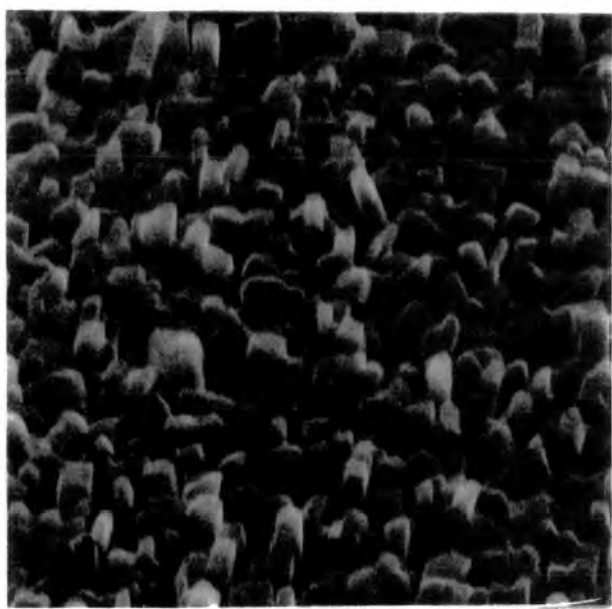
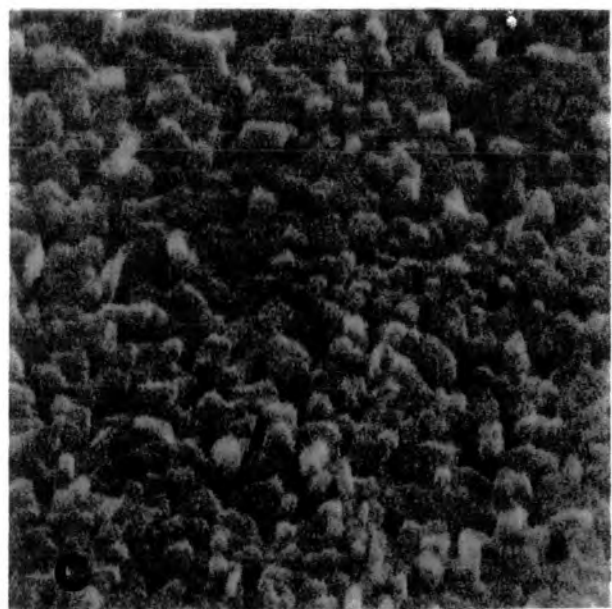
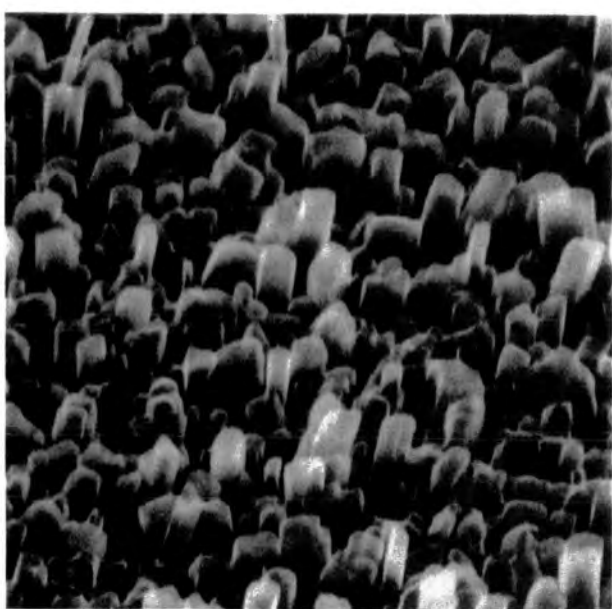
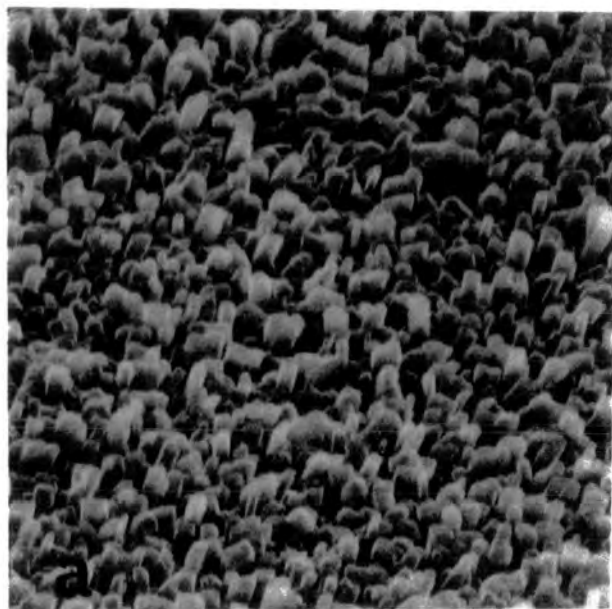


Figure 4.14

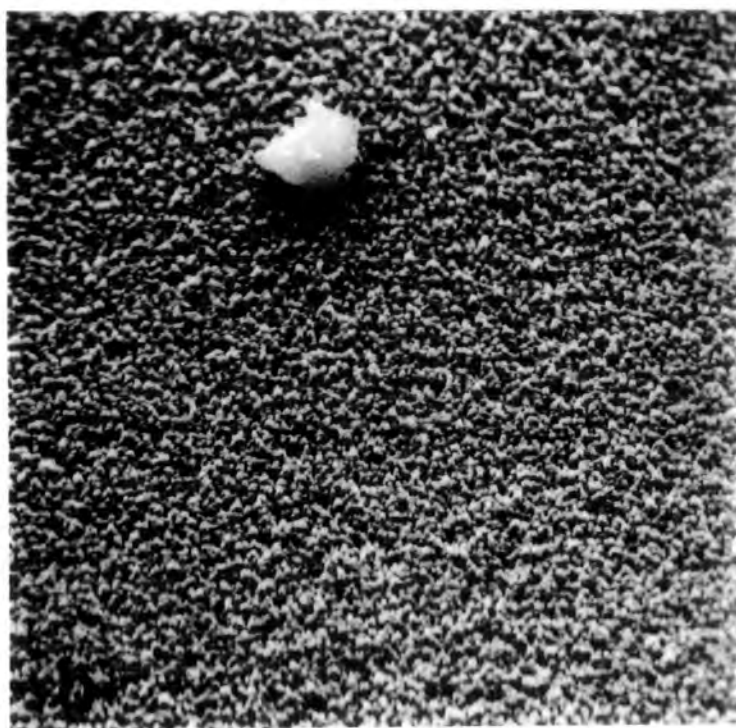
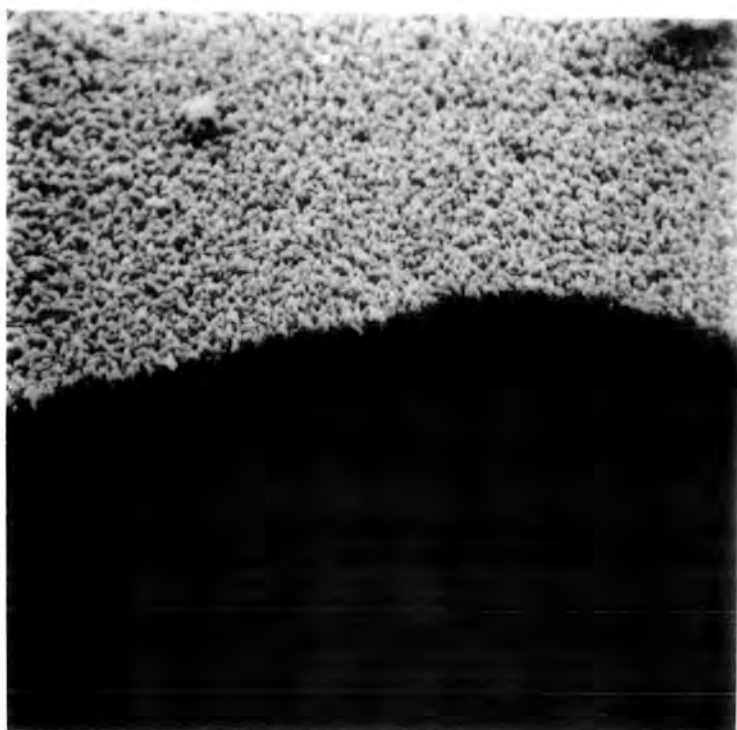
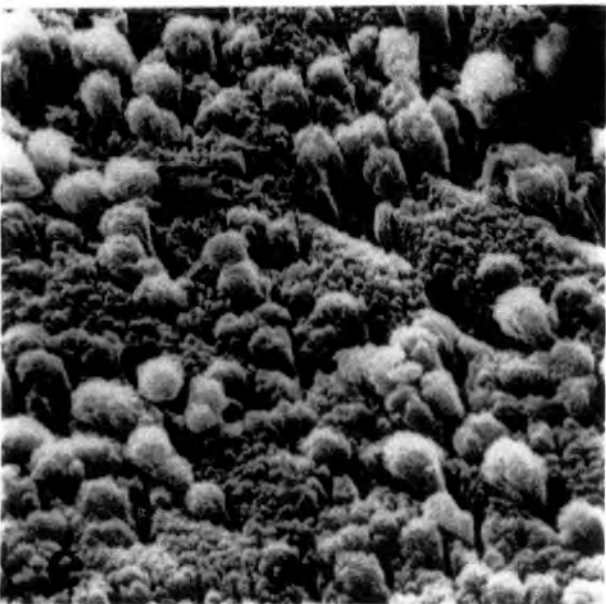
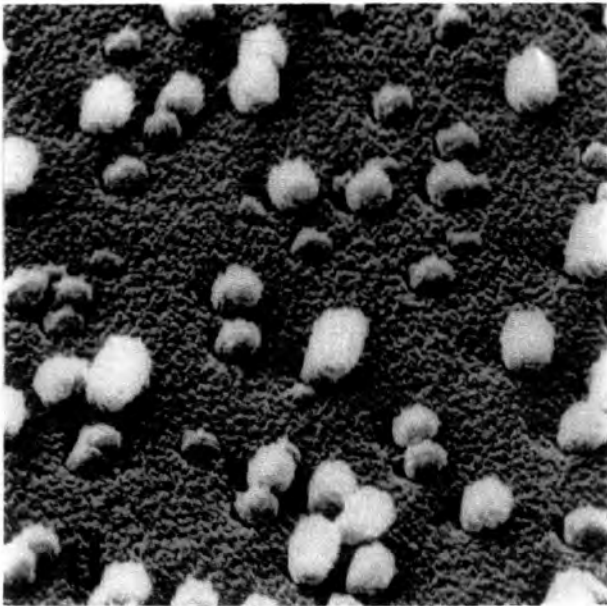
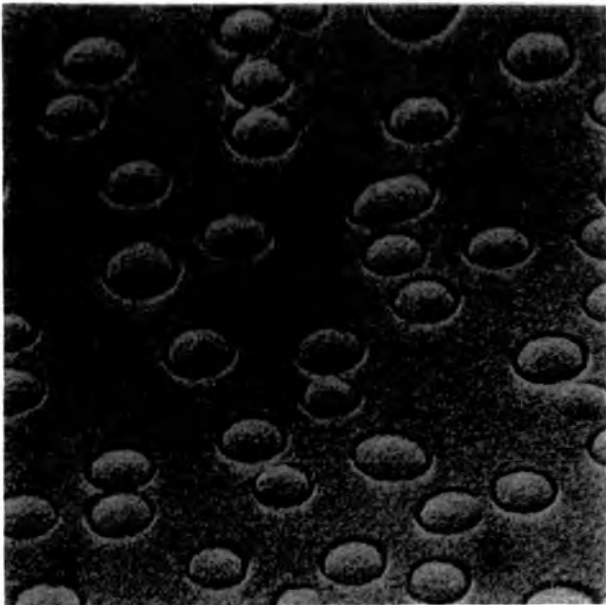


Figure 4.15



213K consist of highly oriented, densely packed crystallites.

(v) Films deposited below 190K

Films deposited below 190K were referred to briefly in the section dealing with the surface replication technique. Examples of films deposited in this substrate temperature region are given in the micrographs in Figure (4.15). The pattern of growth is very different below 190K, the major change being that growth and restructuring appears to occur on annealing. Those areas of film covered with metal prior to annealing were fine grained and had a poorly defined crystallite structure, for example, m.g(c). Although the film deposited at 160K m.g.(e) contains a large number of the cauliflower-like structures in the as deposited state, which are presumably regions of crystallite growth, there was little evidence of growth in the as deposited film at 120K m.g.(c). On annealing the amount of crystalline material present in the film increased in both cases although comparatively few crystallites had grown from the 120K deposit m.g(d). In both cases, however, it is definitely established that growth of crystalline material occurs from the underlying film, although it is possible that the crystalline phase was nucleated during deposition.

At very low deposition temperatures, viz. <20K, films were extremely fine grained and exhibited a somewhat unusual growth behaviour on annealing. Even after annealing at room temperature for several weeks there was no evidence of the cauliflower-like growth which was observed in films deposited at 120K and 160K. However, circular regions of between 25-50,000^oÅ in diameter were observed and these were evenly distributed across the whole surface of the film. An example of this structure is shown in m.g(a) in Figure (4.15).

Higher magnification micrographs revealed that each circular disc was separated from the main body of the film by a deep trough. When the film was coated with metal prior to annealing, as for example in m.g(b), the circular discs were still observed, and in the same concentration. However, significant changes had obviously occurred during the annealing process resulting in the formation of a network of cracks in the metal film. These cracks appeared to originate from the circular discs suggesting that growth was occurring in these areas. Neither the size nor the number density (ca. $10^6/\text{cm}^2$) of circular discs was changed by the presence of the metal film.

Apparently then, minor changes do occur in the low temperature film of (TTF)(TCNQ) after deposition of the metal surface layer, presumably because of considerable stresses generated on annealing. Despite protracted attempts it wasn't possible to determine if the disc like structures were formed during deposition or during the annealing process. They were not observed in films less than $1500\text{\AA}$ thick, or at temperatures of deposition above 30K. Their cause was not established, although a number of possible explanations were considered including: nucleation and growth of the crystalline phase of (TTF)(TCNQ), resulting in a decrease in the molar volume within the area of the disc; differential thermal expansion of the TTF/TCNQ film and the substrate on annealing; or re-evaporation of co-deposited water vapour which will almost certainly be present in films deposited at these low temperatures. However, since the study of (TTF)(TCNQ) was mainly concerned with films deposited above about 160K, further examination of these very low temperature deposits to determine the cause of the unusual disc-like structures was not carried out.

4.3.4 X-Ray Diffraction of TTF TCNQ Films

The X-ray diffraction patterns of annealed films of TTF TCNQ were obtained using the spectrometer described in Chapter 2. Copper K_{α} radiation was used. The diffraction pattern obtained for a film deposited at 273K is shown in Figure 4.16. There were three reflections at θ : 9.8° , 18.6° and 39.6° corresponding to the (002), (004) and (008) (hkl) planes of the complex⁽¹⁷⁾. 'd' Spacings were determined from the single crystal data of Kistenmacher⁽¹⁾ and these are listed in Appendix 3. The (008) reflection was shifted by about 3° from the position predicted from the single crystal data.

Chen and Schectman⁽¹⁷⁾ also observed a strong (0,0,1) orientation in films deposited at 210K and reported a diffraction pattern identical to that given in Figure (4.16). It corresponds to an orientation in which the ab plane of crystallites is parallel to the film plane. A scanning electron micrograph of a film deposited at this substrate temperature was given in Figure (4.10) in Section (4.3.3) and clearly shows the large ab face of the crystallites. This orientation persisted until a substrate temperature of 250K, however, between 273K and 250K the intensity of the (0,0,2) reflection diminished rapidly to zero as shown in Figure (4.17). Below a deposition temperature of 250K there were no prominent reflections, although several very weak ones were observed at 15.1° , 24.4° and 25.6° in separate films. Very weak reflections at 24.4° and 25.6° were reported⁽¹⁷⁾ for films of (TTF)(TCNQ) deposited at 77K but remain unassigned. In the present study no reflections distinguishable from the background were obtained from films deposited below 235K.

Figure 4.16. X-Ray diffraction pattern of a (TTF) (TCNQ) film deposited at 273K showing 0,0,1 reflections.

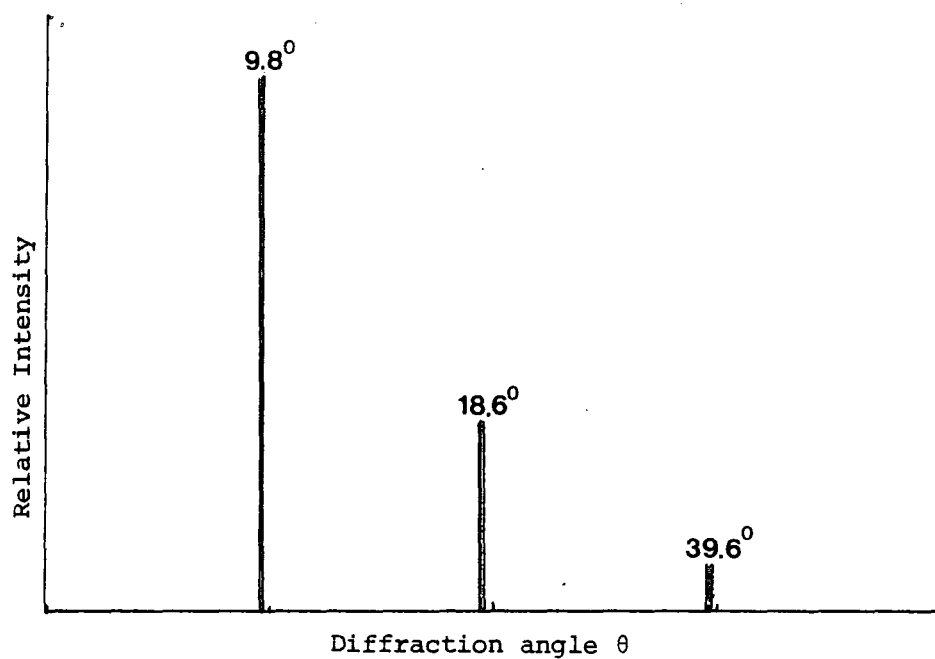
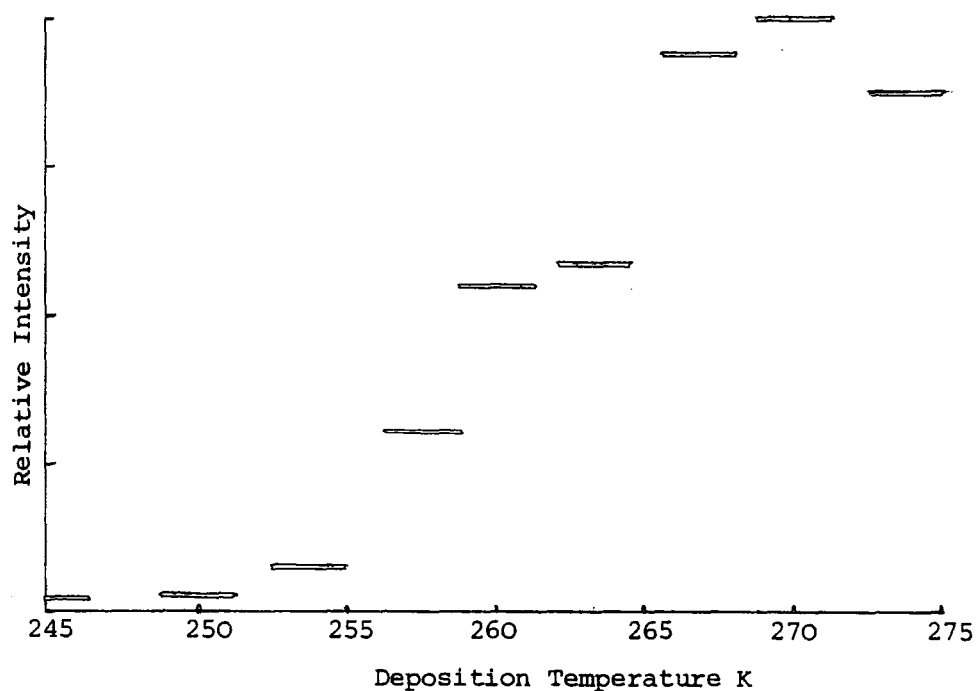


Figure 4.17. Decrease in intensity of the (0,0,2) reflection as a function of substrate temperature 275K and 250K.



4.3.5 Electron Diffraction of (TTF)(TCNQ) Films

Diffraction data obtained from a film deposited using the gradient technique are collected in Table 4.1. The substrate temperature during deposition is given in column 1 and corresponds to the point on the gradient ($\pm 2.5^\circ$) from which the diffraction data were taken. Lattice 'd' spacings were determined from the experimental diffraction patterns and are listed in column 2. The final column contains the most probable Miller indices assignment, which is based upon a comparison with 'd' spacings given in Appendix 3. When more than one assignment was possible both are given. Bracketed numbers refer to the calculated 'd' spacings of the corresponding indexed plane.

With the exception of the 275K deposit, all films exhibited a (h,o,l) orientation. Deposits intermediate in deposition temperature between those given in Table (4.1) also showed similar diffraction behaviour. The diffracting planes in the 275K deposit were predominantly (o,o,l), which corresponds to a crystallite orientation in which the ab planes are parallel to the substrate surface. This was the orientation observed in X-ray diffraction from thicker films.

Transmission micrographs of four areas, corresponding to deposition temperatures of; 270K, 260K, 250K and 228K, are shown in Figure (4.18) a to d respectively. The film deposited at 270K is very similar in appearance to the SEM micrographs in Figure (4.10), in that it consisted of large (ca. 20,000Å) well defined crystallites elongated along one axis (presumably the b-axis), with large areas of the film free of crystallites. This mode of growth is consistent with appreciable diffusion of ad-molecules on the surface prior to

Table 4.1. Crystallite Orientation as a Function of Substrate Temperature for (TTF)(TCNQ) films as determined by TEM.

Deposition Temperature	Observed 'd' Spacing Å	Probable Miller Indices Assignment and Calculated 'd' Spacings
275K	5.80	003 (5.93)
	3.58	005 (3.56)
	2.98	006 (2.97)
270K	5.1	201 (5.24)
	2.53	402 (2.62)
	2.04	108 (2.09)
260K	6.55	102 (6.44)
	3.89	104 (3.87) 300 (3.95)
	3.34	302 (3.32)
	2.68	106 (2.72) 304 (2.64)
	2.05	108 (2.09)
250K	VERY WEAK DIFFRACTION PATTERN	
228K	6.36	102 (6.44)
	3.92	104 (3.87) 300 (3.95)
	3.64	301 (3.66) $\bar{1}$ 05 (3.67)
	3.24	302 (3.31) 105 (3.20)
210K	6.45	102 (6.44)
	3.92	104 (3.87) 300 (3.95)
	3.28	302 (3.31)
UNSTABLE IN THE BEAM		

desorption. However, with decreasing substrate temperature, surface area coverage increased, until by 260K the unusual structure shown in Figure (4.18(b)) was obtained. Crystallites were also much smaller in the b-axis direction at 260K, although apparently growth was still predominantly 2-dimensional and controlled by surface diffusion. The product of surface area coverage and crystallite size was a maximum in the vicinity of 265K. Below this temperature crystalline size began to decrease.

Below 260K, deposits consisted of small needle-like crystallites as shown in Figure (4.18) (c) and (d). The 210K deposit was similar to Figure (4.18) (d) except that crystallites were smaller. Although apparently quite unlike the micrographs obtained using the scanning electron microscope, it should be remembered that Figures (4.8) (a) to (d) were obtained for much thinner films and will therefore reflect the earlier stages of growth. They were also viewed in transmission at 90° to the film phase and there is consequently no perspective, i.e. they are essentially 2-dimensional images. Nevertheless the same general trends were observed in both the scanning and transmission modes.

In general the diffraction patterns obtained consisted of a series of rings, which is normal for polycrystalline samples. Areas of the film deposited in the high temperature region at 260K and above did, however, show some tendency for the diffraction rings to break up, suggesting that crystallites adopted a preferred alignment with respect to the undiffracted beam. The diffraction pattern in Figure (4.19) shows this most clearly. It was obtained for the 260K deposit and corresponds to the micrograph shown in Figure (4.18) (b).

Figure 4.18. The effect of deposition temperature on the structure of (TTF)(TCNQ) films as shown by TEM

- (a) Film deposited at 270K
- (b) Film deposited at 260K
- (c) Film deposited at 250K
- (d) Film deposited at 228K

Magnification $\times 20,000$ (1 cm = 5,000Å)

Figure 4.19. Transmission electron diffraction pattern for a (TTF)(TCNQ) film deposited at 260K.

Figure 4.18

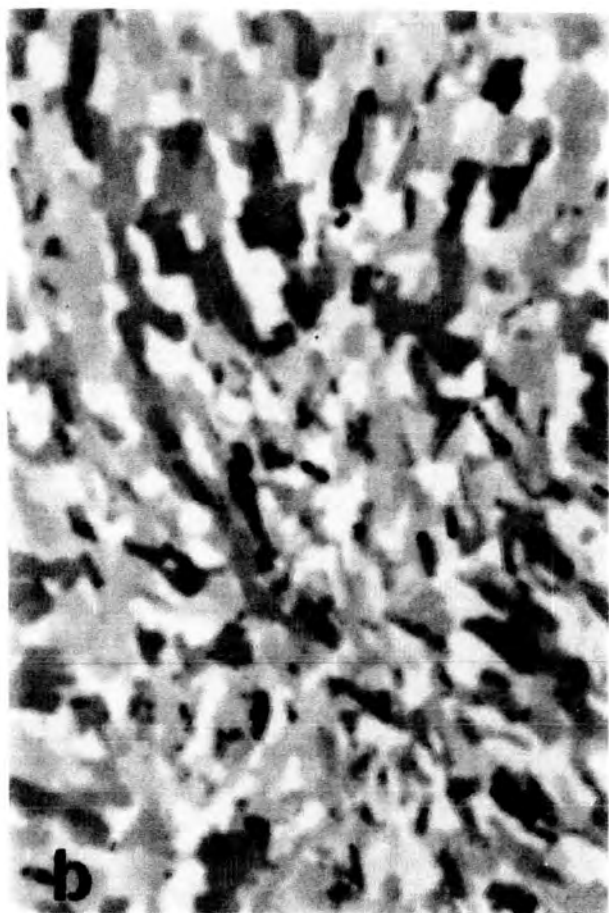


Figure 4.19



In addition to the diffraction spots, an unusual striation of the line corresponding to the 104 (or 300) plane was observed. A similar, but less pronounced effect was observed for areas of the film deposited between 260K and 275K. Linear structure of this kind may be caused by samples which are extremely thin in the diffraction direction⁽²⁹⁾.

4.4 Discussion

It is apparent from the SEM results that the temperature of the substrate during deposition has a marked influence on the topography of (TTF)(TCNQ) films. Because of the strong preference for growth along the b-axis, changes in topography were very pronounced and it was possible to identify transition points between various modes of growth with reasonable accuracy. Five substrate temperature regimes were thus identified which had the following characteristics.

a) Films deposited above 255K

Large well formed platelets with their ab planes oriented out of the film plane were observed above about 265K. At lower substrate temperatures the angle at which these crystallites were inclined to the surface was reduced, culminating in crystallites growing with their ab planes parallel to the film surface.

b) Films deposited between 235K and 255K

The pattern reversed in that the predominant trend was to out of plane growth, with the concentration of crystallites increasing at lower substrate temperature. At 235K a pronounced alignment of crystallites was observed with their long axis oriented out of the film plane. The lack of XRD reflections and weak electron transmission intensities suggests that films deposited below 250K were strongly disordered.

c) Films deposited between 235K and 220K

There was considerable evidence for re-evaporation from 'disordered' regions of films deposited in this regime during annealing. This was accompanied by pronounced changes in their topography. The relative proportion of crystalline to disordered material decreased at lower temperatures and there was a marked decrease in the thickness of deposits.

d) Films deposited between 220K and 190K

An increase in film thickness occurred reaching a maximum between 210-215K. A pronounced out of plane alignment of the long-axis of crystallites was also observed in this substrate temperature regime. Between 210-215K films had a dense columnar structure with a smooth surface. At lower temperatures well formed square prismatic crystallites were observed, with an out of plane orientation.

e) Films deposited below 190K

Films initially had a disordered structure particularly at low temperatures with the number of crystalline centres increasing with increasing substrate temperature. On annealing, further crystallites were formed, although their concentration in the fully annealed film was dependent on deposition temperature. At low deposition temperatures very few larger crystallites were formed even after annealing.

The topographical spectrum observed for (TTF)(TCNQ) films provides a classic example of the changes which occur when progressively non-equilibrium conditions of growth are employed. Thus, under essentially equilibrium conditions, such as occur at high substrate temperatures and low supersaturation, film topography and crystal morphology are largely determined by thermodynamic considerations. The morphology of crystals will, under these circumstances, approximate

to the equilibrium form which is subject to the condition⁽³⁰⁾:

$$\sum \sigma_i A_i = \text{minimum}$$

where σ_i is the specific surface free energy of the i th face and A_i its area. On the basis of PBC theory the ab face of (TTF) (TCNQ) is expected to predominate at low supersaturation and this was shown by XRD and TEM to be the case for films deposited above 260K. At low substrate temperatures and high supersaturations on the other hand kinetic considerations, for example the surface mobility of ad-molecules, become important. Under these conditions b-axis growth should predominate, since this is the strong growth direction. This accounts for the pronounced out of plane b-axis growth observed for films deposited at 235K (Figure (4.11)). In general, therefore, it is possible to provide an adequate description of the topography of films deposited at 235K in terms of nucleation and PBC theories. However, since it is the substrate temperature regime below 240K which is of primary interest, vis a vis the optimum substrate temperature effect, a detailed discussion of the topography of films deposited above 240K is left until Section (4.4.2).

4.4.1 Films Deposited Below 240K

(i) Evidence for re-evaporation

The micrographs of Figures (4.11) and (4.12) suggests that the rate of nucleation of the crystalline phase, during deposition, reaches a maximum in the vicinity of 235K. Below this temperature, nucleation rate decreases, presumably because of a decrease in the surface mobility of ad-molecules, as predicted by equation (1.7). In the absence of nucleation, molecules may either re-evaporate or, alternatively, become trapped by the impinging flux before they have time to re-evaporate from the surface, as discussed in Chapter 3.

Re-evaporation should, of course, cause a reduction in the mass of material deposited relative to films prepared above 235K. Figure (6.13) Chapter 6 does, in fact, show that a marked decrease in the thickness of films did occur for deposition temperatures between 235K and 220K, although it increased again below 220K. However, on closer examination of Figures (4.7) and (4.12) it was definitely established that re-evaporation took place as a result of annealing. This does not, of course, exclude the possibility that re-evaporation also took place during deposition.

The amount of material which re-evaporates from disordered regions on annealing does appear to depend upon the concentration of crystalline centres present in as-deposited films. The micrographs in Figure (4.12) show this clearly. The concentration of stalagmite-like crystals growing out of the plane of the film which are interpreted as sites of nucleation in the as-deposited film, decrease with decreasing substrate temperature between 235 and 220K. It is proposed that on annealing these nucleation centres act as sites for further growth by capturing molecules as they re-evaporate from disordered regions of the film. Since re-evaporating molecules will have a large component directed out of the film plane this would explain the unusual mode of growth observed in Figure (4.12). The amount of material retained in this way will depend upon the relative rates of re-evaporation from disordered regions and growth of these nuclei. It is possible to understand, therefore, why film thickness increases rather than decreases in going from 220K to 235K. Although the occurrence of nucleation is possible within the disordered phase as a result of annealing, as will be shown in Chapters 5 and 6, this does not take place until films are annealed above 270K, whereas re-evaporation and growth of existing nuclei begin immediately above the

temperature of deposition.

(ii) Location of the OST for (TTF)(TCNQ)

The observation of re-evaporation is important because it appears to substantiate VBR's proposal that the OST effect is associated with loss of material from disordered regions of the film, whether it be during deposition or annealing. This makes 235K a possible candidate for the OST in (TTF)(TCNQ) films. The pronounced out-of-plane b-axis alignment observed at this temperature gives way to a more disordered crystallite array at higher temperatures, which is reminiscent of VBR's observations of the OST in anthracene. Their SEM results for anthracene, and those for phthalocyanine⁽³⁷⁾ show a finer grained structure at the OST, which would be consistent with a maximum in nucleation rate, such as was observed for (TTF)(TCNQ) films at 235K. It is not immediately apparent, however, why the location of a maximum in nucleation rate of the crystalline phase should be related to the boiling point of a liquid rather than the sublimation of a solid.

It was not possible to determine the normal boiling point of (TTF)(TCNQ) because it decomposes prior to melting at atmospheric pressure. However, comparing it with other aromatic compounds of similar molecular weight helps to define a fairly broad substrate temperature interval between 180K and 240K within which the OST for (TTF)(TCNQ) might be expected to occur, i.e. assuming the OST is located at one third of the normal boiling point. Within this temperature regime there is, in fact, a second possible candidate for the OST, located at approximately 213K. Since films deposited at both 235K and 213K exhibited similar topographical features, i.e. a pronounced columnar type of growth with densely packed crystals oriented out of the film plane, it is not possible to state categorically

which of these two temperatures is the OST, on the basis of the SEM results alone. Furthermore, XRD and TEM both failed to give any useful information about film structure in this temperature regime, on which to base a decision about its location. Hence the need to carry out infrared and electrical measurements, which are discussed in Chapters 5 and 6, respectively. Certain features of the SEM results do, however, allow an educated guess about the location of the OST in (TTF)(TCNQ).

The study of aromatic hydrocarbons presented in the previous chapter strongly suggests that the OST effect is associated with a transition between disordered and ordered phases of these compounds. Similar arguments should also extend to (TTF)(TCNQ). For example, a reasonable interpretation of the micrographs in Figure (4.15) is that films deposited below about 200K are initially obtained with a highly disordered structure which only crystallises on annealing. Thus the results obtained for the film deposited at 120K m.g's(c) and (d) are consistent with a small concentration of nuclei in the as-deposited film which act as centres for growth on annealing. The concentration of such nuclei in these thicker films increase at higher substrate temperatures to reach a maximum in the region of 213K. At this temperature crystallites are most densely packed resulting in the structure shown in Figure (4.14a) which is a cross section through the film. Unlike the region between 220K and 235K, growth which occurs as a result of annealing in films prepared below 213K appears to involve the formation of new nucleation centres within the disordered regions, rather than re-evaporation and subsequent growth on nucleation centres introduced into the film during deposition. Although Figure (6.13) shows that there was a small decrease in film thickness below 213K there was very little visual evidence to suggest that substantial

re-evaporation had taken place. Further evidence to support this conclusion was obtained from annealing experiments, which are discussed in Chapter 6.

On the basis of the SEM evidence it is inferred that there are two substrate temperature regimes; between 235 and 220K, and below 210K, respectively, within which deposition produces films containing both the disordered and crystalline phases of (TTF)(TCNQ). At intermediate substrate temperatures (210K to 220K), however, an as yet unspecified ordering process leads to an increase in film thickness and is responsible for the densely packed structure observed after annealing to room temperature. This, it is proposed, is the region of the OST for (TTF)(TCNQ), because as will now be discussed it appears to coincide with the boundary line between the liquid and vapour phase and should therefore be related to the nominal boiling point.

(iii) An explanation of the OST effect

An explanation of the OST effect is provided with reference to Figure (4.20), which is a generalised phase diagram for a solid/liquid/vapour system, with effective pressure or deposition rate plotted against substrate temperature. The solid lines (AB), (BC) and (BD) represent the thermodynamic boundaries between the three phases, while the dashed line (BE), dividing regions (1) and (4), is an extrapolation of the liquidus line (BC) into the region of the diagram where crystalline solid is thermodynamically the most stable phase. The line (BE) implies the existence of a metastable equilibrium between the liquid and vapour phase in the absence of crystallisation. Because of the very high quenching rates achievable with vapour deposition onto cooled surfaces it is a most effective method of by-passing the crystalline state and has been used extensively to prepare amorphous or glassy solids⁽³¹⁾.

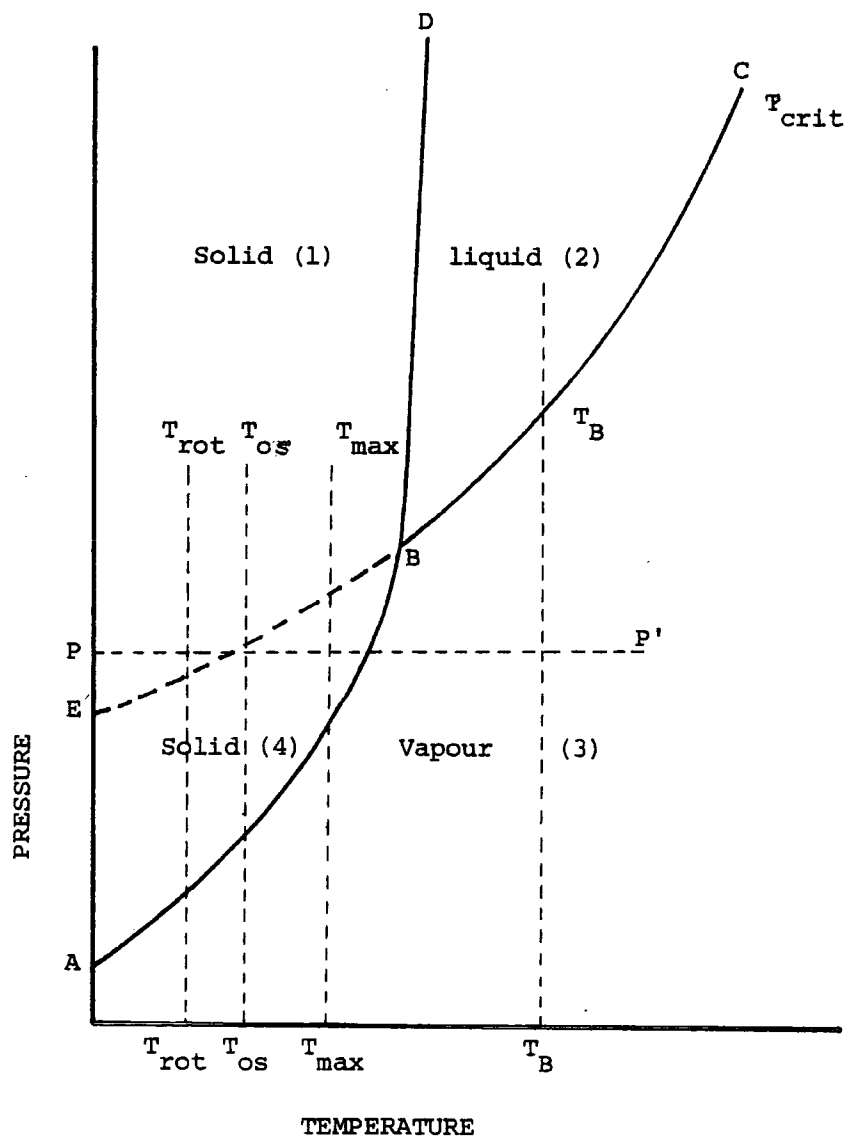


Figure 4.20. Idealised phase diagram for a solid/liquid/vapour system showing the formation of a metastable liquid phase below the melting point (line BE)

At constant impingement rate, the influence of temperature on the nature of the condensate can be followed by traversing a line PP'. Beginning at high substrate temperatures, where the line PP' crosses AB, nucleation of the crystalline phase is thermodynamically possible and the rate of nucleation increases with decreasing substrate temperature to a maximum at $T_{\max}$. This region corresponds to substrate temperatures above 235K for TTF TCNQ. Below $T_{\max}$ the rate of nucleation decreases for kinetic reasons and individual molecules are stable entities under the conditions of deposition and comprise the first disordered phase. Thus, although the crystalline phase of the complex is thermodynamically the most stable phase below $T_{\max}$ its nucleation is prevented by the low mobility of ad-molecules. Within disordered regions of the condensate, molecules presumably adopt a random orientation. Without the stabilising influence of lattice formation the net interaction energy between molecules must, of course, be repulsive since only the crystalline phase is stable in this substrate temperature regime. The disordered phase is therefore thermodynamically unstable, which would explain the tendency to re-evaporate during annealing.

At the point T_{OS} where the line PP' crosses the extrapolated liquid equilibrium line (BE) the liquid phase is in true metastable equilibrium with the vapour phase, despite the fact that substrate temperature is several hundred degrees below the melting point. Films deposited at T_{OS} are therefore properly described as liquid-like rather than solid or disordered, because although they do not possess long range order (LRO) they do possess short range order (SRO) as does a liquid. Although this may appear to be a subtle distinction to make, it is, in fact, crucial for understanding the OST effect since it provides a

straightforward explanation for the generality of relationship between T_{OG} and the normal boiling point of the liquid phase of materials in terms of fundamental forces of attraction and repulsion which exist between molecules, as will now be discussed.

(iv) The Principle of Corresponding States⁽³²⁾

The properties of a non-ideal gas may be treated approximately in terms of the well known Van der Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad (4.1)$$

where the term a/V^2 is a measure of the attractive interaction between molecules; for a given gas a is a constant and V is the molar volume; b , the effective volume of a molecule is approximately four times the measured volume. b is related to both the repulsive and attractive interaction between molecules. The other symbols have their usual meaning.

The pressure, volume and temperature may be expressed in terms of the critical pressure, volume and temperature, respectively.

$$P = \pi P_C \quad V = \phi V_C \quad T = \theta T_C$$

and it is then possible to write the Van der Waals equation in terms of the reduced pressure π , volume ϕ and temperature θ .

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta \quad (4.2)$$

In its reduced form the Van der Waals equation is perfectly general, and represents qualitatively the behaviour of all substance in both the liquid and gaseous states. Thus substances with the same reduced pressure π when at equal reduced temperatures θ have the same reduced volumes V_C , which is a statement of the Law of Corresponding States. While equation (4.2) is perfectly general for VDW type molecules it

suffers from the same limitations as the VDW equation with regard to molecular association.

A consequence of the Law of Corresponding States is that the normal boiling point is a corresponding temperature, i.e., it is a constant fraction (0.6)⁽³³⁾ of the critical temperature. This is approximately true for a variety of substances, normal as well as associated. By the same token all points on the liquidus curve (CE) including the portion (BE) in Figure (4.20) can be considered to be corresponding temperatures, thus the optimum substrate temperature T_{OS} which is one third of the normal boiling, has a value of $0.2 T_{crit}$ (0.6/3). The same will be approximately true for all substances whose molecules interact substantially through VDW forces. Neutral organic substances, which includes aromatic molecules such as anthracene, (TTF) and (TCNQ), fall into this category although electronic effects are clearly important in the complex (TTF)(TCNQ).

The reason for drawing attention to the VDW equation and the Law of Corresponding States is to emphasise; a) that the significant relationship is that between T_{OS} and T_{crit} rather than that between T_{OS} and T_B , and b) that T_{crit} and hence T_{OS} are determined by the relative magnitudes of the repulsive and attractive interactions between molecules, since

$$T_{crit} = \frac{8a}{27Rb} \quad \text{and} \quad T_{OS} = 0.2 T_{crit}$$

At the point where PP' crosses the thermodynamic boundary line (BE) in Figure (4.20) the net interaction potential will change sign, becoming attractive on the LHS of (BE). It is proposed therefore that films deposited in the vicinity of the boundary line owe their additional stability to a net short range attractive interaction between molecules

and it is this which is responsible for the OST effect.

The situation envisaged during deposition at the OST is one in which molecules are able to relax by rotation, relative to their nearest neighbours. This enables us to maximise short range attractive forces and so establish a structure which possesses short range order. At higher temperatures short range repulsive forces will begin to dominate, presumably because of the increase in the effective volume of molecules⁽³³⁾, which will prevent them adopting a minimum potential energy configuration. At the same time their severely curtailed translation freedom prevents molecules from undergoing nucleation until a deposition temperature of 235K, in the case of (TTF)(TCNQ) films, rendering them thermodynamically unstable. Below the OST, on the other hand, the rate of rotational relaxation of molecules (τ_{rot}), which is an activated process, normally obeying an equation of the same form as equation (1.6), i.e.

$$\tau_{rot} = \frac{1}{\nu_{rot}} \exp \frac{-E_{rot}}{kT} \quad (4.3)$$

will decrease. ν_{rot} is a molecular rotation frequency and E_{rot} is the activation energy associated with the process of rotation. At temperatures sufficiently low to cause a significant reduction in τ_{rot} molecules will be prevented from adopting a minimum energy configuration, with respect to nearest neighbours leading to a second region of disorder and a reduction in SRO. The temperature at which this occurs, which is designated T_{rot} in Figure (4.20), defines the lower limit of existence of the metastable liquid phase, for a given deposition rate. From the SEM data obtained for (TTF)(TCNQ) films deposited at about $1 \text{ \AA sec}^{-1}$ the apparent range of existence of the metastable liquid phase in the as-deposited state extends from about

190K up to 213K.

The existence of an SRO phase in the vicinity of the OST, also infers that films deposited below 190K consist of a disordered phase, containing regions of SRO rather than crystallites. However, the film deposited at 160K (m.g 4.15(d)) for example, appears to contain crystalline regions in the as-deposited state. In order to explain these apparently conflicting results it is necessary to consider that bonding between nearest neighbours in the SRO state is similar to that in the crystalline phase of (TTF)(TCNQ) and is largely determined by the out-of-plane interaction between molecules. This may still result in a preference for molecular stacking, even in the absence of LRO and would explain the striking similarity between films deposited at 235K and those deposited at the OST. Thus it is envisaged that in the metastable state segregated stacks may still be formed but within these stacks positional or orientational disorder prevents the establishment of SRO. Furthermore, it is likely that on annealing the metal replication technique would not prevent crystallisation of these disordered stacks so that they appear as crystallites in metallised films.

(v) Dependence of the OST on deposition rate

Since the OST falls on the extrapolated liquidus line its dependence on deposition rate, or effective vapour pressure, should be given by the Clausius-Clapeyron equation. However, the substrate temperature range over which it is possible to observe the OST effect will have an upper limit, which coincides with $T_{\max}$ and a lower limit determined by T_{rot} . Above $T_{\max}$, nucleation of the crystalline phase will occur during growth. Furthermore, in the regime $T_{\max} - T_{\text{opt}}$ nucleation should still be possible, albeit at a lower rate so that in this co-existence region both the crystalline and metastable liquid

phase will be formed at higher deposition rates than $P P'$, it is assumed that at this deposition rate, the nucleation rate of the crystalline phase is negligible. Below T_{rot} of course condensed film will always contain a proportion of the disordered phase in the as-deposited state because of the reduced relaxation rate of molecules. Thus, although there is not a unique value for the OST the range of existence of the metastable liquid phase covers a relatively small substrate temperature interval, which in the case of (TTF)(TCNQ) falls between about 190K and 235K, depending upon the rate of deposition.

T_{rot} and T_{max} in Figure (4.20) are shown as being independent of deposition rate (R) for the sake of clarity. The latter should, in fact, be depicted as exhibiting a weak dependence, as outlined in Section (1.2). The influence of R on T_{rot} has not been ascertained, but since it is likely to influence only the pre-exponential term in equation (4.3) and τ_{rot} is dominated by the exponential term, it is likewise thought to be relatively weakly dependent on R .

(vi) Summary of the study of films deposited below 235K

Films deposited above about 235K were essentially crystalline in the as-deposited state and were considered not to be relevant to the main theme of this thesis, which is concerned with a study of the OST effect. Thus the following section, while of interest in connection with the mechanism of crystal growth from the vapour phase, at relatively low supersaturations, may be safely omitted if the readers main purpose is to gain further insight into the OST effect. A summary of the conclusions derived from the SEM study of (TTF)(TCNQ) films deposited at 240K and below will therefore be given at this point, so that the reader may proceed directly to Chapter 5 is desired. The important conclusions were:-

- a) A maximum in the rate of nucleation of the crystalline phase occurred in film deposited in the vicinity of 235K, which marks the boundary between the high temperature crystalline phase and low temperature disordered state of (TTF) (TCNQ).
- b) In the substrate temperature regime between 235K and 220K both crystalline and disordered regions were formed during deposition. Re-evaporation of disordered material, which occurred on annealing, was considered to be responsible for a reduction in the thickness of films deposited between 220K and 235K.
- c) It was proposed that a metastable liquid-like film possessing SRO was deposited below 220K and, furthermore, it was concluded that this was the cause of the OST effect. The OST for (TTF) (TCNQ) films deposited at $1\text{\AA sec}^{-1}$ was located at 213K.
- d) Below 190K a reduction in the molecular relaxation rate was considered to be responsible for an increase in the degree of disorder incorporated into films during deposition. Crystallisation was observed to occur within disordered regions of low temperature condensates on annealing.
- e) The pronounced out-of-plane b-axis alignment of crystallites observed at 235K, which coincided with a maximum in film thickness, was ascribed to a high rate of nucleus formation during deposition. These acted as centres for further growth when material was re-evaporated from disordered regions of a film on annealing.
- f) Films deposited in the vicinity of 213K showed characteristics similar to those prepared at 235K but crystallites were, if anything, more densely packed and the surface was smoother in the former case. This latter structural optimum is thought to be associated with establishment of SRO at the optimum substrate temperature.

Since XRD and TEM failed to provide any useful information about the structure of films deposited below 250K the conclusions given above are largely based on conjecture, which although not unreasonable is not entirely satisfactory. Thus for the moment they should be considered as proposals rather than conclusions. However, an important objective in carrying out a study of the topography of (TTF)(TCNQ) films was to establish the existence of a structural optimum, and its location, and this objective has almost certainly been realised. In the process a number of highly pertinent questions have been raised in respect of the nature of films deposited below 235K. For example, proposals concerning the reasons for the observation of an OST in vacuum deposited films hinge upon the formation of a disordered phase below 235K and the consequent loss of LRO, and in particular upon the possibility that a metastable liquid-like phase possessing SRO is formed in the vicinity of a structural optimum. Clearly in order to establish the existence of both the disordered and metastable phases it is necessary to investigate the properties of films in the as-deposited state. This is then the main theme of Chapter 5 which is devoted to an infrared study of (TTF)(TCNQ) films.

Having established the existence of a structural optimum in (TTF)(TCNQ) films it becomes necessary to demonstrate that it leads to an optimisation of film properties. This was the main purpose for carrying out the electrical conductivity measurements, which are described in Chapter 6.

4.4.2 Films Deposited at Substrate Temperatures Above 235K

On crossing the solidus line (AB) in Figure (4.20) nucleation of the crystalline phase will occur, the concentration of nuclei increasing with decreasing substrate temperature, as predicted by equation (1.7). Substantial re-evaporation is expected in this

region, as determined by equation (1.6), coupled with a high relative surface mobility whose temperature dependence is given by equation (1.5). Thus, in the substrate temperature regime above 250K film topography can be explained qualitatively by combining equations (1.6) and (1.5) i.e. the relative rates of surface migration and re-evaporation, as will now be discussed.

(i) Films deposited at substrate temperatures above 255K

The mean displacement ($\bar{x}$) of an ad-molecule on a surface after impingement, but prior to desorption, is given by equation (1.9) which is repeated here for convenience

$$\bar{x} = |D_a \tau_a|^{\frac{1}{2}}$$

As outlined in Section (1.2.2) D_a and τ_a have opposite temperature dependencies hence equation (1.9) predicts that $\bar{x}$ goes through a maximum at a temperature determined by $\Delta G_{des} - \Delta G_{sd}$ assuming that the barrier to nucleation ΔG^* is negligible by comparison. As outlined in Chapter (1) the rate of growth of a crystal face depends upon the rate of advance of steps upon that face. Since the latter rate is proportional to ($\bar{x}$) the dimensions of crystallites growing in the film plane should also go through a maximum. Experimental evidence for this maximum is given m.g(a) to (e) in Figure (4.10) for a film deposited at a rate of 70Å/min. This is the deposition temperature regime in which the ab plane of crystallites was shown by XRD to be parallel to the substrate i.e. the strong growth 'b' direction is oriented in the film plane. This is consistent with PBC theory. Because of the high degree of supersaturation at the surface the strongest growth direction should be oriented in the film plane. The maximum in the size of the ab face of crystallites growing in the film plane occurred at 258K to 261K i.e. m.g's(b) and (c) of

Figure (4.10).

Two other features of Figure (4.10) require further comment. At low temperatures, m.g.(a) (257K), there is evidence of out-of-plane growth, although the underlying surface film has a smooth appearance with poorly defined grain boundaries. At high temperatures (268K), on the other hand m.g.(e) shows that the in-plane crystallite aspect ratio is much closer to unity, and that grain boundaries are more clearly defined than in the low temperature deposits. These changes infer that as deposition temperature increases re-evaporation becomes the dominant influence on film topography rather than surface diffusion, and this is supported by the results for films deposited at high temperatures.

At higher substrate temperatures ΔG_{sd} , which is generally much less⁽³⁴⁾ than ΔG_{des} , can be neglected and the latter determines $\bar{x}$ through equation (1.9). Since the average number (n_1) of adsorbed molecules is given by equation (1.6)

$$n_1 = \frac{R_i}{v_o} \exp (\Delta G_{des}/kT)$$

where R_i is rate of impingement, when $n/\tau_a \rightarrow R_i$ a significant proportion of ad-molecules will desorb before they are able to diffuse to a site of attachment and become incorporated into growing crystallites.

When the situation is such that the rate of desorption (R_d) approaches R_i the concentration of molecules in the vicinity of the surface is determined by both R_i and R_d . If ad-molecules are assumed to leave the surface with a Maxwellian distribution of velocities⁽³⁵⁾, then the re-entrant flux will decrease with distance (d) from the surface as $(1/d)^2 R_d$. The effective concentration (C) of molecules as a function

of distance above the surface is then given approximately by

$$C_{(d)} = \frac{1}{d^2} R_d + R_i, \quad (4.4)$$

This corresponds to an increase in supersaturation above the surface when compared to a situation where $R_d \ll R_i$. PBC theory would predict, therefore, that the strongest bonding axis of crystallites should have an out-of-plane component at high temperature, i.e. when the ratio $\frac{R_d}{R_i}$ becomes appreciable. Therefore, the angle which the b-axis adopts relative to the surface should increase with increasing substrate temperature. A comparison with the experimental results for films deposited above 270K (Figure (4.8)) bears out this prediction. Crystals which grow out of the film plane, as can be seen in Figure (4.8(b)) have large well formed ab faces and are very thin, often transparent in the C direction which is reminiscent of solution grown crystals produced under the equilibrium conditions.

The topography of films deposited above 270K is exemplified by the micrographs given in Figures (4.8) and (4.9). The background network of crystals growing in the plane of the film is clearly visible in all six micrographs of Figure (4.8). On average the in-plane dimensions of these crystallites increase with temperature by a factor of two or three in going from 272K (m.g(a)) to 291K (m.g(f)). This increase in crystallite size presumably reflects the higher surface mobility of ad-molecules predicted by equation (1.5). However, in spite of the fact that considerable out of plane growth appears to be occurring at 282K, as is evident from m.g(b), the predicted decrease in size of crystallites growing in the film plane had not materialised by 292K. It is possible that the absence of a maximum is due to the very high rate of deposition, used (10^8 sec^{-1}) to produce the film,

from which the micrographs of Figure (4.8) were taken. Certainly it is apparent from m.g(f) that the underlying film began to break up at higher substrate temperatures. Furthermore, there was a trend away from a film with a smooth appearance, such as m.g(a) with its poorly defined grain boundaries, to a situation where grain boundaries became pronounced, as in m.g's(e) and (f), which again is consistent with an increased rate of desorption at higher substrate temperatures.

In m.g's(c) to (f) closer observation shows that to one side of each of those crystallites growing out of the film plane, the underlying in plane growth is depleted, as if the incoming molecular flux has been prevented from impinging onto the substrate. These depleted areas are very sharply defined by the outline of the associated crystallite. The effect is more easily discernible in the lower magnification micrograph (d) in Figure (4.8). Evidence for this shadowing effect was sometimes observed at lower substrate temperatures. In such cases, however, the outline of the crystal as projected onto the underlying film, had rounded edges and was much less well defined than that in m.g(a). These results are interpreted, therefore, in terms of a decrease in the residence time (τ_a) of ad-molecules on the surface, after impingement, with increasing substrate temperature. The larger diffusion distance of ad-molecules at the lower temperature of 261K is responsible for poorer definition of the depleted area observed in Figure (4.8)a.

The results of Figure (4.9) provide further evidence for the importance of desorption in determining film topography in the region above 270K. These low magnification micrographs show very clearly, the dramatic increase in the out-of-plane contribution which occurs in the vicinity of 270K. Micrographs (b) to (f) represent a deposition temperature increase of only 12K, from 262K to 274K. The

temperature at which this change took place is somewhat lower than expected, in view of the high deposition rate used (10^8 Å sec^{-1}) to prepare the film. The film depicted in the previous Figure was prepared at a deposition rate of only 5 Å sec^{-1} and yet the transition to out-of-plane growth did not begin until 272K i.e., some ten degrees higher. However, as stated earlier, although the same general pattern of growth was observed, irrespective of the deposition rate, it was not possible to quantify the effects of deposition rate because of the difficulty encountered in making a meaningful comparison between different samples.

Desorption Free Energy of ad-molecules

The temperature $T_i \rightarrow o$ at which the transition from in-plane to out-of-plane growth occurs, thus signifies the onset of re-evaporation and as such is a function of ΔG_{des} , which itself is determined by the strength of the interaction between ad-molecules and the sites of attachment on a crystal surface.

A crude estimate of the magnitude of ΔG_{des} can be made from equations (1.6) and (1.6a) if it is assumed that $T_i \rightarrow o$ (270K) corresponds to the temperature at which $\frac{R_d}{R_i} \rightarrow 0.1$. If $R_i \approx 10^{14} \text{ molecules cm}^{-2} \text{ sec}^{-1}$ and ν_o is of the order of a molecular vibrational frequency i.e. 10^{14} sec^{-1} , $\frac{R_d}{R_i} \rightarrow 0.1$ if $\tau_d \sim 10 \text{ sec}$. Substituting into equation (1.6) gives a value of approximately 70 kJ mole^{-1} for ΔG_{des} , which is nearly a factor of four smaller than the sublimation enthalpy⁽²⁶⁾ (260 kJ mole^{-1}). This result infers that ΔG_{des} in the present case does not correspond to removal of molecules from kink sites, but is determined by a van der Waals type interaction between ad-molecules and the surface onto which they impinge.

As remarked earlier both XRD and TEM showed that films deposited above 260K contained crystals which were oriented with their ab planes parallel to the substrate surface i.e. corresponding to the type of growth exemplified by the micrographs of Figure (4.10). Hence, ad-molecules may in such cases be envisaged as diffusing over the ab face of crystallites previously formed. Reference to the crystal structure of (TTF)(TCNQ) in Figure (4.1) shows that the ab face contains molecules of TTF and TCNQ which have their long axis' parallel and their short in-plane axis perpendicular to the ab plane, i.e. their strong bonding direction is parallel to both the ab face and to the plane of the film. Therefore, at low supersaturation, when the mechanism of growth is such that one layer of the crystal is completed before the next layer is nucleated⁽³⁶⁾, impinging molecules must diffuse to steps on a face, or to its edge, in order to attach themselves to growing crystallites. Since the energy of interaction in the b-direction is much larger than that in the a or c direction the attachment energy is to a reasonable approximation simply that between first nearest neighbours and may be equated with the energy of vapourisation per molecule. Since vapourisation of the crystalline complex at 10^{-6} torr does not become appreciable until around 400K it would appear that the rapid increase in out-of-plane crystal growth at 270K does not involve the removal of molecules from kink sites.

In view of the observation made earlier that the diffusion distance of ad-molecules on the surface is very limited in the vicinity of 270K it is probable that τ_a is very short and that molecules desorb before reaching a kink site. The activation energy for desorption ΔG_{des} is likely, therefore, to be determined by the strength of the interaction between ad-molecules and the ab face of crystallites onto which they impinge, in the same way as ΔG_{sd} . However, because

desorption involves complete removal of molecules from the surface

$\Delta G_{\text{des}} > \Delta G_{\text{sd}}$. Although unlike the situation for metals, for which

$\Delta G_{\text{des}} \approx 4\Delta G_{\text{sd}}$ ⁽³⁸⁾, it is probable that in the case of (TTF)(TCNQ)

ΔG_{des} and ΔG_{sd} are of similar magnitude since they are both determined by the interaction energy between ad-molecules and the ab plane.

(ii) Films deposited between 235K and 255K

At lower substrate temperatures, when $\tau_a \rightarrow \infty$, $\bar{X}$ in equation (1.9) is determined by the diffusion coefficient D_{sd} according to equation (1.10). Because of the reduced surface mobility of ad-molecules at low temperatures, out-of-plane growth once again begins to dominate over in-plane growth, as shown in the series of micrographs given in Figure (4.10), which cover the temperature interval between 268K and 255K. A major difference between the last two micrographs (e) and (f) in Figure (4.10) and those taken of films deposited at higher substrate temperature (i.e. m.g's (a) to (d), is the apparent disruption of the underlying in-plane growth. This probably occurs because of an increase in the rate of nucleation brought about by the increased supersaturation, which when coupled with a reasonable surface mobility encourages the growth of poorly oriented crystallites. The change to columnar growth, which is most marked in micrograph (c) of Figure (4.11) is a characteristic feature⁽³⁹⁾ of films grown at low deposition temperatures and particularly of amorphous films⁽⁴⁰⁾.

The substrate temperature interval between 255K and 235K is thought to correspond to the region of Figure (4.20) between $T_i \rightarrow 0$ and T_{max} , the maximum rate of nucleation. According to equation (1.7) the rate of nucleation increases with supersaturation reaching a maximum at T_m and then decreases again because of the low surface mobility of ad-molecules. An examination of the m.g's in Figure (4.12) reveals

what appear to crystalline inclusions in the as-deposited film prepared between 230K and 240K. These inclusions reached a maximum concentration in the vicinity of 233K (m.g.(c)). The dramatic change in film structure which took place when this same film was annealed, can be seen by comparing the micrographs in Figure (4.12) with those of Figure (4.7). The lath-like crystals which are observed to be growing out of the film plane in Figure (4.12) also reach a maximum in concentration and it is inferred therefore that inclusions present in the as-deposited film are active sites for subsequent growth, which occurs when molecules begin to re-evaporate from disordered regions on annealing. A discussion of the significance of the observation of re-evaporation was given in the previous section. So, for the present it is sufficient only to stress the point that it (re-evaporation) appears to take place primarily on annealing and not during film deposition.

As explained earlier the re-entrant molecular flux leads to a high supersaturation in the vicinity of the surface, with a large out-of-plane component, which promotes growth along the strong bonding or b-axis direction. Thus it is proposed that the highly characteristic columnar type of growth observed at deposition temperatures in the vicinity of 235K consists of crystallites oriented with their b-axis directed out of the film plane. Furthermore, it is also proposed that the maximum in both crystallite concentration and film thickness (Figure (4.12)) observed at this deposition temperature is due to the fact that 235K was also the location of T_m , the position of the maximum rate of nucleation.

As the rate of nucleation decreases at high substrate temperature and surface diffusion rate increases, the probability that molecules

will encounter a nucleus before desorbing will also decrease, leading to thinner films above 235K as found in Figure (6.13). The increased surface mobility of molecules also increases the tendency toward growth in the plane of the film as shown by the change from an oriented to a disoriented structure in m.g's(e) of Figure (4.11). This leads eventually to the (0,0,1) type of growth observed at substrate temperatures above 255K.

Unfortunately, both TEM and XRD failed to provide any useful information about the structure of films deposited in the substrate temperature region between 250K and 235K with which to corroborate the evidence obtained from SEM. Below 250K only a weak electron diffraction pattern was obtained which coincided with the disappearance of the (0,0,1) reflection observed in films deposited at higher substrate temperature. Both observations are consistent with the random nature of crystal growth observed by SEM between 240K and 255K.

In conclusion, the SEM study of (TTF)(TCNQ) films prepared above a substrate temperature of 250K have shown that crystallisation and growth occurs largely during deposition and that the changes which occur on annealing to room temperature are relatively minor. Significant desorption of ad-molecules takes place during the deposition process at substrate temperatures above 270K and is probably responsible for the observed out-of-plane crystallite growth. Between 265K and 255K in-plane growth predominates due to the a balance between the surface mobility of ad-molecules and their tendency to desorb.

Between 255K and 235K an out-of-plane re-alignment of the b-axis of crystallites was observed, as a result of reduced surface mobility, which culminated in a maximum in nucleation rate at 235K. This maximum was marked by a pronounced structural singularity in the vicinity of 235K. It is proposed that at the lower temperature end of

this substrate temperature interval significant topographical changes took place due to re-evaporation from disordered regions of the film which were incorporated during deposition.

References for Chapter 4

1. Kistenmacher, T.J., Phillips, T.E. and Cowan, D.O., Acta Cryst. B30, 763 (1974).
2. Blessing, R.H. and Coppens, P., Sol. State Comm., 15, 215 (1974).
3. Berlinsky, A.J., Rep. Prog. Phys., 42, 1243 (1979).
4. Comes, R., Shapiro, S.M., Shirane, G., Garito, A.F. and Heegar, A.J., Phys. Rev. Lett., 35, 1518 (1975).
5. Donoyer, F., Comes, R., Garito, A.F., Heegar, A.J., Phys. Rev. Lett., 35, 445 (1975).
6. Keller, H.J., Low-dimensional Cooperative Phenomena. The Possibility of High Temperature Superconductivity 1975 (Plenum: New York).
7. Ferraris, J., Cowan, D.O., Walatka, V. and Perlstein, J.H., J.A.C.S., 95, 948 (1973).
8. Vincett, P.S., Barlow, W.A. and Roberts, G.G., Nature, 255, 542 (1975).
9. The gradient sublimation technique was used to investigate the effect of substrate temperature upon the topography of pyrene and perylene films, but a pronounced structural singularity was not observed in either case.
10. Hartman, P., in 'Physics and Chemistry of the Organic Solid State', Interscience (1963) p.382, Vol.1
11. See references (15) to (18).
12. Begg, I.D., Narang, R.S., Roberts, K.J., Sherwood, J.N., J. Cryst. Growth, 49, 735 (1980).
13. Coleman, L.B., Ann. New York Acad. Sci., 313, 316 (1978).
14. Gavezzotti, A. and Simonetta, M., Acta Cryst., A32, 997 (1976).

15. Chandhari, P., Scott, B.A., Laibowitz, R.B., Tankiewicz, Y.
and Torrance, J.P., Appl. Phys. Lett., 24, 439 (1974).
16. Simonyi, E.E., Scott, B.A. and White, E.A.D., Mat. Res. Bull.
11, 347 (1976).
17. Chen, T.H. and Schechtman, B.H., Thin Sol. Films, 30, 173 (1975).
18. Reinhardt, C., Vollman, W., Hamann, C., Libera, L., Trompler, S.,
Kristall und Technik, 15, 243 (1980).
19. Nielsen, P., Epstein, A.J., Sandman, D.J., Sol. State Comm.,
15, 53 (1974), and Simonyi, E.E., Graczyk, J.F. and Torrance, J.B.,
IBM J. Res. Dev., 22, 315 (1978).
20. Wozniak, W.T., Deparquali, G., Klien, M.V., Sweany, R.L. and
Brown, T.L., Chem. Phys. Lett., 33, 33 (1975).
21. Lin, S.F., Spicer, W.E. and Schechtman, B.H., Phys. Rev.,
B12, 4184 (1975).
22. Siedle, A.R. and Hertz, H.S., Mat. Res. Bull. 11, 1185 (1976).
23. Sandman, D.J., Epstein, A.J., Chickos, J.S., Ketchum, J.,
Fu, J.S. and Scheraga, H.A., J. Chem. Phys. 70, 305 (1979).
24. Boyd, R.H., J. Chem. Phys. 38, 3529 (1963).
25. de Kruif, C.G., Govers, H.A.J., J. Chem. Phys. 73, 553 (1980).
26. Metzger, R.M., J. Chem. Phys., 66, 2525 (1977).
27. see Glasstone, S., 'Text Book of Physical Chemistry', p.410,
Macmillan. 2nd edition (1948).
28. see p.828 of reference (27).
29. Private communication with R.T. Murray.
30. p.372 in reference (10).
31. Skripov, V.P., in 'Crystal Growth and Materials', North Holland
1976, p.328, Ed., Kaldis, E. and Scheel, H.J.
32. p.439 in reference (27).

33. p.440 in reference (27).
34. in 'Handbook of Thin Film Technology' p.1-32, Ed. Maissel, L.I. and Glang, R., McGraw-Hill (1970).
35. Dunning, W.J. in reference (10) p.411.
36. Vincett, P.S., Popovic, Z.D. and McIntyre, L., Thin Sol. Films, 82, 357 (1981).
37. p.8-29 in reference (35).

CHAPTER 5

INFRARED SPECTROSCOPY OF (TTF)(TCNQ) FILMS

5.1 Introduction

Chen & Schectman⁽¹⁾ pointed out that films of TTFTCNQ deposited at 77K had a metastable structure and were only converted to the stable state on annealing near room temperature. Evidence for this metastable state has also been obtained by Lin et al.⁽²⁾ who used ultraviolet photoemission (UPS) measurements to monitor the effect of annealing on the surface composition of TTFTCNQ films. Changes in the UPS spectra were observed at 195K and between 249 to 265K. Between 195 and 249K the spectra remained virtually unchanged. To account for these changes Lin et al. proposed a model which postulates that during sublimation TTFTCNQ dissociates to some extent, so that condensates formed at liquid nitrogen substrate temperatures contain a percentage of uncomplexed TTF° and TCNQ° , as well as the associated complex TTF-TCNQ. As the sample temperature was increased, above 195K molecular re-orientations were thought to take place, resulting in an enrichment of the surface layer of TTF° , which has the highest vapour pressure. TTF° was the most prominent emission in UPS spectrum in the region above 195K. It was shown that the electron escape depth from TTFTCNQ was less than $10\text{\AA}$. Therefore, UPS samples only the surface layers, so that the increase in TTF° emission was thought to be consistent with surface enrichment of this species. The change at higher temperatures, i.e., above 265K, was thought to be associated with changes in the electronic structure of TTFTCNQ and it was postulated that in films deposited at liquid nitrogen temperatures the associated pairs of TTFTCNQ involved only slight charge transfer, and that this charge transfer increased upon warming to give the ionized complex.

The changes observed in the UPS spectrum were confirmed by differential thermal analysis (DTA) of films deposited at liquid nitrogen temperatures, although the transformations took place at 223 and 258K and not 195 and 249K as observed for UPS. A further peak in the ΔT vs T data was observed at 273K which was thought to be due to condensed water undergoing melting. All three peaks were endothermic. Both DTA and UPS experiments established that the transformations observed were irreversible. The DTA results also indicate that the transformations observed occur in the bulk of the film as well as on the surface.

Further evidence for the existence of a metastable form of TTFTCNQ has been reported by Wozniak et al.⁽³⁾ who examined the infrared spectra of films of TTFTCNQ deposited at low temperatures. Using matrix isolation techniques they observed that both TTF^O and $TCNQ^O$ were present in films deposited at 10K and suggested that they might also be present in crystalline TTFTCNQ at room temperature, which, they conjectured, might account for the variation in conductivities observed by many workers. There were a number of bands in the spectrum of the matrix isolated material which they assigned to the complex, but no rationale for the assignment was given. Wozniak et al. also observed that the spectrum of thin films deposited at liquid nitrogen temperature, changed on annealing at 233 and 263K, which agrees approximately with the UPS observations of Lin et al. discussed earlier.

Interestingly, the structural studies of Chapter 4 showed that a pronounced alignment of microcrystallites occurred in $(TTF)(TCNQ)$ films deposited in the vicinity of 200 and 235K, i.e. at temperatures which were coincident with certain of the transformations mentioned

above. Furthermore, the study of aromatic hydrocarbons described in Chapter 3 provided evidence that the structural optimum in films of anthracene was associated with a transformation from a metastable to a stable state. The inference is then that the optimum temperature effect is, in some way, associated with a disorder-order transition, which is consistent with the model of film growth already outlined in Chapter 4. This model emphasises the importance of short range intermolecular, or nearest neighbour, interactions in determining film structure. Since the vibrations of molecules in the condensed state are often sensitive to these same interactions, infrared spectroscopy has been used to probe the 'local' structure of (TTF) (TCNQ) films in the as-deposited state. Changes in the molecular interaction potential have also been monitored as a function of annealing temperature, to provide further information about how the structure of films evolve after deposition.

The interpretation of the infrared spectra of films of the complex requires a knowledge of the vibrational spectrum of the precursor molecules TTF and TCNQ, consequently, before proceeding with the presentation of the experimental results the rationale for the band assignments given is briefly discussed. This first section also contains a review of 'vibronic effects' in charge transfer complexes which is essential for understanding the spectra of low temperature deposits.

5.1.1 Band Assignments in TTF and TCNQ

The assignment of vibrational bands in the infrared spectra of (TTF) (TCNQ) films is based upon the work of Bozio et al.⁽⁴⁾ who have made an extensive study of TTF and TCNQ and their compounds. When assigning bands the normal convention was adopted to denote the

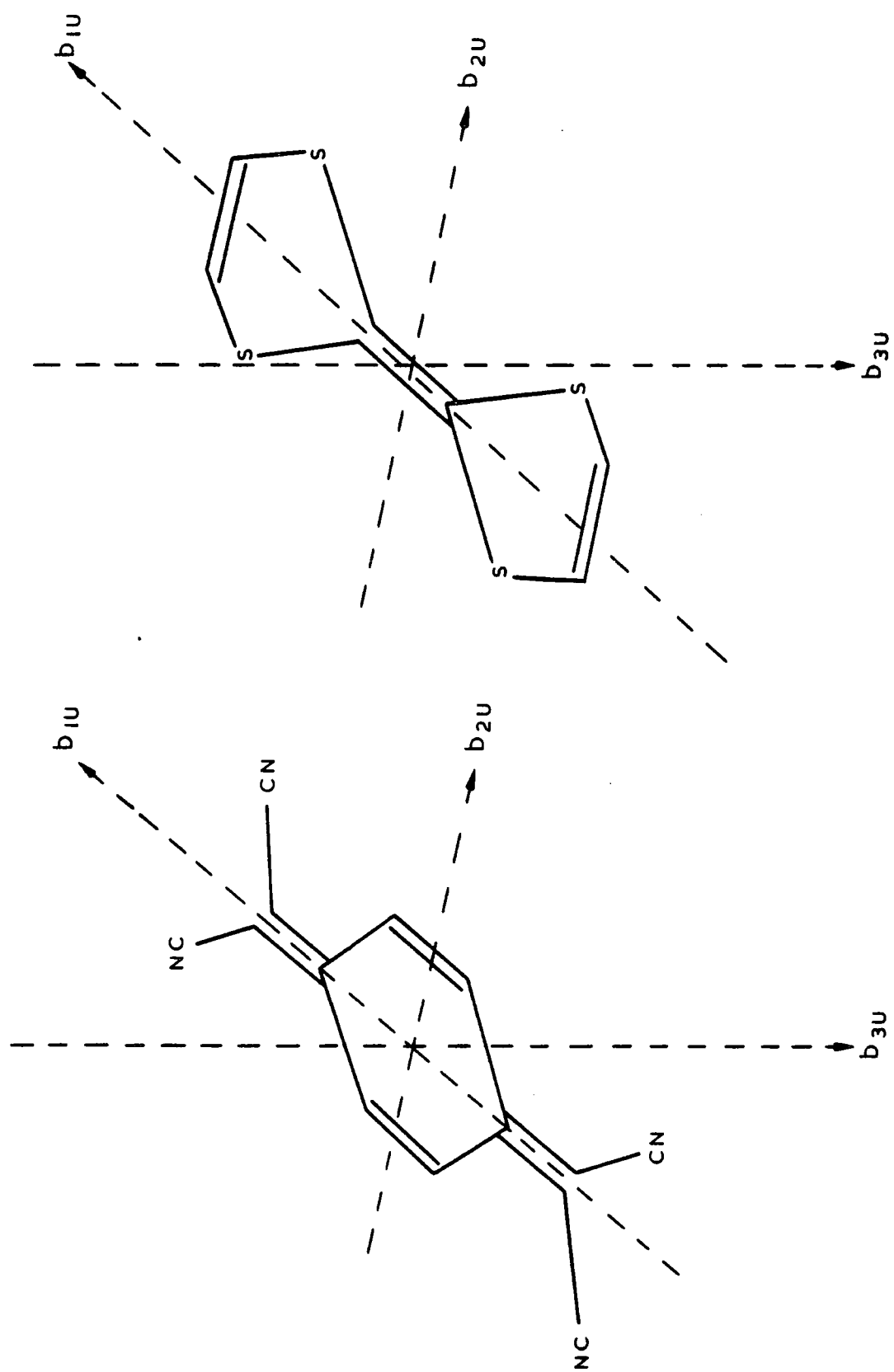


Figure 5.1. Symmetry Axes of TCNQ and TTF

molecular symmetry axis, and this is shown with reference to both molecules in Figure 5.1. The in-plane long and short axis are labelled b_{1u} and b_{2u} respectively, whilst b_{3u} is the axis normal to the molecular plane. The (a_g) band notation refers to totally symmetric vibrational modes, which in the present context have an out of plane polarisation. Polarisation and charge effects are two important factors for determining band intensities and frequencies as will now be discussed.

Polarisation Effects

Since the transition moment for a given vibrational transition is in general different for each of the three principle molecular axis,⁽⁵⁾ the relative intensities of infrared bands are dependent upon the orientation which a molecule adopts with reference to the electric vector of the incident light beam. Using an oriented gas model, Bozio et al.^(4b) were able to predict band intensity ratios for light polarised parallel and perpendicular to the b-axis of a monoclinic crystal of TTF. Table (5.1a) lists the proportionality factors for the infrared intensities of the (102) face of a monoclinic crystal of TTF. From Table (5.1a) it can be seen that bands of b_{2u} symmetry are of weak intensity when using light polarised parallel to either the a or b axis. Similarly, with light polarised parallel to the c-axis, any contribution from bands of b_{1u} or b_{3u} symmetry will also be weak. When a sample consists of randomly oriented polycrystallites however, bands of all symmetries will be observed since crystals of all orientations will be present. Similar arguments can also be extended to vibrations of TCNQ,⁽⁶⁾ for which the proportionality factors are given in Table (5.1b).

Changes in the weighting of a particular molecular orientation within deposits of (TTF) (TCNQ), which are induced by changes in the

Table 5.1. Proportionality Factors for Band Intensities

a) TTF^(4b)

	Z	Y	X
Crystal Direction	b_{1u}	b_{2u}	b_{3u}
a ⁽¹⁾	0.79	0.04	0.17
b	0.19	0.00	0.81
c ⁽²⁾	0.02	0.96	0.02

(1) (2a-c) crystal direction, perpendicular to the
'b' axis

(2) normal to the 102 crystal face

b) TCNQ⁽⁶⁾

	Z	Y	X
Crystal Direction	b_{1u}	b_{2u}	b_{3u}
a	0.43	0.56	0.00
b	0.07	0.09	0.84
c* ($\perp$ a b)	0.49	0.35	0.16
a* ($\perp$ b c)	0.58	0.42	0.00
b	0.07	0.09	0.84
c	0.35	0.49	0.16

* electric vector parallel to designated crystal direction

substrate temperature of deposition, or as a consequence of annealing, should alter the relative intensities of bands with different symmetry axis'. In principle, therefore, it should be possible to identify substrate temperature dependent molecular orientation effects from an analysis of band intensity ratios.

The Effects of Charge

Since the dipole moment change accompanying a vibrational transition determines both the intensity and frequency of an infra-red vibrational band,⁽⁷⁾ the spectra of TTF and TCNQ are changed upon ionisation by an amount which is dictated by the precise details of the charge distribution around the molecule. For example, using the simplifying assumption that the relation between the charge present on a molecule and the Raman line shift was linear to first order, Kuzmany and Stulz⁽⁸⁾ have estimated that the average degree of charge transferred from TTF to TCNQ in the complex (TTF)(TCNQ) is 0.5. This is in reasonable agreement with the value of 0.59 obtained from diffuse X-ray scattering⁽⁹⁾ and X-ray diffraction data⁽¹⁰⁾. In the peculiar time scale of molecular vibrations ($\nu \approx 10^{-13} \text{ sec}^{-1}$) electrons are considered to be localised on a given molecule,⁽¹¹⁾ during the period of a single vibration, i.e. in the absence of vibronic effects of the type discussed below. The relative concentration of the various charged species present in films of (TTF)(TCNQ), even in the presence of each other, can therefore, be determined from an analysis of their respective vibrational frequencies.

5.1.2 Vibronic Effects

In 1975 Anderson and Devlin⁽¹¹⁾ showed that many of the dominant bands in the infrared spectrum of K TCNQ had no counterpart in the spectra of either TCNQ⁰ or TCNQ⁻. They were able to show with the aid of single crystal reflectance studies that all of these anomalous bands displayed an intense polarisation in a direction perpendicular to the plane of TCNQ molecules in the complex. Furthermore, they were located at frequencies which corresponded closely with the totally symmetric (a_g) molecular vibrations of neutral TCNQ. Under normal circumstances these are infrared inactive. Anderson and Devlin proposed that the a_g vibrational modes were rendered infrared active by a vibronically based charge oscillation between neighbouring TCNQ molecules in a way which is analogous to vibronic effects in halogen complexes of aromatic hydrocarbons in solution.⁽¹²⁾ Hinkel and Devlin⁽¹³⁾ had previously established that vibronic effects were responsible for each of the dominant features observed in the infrared spectrum of the planar tetracyanoethylene (TCNE) anion in the solid state.

The origin of vibronic effects

In the model originally proposed⁽¹⁴⁾ and ⁽¹⁵⁾ to account for the observation of vibronic effects in weak charge transfer complexes,⁽¹⁶⁾ the increased intensity and shift in frequency of bands was considered to arise as a result of coupling between; intramolecular bands on the donor (D) and acceptor (A), and the highest occupied molecular orbital. Just how this accounts for increased infrared activity of the A_g vibrational modes is best explained in terms of charge transfer theory.⁽¹⁷⁾

A charge transfer complex is considered to be a resonance hybrid between two states; ⁽¹⁸⁾ a lower energy no bond state $\Psi_{(D,A)}$, and a higher energy ion pair state, $\Psi(D^+A^-)$, which arises as a result of a one electron transfer from D to A. Mixing of the two states produces a stabilised ground state Ψ_N and an excited state Ψ_E .

$$\begin{aligned}\Psi_N &= a\Psi(D,A) + b\Psi(D^+A^-) \\ \Psi_E &= -b\Psi(D,A) + a\Psi(D^+,A^-)\end{aligned}\tag{5.1}$$

The magnitude of the coefficients a and b determines the degree of charge transfer, for a weak complex $a \gg b$. The ground state Ψ_N will, in the case of a weak complex, have primarily the character of the no-bond (D,A) state while the excited state has an ion-pair character (D^+,A^-). Consequently, in undergoing a transition from the ground state to the excited state an electron displacement from D to A occurs. The difference in energy between the no-bond $E_{(D,A)}$ and ionic $E_{(D^+A^-)}$ states is given ⁽¹⁹⁾ by:

$$E_{(D^+A^-)} - E_{(DA)} = I_D - A_A - C\tag{5.2}$$

C is the difference in stabilisation energy between the excited state and the ground state of the complex.

To a first approximation intramolecular vibrations do not change the distance between the donor and acceptor, and C is relatively insensitive to these vibrational coordinates. However, Ferguson and Matsen (F-M) ⁽¹⁴⁾ and Friedrich and Person ⁽¹²⁾ have pointed out that totally symmetric (a_g) vibrations can produce a change in the vertical ionisation potential of the donor or the acceptor, or both. It can be seen from equation (5.2) that a change in either I_D or A_A

will alter $E_{(D^+,A^-)} - E_{(D,A)}$. This in turn alters the mixing coefficients for the no-bond and dative states causing a modulation of the amount of charge transferred from D to A. The oscillation in transition dipole moment is directed along a line joining D and A, causing an out of plane polarisation of totally symmetric modes and resulting in anomalous infrared activity.

Modes which exhibit anomalous infrared activity

The intensity of the i th vibrational mode is given by^{(14), (20)}

$$A_i = \frac{N\pi}{3C^2} \left(\frac{\partial \mu}{\partial Q_i} \right)^2 \quad (5.3)$$

where N is the Avogadro number, Q_i is the normal coordinate of the i th vibrational mode and μ is the dipole moment. In the present case only linear coupling between electrons and intramolecular vibrations need be considered. These interactions result from a modulation of the molecular orbital eigen values, or transition state energies, by the intramolecular vibrational modes. According to Duke⁽²¹⁾ terms linear in the normal mode coordinates must be associated with totally symmetric (a_g) (infrared inactive) vibrations for non-degenerate electronic states. Linear coupling to a non-totally symmetric mode leads to a change of symmetry of the molecule in that state and is forbidden on the basis of group theoretic symmetry arguments.⁽²²⁾ Consequently coupling to vibrational modes which are normally infrared active, does not occur, because in order to be infrared active they require a change in dipole moment and are therefore non-totally symmetric by definition.

Ferguson⁽²³⁾ has pointed out that vibrations which change the overlap integral between donor and acceptor orbitals, that is inter-molecular vibrations, change the relative magnitudes of the coefficients a and b in equation (5.1) and will also have increased infrared

activity. However, intermolecular vibrations normally occur at low frequencies ($<400\text{ cm}^{-1}$) and fall outside the spectral range examined in the present study.

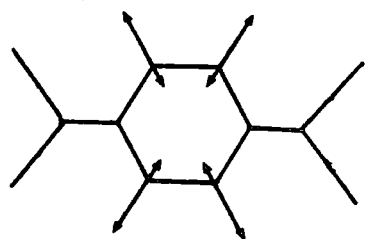
It is emphasised at this point that the totally symmetric vibrational modes are infrared 'inactive' in both the donor and the acceptor, in the uncomplexed state. Their presence in the infrared spectrum must, therefore, signify an increased intermolecular electronic interaction. Although the molecular orbital couples to the a_g vibrational modes which are normally Raman active, Girlando et al.⁽²⁹⁾ have pointed out that this coupling is out of phase rather than in phase. Consequently, the frequency of the anomalous infrared band will not occur at the same position as the frequency shift of the analogous Raman band.

A further feature of vibronically coupled charge oscillations is that their transition dipole is directed along a coordinate joining donor and acceptor, which in the case of planar aromatic compounds corresponds to an out of plane polarisation. This is precisely what Anderson and Devlin⁽¹¹⁾ observed for $K^+(\text{TCNQ})^-$. In $K^+(\text{TCNQ})^-$ as in many other TCNQ compounds, the aromatic molecules are arranged in columnar stacks, in which the planes of adjacent molecules are parallel. As discussed in Chapter 4 (section 4.1.1) this is also the configuration adopted by both TTF and TCNQ in the charge transfer complex. It is responsible for its highly anisotropic properties because it facilitates electron transfer between molecules in the stack. The situation is analogous to that observed in aromatic/halogen charge transfer complexes because, although neighbouring molecules in the stack are identical, it is the oscillation of electronic charge between them that is responsible for the activation of the a_g vibrational modes.

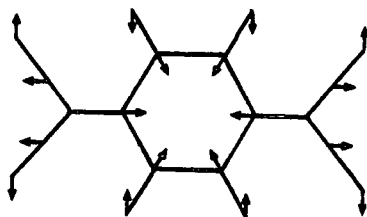
The original ideas of Ferguson and Matsen have been modified and extended to explain the infrared properties of TCNQ and TTF salts, and have been included in a description of electrical conduction⁽²⁴⁾ and Charge Density Waves (CDW's) in TTFTCNQ. In a series of papers, Rice⁽²⁵⁾ and his co-workers have discussed two mechanisms which describe the infrared properties of TCNQ salts. The first of these mechanisms⁽²⁶⁾ considers phase oscillations of intramolecularly stabilised CDW's. It is appropriate for organic linear chain semiconductors of the type $R^+(TCNQ)^-$ in which the semiconducting state is due to an intermolecular Peierls distortion.⁽²⁷⁾ The second approach⁽²⁸⁾ has been applied to complexes of the type M^+TCNQ^- and is referred to as the dimer charge transfer oscillation mechanism. It is relevant to isolated radical ion dimers such as occur in solution,⁽²⁹⁾ or for linear chain structures of interacting dimers of the type found in K-TCNQ. It is the solid state analogue of the (F-M) model discussed earlier.

The consequences of both mechanisms are very similar and either can be used to provide a qualitative explanation of the infrared spectra of TCNQ and TTF compounds. Like the F-M model they both consider that it is the (a_g) vibrational modes of parent neutral molecules, in our case TTF and TCNQ, which couple to the appropriate non-degenerate molecular orbital, i.e. $B_{2g}(\pi)$ and $B_{1u}(\pi)$,⁽³⁰⁾ respectively. The analysis of the infrared spectra is simplified by the fact that, of the 54 normal vibrational modes of TCNQ, only 10 are a_g modes, and of the 36 modes of TTF there are only 7 a_g modes. These are shown in Figures 5.2 and 5.3 and in the parent molecule occur at the frequencies indicated.

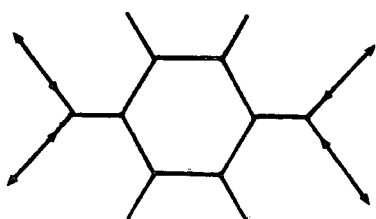
Figure 5.2. (30) Schematic Diagram of the normal mode amplitudes for the ten a_g symmetry vibrations of TCNQ, showing their dominant character and respective coupling constant (g)



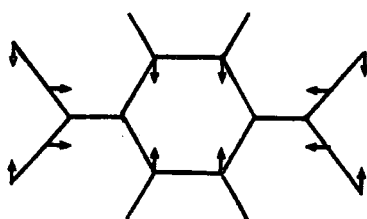
ν_1 : 3052, g : 0.01
C-H stretch



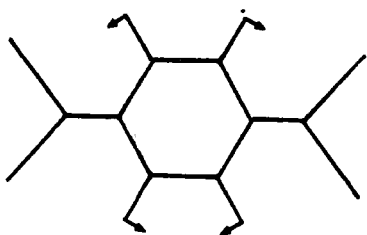
ν_6 : 932, g : 0.25
C-C ring stretch



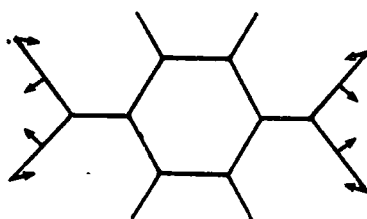
ν_2 : 2230, g : 0.19
C $\equiv$ N stretch



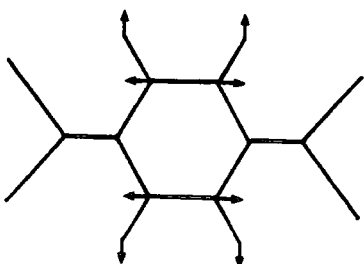
ν_7 : 726, g : 0.37
c-C ring stretch



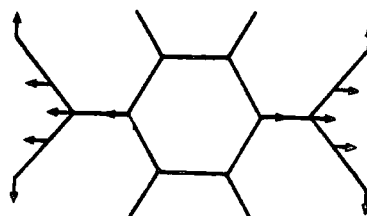
ν_3 : 1602, g : 0.66
C=C ring stretch, C-H bend



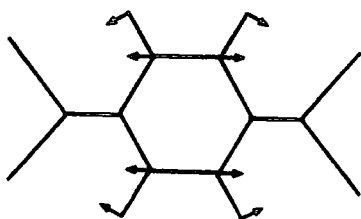
ν_8 : 600
C(CN)₂ scissor, C-C wing deformation



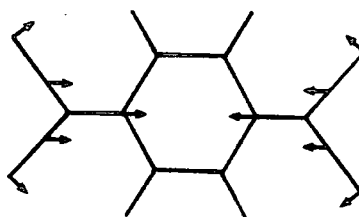
ν_4 : 1453, g : 0.27
C=C wing stretch



ν_9 : 338, g : 0.58
ring deformation

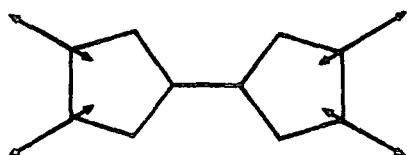


ν_5 : 1207, g : 0.19
C-H bend, C=C ring stretch

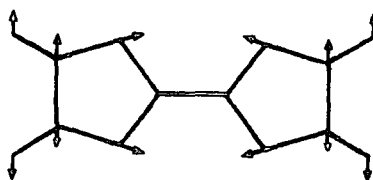


ν_{10} : 126, g : 0.49
C-C $\equiv$ N bending

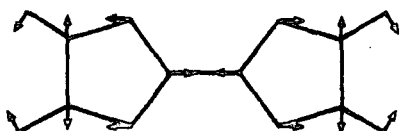
Figure 5.3.⁽²¹⁾ Schematic diagram of the normal mode amplitudes for the seven a_g symmetry vibration of TTF, showing their dominant character and respective coupling constant (g)



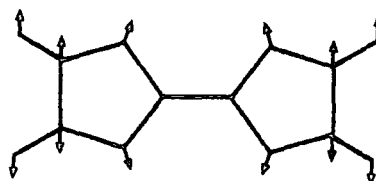
ν_1 : 3099, g : 0.03
C-H stretch



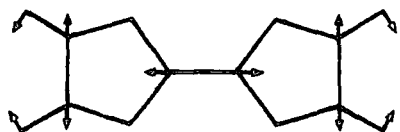
ν_5 : 740, g : 0.49
S-C stretch



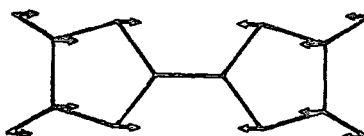
ν_2 : 1559, g : 0.23
C-C stretch



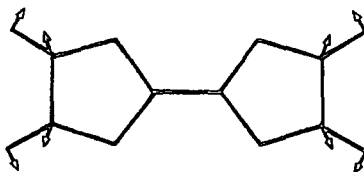
ν_6 : 472, g : 1.33
C-S stretch C-S-C bend



ν_3 : 1518, g : 0.62
C-C stretch



ν_7 : 253, g : 0.16
S-C-S bend C-S-C bend



ν_4 : 1077, g : 0.16
S-C-H bend

- a) after Duke, reference 21
- b) after Bozio et.al., reference 36
- c) after Rice and Lipari, reference 32

Anomalous mode intensities

Rice⁽²⁶⁾ has expressed the electron-vibrational interaction in terms of the notion that the energy E , of the molecular orbital which accommodates the radical electron, is a function of the instantaneous nuclear geometry of the molecule. For sufficiently small nuclear displacements E is given by,

$$E = E_0 + \sum_i g_i Q_i \quad (5.4).$$

where E_0 is the equilibrium molecular orbital energy, g_i , the linear electron vibrational coupling constant ($e-mv$) is the partial derivative of E with respect to Q_i the normal mode coordinate of the i th a_g vibrational mode. (g_i) is a measure of the strength of coupling between the molecular orbital and the i th vibrational mode and has been calculated for each of the a_g modes of TTFTCNQ. Their values are shown alongside the corresponding mode in Figures 5.2 and 5.3.

Bozio et al.⁽³¹⁾ have shown that the intensity gain which occurs as a result of the electron molecular vibrational interaction for a radical cation dimer is given by

$$(\vec{\mu} \text{ del})_n = - \frac{4t\hbar\omega_n}{U^2} (g_n^+ + g_n^0) \vec{\mu} C_T \quad (5.5)$$

where t is the electron transfer integral, $U \equiv U_0 - V$ is the effective coulomb interaction where U_0 is the intramolecular Coulomb repulsion energy between two electrons on the same TTF molecule and V is the Coulomb repulsion energy between adjacent molecules, $\vec{\mu} C_T$ is the transition dipole moment of the electronic charge transfer absorption, ω_n , g_n^+ and g_n^0 are the frequency of the n -th totally symmetric mode and its $e-mv$ coupling constants for the half and fully occupied molecular orbital of the parent molecule. A similar expression

will apply for TCNQ radical anion dimers. For a given transition equation (5.5) shows that the gain in intensity, as a result of electron vibrational coupling, depends upon the sum of the electron vibrational coupling constants for the half and fully occupied molecular orbital. These have been calculated by Rice and Lipari⁽³²⁾ for TTF and TCNQ. The last column in Table (5.3) gives the sum of the two coupling constants from which it is possible to rank the relative intensities of the a_g modes in the radical ion dimers of TTF and TCNQ. Of the TTF modes, ν_1 to ν_6 fall in the region of the infrared spectrum examined in the present work and of these, bands ν_3 ν_5 and ν_6 should exhibit the strongest coupling to the $b_{1u}(\pi)$ orbital and show appreciable intensity in $(TTF^+)_2$. Bands ν_1 to ν_9 for TCNQ fall into the region studied and similarly of these ν_2 ν_3 ν_4 ν_5 ν_6 ν_7 and ν_9 are expected to exhibit appreciable intensity in the infrared spectrum of the $(TCNQ^-)_2$ dimer. A detailed discussion of the theory of electron, molecular vibration interaction is given in references (24) and (26).

Evidence for Vibronic effects in TCNQ and TTF compounds

The ideas outlined above have been confirmed by a number of experimental studies. Rice et al.⁽²⁶⁾ calculated the spectrum of KTCNQ using the charge transfer oscillation theory and has shown excellent agreement with the infrared reflectance results of Tanner et al.⁽³³⁾ and Anderson and Devlin.⁽¹¹⁾ Similar agreement has been established between the data for $[\text{triethyl ammonium}]^+(\text{TCNQ})_2^-$ ⁽³⁴⁾ and the phase oscillation theory of Rice.⁽²⁸⁾ Strong coupling between TCNQ intramolecular vibrations and molecular orbitals has been observed in $(\text{methyltriphenylarsonium})^+(\text{TCNQ}_2)^-$ ⁽³⁵⁾. Solution studies of TCNQ salts also point to the importance of vibronic effects. LiTCNQ for example is known to undergo self dimerisation in concentrated

solution,⁽³⁶⁾ which is accompanied by an enhancement of the a_g modes of TCNQ. Bozio et al.⁽³⁶⁾ have also shown from a study of two polymorphic forms of Rb TCNQ that the intensity of vibronic features is sensitive to different types of anion stacking in the two structures.

Polarised single crystal data for $\text{TTF}(\text{ClO}_4)$ ⁽³⁷⁾ and the infrared powder spectrum of $\text{TTF Br}_{1.0}$ are thought to exhibit effects which are vibronic in origin.⁽⁴⁶⁾ Furthermore, infrared solution studies⁽⁴⁶⁾ of $\text{TTF}^+(\text{ClO}_4)^-$ have shown that dimerisation of TTF^+ which is known to occur in solution at low temperatures⁽³⁸⁾ is accompanied by the observation of new bands which have been assigned to vibronically enhanced a_g vibrational modes. It would appear therefore that the experimental studies of radical cation salts are completely analogous to the situation existing in TCNQ compounds, and that vibronic effect must be taken into account when considering the infrared spectrum of $(\text{TTF})(\text{TCNQ})$ films.

5.2 Experimental Results

5.2.1. The Spectra of Films in the As-deposited State

Films of the complex were deposited at substrate temperatures between 80K and 300K using the techniques described in section 2.3.1. Their spectra were recorded in the as-deposited state prior to annealing. Because of their somewhat different vibrational properties, films deposited below 190K are considered separately. Results for films deposited above 190K are presented first.

Films Deposited above 190K

The four spectra given in Figures 5.4 to 5.7 are representative of film deposited above 190K. The main bands observed in the spectra of these four films are listed in columns 1 to 4 of Table 5.2.

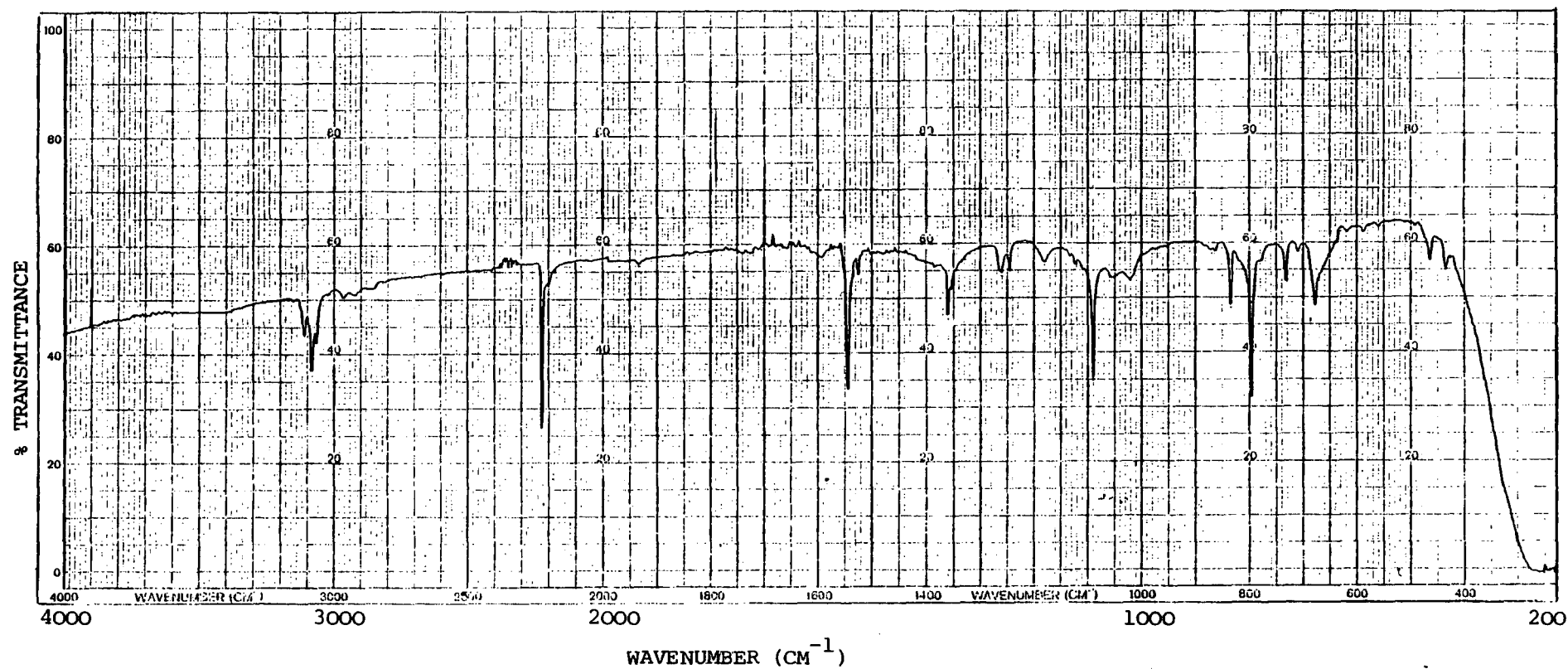


Figure 5.4. Infrared absorption spectrum of a (TTF)(TCNQ) film deposited and recorded at 205K

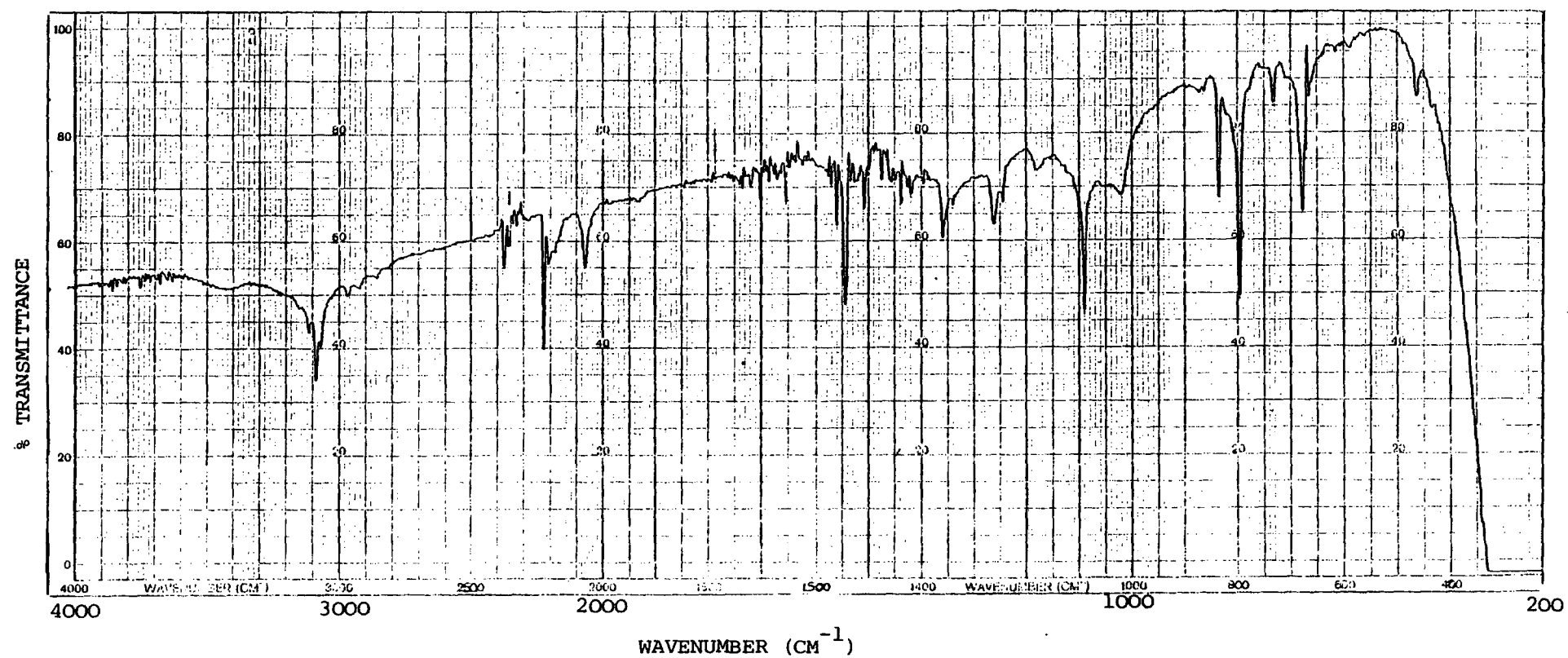


Figure 5.5. Infrared absorption spectrum of a (TTF)(TCNQ) film deposited and recorded at 230K

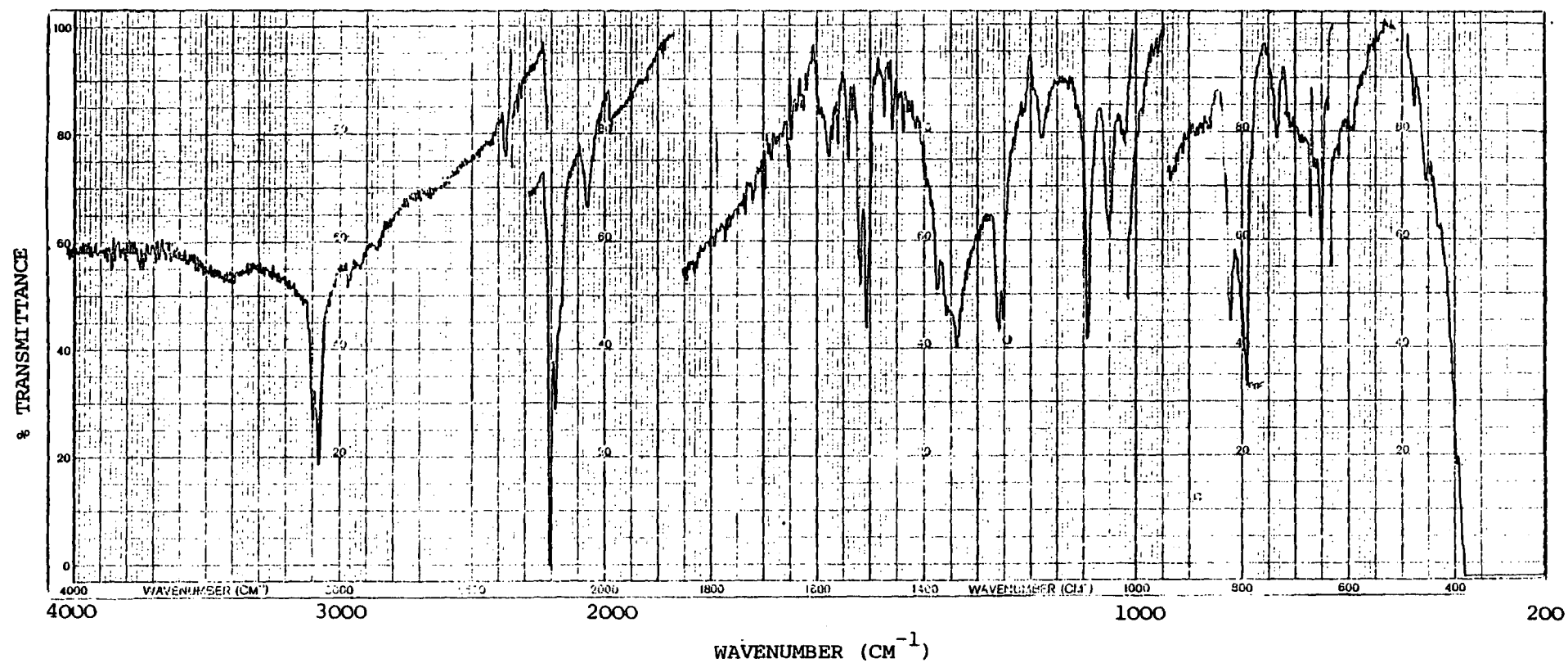


Figure 5.6. Infrared absorption spectrum of a (TTF)(TCNQ) film deposited and recorded at 240K

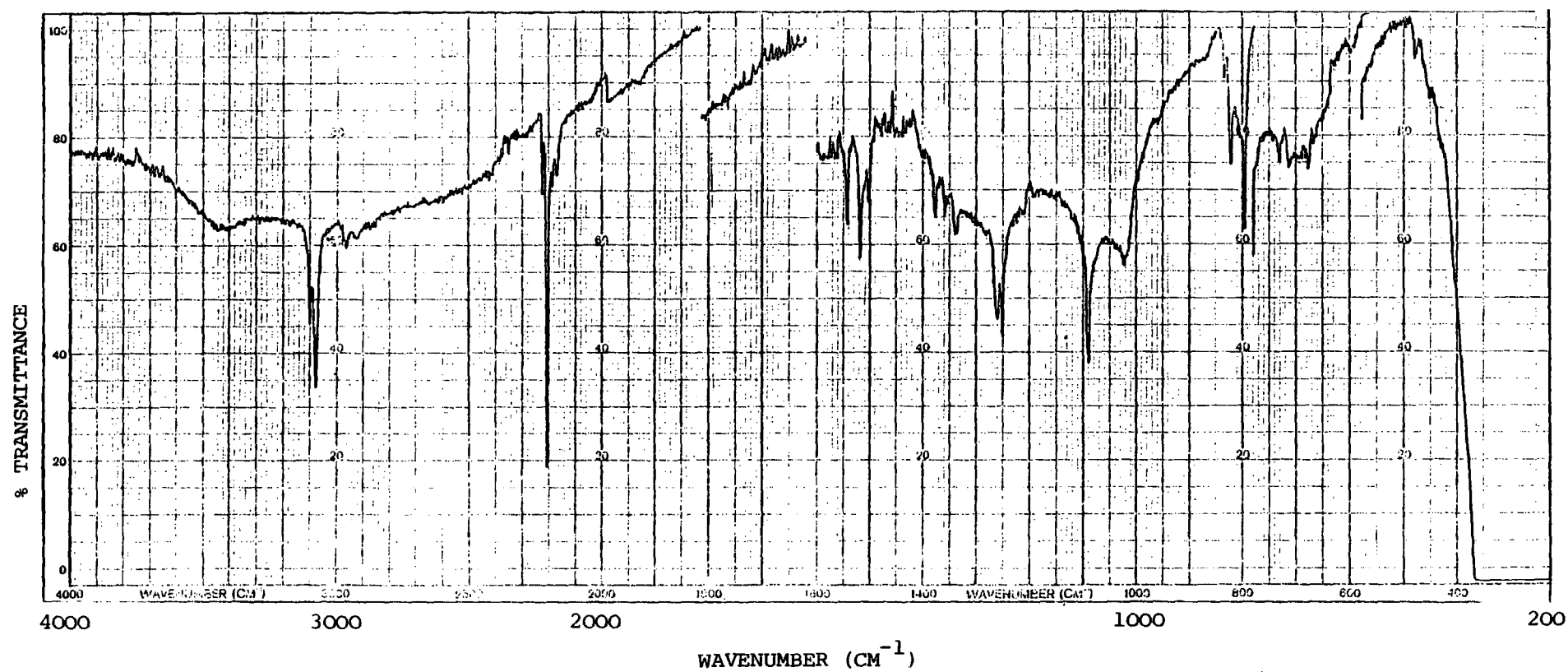


Figure 5.7. Infrared absorption spectrum of a (TTF)(TCNQ) film deposited and recorded at 250K

Absorption band frequencies from the spectra of the four precursors i.e. $(\text{TTF})^0$, $(\text{TTF})^+$, $(\text{TCNQ})^0$ and $(\text{TCNQ})^-$ are also listed in Table 5.2 in columns 5, 6, 8 and 9 respectively. Frequencies listed for $(\text{TTF})^+$ are taken from the results of Girlando et al.⁽⁴⁶⁾ for $(\text{TTF})^+ \text{Br}_{1.0}^-$. The other spectra were obtained using KBr dispersions of the appropriate compound. $\text{Li}^+(\text{TCNQ})^-$ was considered to be representative of TCNQ radical ion species. Columns 7 and 10 of Table 5.2 list the most probable assignments of TTF and TCNQ absorptions observed in the spectra of the four films. With very few exceptions bands present in each of the four films could be assigned to one of the four precursor molecules. Those bands which had no counterpart amongst the precursors were generally vibronic in origin and are discussed in the following section. Three substrate temperature regimes were identified for film deposited above 190K which were characterised by marked differences in their infrared spectra.

195 - 230K

Films deposited at 205 and 230K were representative of this deposition temperature interval.

Several infrared vibrations are diagnostic of differently charged TCNQ and TTF molecules.

TCNQ Species

Thus for $(\text{TCNQ}; \text{TCNQ}^-)$ Girlando⁽³⁹⁾ has determined that bands at the following frequencies indicate the amount of charge on a molecule. $b_{3u} \nu_{52}$: 475, 485 cm^{-1} ; $b_{3u} \nu_{50}$: 859, 823 cm^{-1} . Bands of medium to strong intensity were present at 468 and 837 cm^{-1} , in the 205K deposit. Because of possible overlap with the $a_g \nu_6$ mode of TTF the band at 468 cm^{-1} could not be positively assigned to $b_{3u} \nu_{52}$. The presence of the band at 837 cm^{-1} suggests that TCNQ may be present as a partially charged species. However, a band at

Table 5.2. The most probable assignment of the vibrational bands observed in the infrared spectra (Figures 5.4 to 5.7) of (TTF)(TCNQ) films deposited at 205, 230, 240 and 250K, respectively

Film Deposition Temperature				TTF ⁰	TTF ⁺	Assign- ment ^(a) TTF	TCNQ ⁰	TCNQ ⁻	Assign- ment ^(b) TCNQ
205K	230K	240K	250K						
3119 (w)	3115 (w)	-	-						
-	-	3100 (m)	3100 (m)						
3084 (s)	3085 (s)	-	-	3083		dimer* ag v ₁			
-	-	3078 (s)	3078 (s)		3073 3079	b _{2u} v ₂₂ b _{1u} v ₁₃			
3070 (sh)	3070 (w)	-	-						
2228 (vs)	2225 (s)	-	2225 (w)				2229 (vs)		b _{1u} v ₁₉ b _{2u} v ₃₃
2212 (sh)	2208 (m)	2205 (vs)	2206 (vs)					2210 (vs)	dimer* ag v ₂
-	-	2185 (m)	2185 (vw)					2181	b _{1u} v ₁₉
-	2068 (m)	2065 (w)							
1545 (s)	1543 (s)	1540 (w)	1542 (w)				1542 (s)	1580	b _{2u} v ₃₄ b _{1u} v ₂₀
1526 (w)	-	-	-	1527 (s)	1478	b _{1u} v ₁₄			
-	-	1518 (m)	1518 (m)			dimer*		1518	b _{2u} v ₃₄
-	-	1507 (m)	1503 (m)					1504	b _{1u} v ₂₀
		1377 (w)	1377 (w)					1388 1363 (vs)	b _{2u} v ₃₅ b _{1u} v ₂₁
1361 (m)	1360 (m)	-	-			dimer*	1355 (m)	1345 (vs)	b _{2u} v ₃₅
-	-	1340 (br.s)	1340 (w)			dimer*			
1265 (w)	1263 (m)	1260 (m)	1260 (m)	1258		dimer* b _{3g} v ₂₉			
1246 (w)	1246 (w)	1250 (m)	1251 (m)	1255 (s)	1237	b _{2u} v ₂₃			
1185 (w.br)	1180 (w)	1180 (w)	-					1185 (s)	dimer* b _{3g} v ₄₅
1090 (s)	1090 (s)	1093 (s)	1090 (m)	1089 (w)	1072	b _{1u} v ₁₅			
-	-	1051 (m)	-						
865 (w)	-	-	-	870 (m)		b _{2u} v ₂₄	865 (vs)	823 829 LiTCNQ	out of plane C-H b _{3u} v ₅₀

Table contd.

837(s)	835(s)	-	-		836	$b_{1u} \nu_{16}$	836	$b_{3u} \nu_{50}$
-	-	820(s)	822(m)		825	$b_{2u} \nu_{25}$	812(vw)	
798(s)	796(vs)	791(s)	795(s)	798(vs)	825	$b_{2u} \nu_{25}$		
780(vw)	-	-	-	780(vs)	836	C-S $b_{1u} \nu_{16}$		
733(m)	732(w)	735(w)	731(vw)	736(m)	751	dimer* $b_{1u} \nu_{17}$		
678(s)	678(s)	-	-		(665)	$b_{2u} \nu_{26}$		
				649(vs)	calc	C-H out plane		
-	-	650(s)	-	637(vs)	705	$b_{3u} \nu_{34}$		
468(m)	463(w)	-	-	470		dimer* ag ν_6^*	478(s)	$b_{3u} \nu_{52}$
436(w)	-	435(vw)	-	436(w)		$b_{1u} \nu_{18}$		

Footnotes

dimer* refers to bands which can also be assigned to infrared inactive fundamentals for the reasons discussed in Section (5.1.2)

the letters in brackets after a given band frequency refer to its relative intensity; vs, very strong, s, strong, m, medium, w, weak and vw, very weak, sh, shoulder, br, broad.

- Frequencies quoted for TTF^+ were taken from reference (46)
- Frequencies quoted for TCNQ^- were taken from reference (36)

Band assignments are as given in references (46) and (6) respectively.

837 cm^{-1} in the spectrum of $\text{C}_{60}(\text{TCNQ})_3$ has been assigned⁽³⁹⁾ to TCNQ^0 . Furthermore, since this band corresponds to an out of plane C-H band it is likely to be sensitive to intermolecular interactions which could be the reason for it being red shifted by 20 cm^{-1} from its position in $(\text{TCNQ})^0$. Further discussion of this point is given in section 5.3.

Further evidence for neutral TCNQ was provided by the presence of a single band in the C=C stretching region at 1547 cm^{-1} , in both the 205K and 230K deposits. In neutral TCNQ, the ring and external C=C bands vibrate at the same frequency (1548 cm^{-1}) whereas in TCNQ^- they are shifted to 1510 and 1580 cm^{-1} respectively, as for example in LiTCNQ .⁽³⁶⁾

Absorption bands in the C≡N stretching region at 2228 cm^{-1} and 2210 cm^{-1} are also diagnostic of the state of charge of the molecule. There is, for example, a single strong band at 2228 cm^{-1} in both the 205 and 230K deposits which by comparison with the spectra of the neutral compound can be positively assigned to $(\text{TCNQ})^0$. The band due to TCNQ^- at 2212 cm^{-1} in the 205K deposit was extremely weak, while that at 2208 cm^{-1} in the 230K film was only slightly longer. In fact all bands associated with $(\text{TCNQ})^-$ were either entirely absent or of very low intensity in both films and those bands which were observed could be readily assigned to $(\text{TCNQ})^0$ or, as will now be discussed, to $(\text{TTF})^0$.

TTF Species

Although a judicious assignment of bands to either $(\text{TTF})^0$ or $(\text{TTF})^+$ was less straightforward than for TCNQ species the band at 798 cm^{-1} has been positively assigned⁽⁴⁶⁾ to $(\text{TTF})^0$ and was present with high relative intensity in the 205 and 230K deposits. However,

other strong bands which are present in neutral TTF, notably those with b_{1u} symmetry, located at frequencies of 1527 cm^{-1} ($b_{1u}v_{14}$) and 780 cm^{-1} ($b_{1u}v_{16}$) were either very weak or completely absent from the spectra of these films. Although of different symmetry to the band at 798 cm^{-1} ($b_{2u}v_{25}$), all three bands are polarised in the molecular plane.

A crystallite orientation is possible in which bands of b_{1u} symmetry are low in intensity compared to those with b_{2u} symmetry from Table 5.1. this corresponds to light polarised in the crystal C direction, i.e. normal to the 102 crystal face. This orientation is consistent with the results of the electron diffraction study in Chapter 4 which showed that films deposited below 260K had a (102) crystallite orientation (see Table 4.1), i.e. with the 102 plane parallel to the surface of the film.

There was a strong absorption present in the spectra of all four films at 1090 cm^{-1} which also has b_{1u} symmetry ($b_{1u}v_{15}$). This band corresponds to the C-H in plane bonding mode of TTF and its observation suggests that factors other than molecular orientation effects are important in determining the spectra of films, since under normal circumstances it might have been expected to have a much reduced intensity in films with a (102) orientation. Similarly the band at 670 cm^{-1} in the 205 and 230K deposits, which is assigned to the $b_{3u}v_{34}$ C-H out-of-plane bending mode, was much stronger than expected. Both of these vibrations are likely to be sensitive to^(4c) intermolecular interactions and it is possible that this is responsible for their higher frequency compared to crystalline TTF. All remaining bands in the spectrum of the 205 and 230K spectrum were consistent with (TTF)⁰.

Since all bands of appreciable intensity in the spectra of films deposited in the region of 195-230K could be assigned to $(\text{TTF})^0$ and $(\text{TCNQ})^0$ it is concluded that charged species, if present, have a very low concentration. Bands of very weak intensity, for example, that in the $\text{C}\equiv\text{N}$ stretching region at 2208 cm^{-1} were observed in the film deposited at 230K and infer that $(\text{TCNQ})^-$ is present, but in low concentration.

230 - 250K

Bands assigned to neutral TCNQ in the previous samples were either absent or very much diminished in the spectrum of the 240K deposit. There were several new bands located at 2205, 2185, 1580, 1515 and 1507 cm^{-1} , which were assigned to $(\text{TCNQ})^-$. The band observed at 820 cm^{-1} may be assigned to either TTF ($b_{2u}\nu_{25}$) or TCNQ ($b_{3u}\nu_{50}$) although the former is more likely since the $b_{3u}\nu_{50}$ vibration is shifted from 865 cm^{-1} in TCNQ^0 to 830 cm^{-1} in $\text{Li}^+(\text{TCNQ})^-$. A further downward shift in frequency in the 240K deposit is unlikely, in view of the smaller degree of charge transfer in the complex.

An additional feature of the 240K spectrum was that the band assigned to the $b_{3u}\nu_{34}$ mode of TTF (650 cm^{-1}) was located very close to its frequency in neutral TTF. This is a shift of 30 cm^{-1} compared to the lower temperature deposits and is in a direction opposite to that expected in going from $(\text{TTF})^0$ to $(\text{TTF})^+$ since the latter is reported to possess an absorption band at 705 cm^{-1} .^(4b) The intensity of this band was also diminished relative to the band at 798 cm^{-1} :

On the basis of the infrared spectrum it was concluded that the 240K deposit contained substantial amounts of the radical ions i.e. $(\text{TTF})^+$ and $(\text{TCNQ})^-$, although the evidence for the former is not substantive. In fact bands due to $(\text{TTF})^0$ were, by comparison with

those of $(\text{TCNQ})^{\circ}$ still intense. For example the band located at 2228 cm^{-1} , which was the most intense absorption in the spectrum of TCNQ° , was completely absent, whilst that due to TTF° at 798 cm^{-1} has not greatly diminished in intensity when compared to lower temperature deposits. Therefore, in addition to $(\text{TCNQ})^{-}$ and $(\text{TTF})^{+}$ the film deposited at 240K also contains $(\text{TTF})^{\circ}$.

There is, in addition to bands associated with intramolecular vibrational modes, a very broad absorption in the $1300 - 1400\text{ cm}^{-1}$ region of the spectrum. A very intense band was also observed at this position in films deposited below 190K and is thought to be 'vibronic' or electronic in origin.

250K deposit

The trend observed in the film deposited at 240K, i.e. an increase in concentration of the radical ion species and a decrease in the intensity of absorptions due to TTF° and TCNQ° , was continued in the 250K deposit. The background absorbance was, however, much stronger than for previous films, indicative of electronic excitations. Bandwidths were generally narrower, and the intensities of all bands were reduced compared to the background absorbance.

Two bands at 1580 and 1504 cm^{-1} , previously attributed to TCNQ^{-} , were no longer present in the spectrum of this film, and the broad absorbance between $1300 - 1400\text{ cm}^{-1}$ observed in the spectrum of the 240K deposit was resolved into three weak bands at 1378 , 1360 and 1337 cm^{-1} . Two of these bands were assigned to TCNQ^{-} (1361 , $b_{1u}v_{21}$; 1388 cm^{-1} , $b_{2u}v_{35}$). Thus, although it is clear that the film deposited at 250K contains primarily charged species, it is not possible, on the basis of the absorption spectrum, to distinguish between the presence of free TCNQ^{-} molecules or charge transfer

complex. A comparison of the 250K spectrum with that obtained in reflection from a film annealed at higher substrate temperatures (Figure 5.8) however, indicates that the film is substantially in the form of the charge transfer complex. The reflectance spectrum was obtained from a film deposited onto conducting tin oxide coated glass at 130K and then annealed to room temperature.

Films Deposited below 190K

The Spectra

The interpretation of the spectra of deposits formed at temperatures below 190K is based upon the assumption that vibronic effects play a significant rôle in determining the vibrational properties of both TTF and TCNQ in these films. Compare, for example, the spectra in Figures 5.9 and 5.10 for the 85K and 160K deposit with that in Figure 5.4 for the 205K deposit. It is immediately apparent that band widths are on average 3 or 4 times greater in the spectra of low temperature films, several absorptions at 2210, 1355 and 1182 cm^{-1} being particularly broad and intense. In addition, many of the bands observed in the film prepared at 85K were not present in the spectra of those deposited above 190K and cannot be assigned to vibrational modes of the parent molecules. A comparison of the frequencies of these bands with those of the a_g vibrational modes of TTF and TCNQ, given in Figures 5.2 and 5.3, suggests these bands are "vibronic" in origin.

In addition to bands of vibronic origin there were also a number of absorptions which have previously been assigned to neutral TTF and TCNQ. The ratio of vibronic to neutral band intensities increased with decreasing substrate temperature indicating a decrease in the relative concentration of neutral molecules. This can be

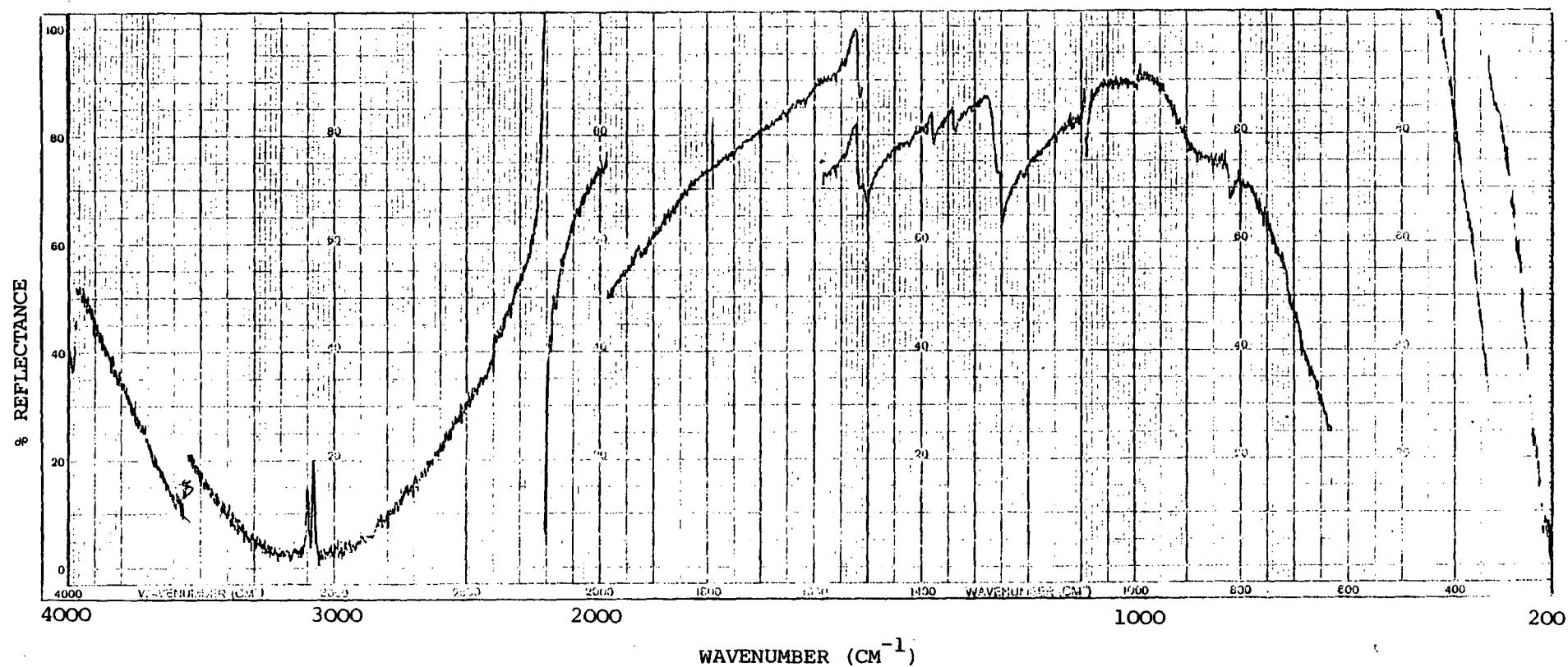


Figure 5.8. Infrared reflectance spectrum, taken at glancing angle (c. 45°), of a film of (TTF)(TCNQ) deposited onto conducting tin oxide coated glass at 130K. The spectrum was recorded after annealing to room temperature.

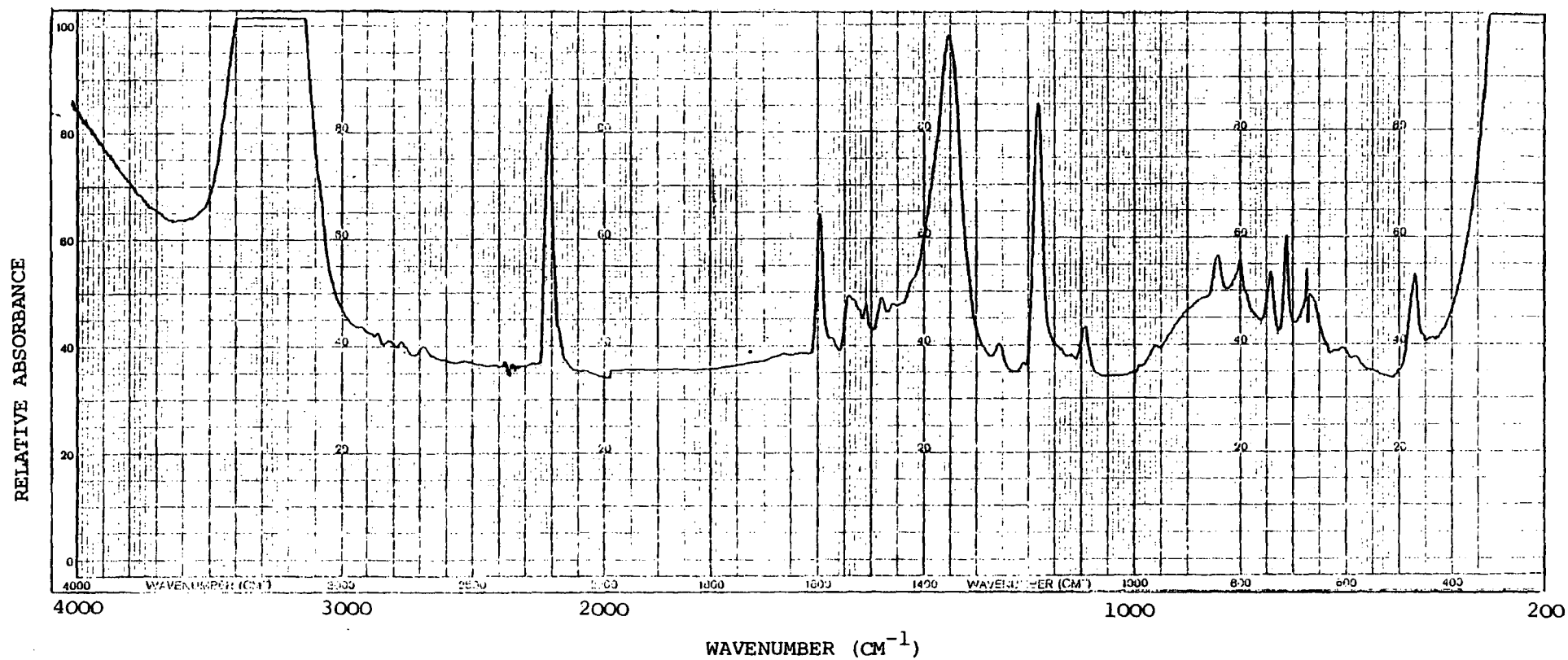


Figure 5.9. Infrared absorption spectrum of a film of (TTF)(TCNQ) deposited and recorded at 85K.

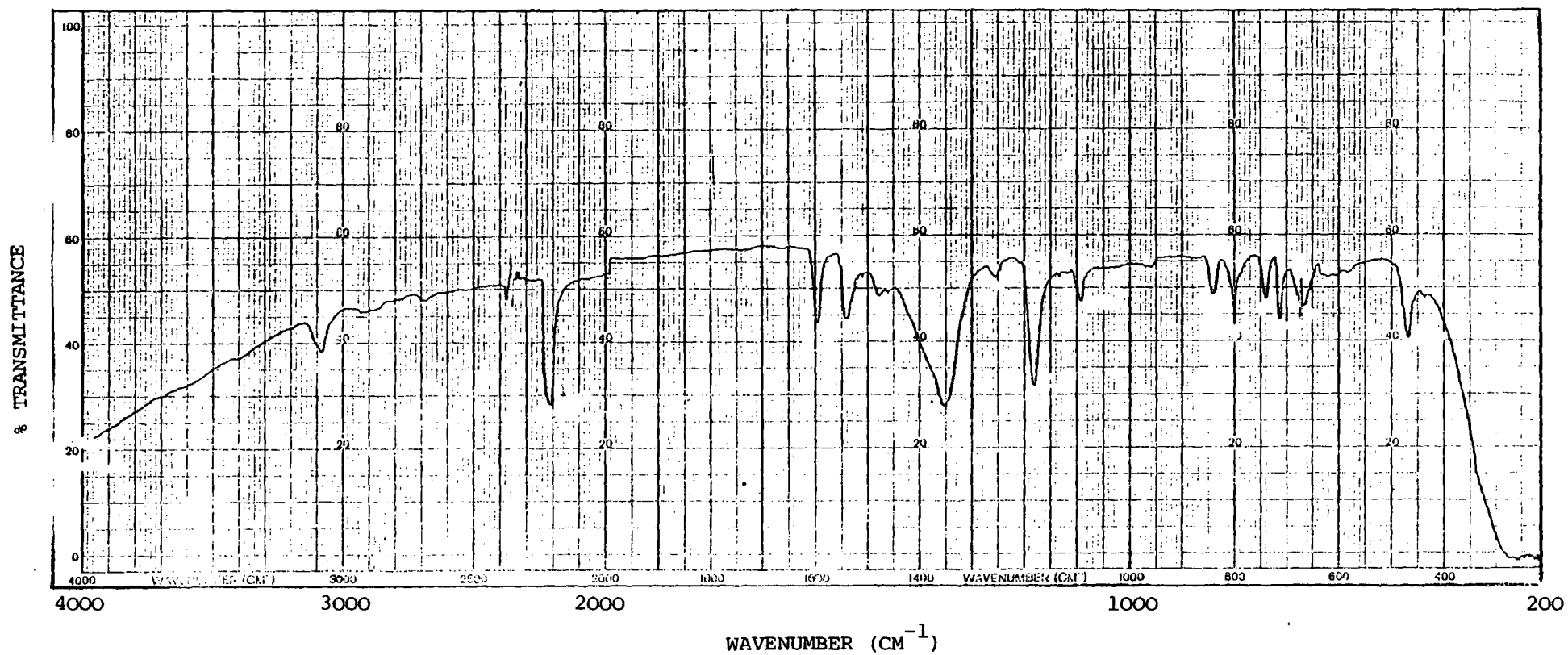


Figure 5.10. Infrared absorption spectrum of a film of (TTF)(TCNQ) deposited and recorded at 160K.

readily seen by comparing the spectra of 85K (figure 5.9) and 160K (Figure 5.10) deposits.

The Interpretation of the Spectra of Low Temperature Deposits

Bands located at 2210, 1595, 1183, 960, 710 and 605 cm^{-1} were assigned to the ν_2 ν_3 ν_5 ν_6 ν_7 and ν_8 a_g modes of TCNQ, while those at 1480, 740 and 468 cm^{-1} are thought to be derived from the corresponding a_g vibrations of TTF, that is ν_2 ν_5 ν_6 , respectively.

The rationale behind the assignment of the above bands to the totally symmetric vibrations of the two parent molecules was discussed in Section (5.1.2). Bozio et al. have studied the infrared spectra of TTF ClO_4 ^(4b) and LiTCNQ⁽³⁶⁾ in solution as a function of concentration. At high concentrations both salts form charged dimeric species in solution which results in an intensity enhancement of their respective a_g vibrations. In the case of LiTCNQ, two bands at 1595 and 1183 cm^{-1} exhibited pronounced enhancement with increased concentration, while a third at 1371 cm^{-1} was only weakly effected. The frequencies of all three bands coincided exactly with absorptions observed in the spectra of low temperature deposits. A similar enhancement of three bands located at frequencies of: 1360, 749 and 492 cm^{-1} was observed in the solution spectra of $\text{TTF}^+ (\text{ClO}_4)^-$; while in the infrared spectrum of TTF (Br)_{1.0}⁽⁴⁶⁾, which is known to form dimers in the solid state, three bands in the low temperature spectrum (20K) at 1450-1350, 742 and 470 cm^{-1} were assigned to the totally symmetric ν_3 ν_5 and ν_6 modes of TTF. The fact that both TTF and TCNQ show increased vibrational intensity in the 1360 cm^{-1} region of the spectrum could account for the extremely broad and very intense band observed at this frequency in the spectra of low temperature films. However, solid alkali metal salts of TCNQ which

are known to contain dimers, also exhibit a very broad intense absorption in this region of the spectrum. This band has previously⁽³⁶⁾ been assigned to the ν_4 totally symmetric mode of TCNQ.

The band at 1360 cm^{-1} in the spectrum of TTF salts was assigned by Bozio et al.^(4b) to the ν_3 (1515 cm^{-1}) mode of TTF. However, an additional low intensity peak was present in the low temperature spectrum at 1480 cm^{-1} . Since all of the a_g vibrations of TCNQ in this region of the spectrum have been accounted for, it is presumably derived from one of two possible TTF a_g modes, that is ν_2 (1555 cm^{-1}) or ν_3 (1515 cm^{-1}). In view of the earlier assignment of the band at 1360 cm^{-1} to the ν_3 a_g mode the most likely candidate for the peak at 1480 cm^{-1} is TTF (ν_2).

The other bands present in the low temperature spectrum, which are assigned to totally symmetric vibrations are given in Table 5.3. The broad absorption in the $-\text{C}\equiv\text{N}$ stretch region centered at 2210 cm^{-1} was resolved on annealing into two bands at 2227 and 2210 cm^{-1} . The latter was observed to decrease in intensity as a result of annealing (Figure 5.11) and for reasons which will be discussed is therefore assigned to the TCNQ a_g ν_2 mode. The frequency of the band at 710 cm^{-1} coincides almost exactly with that expected for the a_g ν_7 mode of TCNQ. The only other possible candidate is the band at 740 cm^{-1} but this is unlikely in view of its earlier assignment⁽⁴⁶⁾ to TTF, a_g ν_5 in TTF (Br)_{1.0}. The work of Bozio et al. also supports the assumption that the band located at 468 cm^{-1} originates from TTF, a_g ν_6 .

Band intensities

With the exception of the ν_1 and ν_4 modes all of the observable, totally symmetric vibrations of TTF are present in the spectra of films deposited at low temperatures. The ν_1 mode which corresponds

to the totally symmetric C-H stretching vibration (3083 cm^{-1}) is according to Rice et al.⁽²⁴⁾ only weakly coupled to the electron molecular orbital ($g \sim 0.01\text{ meV}$) and is not expected to show a pronounced anomalous infrared activity. Therefore, although several bands are present in the C-H stretch region, it is not possible to assign these to the ν_1 mode with any confidence. Similar considerations apply to the ν_1 mode (3048 cm^{-1}) of TCNQ ($g \sim 0.01$). However, according to Rice the ν_4 mode of TTF should be strongly coupled and although a band was observed at 1091 cm^{-1} , which is close to the frequency expected for the ν_4 mode of TTF (1094 cm^{-1}), it did not show the annealing behaviour (see later) expected for an a_g vibration. It is probable that this absorption belongs to the normally infrared active C-H in plane bending ($b_{1u}\nu_{15}$) mode of TTF, and the $a_g \nu_4$ mode remains unaccounted for.

The two weak bands located at 960 and 605 cm^{-1} complete the assignment of observable TCNQ a_g vibrations. Both are absent from the spectra of films deposited above 190K . The latter originates from $a_g \nu_8$, its low intensity possibly being due to a small value of the coupling constant ($g \approx 0.03\text{ meV}$). In view of the somewhat higher value of the coupling constant of the ν_6 totally symmetric vibration (948 cm^{-1} , $g \sim 0.25\text{ meV}$) a greater intensity was expected for this band. However, there appears to be very little correlation between the calculated values of the coupling constant listed in column 7 of Table 5.3 and the observed band intensities of the spectra of films deposited at low temperature.

If it is assumed that the anomalous infrared activity is derived entirely from the electron vibrational interaction then the intensity gain should be directly related to the sum of the coupling constants

by equations (5.4) and (5.5). According to this simple analysis the electron, vibrational coupling strength for the bands observed in the spectra of low temperature deposits, should scale as $\nu_5 \sim \nu_2 > \nu_3 > \nu_7 > \nu_6 > \nu_8$ for TCNQ and as $\nu_6 > \nu_5 > \nu_2$ for TTF. Since the band centered at 1360 probably consists of the ν_3 and ν_4 modes of TTF and TCNQ, respectively, it was not possible to determine the relative coupling strengths of these two vibrational modes.

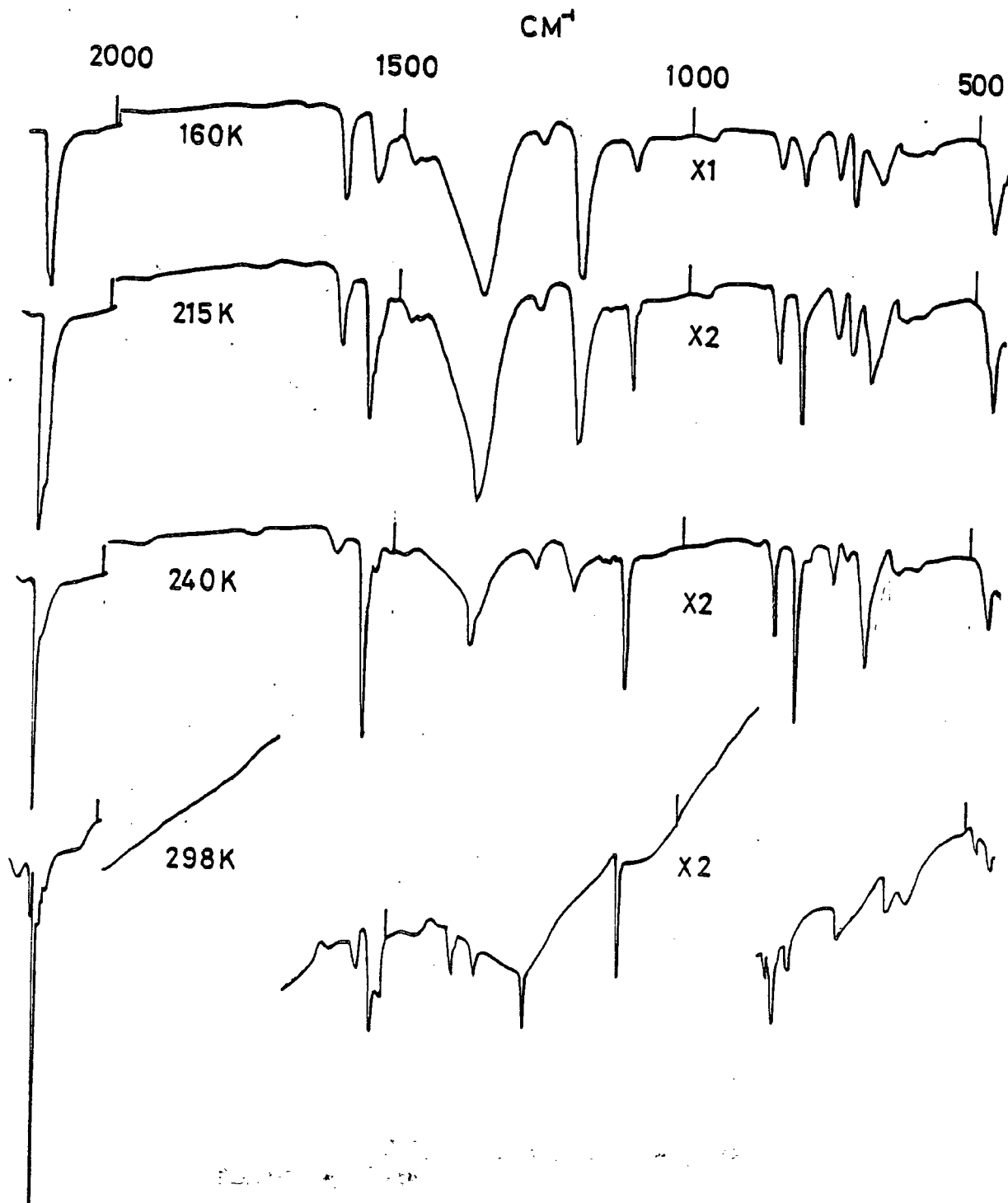
5.2.2 Annealing Studies

Annealing at low temperatures

The changes which occur when a film of TTFTCNQ is deposited at substrate temperatures below 190K and then subjected to annealing were referred to in passing in section 5.2.1. The infrared spectra of a film deposited at 160K, and then annealed stepwise at progressively higher temperatures are shown in Figure (5.11). It was pointed out earlier that films deposited above a characteristic temperature, which in the case of TTFTCNQ appears to be about 190K, did not contain any anomalous infrared absorption bands associated with a_g vibrational modes. It is clear from Figure (5.11) that annealing is also instrumental in reducing the intensity of bands assigned to a_g vibrational modes which were present in the spectra of films deposited onto substrates below 190K. The intensities of all bands assigned to totally symmetric a_g vibrational modes of TTF and TCNQ which are listed in Table 5.3 were progressively reduced as the temperature was increased, although the more intense absorptions at 2210, 1595, 1183 and 468 cm^{-1} were still very much in evidence at 240K.

In addition to those bands which were associated with the totally symmetric vibrations of TTF and TCNQ, the spectra of films deposited below 190K also contained absorptions which are normally

Figure 5.11. Stepwise annealing of a film deposited at 160K.
Spectra were recorded at 160, 215, 240 and 298K.



infrared active. All of these additional absorptions are thought to derive from neutral TTF and TCNQ. The basis for their assignment has already been discussed in connection with the spectra of films deposited at temperatures above 190K. A further point to consider is that while annealing causes a reduction in the intensity of a_g vibrational modes it also results in an increase in the strength of those absorptions which have been assigned to neutral TTF and TCNQ. The absorption bands which increase in intensity are readily located in Fig. 5.11. For reasons which will be discussed, a_g modes are thought to originate from the charge transfer interaction between TTF and TCNQ, i.e. the formation of a charge transfer dimer (CTD). An approximate value for the relative amounts of dimer and monomer present in the 160K film was obtained from the change in the intensities of their respective absorption bands. On annealing from 160K to 240K the absorption band at 1595 cm^{-1} decreased from an initial relative intensity of 64 to 7, while that at 1545 cm^{-1} increased from 42 to 64 over the same temperature range. Assuming that the loss in intensity of the CTD band at 1595 cm^{-1} was due to dissociation, resulting in the formation of TCNQ^0 (1545 cm^{-1}) the band intensity ratio, i.e. $1595:1545\text{ cm}^{-1}$ was approximately 2.5 : 1. Since the initial ratio of the two band intensities was 3 : 1, respectively, the ratio of CTD to TCNQ^0 at 160K was estimated to be 0.6 : 1. A similar ratio was found when the intensities of TCNQ bands in the CTD at 1183 and 710 cm^{-1} were compared with the TCNQ^0 absorption at 1545 cm^{-1} .

Unfortunately, the only band of appreciable intensity which could be definitely assigned to TTF in the CTD was that at 468 cm^{-1} ($a_g \nu_6$) and this overlapped with a TCNQ^0 band ($b_{3u} \nu_{32}$, 478 cm^{-1}).

Consequently it was not possible to make an accurate determination of the ratio of CTD to neutral TTF on the basis of TTF vibrational modes. However an approximate value was obtained by comparing the intensity of the bands at 468 cm^{-1} ($a_g \nu_6$) and 797 cm^{-1} ($b_{2u} \nu_{25}$) the latter having already been assigned to TTF^0 . The small contribution from the $b_{3u} \nu_{32}$ mode of TCNQ was ignored. The relative concentration (normalised to that at 160K) of CTD, based on the $a_g \nu_3$ mode of TCNQ (1595 cm^{-1} , curve a) and the $a_g \nu_6$ of TTF (468 cm^{-1} , curve b), is given in Figure (5.12), as a function of annealing temperature, for a film deposited at 160K. The lack of coincidence of the two curves in the high temperature region is presumably due to the presence of the $b_{3u} \nu_{32}$ mode of TCNQ. The data given in Figure 5.12 illustrates very clearly the rapid decrease in concentration of CTD above 200K, with the maximum rate of dissociation close to 215K, in both cases.

The data shown in Figure 5.12 were obtained by annealing the film deposited at 160K in a stepwise manner. At each stage in the annealing process the film was annealed at constant temperature for at least 30 mins during which time the intensity of bands in the $\text{-C}\equiv\text{N}$ stretching frequency region ($2300 - 2100\text{ cm}^{-1}$) was monitored using the repeated scan facility of the model 580 spectrometer. The results are given in Figure (5.13) in which the absorbance intensity of the band at 2210 cm^{-1} relative to that at 205K is plotted as a function of time, for each of the temperatures indicated. At temperatures up to 215K the rate of decay was effectively constant, i.e. temperature independent and the absorbance (concentration) decreased linearly with time. Between 215 and 220K the rate of dissociation of CTD increased becoming non-linear but then returned

Figure 5.12. The change in peak intensity of; the $a_g \nu_3$ mode (1595 cm^{-1}) of TCNQ, Curve (a); and the $a_g \nu_6$ mode (468 cm^{-1}) Curve (b) of a film deposited at 160K.

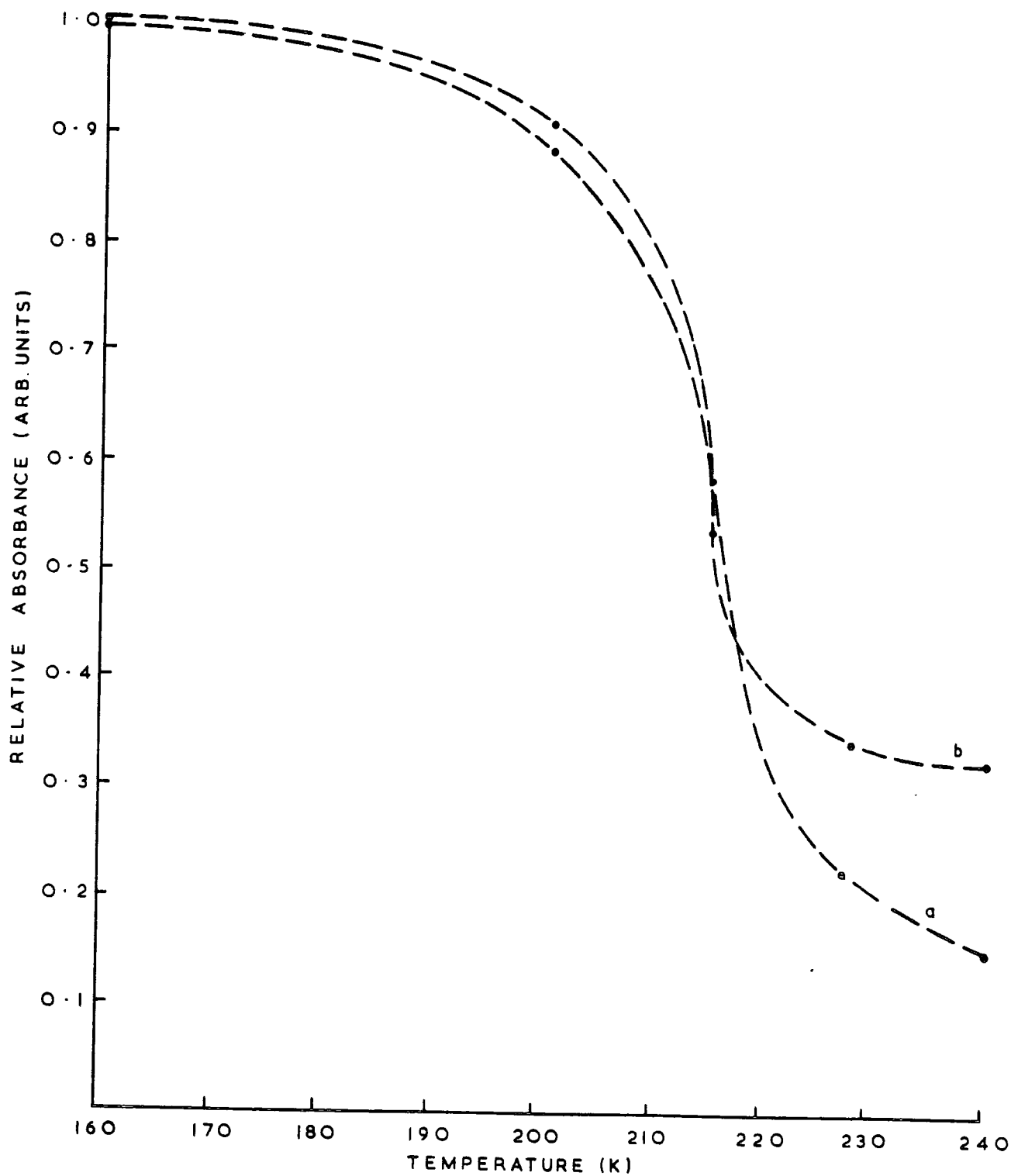


Figure 5.13. The decrease in peak intensity of the -C≡N stretching band intensity (2210 cm^{-1}) as a result of stepwise annealing at 205, 210.5, 215.5, 220 and 225K for a film deposited at 160K

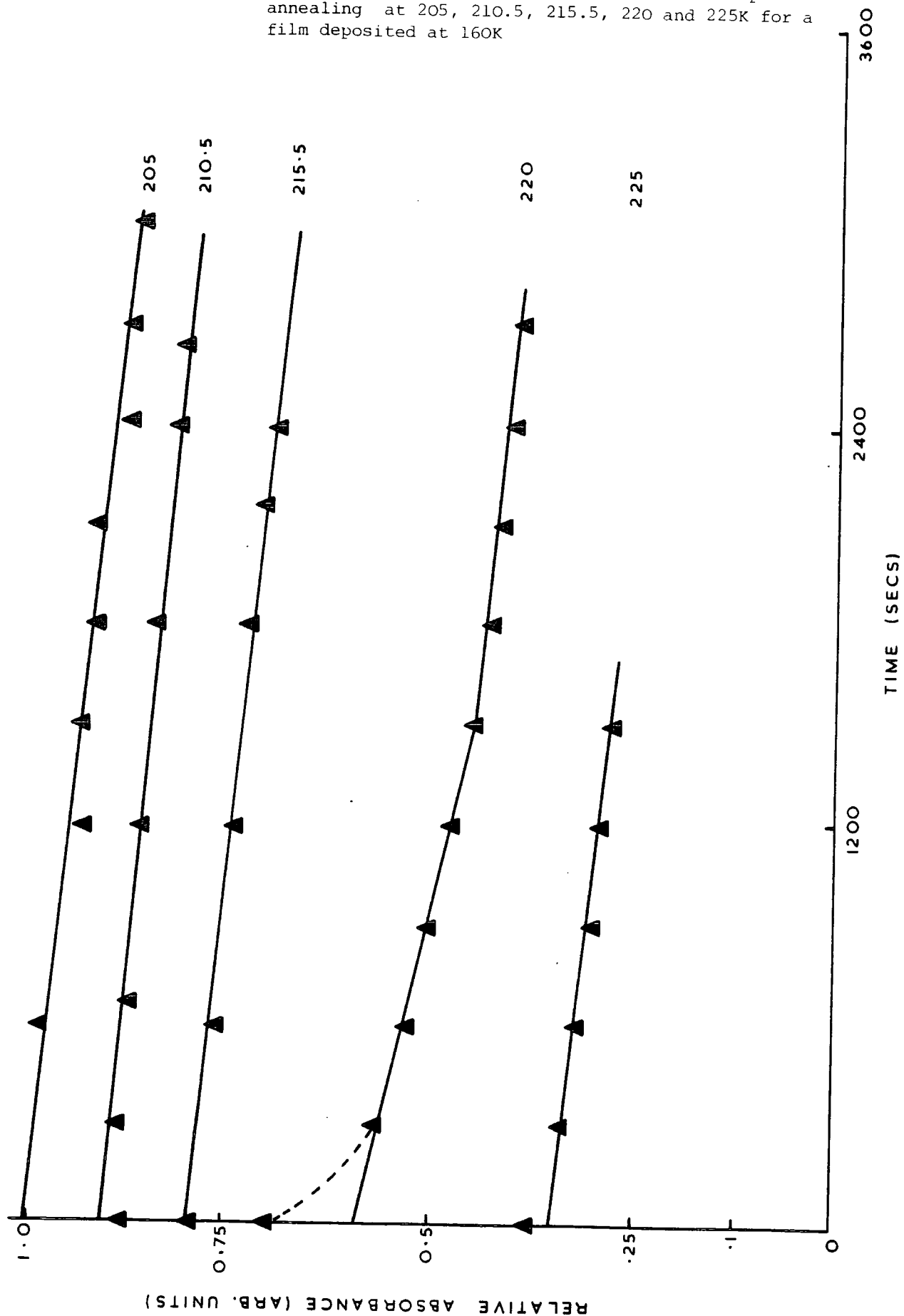


Table 5.3

Infrared bands which decrease in intensity when films deposited below
190K are annealed

Frequency of observed band (cm^{-1})	Intensity ^(a) reduction	ag vibrational modes (cm^{-1})				g (meV) ^(e)
		TCNQ ^(b)	TCNQ ⁻ (c)	TTF ^(d)	TTF ⁺	
2205 (vs)	4/5	2229 (ν_2)	2210	-	-	0.19
1595 (s)	6/7	1602 (ν_3)	1580	-	-	0.66
1540 (sh)	-	-	-	-	-	-
1480 (w)	-	-	-	1555 (ν_2)	1505	0.23
				1515 (ν_3)	1420	0.62
1360 (vvs)	4/5	1454 (ν_4)	1370- 1330	-	-	0.27
1183 (vs)	4/5	1207 (ν_5)	1185	-	-	0.19
960 (w)	-	948 (ν_6)	978*	-	-	0.25
740 (m)	-	-	-	735 (ν_5)	758	0.49
710 (m)	7/8	711 (ν_7)	723	-	-	0.37
605 (vw)	-	602 (ν_8)	613*	-	-	0.03
468 (s)	$\frac{1}{2}$	-	-	468 (ν_6)	501	1.33

(a) On annealing from 160-227K. The non-Gaussian shape and low intensity of many bands prevented a meaningful determination of the reduction in their intensities.

(b) ref (36) (c) taken*from the spectra of LiTCNQ

Frequencies marked with * were taken from ref (36)

(d) ref (46) (e) ref (32)

FIGURE 5.14a

The decrease in intensity of the $a_g \nu_2$ mode of TCNQ (2206 cm^{-1}), as a function of temperature, for a constant annealing rate of $0.5^\circ\text{C}/\text{min}^{-1}$, for a film deposited at 85K

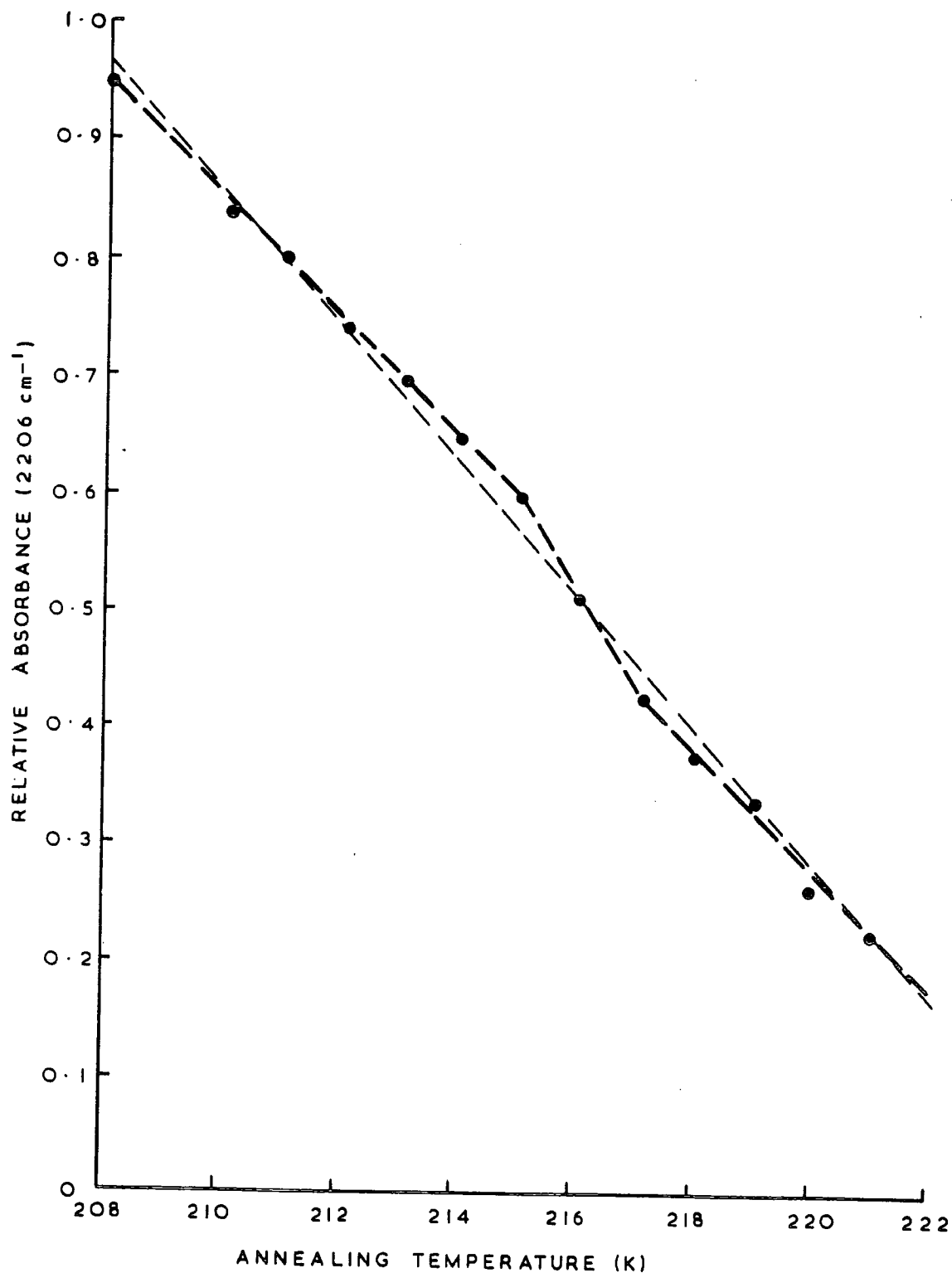
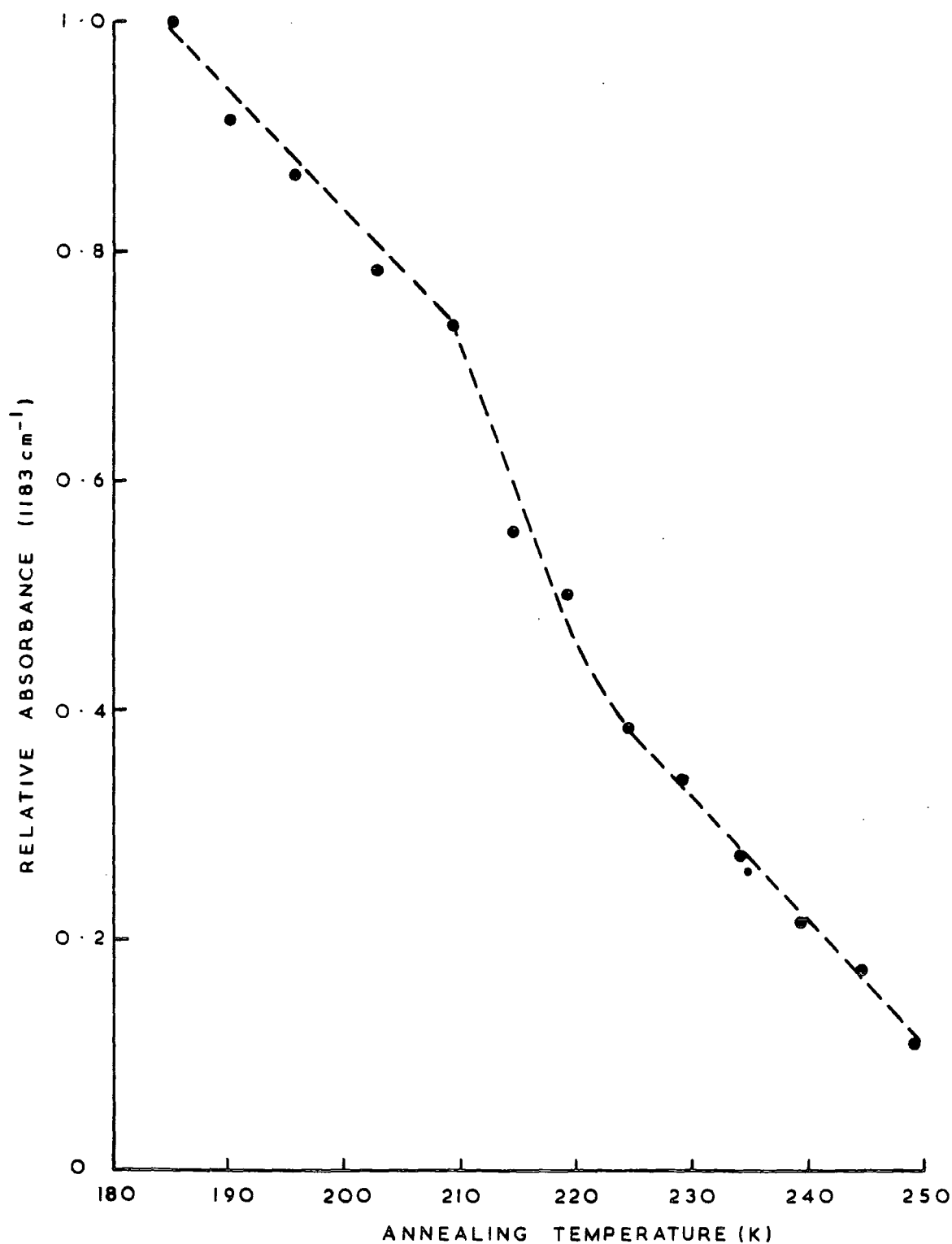


FIGURE 5.14b

The decrease in intensity of the a_g ν_5 mode of TCNQ (1185 cm^{-1}), as a function of temperature, at constant annealing rate ($0.5^\circ\text{C}/\text{min}^{-1}$), for a film deposited at 160K



to the initial rate.

It appears from Figure (5.13) that the rate of dissociation was, apart from the region between 215 and 220K, independent of temperature. This is shown convincingly in Figures (5.14(a) and (b)) which shows data obtained from films deposited at 85K and 185K, respectively. In both cases a change in slope was observed in the vicinity of 215K, but above and below this temperature the rate of decrease of CTD concentration was constant. Data in Figure (5.14) was obtained by annealing both films at a constant rate of temperature increase ($0.5^{\circ}\text{C. min}^{-1}$). The relative absorbance of the TCNQ ($a_g \nu_2$) band at 2206 cm^{-1} is plotted as curve a and that of TCNQ ($a_g \nu_5$) at 1185 cm^{-1} as curve b. Both absorption bands are associated with the CTD as discussed earlier.

5.2.3 Annealing in the high temperature region

When films deposited below 190K were annealed beyond the point at which a_g mode intensities were reduced to zero, further changes in their vibrational spectra were observed. Figure (5.15) illustrates the dramatic change which occurred between 267K (spectrum a) and 270K (spectrum b) in the spectrum of a film deposited at 100K and then annealed. Bands due to molecular vibrations almost entirely disappeared into the background and the film became strongly absorbing across the whole of the spectrum, above a frequency of about 1000 cm^{-1} . Below this frequency the transmittance of the film increased to a maximum at approximately 400 cm^{-1} and then decreased rapidly. For films deposited at other substrate temperatures, particularly above 190K, this change was less dramatic, as illustrated in Figure (5.16) for a sample prepared at 214K. Spectrum (a) was obtained for the film in the as-deposited state, whilst spectrum (b) was that of the same sample after annealing to 300K. The main bands

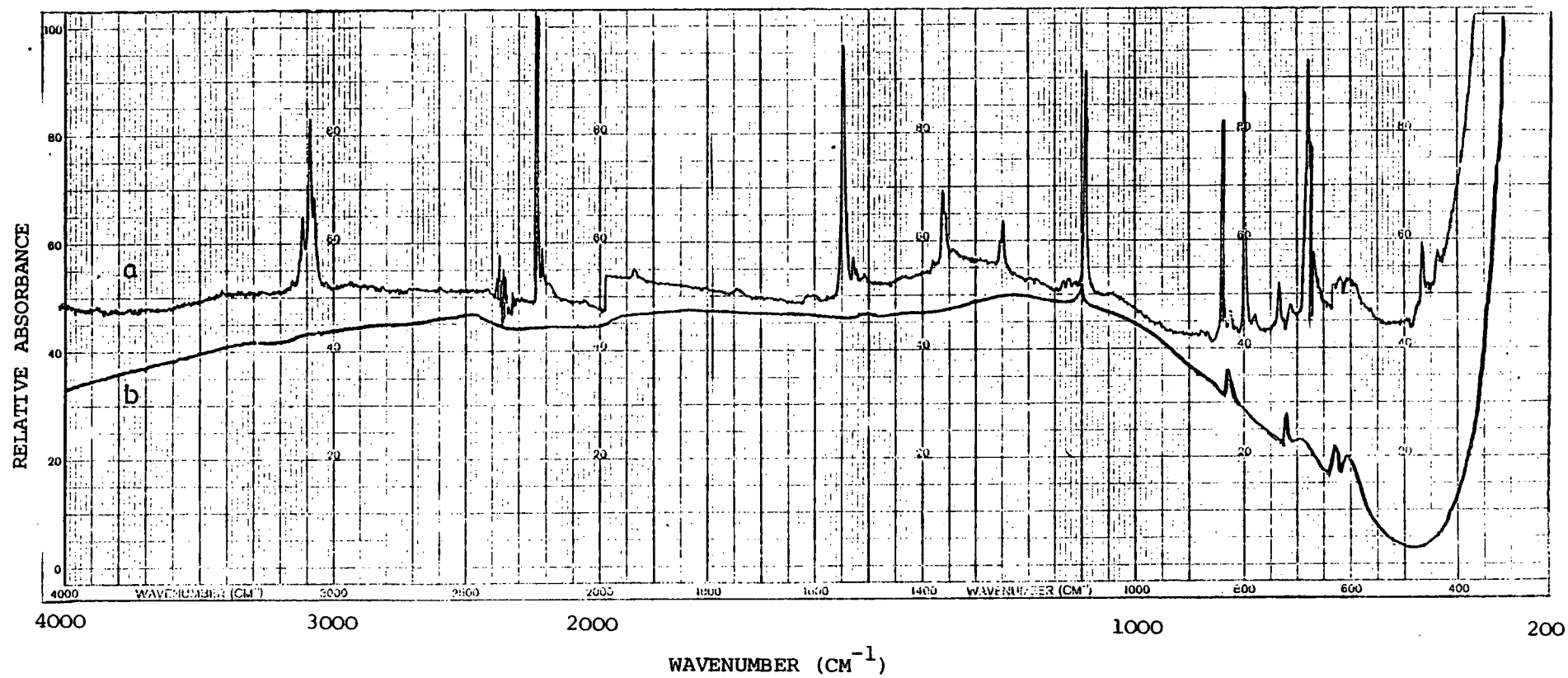


Figure 5.15. Infrared spectra of a film of (TTF)(TCNQ) deposited at 100K, and recorded at 267K (Curve a) and then annealed and recorded at 270K (Curve b).

Figure 5.16. Infrared spectra of a film of (TTF)(TCNQ) deposited and recorded at 214K (Curve a) and then annealed and recorded at 300K (Curve b).

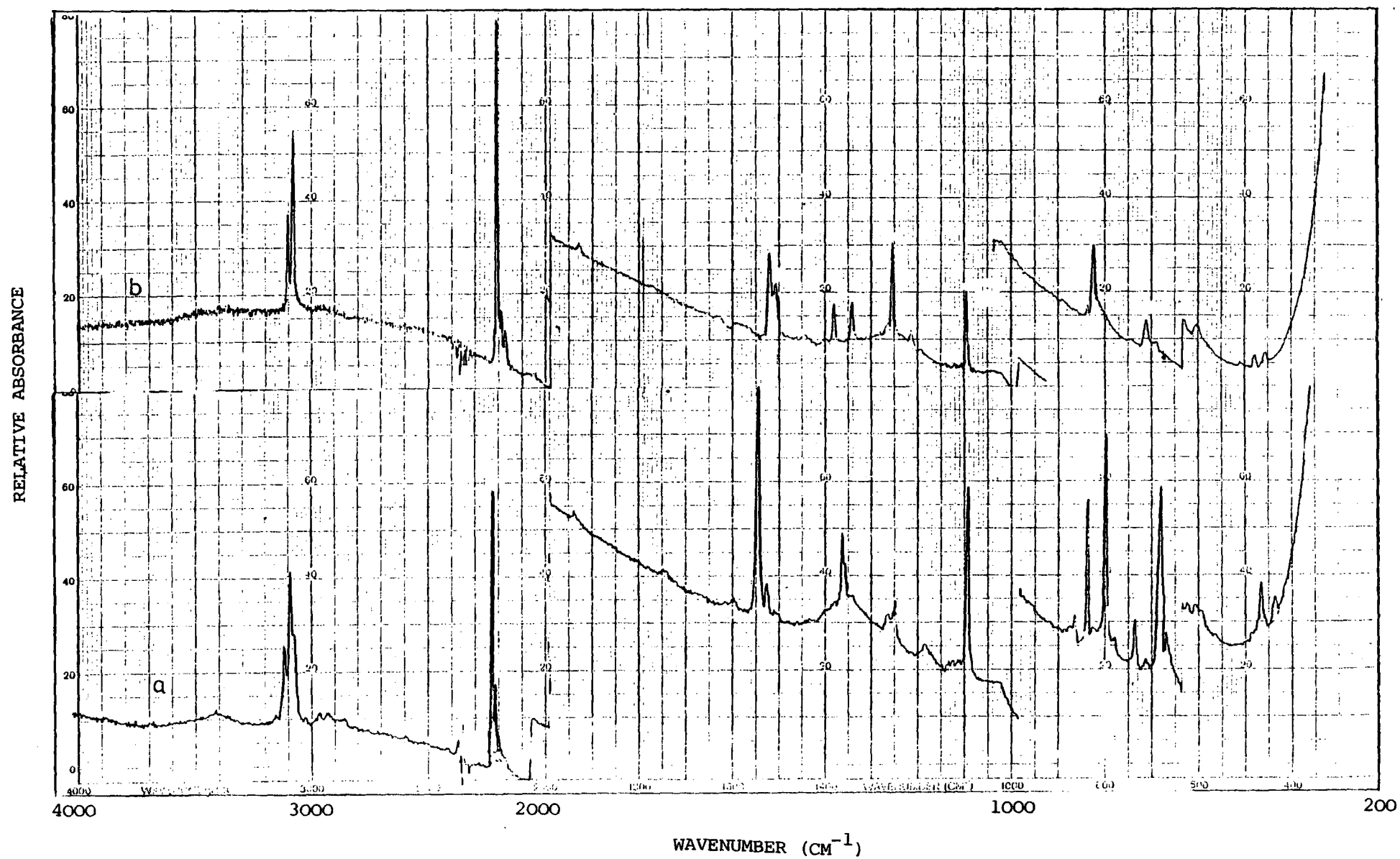


Table 5.4. The assignment of bands in the spectra of Figure 5.16.

Frequency (cm ⁻¹)	214 K Relative Intensity (a)	Frequency (cm ⁻¹)	300 K Relative Intensity (b)	Assignment (c)
3118	19			TTF ⁰ , b _{1u} v ₁₃
		3102	28	)
3090	45			) ?
		3080	49	)
				TTF ⁺ , b _{1u} v ₁₃
3070	(Sh)			TCNQ ⁰ , b _{1u} v ₁₈ TTF, b _{2u} v ₂₂
2228	82			TCNQ ⁰ , b _{1u} v ₁₉
				b _{2u} v ₃₃
2210	21	2210	100	TCNQ ⁻ , ag v ₂ ? b _{1u} v ₁₉
		2184	10	TCNQ ⁻ , b _{1u} v ₁₉ b _{2u} v ₃₃
		2166	10	TCNQ ⁻ , b _{2u} v ₃₃
1547	66			TCNQ ⁰ b _{2u} v ₃₄
				b _{1u} v ₂₀
1527	9			TTF ⁰ , b _{1u} v ₁₄
		1521	24	TCNQ ⁻ , b _{2u} v ₃₄
		1507	14	TCNQ ⁻ , b _{1u} v ₂₀
		1381	10	TCNQ ⁻ , b _{2u} v ₃₅
1363	19			TCNQ ⁻ , b _{1u} v ₂₁
		1342	10	TCNQ ⁻ , b _{2u} v ₃₅
1265	5			TTF ⁰
		1255	27	TTF ⁺ } b _{2u} v ₂₃
1249	10			TTF ⁰)
1093	56	1095	22	TTF ⁰ ; TTF ⁺ , b _{1u} v ₁₅
865	7			) TTF ⁰ , b _{2u} v ₂₄ ;
837	79	837	3	) TCNQ ⁰ , b _{3u} v ₅₀
825	1	824	22	TTF ⁺ , b _{2u} v ₂₅
798	100			TTF ⁰ , b _{2u} v ₂₅
737	14			TTF ⁰ , b _{1u} v ₁₇
712	3	712	8	ag v ₇
680	56			TTF ⁰ , b _{2u} v ₂₆
600	4	600	5	ag v ₈
467	14	467	3	) TCNQ ⁰ , b _{3u} v ₅₂
		455	3	)
437	7			TTF ⁰ , b _{1u} v ₁₈

a) Relative to the band at 798 cm⁻¹. b) Relative to the band at 2210 cm⁻¹.
c) Based upon the analysis of references (4b) and (36)

in both spectra of Figure (5.16) are listed, in columns 1 and 3 of Table 5.4 and their relative intensities in columns 2 and 4, respectively. The final column contains the most probable assignments of bands, based upon the analysis of Bozio et al. (4b) and (36)

Almost without exception, those bands present in the low temperature spectrum (a), belonged exclusively to neutral TCNQ or TTF species and exhibited a marked reduction in intensity on annealing to 300K. Furthermore all bands present in the high temperature spectrum (curve b) could be assigned to charged $(\text{TCNQ})^-$ and $(\text{TTF})^+$ species. With the exception of the band at 2210 cm^{-1} , all bands which were previously assigned to totally symmetric modes are either very weak (712 cm^{-1} and 600 cm^{-1}) or completely absent. Weak broad features which were observed at $1300 - 1400\text{ cm}^{-1}$ and 1180 cm^{-1} in the 214K spectrum, were probably due to totally symmetric vibrations. Both had disappeared at 300K. Since the C≡N stretching band in the dimer was located at a slightly different frequency (2205 cm^{-1}) it is possible that the band observed at 2210 cm^{-1} can be assigned to a normally infrared active band ($b_{1u} \nu_{19}$) and not to $a_g \nu_2$.

The two main bands in the C≡N stretching region (TCNQ^0 , 2210 cm^{-1} ; TCNQ^- , 2210 cm^{-1}) were extremely narrow and intense and were easily resolved. Figure 5.17 shows the region between 2250 and 2150 cm^{-1} for a film deposited at 195K. On annealing, the band due to TCNQ^0 at 2228 cm^{-1} was seen to decrease, while that due to TCNQ^- at 2210 cm^{-1} increased in intensity, above a temperature of 275K. This change was accompanied by an increase in the background absorbance which was remarked upon earlier. In Figure (5.17) the effect of the increased background absorbance was to reduce the intensity of both bands simultaneously. Both processes, i.e. the increase in background absorbance and the change in band intensity in the C≡N stretching

WAVENUMBER(CM.⁻¹)

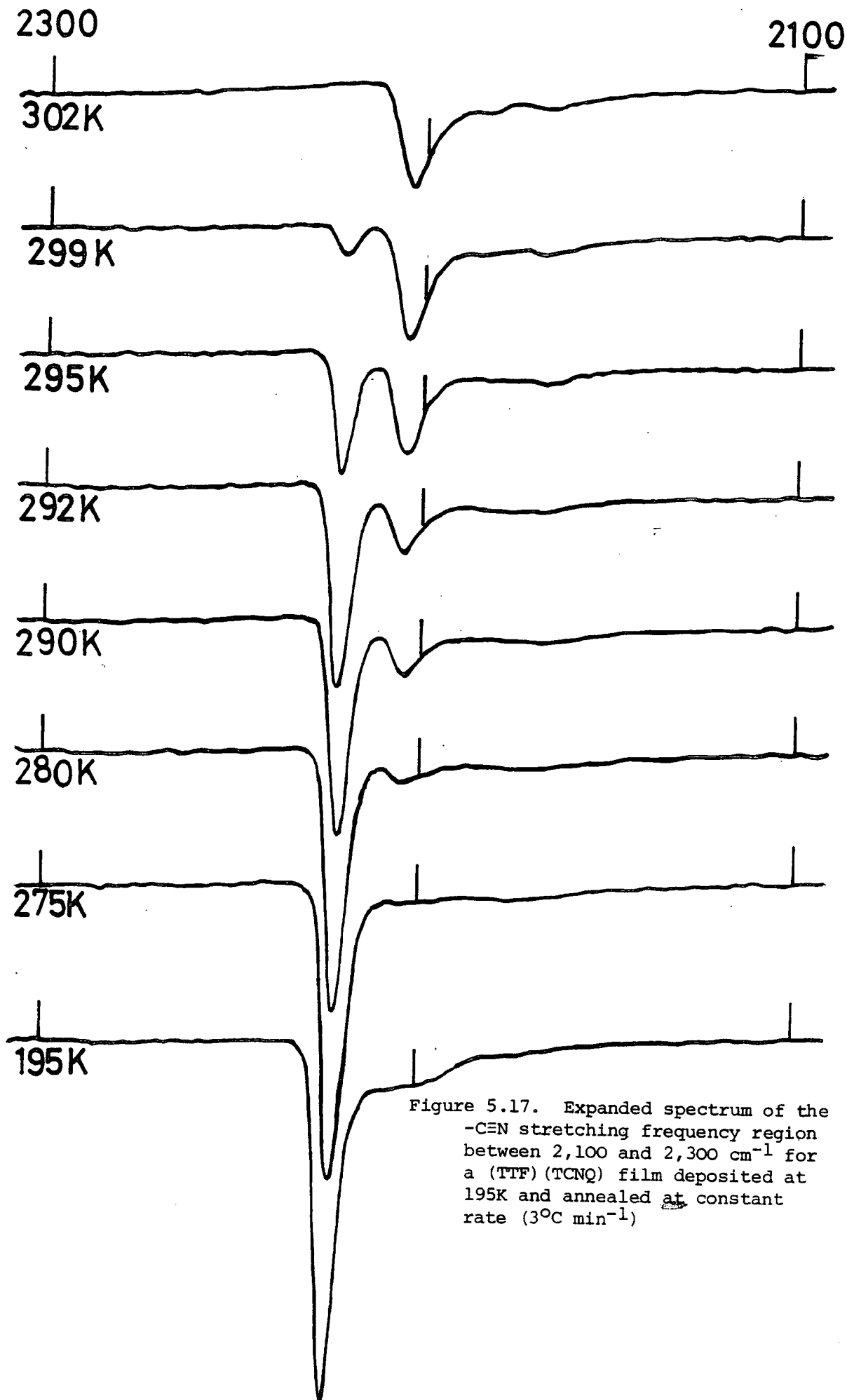


Figure 5.17. Expanded spectrum of the -C≡N stretching frequency region between 2,100 and 2,300 cm⁻¹ for a (TTF)(TCNQ) film deposited at 195K and annealed at constant rate (3°C min⁻¹)

FIGURE 5.18

Decrease in intensity of the $\text{-C}\equiv\text{N}$ stretching vibration of TCNQ^0 (2228 cm^{-1}) as a function of annealing temperature for films of (TTF)(TCNQ) deposited at various substrate temperatures

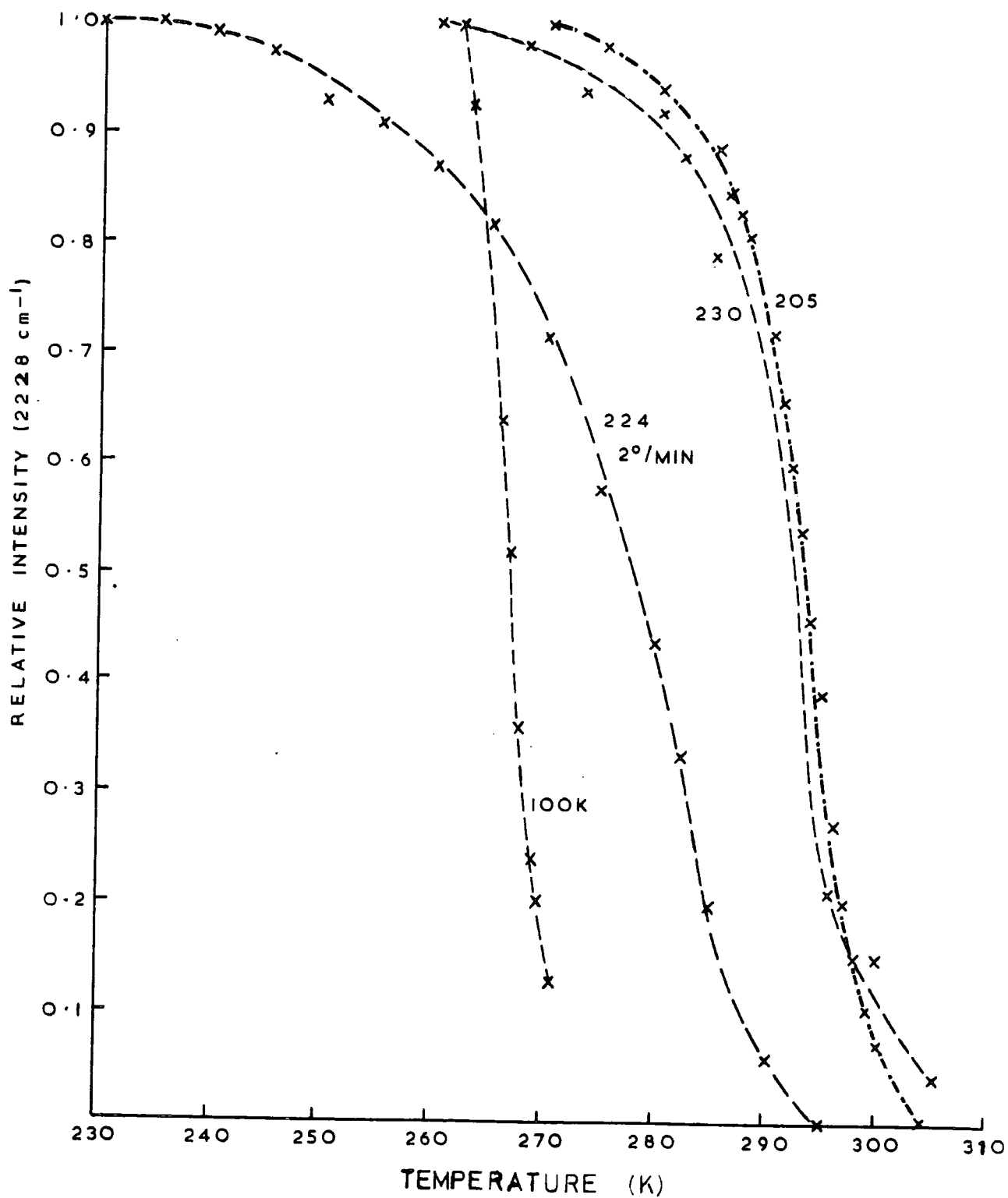


FIGURE 5.19

Increase in intensity of the $\text{-C}\equiv\text{N}$ stretching vibration of TCNQ^- (2206 cm^{-1}) as a function of annealing temperature for films of (TTF)(TCNQ) deposited at various substrate temperatures

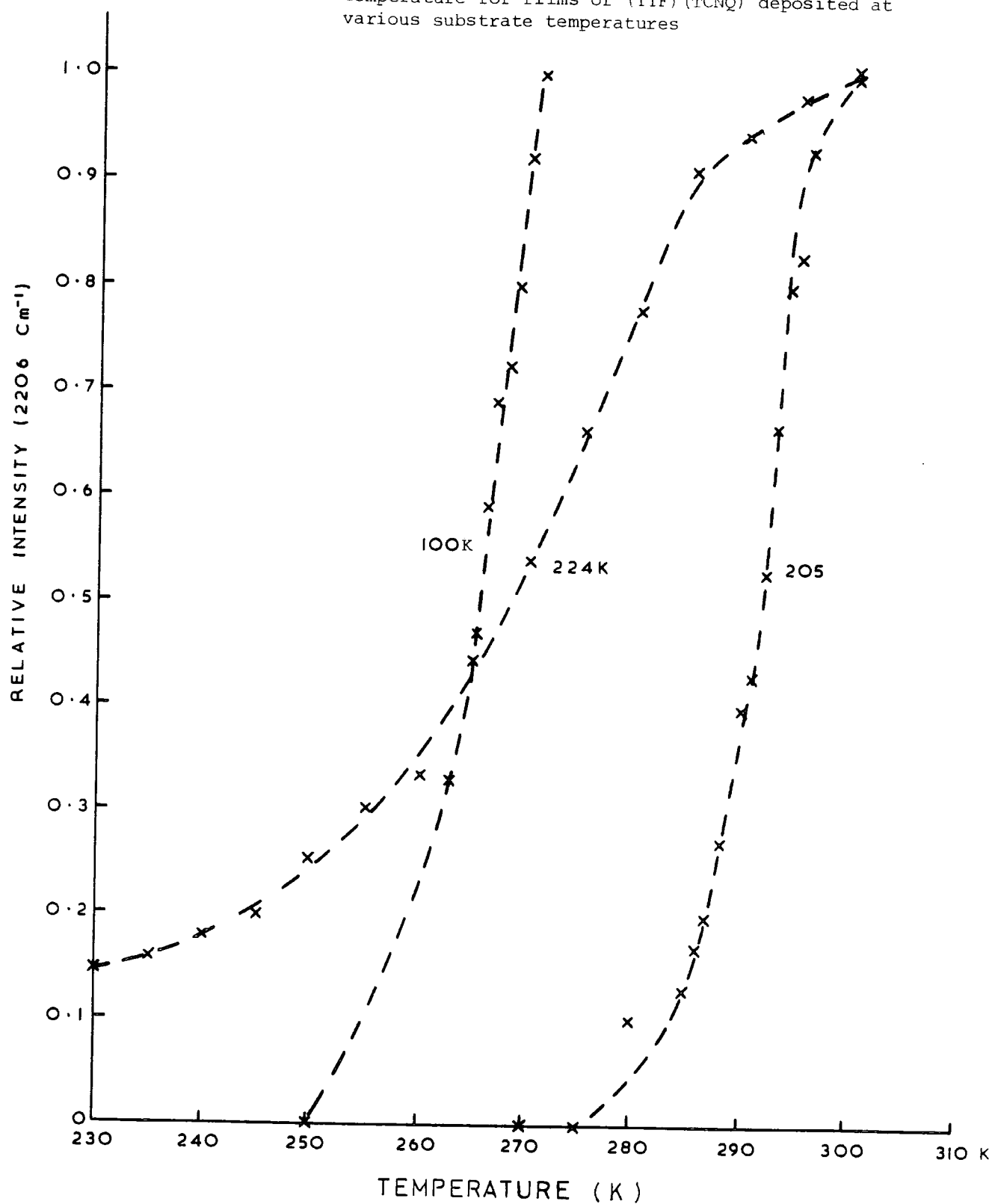


FIGURE 5.20 Decrease in background transmittance in the spectral region (2100-2300 cm^{-1}) as a function of annealing temperature for (TTF)(TCNQ) films deposited at various substrate temperatures

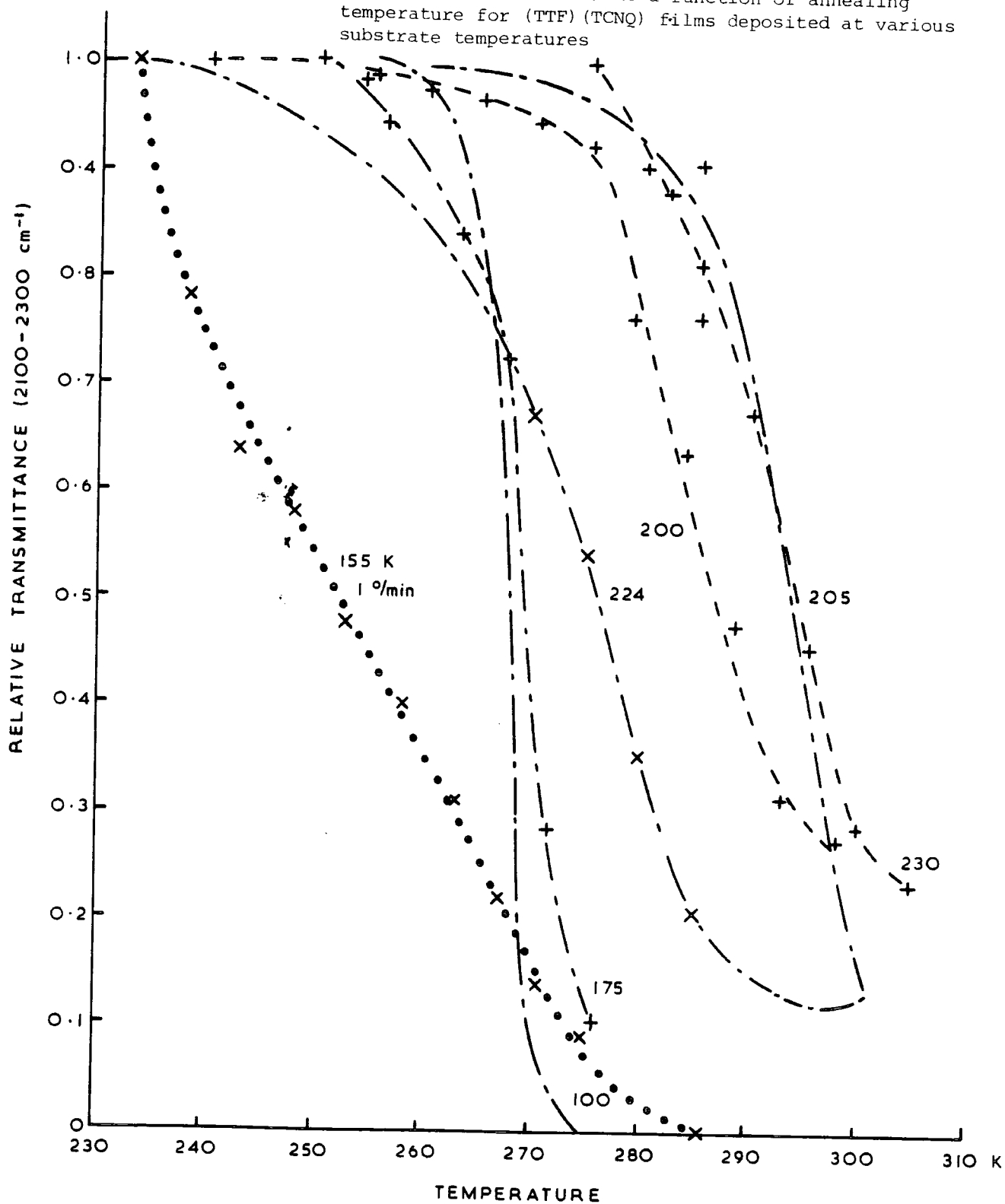
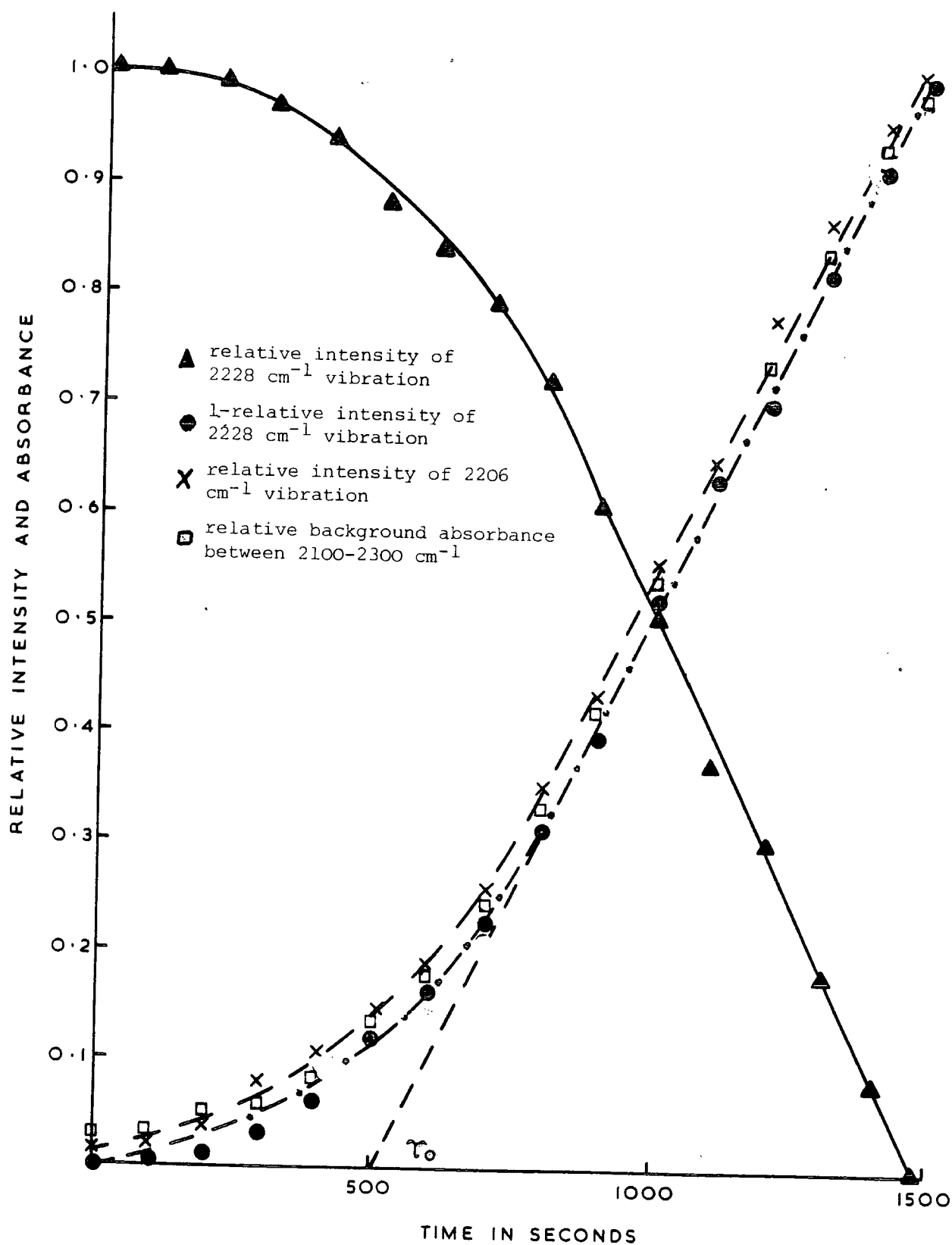


FIGURE 5.21

Time dependence of the change from TCNQ^0 to TCNQ^- for a film deposited at 160K and annealed at a constant temperature of 265K



region, were monitored with the aid of the repeated scan facility of the model 580 spectrometer. The region between 2300 and 2100 cm^{-1} was scanned once every 25 seconds. The decrease in intensity of the TCNQ° band at 2228 cm^{-1} , which occurred as a result of annealing, is shown in Figure (5.18) for a series of films deposited at 85, 195, 214 and 222K, respectively. Annealing rates of between 1 and 2 $^{\circ}$ /min were used. Band intensity, relative to that at maximum absorbance, is plotted on the ordinate axis. Similar curves are plotted in Figures (5.19) and (5.20) for the observed increase in the 2206 cm^{-1} (TCNQ^{-}) band intensity and decrease in background transmittance, respectively. The temperature of deposition and the annealing rate used are given in the diagrams alongside the appropriate curve.

It would appear from the data in Figures (5.19) to (5.21) that all three processes are related, i.e. the increase in background absorbance exhibits the same temperature dependence as the conversion of TCNQ° to TCNQ^{-} , for a given film. This point is emphasised by the curves plotted in Figure (5.21) for a film deposited at 160K and then annealed at a constant temperature of 265K. The time dependence of all three processes are practically identical. Both the relative intensity and one minus this quantity for the 2228 cm^{-1} band (TCNQ°) are plotted in order to illustrate that all three processes have the same time dependence in the film deposited at 170K.

Two films deposited at 155K and 224K showed somewhat different annealing behaviour than those deposited at other substrate temperatures. In the case of the 224K film the increase in the background absorbance and the process of ionisation i.e. $\text{TCNQ}^{\circ} \rightarrow \text{TCNQ}^{-}$, both began at about 230K, lower than observed for other films, which only began

to change around 260K. Similar behaviour was observed when the annealing process, for films deposited at 222K and 235K, was monitored electrically. As already remarked earlier, films deposited between 220K and 235K often showed irreproducible annealing behaviour, with films deposited at nominally the same substrated temperature displaying both types of behaviour, i.e. a gradual change beginning just above the deposition temperature. The pattern of annealing of the 155K deposit was similar to that observed for alloys of metals.⁽⁴⁰⁾ It is indicative of a two stage ordering process;⁽⁴¹⁾ the first involving the establishment of short range order at low temperatures which corresponds to the rapidly decreasing portion of the film at low temperatures, followed by a constant rate long range ordering process at higher temperatures. This behaviour was only exhibited by the 155K deposit.

5.3 Discussion

The infrared results have shown that the nature of the interaction between molecules within films is a function of the substrate temperature during deposition. From the infrared spectra three well defined substrate temperature regimes were identified with the following characteristic features.

a) Below 190K

The observation of anomalously active a_g vibrational modes signifies the existence of electron-vibrational coupling and provides evidence for a strong intermolecular interaction.

b) 190K to 230K

The only infrared bands of appreciable intensity could be assigned to either neutral TCNQ^0 or neutral TTF^0 . The absence of bands due to radical ion species is consistent with the formation of a 'neutral lattice' in this substrate temperature regime.

c) Above 230K

The concentration of neutral species diminished and the intensity of bands due to radical ions increased with increasing substrate temperature. Absorptions due to electronic transitions were observed to increase in intensity as the concentration of radical ion species increased and eventually dominated the spectrum of films deposited above 250K.

One important conclusion to be derived from these results is that at low deposition temperatures films are formed with non-equilibrium structures. Only above 250K does the molecular type spectrum observed at low temperatures give way to that normally observed for the crystalline complex. A typical example of the spectrum of the complex, which is dominated by electron transitions, was shown in Figure (5.8). This spectrum was obtained using the reflectance method described in section (5.2.1). A number of 'molecular' features are apparent, but of low intensity. The strong electronic transitions have their origin in the metallic nature of the complex as will now be discussed.

5.3.1 Electronic Transitions in TTFTCNQ

(TTF) (TCNQ) is a highly anisotropic 1-d metal, with a high conductivity along the b-axis. As with normal metals its frequency dependent dielectric function $\epsilon(\omega)$, is given by the semi-classical Drude expression. ⁽⁴²⁾

$$\epsilon(\omega) = \epsilon_{\text{core}} - \frac{\omega_p^2}{(\omega^2 + i\omega\tau_e^{-1})} \quad (5.6)$$

Where $\omega_p^2 = 4\pi Ne^2/m^*$, ϵ_{core} is the residual dielectric constant at high frequency arising from the core polarisability, τ_e is the electronic relaxation time, N is the electron density, ω_p the plasma frequency and m^* the effective optical mass of the conduction

electrons. Dividing the RHS of equation (5.6) by ϵ_{core} gives

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\epsilon_{\text{core}} (\omega^2 + i\omega\tau_e^{-1})} \quad (5.7)$$

For simplicity it is assumed that for TTFTCNQ the free electron gas⁽⁴³⁾ model applies. Equation (5.7) reduces to,

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \quad (5.8)$$

where the effective mass is replaced by m , the mass of a free electron.

At frequencies below ω_p , $\epsilon(\omega)$ in equation (5.8) is negative. As there are no wave-like solutions for electromagnetic waves when $\epsilon(\omega)$ is negative incident photons of frequencies less than ω_p cannot propagate within a crystal, and are reflected.

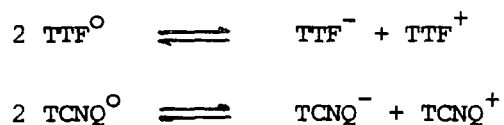
The plasma edge of TTFTCNQ is located at $1.3\mu\text{m}$ ^{(44), (45)} so according to this simple analysis the infrared region should be obscured by intraband electronic transitions. Consequently, the observed intensity of simple intramolecular vibrations is substantially reduced. Previous studies of single crystals have, for this reason, failed to provide information of a molecular nature. Although weak molecular bands were observed,⁽⁴⁶⁾ these could not be assigned with any certainty. In a recent study, reported sometime after the present work was completed, Bozio and Pecile⁽⁴⁷⁾ have presented a complete assignment of vibrational fine structure observed in the infrared spectra of the semiconducting phases of (TTF)(TCNQ) single crystals which are formed at low temperatures. They identified a number of features in the spectrum with the interaction between conduction electrons and intramolecular modes of both TTF and TCNQ. They also observed a number of Fano-like⁽⁴⁷⁾ antiresonance dips which disappeared

above the metal-insulator phase transition temperature. Many of these antiresonance dips were assigned to the same a_g vibrational modes, observed in films deposited below 190K in the present study and were discussed within the framework of the phase phonon mechanism. While it appears certain that the phase phonon⁽²⁶⁾ mechanism, referred to in section (5.1.2) is appropriate for the highly conducting form of the complex, with its regular one-dimensional lattice, an alternative explanation of anomalous infrared activity (a_{ia}) is required for what is very much a molecular lattice, such as that obtained in films at low deposition temperatures.

5.3.2 The Origin of Anomalous Infrared Activity in Films Deposited Below 190K

The poor electrical conductivity (see Chapter 6) and the lack of electronic absorptions in the infrared, support the view that low temperature deposits have a disordered rather than a well ordered one-dimensional structure. This suggests that either the charge transfer mechanism of Ferguson and Matsen⁽¹⁴⁾ or the charged dimer oscillation theory⁽²⁶⁾ is applicable for these films. Both mechanisms are appropriate for a situation involving a strong inter-molecular interaction between pairs of molecules, or dimers.

It is possible to rule out the interaction of identical neutral molecules as the origin of the observed anomalous infrared activity, because a_g mode enhancement requires the oscillation of electron density and the disproportionation reactions, are energetically



unfavourable at ordinary temperatures and pressures. However, this still leaves a number of other possibilities. If strongly inter-

acting pairs of molecules are treated as dimers then (aia) may originate from either homomolecular dimers, such as $(\text{TTF}_2)^+$, $(\text{TTF}_2)^{2+}$, $(\text{TCNQ}_2)^-$ and $(\text{TCNQ}_2)^{2-}$ or from the isolated heteromolecular charge transfer complex $(\text{TTF}^{\delta+} \text{TCNQ}^{\delta-})$. Since all of these species are expected to show a_g mode enhancement at similar frequencies, it is not possible to determine unequivocally which of them is responsible for the observed (aia). On the basis of the available theoretical and experimental evidence it appears however that it originates from the complex, i.e. the heteromolecular species $(\text{TTF}^{\delta+}, \text{TCNQ}^{\delta-})$.

An examination of Figure (5.12) shows that the intensity of both TTF and TCNQ a_g vibrations decreased simultaneously, with the maximum rate of decay occurring at 215K. Had TTF and TCNQ been part of separate homomolecular dimers different rates of decay might have been expected, although simultaneous decay of both types of dimer cannot be entirely discounted. However, the formation of charged homomolecular dimers on film deposition obviously requires the presence of charged molecules, either as dimers or monomers, in the vapour phase. The former is ruled out by the effusion experiments of de Kruif and Govers⁽⁴⁸⁾ who established that the vapour above (TTF)(TCNQ) contains only monomeric species. This conclusion is supported by theoretical calculations⁽⁴⁹⁾ which indicate that whilst the formation of charged homomolecular dimer is energetically favourable at low temperatures, the intermolecular interaction is not sufficiently strong to prevent dissociation at the temperature of vapourisation (ca. 430K). It was also concluded from the simple analysis outlined in Chapter (4) that in a situation where the vapour phase is made up of monomers, the concentration of charged $(\text{TTF})^+$ and $(\text{TCNQ})^-$ is

negligible.

There is then no mechanism for the formation of homomolecular dimers, either in the vapour phase, or as a result of diffusion on the substrate after impingement. By a process of elimination it is concluded that the (a_{1g}) observed in films deposited below 190K is due to heteromolecular charge transfer dimers (CTD), which are presumably formed on the substrate after impingement as a result of the interaction between TTF⁰ and TCNQ⁰.

A possible structure of the CTD is one in which the donor and acceptor adopt a configuration with their molecular planes parallel, since it provides for maximum overlap of their π electron orbitals and the strongest possible non-bonded interaction. There is no direct experimental evidence of a 'sandwich' structure of (TTF⁺TCNQ⁻), however, molecular orbital calculations of Berlinskii et al.⁽⁴⁹⁾, Silverman⁽⁵⁰⁾ and Govers,⁽⁵¹⁾ for (TTF₂) and (TCNQ₂) dimers, suggest that a sandwich structure is energetically the most likely configuration for the CTD. Atom-atom potential calculations,⁽⁵²⁾ and fluorescence measurements⁽⁵³⁾ on planar aromatic molecules also indirectly support this configuration.

Experimental evidence from the present work which supports such a structure is the observation of anomalous infrared activity of the a_g vibrational modes, which are polarised in a direction perpendicular to the molecular plane. Their very existence is indicative of a strong out of plane electronic interaction such as occurs in planar charge transfer complexes, in which the transition moment for charge transfer is directed along a line perpendicular to the molecular plane. It is possible that rather than adopting a structure in which the molecular planes are parallel, pairs of molecules in the 'dimer' are inclined at an angle, such as occurs in the 55° dimer of

anthracene.⁽⁵⁴⁾ This structure would still allow for partial overlap of π orbitals on adjacent molecules. In reality, because films have a disordered structure a distribution in the angle between planes of adjacent molecules is probably obtained, which would introduce a variable degree of charge transfer between molecular pairs. This could account for the annealing behaviour of films, which as discussed in section (5.3.4) appears to reflect a distributed activation energy for the disappearance of a_g vibrational modes.

The Formation of Charge Transfer Dimers

Both TTF and TCNQ form aggregated one-dimensional stacks in many of their compounds, including (TTF)(TCNQ), therefore, it is natural to assume that the attractive interaction between like species is greater than that between donor and acceptor. To some extent this assumption conflicts with the results of molecular orbital calculations,⁽⁴⁹⁾ from which it was concluded there was no net attractive interaction between monomers within neutral homomolecular dimers of either TTF or TCNQ. However, non-bonded van der Waals interactions, which are responsible for binding in closed shell systems were neglected in these calculations. When such effects are included, as for example in the atom-atom potential calculations of Silverman⁽⁵⁰⁾ and Govers⁽⁵¹⁾ and the method of close packing of van der Waals hard spheres,⁽⁵⁰⁾ a minimum energy configuration was predicted⁽⁵⁰⁾ for a (TTF)₂⁰ dimer with slipped geometry and for (TCNQ)₂⁰ with fully eclipsed geometry.

Although no such calculations have been carried out on a CTD,⁽⁵⁰⁾ it was established from annealing experiments that they are unstable above 215K. For example Figure (5.11) shows that a decrease in the

intensity of a_g vibrational modes is accompanied by an increase in those infrared active modes assigned to neutral TTF and TCNQ. This infers that CTD's dissociate to give neutral molecules, which is consistent with the observation that no a_g modes were observed in those films deposited above 190K. Since CTD's are unstable, their formation provides clear evidence that kinetic rather than thermodynamic considerations are responsible for determining the structure of films deposited below 190K. In other words the observation of (aia) is an indication of the formation of a disordered phase which for kinetic reasons is unable to relax to give a thermodynamically more stable phase. A consideration of the short range interaction between molecules shows why, in the case of (TTF)(TCNQ) films, disorder should manifest itself as CTD formation.

Inter-Molecular Interactions

Despite the absence of Long Range Order (LRO) within amorphous solids and glasses, Radial Distribution Function (RDF) analysis⁽⁵⁵⁾ has shown that such materials are ordered at a microscopic level, i.e. there is some Short Range Order (SRO). On average each molecule or atom has the same distribution of nearest neighbours and it is only when the second, third and subsequent coordination shells are analysed that disorder becomes apparent. The reason for this is that the tendency to minimise atom-atom interaction potentials plays a crucial role in determining the nearest neighbour configuration and thus the SRO of solids.

By analogy with binary alloys,⁽⁵⁶⁾ the role of intermolecular potentials in films of (TTF)(TCNQ) can be represented by the equation

$$V = \frac{1}{2} (V_{DD} + V_{AA}) - V_{AD} \quad (5.9)$$

where V_{DD} , V_{AA} and V_{AD} are the molecular interaction potentials between

donors (D), acceptors (A) and donor/acceptor, nearest neighbours, respectively.

The significance of equation (5.9) is that it predicts that when V is negative, i.e. when the attractive interaction between like species ($V_{DD} + V_{AA}$) is greater than that between donor and acceptor, then it is energetically favourable for the number of AA and DD nearest neighbour pairs to increase at the expense of AD nearest neighbour pairs. The opposite is true when V is positive.

If these are the only interactions which need to be considered, then it would appear that V in equation (5.9) is in fact negative, since CTD's were observed to dissociate on annealing. If this is so then an activation energy barrier must exist for diffusion of molecules either translational or rotational, which prevents them from adopting a minimum energy configuration with respect to nearest neighbours. The nature of this barrier is discussed in Section (5.3.4).

In a two sub-lattice system there is equal probability that a molecule which impinges randomly from the vapour phase will be initially located on either the TTF or TCNQ sub-lattice. Thereafter, molecular relaxation will occur at a rate (τ) which is determined by substrate temperature according to

$$\tau = v_0 \exp \frac{-E_{rel}}{kT} \quad (5.10)$$

where E_{rel} is the activation energy for the relaxation process and v_0 is an attempt frequency of the same order as the frequency of a molecular vibration and is approximately $\left(\frac{h}{kT}\right)$. Because of the exponential term in equation (5.10) the rate of relaxation is a rapidly varying function of temperature. With a value of 0.35 eV for E_{rel} , τ decreases by a factor of 10^9 between 200K and 100K and has a

value of the same order as the time taken to deposit a monolayer (at $1\text{\AA}/\text{sec}$) between about 160K and 190K, assuming $v_0 \sim 10^{12} \text{ sec}^{-1}$. Although very approximate, these values indicate the possibility of molecules becoming trapped in non-equilibrium configurations during film deposition at temperatures which correspond to the observation of (aia) in (TTF)(TCNQ) films.

If a face-to-face molecular configuration is adopted on deposition then the number of nearest neighbours is two for both TTF and TCNQ. In the absence of relaxation processes there is then a 75% probability that each TTF molecule will have one or more TCNQ nearest neighbours, and vice-versa, immediately after deposition. There is also a 25% probability that either AAA or DDD interactions will occur. Since (aia) is the result of interactions between TTF and TCNQ it is apparent that even at the very lowest temperatures, bands due to neutral molecules will still be observed.

Because V in equation (5.9) is negative, an increased tendency toward AAA and DDD type interactions is predicted at higher substrate temperatures, and this is what is observed in Figures (5.9 and 5.10). Although the ratio of the intensities of a_g vibrational modes compared to normal infrared vibrational modes, tends towards a maximum at low temperatures the latter are still very much in evidence at a deposition temperature of 85K. The matrix isolation studies of Wozniak et al.⁽³⁾ also showed that bands which could be assigned to the normal infrared active vibrational modes of TTF and TCNQ were present in films prepared at deposition temperatures as low as 10K.

Summarising, the situation envisaged for films of (TTF)(TCNQ) deposited below 190K involves the interaction between molecules of TTF and TCNQ which are trapped on adjacent sites. The steric inter-

action between neighbouring molecules prevents them from relaxing to give a more stable configuration at low temperatures. As the deposition temperature is increased there is a tendency to increase the number of AA and DD interactions because of the sign of the interaction potential in equation (5.9).

When donors and acceptors are trapped on adjacent sites in a face-to-face configuration the overlap of π orbitals enables charge transfer to occur. The degree of charge transfer is modulated as a result of an intermolecular vibration in a direction perpendicular to the molecular plane, and it is this which is responsible for the (a_{1g}) of a_g vibrational modes, as explained in section (5.1.2).

During deposition at substrate temperatures above 190K, or as a result of annealing above 215K, molecules are able, by relaxation, to minimise their nearest neighbour interaction potentials. Consequently, a_g modes are no longer observed, or are reduced in intensity on annealing. However, the highly conducting phase of the complex is not formed until deposition temperatures above 235K, which raises a number of questions regarding the nature of those films deposited between 190K and 235K.

5.3.3 The Formation of a Neutral Lattice Between 190 and 230K

Films deposited at substrate temperatures between 190 and 230K consisted almost entirely of neutral TTF and TCNQ with very little evidence for the presence of charged species. This result is all the more remarkable when it is considered that molecules of TTF and TCNQ are in such close proximity, and yet, charge transfer does not occur. Reference to the energy cycle for (TTF)(TCNQ), which

is given in Figure 4.2, provides a reasonable explanation of why charge transfer is not observed.

Transfer of charge from TTF to TCNQ is a net energy consuming process, which in the absence of crystallisation does not occur.

Using the arguments advanced by Metzger⁽⁵⁷⁾ if;

$$E_c + I_D - A_A < 0 \quad (5.11)$$

then an ionic crystal is observed, but if

$$E_c + I_D - A_A > 0 \quad (5.12)$$

then the crystal is not ionic and must exist as a van der Waals solid. E_c is the theoretical Madelung energy given by;

$$E_c = \sum_{i>j} \sum \frac{Z_i Z_j}{|r_i - r_j|}$$

i.e. a double lattice sum over all ions of a unimolecular crystal at lattice positions r_i, r_j (excluding the ones on the same ion) carrying formal electric charges Z_i and Z_j , respectively. I_D is the ionisation potential of TTF and A_A is the electron affinity of TCNQ. Metzger⁽⁵⁷⁾ has calculated E_c for (TTF)(TCNQ) and finds that it fails to explain the ionicity of the complex for all uniform values of the charge transferred, i.e. equation (5.12) above applies. He concluded that 'the crystal must obviously maximise a binding energy other than just E_c ' and listed the following possible contributions: a) partial charge transfer, b) polarisation effects, c) random-phase charge-density waves, d) and exchange coulomb effects which reduce the true Coulomb energy below the value of E_c .

The absence of long range order (LRO) should exclude some of these additional contributions to the crystal binding energy, viz.,

random-phase charge density waves, and exchange interactions along the linear stacks of TTF and TCNQ. Even the most favourable calculations,⁽⁵⁸⁾ for a charge transfer of 0.5, which include reliable estimates for polarisation effects and conduction electron contribution to the binding energy, fail to account for the experimental crystal binding energy⁽⁵⁹⁾ ($U_{\text{exp}} = -4.88$ eV/molecule) by almost 3 eV. This suggests that the additional factors listed above make a considerable contribution to the stabilisation of an ionic lattice and in the absence of LRO it is possible to understand why charge transfer does not occur. Films deposited between 190 and 230K are, therefore, characterised by the lack of LRO although the small half width of their infrared bands suggests there is significant short range order (SRO).

Without lattice formation to compensate for the increase in energy associated with the transfer of charge, molecules will retain their neutral oxidation state. In this event the film must be held together by van der Waals forces i.e. short range non-bonded interactions, which determine the magnitude and sign of the potential V in equation (5.9). The configuration which molecules adopt with respect to each other, i.e. whether there is a repulsive or attractive interaction between molecules is a matter for conjecture. The absence of a_g vibrational modes in films deposited above 190K is consistent with there being no interaction between π -orbitals on TTF and TCNQ, however, an attractive interaction between neutral molecules of the same species cannot be discounted in films deposited between 190K and 230K. Indeed the observation that the C-H out-of-plane bending vibrations of TCNQ ($b_{3u} \nu_{50}$) and TTF ($b_{3u} \nu_{34}$) are located at the same frequency, in films deposited between 190K and 230K, and in those

deposited below 190K, suggests that the interaction between molecules is similar in both cases.

Neutral Dimers

Since a a_g mode enhancement is associated with the interaction between intramolecular vibrational modes and a fluctuating charge density, 'neutral dimers' are not expected to exhibit (aia). However, eximer fluorescence from films of aromatic hydrocarbons (Chapter 3) established that charge transfer between molecules in the ground state is not a pre-requisite for a strong intermolecular interaction in films deposited at low temperatures. Thus, by analogy with aromatic hydrocarbons, 'neutral dimers' should also be formed at low temperatures in films of (TTF)(TCNQ).

The evidence for 'neutral dimers' of TTF and TCNQ is somewhat limited. It is derived mainly from shifts in the frequency of the C-H out-of-plane bending vibrations, relative to their positions in the pure parent compounds. Because of their out-of-plane symmetry the respective vibrational mode on both TTF and TCNQ should be relatively sensitive to interactions with neighbouring molecules and should provide a good indication of the strength of intermolecular forces. This is also true to a lesser extent for in-plane bending vibrations. In the monoclinic crystal form of TTF, for example, the in-plane and out-of-plane C-H vibrational modes i.e. $b_{1u} \nu_{15}$, $b_{3u} \nu_{34}$ both show large Davydov or factor group splittings of 10 (1079; 1089 cm^{-1}) and 20 cm^{-1} (634; 654 cm^{-1}) respectively, which, it was suggested,⁽³⁷⁾ is related to short intermolecular hydrogen-hydrogen distances.

In films deposited below 230K the out-of-plane C-H bending modes of TTF and TCNQ exhibit opposite frequency shifts when compared to spectra of the parent molecules. The $b_{3u} \nu_{50}$ mode of TCNQ is shifted

to lower frequency (865 to 835 cm^{-1}) while that of TTF ($b_{3u}v_{34}$) is shifted c.a. 650 cm^{-1} to the higher frequency of 680 cm^{-1} , the latter mode showing considerable asymmetry on the low frequency side, which may be caused by increased intermolecular interaction.⁽³⁷⁾

The shift to lower frequency in the case of the $b_{3u}v_{50}$ mode of TCNQ is presumably due to a decrease in the repulsive interaction between neighbouring molecules, when compared to crystalline TCNQ, which reduces the energy of the excited state relative to the ground state. The shift to higher frequencies implies that the opposite is true for TTF, i.e. there is an increase in the repulsive interaction. The behaviour of the $b_{3u}v_{50}$ mode of TCNQ is consistent with the fact that in crystalline TCNQ there is a short N---H intermolecular contact, although it is difficult to reconcile the blue shifted $b_{3u}v_{34}$ mode of TTF with the known crystal structure of TTF, which has been shown to contain strongly interacting 'dimers'.

Without additional information it is futile to speculate further about the nature of the interaction between neutral molecules. Particularly since there is likely to be a distribution in the intermolecular interaction potential because of the lack of LRO within these films, although it is possible that this disorder is reflected in the width and asymmetry of the $b_{3u}v_{34}$ vibration of TTF.

SRO between 190 and 230K

The absence of a_g vibrational modes in films deposited between 190K and 230K suggests that TTF and TCNQ form separate sub-lattices even in the absence of LRO. It is possible that these separate sublattices segregate to form orientationally disordered one or two dimensional structures, which would also explain the lack of charge transfer bands in the UV/visible spectrum of the film deposited

at 214K (Figure (5.16(a)). Indeed it is difficult to envisage an alternative molecular arrangement which does not allow for some overlap at the boundary between adjacent TTF and TCNQ sub-lattices, and the consequent observation of charge transfer bands or (aia). Such a structure could also provide a precursor state for the formation of the one-dimensional lattice of the metallic phase of the complex.

It is concluded on the basis of the discussions so far, that the amount of disorder incorporated into a film during growth decreases with increasing deposition temperature, becoming zero above 190K, when defined in terms of the SRO parameter $S^{(68)}$ which is given by

$$S = (q_R - q_W) / (q_R + q_W) \quad (5.13)$$

where q_R and q_W are the number of right and wrong nearest neighbour pairs counted over all lattice pairs. The ratio of intensities for a_g and normal infrared modes which essentially reflects the change in the SRO parameter with deposition temperature dropped rapidly above 185K. Since a_g vibrational modes were not observed in the infrared spectra of films deposited between 190K and 230K, it is inferred that $q_R = 1$ and $q_W = 0$. Therefore, from equation (5.13) $S = 1$ for films deposited in this temperature interval. A deposition temperature of 190K would thus appear to represent the boundary line between the disordered and SRO state of (TTF)(TCNQ). Further insight into the nature of the disorder $\rightarrow$ SRO transformation was provided by a study of the annealing behaviour of low temperature deposits which will now be discussed.

5.3.4 The Disorder - SRO Transformation in (TTF)(TCNQ) Films

It was shown in Figure (5.11) that when films deposited below 190K are annealed there was a decrease in the intensity of a_g vibrational modes and a corresponding increase in the intensity of normally infrared active modes. The maximum rate of change of the a_g mode intensities occurred at 215K for both TTF and TCNQ, but the change did not begin to occur until above about 200K. This was true of all films deposited below 190K, irrespective of deposition temperature.

It is obvious from the previous discussion that these changes correspond to the dissociation of CTD's, leading to an increase in the SRO parameter. Since no a_g vibrations were observed in films deposited above 190K it would appear that the activation energy for the disorder $\rightarrow$ SRO transformation is associated with the relative ease with which molecules are able to move on the surface after deposition. Once molecules are incorporated into a growing film, for steric reasons the activation energy for molecular relaxation increases, hence the observation of a_g vibrational modes at annealing temperatures as high as 255K.

The value of the activation energy E_{rel} is indicative of the mechanism of the elementary ordering process. A crude estimate of E_{rel} can be obtained from the temperature of the transition, which according to Waugh⁽⁶⁰⁾ is given by

$$E_{rel} \sim 155 T_m \text{ j mole}^{-1}$$

T_m is the temperature at which the maximum rate of change occurred. According to Figure (5.12) T_m for the disorder $\rightarrow$ SRO transformation occurred at 215K, which gives a value for E_{rel} of 32 Kj mole^{-1} . This

rules out a relaxation process involving bulk translational diffusion, which in organic molecular crystals occurs with activation energies of about twice the sublimation energy⁽⁶¹⁾ and corresponds to about 260 KJ mole⁻¹ ⁽⁵⁷⁾ for (TTF)(TCNQ). Although translational diffusion along grain boundaries⁽⁶²⁾ often occurs with much lower activation energies, a comparison with data for other molecular solids favours a relaxation mechanism involving molecular rotation.

Rotation in Molecular Solids

Numerous theoretical and experimental studies have established that molecular rotation in organic solids occurs with activation energies similar to that estimated for the disorder $\rightarrow$ SRO transformation. Pyrene for example re-orientates between equivalent sites at room temperature with an activation energy of 56 KJ mole⁻¹.⁽⁶³⁾ With the aid of potential energy calculations⁽⁶⁴⁾ this was shown to correspond substantially to rotation about an axis perpendicular to the molecular plane, but with additional rotation about other axes. Similarly, an NMR determination⁽⁷⁵⁾ of the molecular relaxation rate gave an activation energy of only 25 KJ mole⁻¹ for the in-plane rotation⁽⁶⁴⁾ of Coronene. Other measurements,⁽⁶⁶⁾ on charge transfer complexes of naphthalene and pyrene with tetracyanoethylene and trinitrobenzene gave values of between 40 and 60 KJ mole⁻¹.

The atom-atom potential energy calculations of Gavezzotti & Simonetta⁽⁷⁷⁾ have shown that the in-plane rotation of a large number of aromatic compounds should occur with activation energies of similar magnitude to those listed above. By way of contrast Sherwood et al.⁽⁶¹⁾ and Labes et al.⁽⁶⁸⁾ have shown experimentally that the activation energy for translational self-diffusion within

organic molecular solids are typically $80\text{--}240 \text{ KJ mole}^{-1}$, which as already stated, corresponds to approximately twice the sublimation energy.

Although attempts were made to determine the activation energy for the transition from the disordered to the SRO state from a measurement of relaxation rate (τ) as a function of temperature, these were not successful. The data of Figure (5.14) shows that the relaxation process does not follow normal behaviour⁽⁴¹⁾ i.e. an exponential temperature dependence. However, an upper limit of about 40 KJ mole^{-1} can be assigned to the activation energy of the disorder $\rightarrow$ SRO transition from the experimental determination of the activation for the high temperature transition in Chapter 6, and from the infrared data in section (5.2.2), Figure (5.18) of this chapter. Calculation of the activation energy from infrared data is deferred until Chapter 6.

It is concluded that there is a barrier to molecular rotation, which is responsible for the formation of disordered films at deposition temperature below 190K. Since rotation about an axis perpendicular to the molecular plane generally occurs with a lower activation energy than rotation about the other principle axis, it is assumed that the former is the mechanism of relaxation. It is envisaged that relaxation involves restricted, rather than free, rotation between potential energy minima, resulting in the formation of a metastable state. Restricted rotation also occurs in aromatic hydrocarbons.⁽⁶⁴⁾ Since the transformation was shown experimentally to be irreversible, it is apparent that once this metastable state has been achieved, further rotation does not occur until high

temperatures, otherwise CTD's would have been reformed on cooling and this was not observed.

Kinetics of the Disorder $\rightarrow$ SRO Transition

The straight line behaviour of Figure (5.13) indicates that the rate of disappearance of a_g vibrational modes, on annealing above 200K, is zero order, i.e. remains constant with time under isothermal annealing conditions. On increasing the annealing temperature the rate remained constant until 215K when it increased suddenly and then returned to its initial value, despite further increases in temperature. This sudden increase in rate in the vicinity of 215K was always observed when low temperature deposits were annealed. The data in Figure (5.14) was obtained from films deposited at 85K and 185K curves (a) and (b), respectively, which were annealed at a constant rate of temperature increase of $0.5^\circ/\text{min}$. In both cases an increase in the rate of disappearance of a_g modes was observed around 215K, whilst either side of this temperature it remained constant.

At this point attention is directed to the results of the structural and electrical studies, which are described in Chapters 4 and 6, respectively. Scanning electron microscopy showed that a pronounced alignment of crystallites occurred in films deposited immediately below this temperature, whilst electrical conductivity measurements indicated that crystallites were aligned with their b-axis perpendicular to the plane of the film. The obvious implication is that 215K is the optimum deposition temperature for (TTF) (TCNQ) films and that the effect is connected with a rapid increase in the rate of the disorder $\rightarrow$ SRO transformation.

If, as previously argued, there is an activation energy for rotation associated with the transformation, then the temperature dependence of the rate of reaction should obey an Arrhenius type of expression.⁽⁶⁹⁾

$$\text{rate} \propto A \exp \frac{-E_{\text{rel}}}{kT} \quad (5.14)$$

In general this equation is accurately obeyed by all chemical reactions.

Apparently the rate of disappearance of a_g modes does not exhibit an exponential temperature dependence. With the exception of the region around 215K, for example, the rate remains virtually constant over a temperature interval of 55K for the film deposited at 185K, shown as curve b in Figure (5.14). Furthermore, at constant temperature, the rate of approach to equilibrium is normally assumed⁽⁷⁰⁾ to be exponential and is given by

$$\delta = \delta_0 e^{-t/\tau} \quad (5.15)$$

where δ is the deviation from equilibrium and δ_0 its value at $t = 0$. τ is the relaxation time. Again it is clear from Figure (5.13) that, with the possible exception of the 215K annealing curve, the above relationship is not obeyed.

The disorder $\rightarrow$ SRO transformation involves an increase in the degree of order within a film, i.e. the change in entropy (ΔS) for the system is negative. As $\Delta S = \frac{\Delta H}{T}$, where ΔH is the enthalpy change accompany the reaction, the transformation is exothermic. If $\Delta H > E_{\text{rel}}$ in equation (5.14), and the heat liberated during the ordering process is re-adsorbed, this would promote further dissociation of CTD's, resulting in an apparently zero-order process. When $\Delta H \gg E_{\text{rel}}$, the normal exponential temperature dependence of the reaction rate would be dominated by the enthalpy change associated with the ordering

process, which provides a possible explanation of the temperature independence of the disorder $\rightarrow$ SRO transformation. Of course, when carried out under ideal isothermal conditions, the rate of the transformation should obey equations (5.14) and (5.15). However, since infrared experiments were carried out in high vacuum, on NaCl or KBr substrates, which have poor thermal conductivity, it is likely that isothermal conditions were not established and that re-adsorption of the heat of transformation occurred.

A more detailed explanation of these experimental observations cannot be given at the present time. However, in a number of ways they are analogous to glass transition phenomena, such as occur on warming glass forming liquids above their glass transition temperature (T_g). The crystallisation process of glasses normally takes place in two steps⁽⁷¹⁾, involving an initial pseudo-second order phase transition at T_g , followed by crystallisation at some higher temperature, such as was observed by Haida⁽⁷²⁾ et.al. for chloroform. On warming, both the entropy and the volume change continuously, although a small endothermic anomaly usually occurs at T_g followed by a larger exothermic anomaly on crystallisation. The former may be associated with a change in the heat capacity (C_p), which should exhibit a discontinuity at T_g ⁽⁷³⁾ if the glass transition were a true second order reaction. Furthermore, the kinetics of the glass transition do not generally obey an Arrhenius relation (equation 5.14). Diffusion in glasses, for example, is often best described by a simple empirical modification of the Arrhenius relation of the type⁽⁷⁴⁾

$$D = A' \exp \frac{-E}{R(T - T_0)} = A' \exp \frac{-B}{T - T_0} \quad 5.16$$

in which $T_g \approx 1.1$ to $1.3 T_0$ and the other terms have their usual meaning. Equation (5.16) implies an apparent activation energy which

varies with temperature according to

$$E = R \frac{d \ln D}{d(1/T)} = B \frac{T^2}{T - T_0} \quad 5.17$$

and increases exponentially with decreasing temperature.

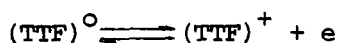
Both equations (5.16) and (5.17), however, infer that the diffusion coefficient should increase very rapidly above some temperature T which will be determined by the activation energy distribution. This is, in fact, contrary to what was observed when annealing in the vicinity of 215K. (Figures 5.13 and 5.14), unless the discontinuity observed at this temperature constitutes the entire glass transition region. Thus, there would appear to be no satisfactory explanation of the results contained within Figures 5.13 and 5.14, within the framework of the theory of glass transitions⁽⁷⁵⁾. It is worth emphasising, however, that the discontinuity which occurred in both sets of data was located at about 215K, which structural studies suggest is the location of the OST for (TTF)(TCNQ).

5.3.5 The SRO → Crystalline Transformation

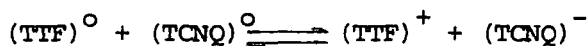
It is possible that the rapid increase in diffusion coefficient predicted by equations (5.16) and (5.17) is responsible for the characteristically sharp transition which occurred in the high temperature regime above 260K (Figures 5.17 to 5.21). This transition, however, is probably associated with the formation of the crystalline state of the complex, rather than a glass transition. As discussed in section 5.3.1, the crystalline form of (TTF)(TCNQ) is highly reflecting below the plasma frequency ω_p , so that the decrease in transmittance which accompanied the reduction



is probably associated with the increased reflectance brought about by crystallisation of the SRO lattice. The fact that both processes showed the same time dependence infers that formation of the charge transfer complex is occurring with simultaneous oxidation of TTF, according to the reaction



Now, it was argued in section 5.3.3, that the reaction,

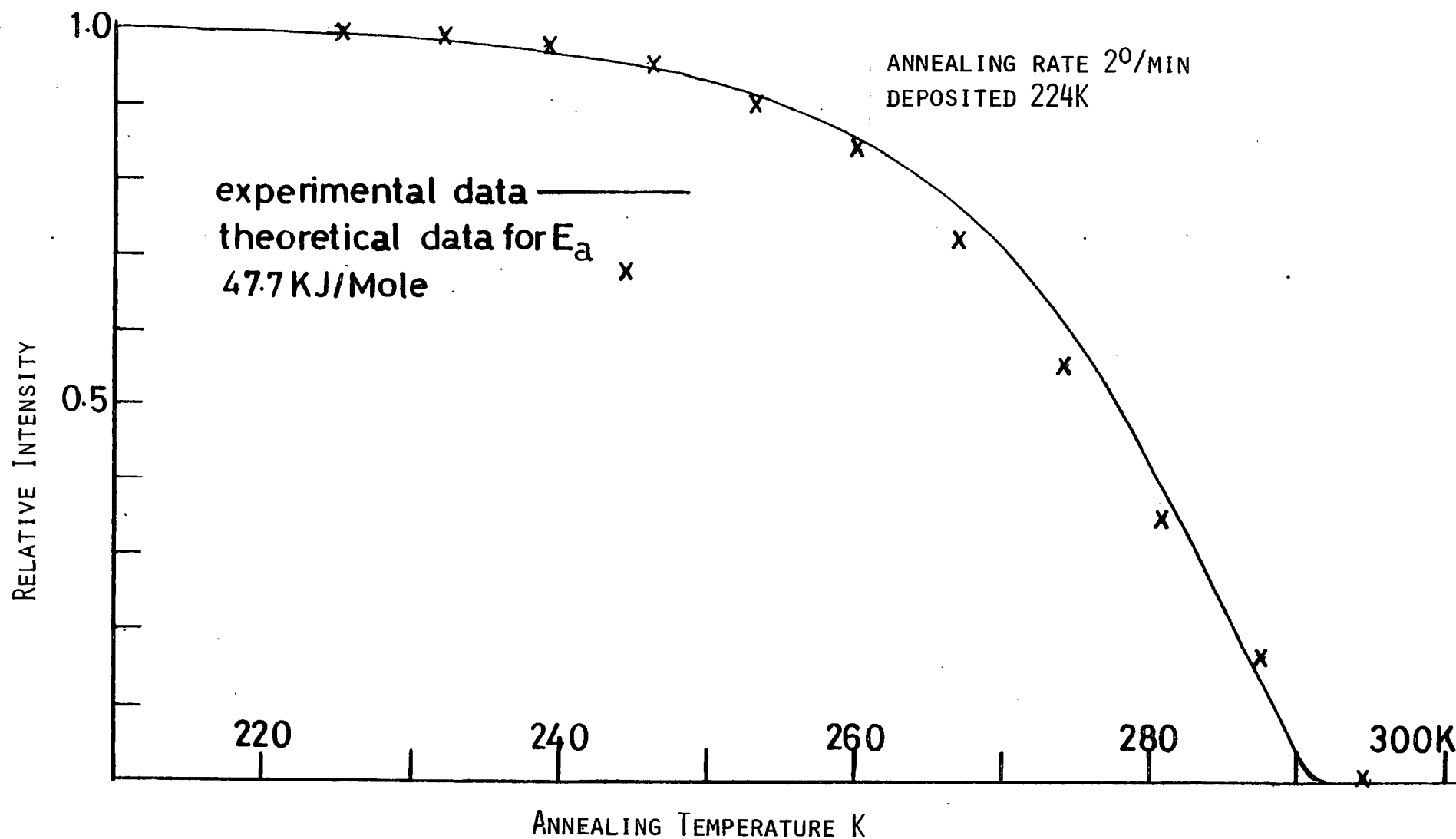


was energetically unfavourable in the absence of crystallisation.

It would appear, therefore, that all three of the above reactions are related and that the rate determining step in the process is diffusion of molecules to give a lattice structure which is then able to undergo crystallisation.

An apparent activation energy (E_a) for the process of about 48 kJ mole^{-1} was obtained from the annealing curve for a film deposited at 224K as shown in Figure (5.22), which shows the decrease in intensity of the 2226 cm^{-1} . C≡N stretching vibration of TCNQ° as a function of annealing temperature. The theoretical points on the curve were calculated using a procedure due to Smith & Aranoff⁽⁷⁶⁾, and assuming the reaction was first order in TCNQ. A value for E_a of 48 kJ mole^{-1} is about 10 kJ mole^{-1} higher than that obtained when using electrical conductivity changes to monitor the crystallisation process, as discussed in Chapter 6. It is, however, consistent with a process involving in-plane molecular rotation, as outlined in Section (5.3.4). Further discussion of this point is deferred until Chapter 6.

FIGURE 5.22. $\text{C}\equiv\text{N}$ PEAK (2226 cm^{-1}) INTENSITY VS TEMPERATURE



Molecular orientation in films of (TTF)(TCNQ)

The results of Figures (5.15) and (5.16) point to a difference in the annealing behaviour between a film deposited at 100K and that deposited near the proposed OST i.e., 214K, respectively. In the former case hardly any molecular features remain after the transformation, in that the spectrum appears to be dominated by electronic transition. Whereas, in the case of the 214K deposit intramolecular vibrations are extremely strong and hardly diminished, despite the fact that the transformation of neutral species to give the complex is essentially complete after annealing at 300K, as shown by Table 5.4. Reference to Figure (5.1) provides a probable explanation for this difference in behaviour in terms of molecular orientation effects.

Electronic transitions in (TTF)(TCNQ) have a large component directed out of the molecular plane and, as discussed in the Introduction to this chapter, couple most effectively to a_g intramolecular modes. Therefore, crystallites in which the high conductivity b-axis (molecular b_{3u} axis) is aligned parallel to the electric vector of the exciting radiation will be highly reflecting as discussed in section (5.3.1). Thus, in deposits containing randomly oriented crystallites electronic transitions will dominate the infrared spectrum at all angles of incidence. On the other hand, it was shown in Chapter 4 that crystallites in films deposited in the vicinity of 213K are oriented with their b-axis directed out of the film plane, i.e. perpendicular to the electric vector for a normal angle of incidence of the exciting radiation. In this event the in-plane (b_{1u} and b_{2u}) molecular vibrations will predominate and as these do not couple effectively to the conduction electrons the infrared spectrum

will be essentially molecular in nature. These results would appear to confirm the proposals of Chapter 4 and are consistent with a molecular orientation more-or-less parallel to the substrate at the OST.

Reflectance and Conductivity

It was assumed earlier that the decrease in transmittance accompanying the formation of the complex was associated with the increased reflectivity of the crystalline phase as compared to the SRO lattice. According to the Hagen-Rubens⁽⁷⁷⁾ relation the increased reflectivity is associated with an increase in the DC conductivity (σ_0), i.e.

$$R \cong 1 - \left(\frac{2\omega}{\sigma\pi_0} \right)^{1/2} \quad 5.18$$

for $\omega\tau \ll 1$. The observed changes in the infrared spectrum should, therefore, be accompanied by a sharp increase in conductivity as crystallisation of the SRO phase commences. This aspect of the annealing process has been dealt with in detail in Chapter 6, however, it is worthwhile just emphasising the point that the infrared results show that the increase in conductivity of films when annealed above about 280K, is associated with a fundamental change in their structure and is not simply due to a reduction of grain boundary effects.

A Summary of the Infrared Study of (TTF)(TCNQ)

The infrared study of (TTF)(TCNQ) films has provided confirmation of many of the ideas outlined in Chapters 3 and 4. In particular it has shown;

- a) that an intermediate phase of (TTF)(TCNQ), which does not possess LRO, but does nevertheless possess SRO and is metastable, is formed at deposition temperatures in the vicinity of the OST, i.e. 213K.

- b) that crystallites are aligned with their molecular planes parallel to the plane of the film in deposits prepared at 214K.
- c) A disordered phase of (TTF)(TCNQ) is formed at deposition temperatures below 190K, which is characterised by anomalous infrared activity of the Ag vibrational modes, due to an enforced interaction between donors and acceptors in the ground state.
- d) Crystallisation of this disordered phase proceeds via the metastable state and does not occur until near room temperature in films deposited below 215K.
- e) The rate of the disorder → metastable transformation reaches a maximum in the vicinity of the OST.

In addition, the observation of a neutral lattice, between 195K and 230K, provides experimental confirmation of the proposal put forward by Metzger⁽⁵⁷⁾ and others⁽⁵⁸⁾, based on lattice energy calculations, that charge transfer in (TTF)(TCNQ) is only made energetically possible by the intervention of lattice stabilisation effects.

References for Chapter 5

1. Chen, T.H. and Schectman, B.H., Thin Sol. Films, 30, 173 (1975).
2. Lin, S.F., Spicer, W.E. and Schectman, B.H., Phys. Rev., B12, 4184 (1975).
3. Wozniak, W.T., Depasquali, G., Klien, M.V., Sweany, R.L. and Brown, T.L., Chem. Phys. Lett., 33, 33 (1975).
4. for example, a) Bozio, R., Girlando, A., Pecile, C., J.C.S. Faraday, 71, 1237 (1975), b) Bozio, R., Zanon, I., Girlando, A. and Pecile, C., J. Chem. Phys. 71, 2282 (1979), c) Bozio, R. and Pecile, C., J. Phys. C13, 6205 (1980).
5. Suzuki, H., "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, (1967), p.69.
6. Takenaka, T., Spectrochim. Acta., 27A, 1735 (1971); Lunelli, B. and Pecile, C., J. Chem. Phys., 52, 2375 (1970).
7. Dows, D.A., in 'Physics and Chemistry of the Organic Solid State' 1, 657 (1963), Ed. Fox, D., Labes, M.M. and Weissberger, A., Interscience.
8. Kuzmany, H. and Stolz, H.J., J. Phys. C., 10, 2241 (1977).
9. Denoyer, F., Coines, F., Garito, A.F. and Heegar, A.J., Phys. Rev. Lett., 35, 445 (1975).
10. Coppens, P., Phys. Rev. Lett., 35, 98 (1975).
11. Anderson, G.R. and Devlin, J.P., J. Phys. Chem., 79, 1100 (1975).
12. Friedrich, H.B. and Pearson, W.B., J. Chem. Phys., 44, 2161 (1966).
13. Hinkel, J.J. and Devlin, J.P., J. Chem. Phys., 58, 4750 (1973).
14. Ferguson, E.E. and Matsen, F.A., J. Chem. Phys., 29, 105 (1958).
15. Ferguson, E.E. and Matsen, F.A., J. Am. Chem. Soc., 82, 3268 (1960).
16. Collin, J. and D'or, L., J. Chem. Phys., 23, 397 (1955), and Ferguson, E.E., J. Chem. Phys., 26, 1357 (1957).

17. Mulliken, R.S., J. Am. Chem. Soc., 74, 811 (1952).
18. in reference (5) p.102
19. in reference (5) p.103
20. Mulliken, R.S., J. Chem. Phys., 7, 14 (1939).
21. Duke, C.B., Ann. N.Y. Acad. Sci., 313, 166 (1978).
22. Duke, C.B., Lipari, N.O. and Pietronero, L., Chem. Phys. Lett., 30, 415 (1975).
23. Ferguson, E.E., J. Chim. Phys., 61, 257 (1964).
24. Rice, M.J., Duke, C.B. and Lipari, N.O., Sol. State Commun., 17, 1089 (1975).
25. see for example, a) Rice, M.J., Phys. Rev. Lett., 37, 36 (1976).
26. Rice, M.J., Lipari, N.O. and Strassler, S., Phys. Rev. Lett., 39, 1359 (1977).
27. Peierls, R.E., 'Quantum Theory of Solids', p.108, Oxford Univ. Press (1965).
28. Rice, M.J., Pietronero, L. and Bruesch, P., Sol. Stat. Commun., 21, 757 (1977).
29. Boyd, R.H. and Phillips, W.D., J. Chem. Phys., 43, 2937 (1965).
30. Lipari, N.O., Rice, M.J., Duke, C.B., Bozio, R., Girlando, A. and Pecile, C., Int. J. Quant. Chem., 11, 583 (1977).
31. Bozio, R., Girlando, A., Zanon, I. and Pecile, C., in Quasi One-Dimensional Conductors, I. Lecture Notes in Physics, Vol. 95, Ed. Barisic, S., Bjelis, A., Cooper, J.R. and Leontic, B., Publ. Springer-Verlag, New York, (1979), p.217.
32. Rice, M.J. and Lipari, N.O., Phys. Rev. Lett., 38, 437 (1977).
33. Tanner, D.B., Jacobsen, C.S., Bright, A.A. and Heegar, A.J., Phys. Rev., B16, (1977) 3283.
34. Brau, A., Bruesch, P., Farges, J.P., Hinz, W. and Kuse, D., Phys. Stat. Solidi, B62, (1974) 615.

35. Petzelt, J., Kral, K., Rysava, N., Dobiasova, Kroupa, J.,
Oswald, J., Szyszkowski, A. and Graja, A., Sol. Stat. Comm.,
32, (1979) 1315.
36. Bozio, R., Zanon, I., Girlando, A., Pecile, C., J. Chem. Soc.
Faraday, 74 (1978) 235.
37. Sugano, T., Yakushi, K. and Kuroda, H., Bull. Chem. Soc. Jap.,
51 (1978) 1041.
38. Torrance, J.B., Scott, B.A., Welber, B., Kaufmann, F.B. and
Seiden, P.E., Phys. Rev., B19, (1979) 730.
39. Girlando, A., Bozio, B. and Pecile, C., Chem. Phys. Lett. 25,
409 (1974).
40. Kaya, S. and Sato, H., Proc. Phys. Math. Soc. Japan, 25, 261
(1943).
41. Sato, H. in 'Physical chemistry an Advanced Treatise', Volume 10,
Ed. Jost, W., p.579, (1970), Academic Press.
42. Heegar, A.J. and Garito, A.F., in 'Low-Dimensional Cooperative
Phenomena', Ed. Keller, H.J., p.89, (1975), Plenum Press.
43. See Kittel, C., 'Introduction to Solid State Physics', 4th Edition,
p.269 (1971), John Wiley and Sons.
44. Bright, A.A., Garito, A.F. and Heegar, A.J., Sol. State Commun.,
13, 943 (1973).
45. Bright, A.A., Garito, A.F. and Heegar, A.J., Phys. Rev. B10,
1328 (1974).
46. see Jacobsen, C.S., in reference (31) p.223.
47. Bozio, R. and Pecile, C., Sol. State Commun., 37, 193 (1981).
48. de Kruif, C.G. and Govers, H.A.J., J. Chem. Phys., 73, 553 (1980).
49. Berlinsky, A.J., Carolan, J.F. and Weiler, L., Sol. State Commun.,
19, 1165 (1976).
50. Silverman, B.D., J. Chem. Phys., 71, 3592 (1979); *ibid*, 72, 5501
(1980).

51. Govers, H.A.J., Acta Cryst., A34, 960 (1978).
52. After completion the paper by Govers, H.A.J., Acta Cryst., A37, 529 (1981), was published which shows that the mixed stack of (TTF) and (TCNQ) proved to be less stable than the segregated homomolecular stack, but only by some tenths of a kJ mole⁻¹.
53. see Chapter 3.
54. Chandross, E.A. and Ferguson, J., J. Chem. Phys., 45, 3554 (1966).
55. Glasstone, S., 'Textbook of Physical Chemistry', p.518, Macmillan 2nd Edition 1948.
56. in reference (41) p.596.
57. Metzger, R.M., J. Chem. Phys., 66, 2525 (1977).
58. Torrance, J.B. and Silverman, B.D., Phys. Rev. B15, 788 (1977).
59. Metzger, R.M., Ann. N.Y. Acad. Sci., 313, (1978).
60. Waugh, J.S. and Fedin, E.I., Sov. Phys. Solid State, 4, 1633 (1963).
61. Burns, G. and Sherwood, J.N., Mol. Cryst. Liq. Cryst., 18, 91 (1972).
62. Gupta, D. and Ho, P.S., Thin Sol. Films, 72, 399 (1980).
63. Fyfe, C.A., Gilson, D.F.R. and Thompson, K.H., Chem. Phys. Lett., 5, 215 (1970).
64. Boyd, B.K., Fyfe, C.A. and Wright, D.A., J. Phys. Chem. Solids, 35, 1355 (1974).
65. Fyfe, C.A., Duneli, B.A. and Ripmeester, J., Cand. Chem., 49, 3332 (1971).
66. Fyfe, C.A., Smith, D.H., Ripmeester, J., J.C.S. Faraday, 72, 2269 (1976).
67. Gavezzotti, A. and Simonetta, M., Acta Cryst. A32, 997 (1976);
ibid, A31, 645 (1975).

68. Lee, C.H., Kevorkian, H.K., Rencroft, P.J. and Labes, M.M.,
J. Chem. Phys., 42, 1406 (1965).
69. Liadler, K.J., 'Chemical Kinetics' 2nd Edition, p.53, McGraw-Hill
(1965).
70. in reference (41) p.669.
71. Rao, K.J., Bull. Mater. Sci., 1, 181 (1979).
72. Haida, O., Suga, H. and Seki, S., J. Non-Cryst. Solids, 22,
219 (1976).
73. Kozak, J.J., in 'Advances in Chemical Physics', 40, 229.
Ed., Prigogine, I. and Rice, S.A., Interscience (1979).
74. Angele, C.A. and Clarke, J.H.R., *ibid*, 48, 397 (1981).
75. Grest, G.S. and Cohen, M.H., *ibid*, 48, 455 (1981).
76. Smith, A.W. and Aranoff, S., J. Chem. Phys., 62, 684 (1958).
77. see Kittel, C., 'Introduction to Solid State Physics',
4th Edition, p.290, Publ., John Wiley & Son (1971).

CHAPTER 6

The Electrical Conductivity of (TTF)(TCNQ) Films

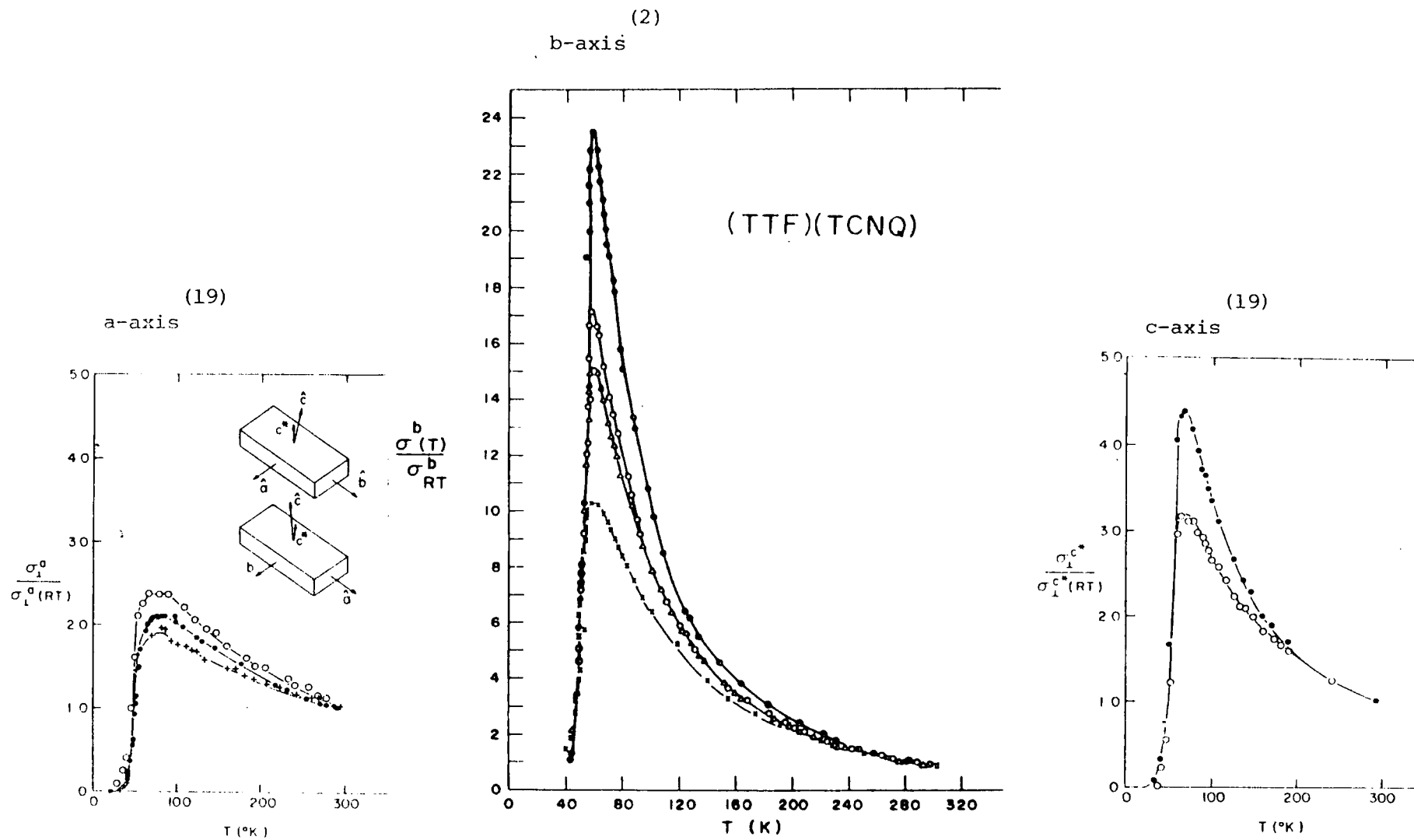
6.1 Introduction

6.1.1 Electrical Conductivity in (TTF)(TCNQ) Single Crystals

At the time of its discovery, (TTF)(TCNQ) was shown⁽¹⁾ to have the highest electrical conductivity of any organic material then known. At room temperature the b-axis conductivity of crystals was found to vary between 200 and 600 ($\Omega\text{.cm.}$)⁻¹. It increased on cooling to a maximum value of 3000 - 15000 ($\Omega\text{.cm.}$)⁻¹ near 60K, i.e. some 10 to 20 times the room temperature value. Below 60K the conductivity was found to be activated and decreased rapidly, with an activation energy of about 0.01 eV. The temperature dependence of the b-axis conductivity of a typical crystal, normalised to the value at room temperature,⁽²⁾ is given in Figure 6.1 (curve b).

Shortly after the results of Ferraris et al. were reported, Coleman et al.⁽³⁾ published b-axis conductivity data on what they regarded as highly perfect single crystals of (TTF)(TCNQ), which had conductivities at room temperature of 1800 ($\Omega\text{.cm.}$)⁻¹, increasing by a factor of 500 to a value of the order of 10^6 ($\Omega\text{.cm.}$)⁻¹, at the maximum near 60K. If a tight binding model⁽⁴⁾ of conduction is assumed the low temperature value of the conductivity corresponds to a mean free path for electrons of the order of $2000\text{\AA}$, or several hundred lattice spacings. Such a high value is not consistent with a single particle scattering mechanism⁽⁵⁾ and a collective mode contribution to the conductivity i.e. fluctuations toward a superconducting state was proposed.⁽⁶⁾ However, despite many attempts the original results of Coleman et al. could not be reproduced. There is now a consensus⁽⁷⁾ that their data was probably wrong and was due to an experimental artefact, such as misalignment of electrical contacts.⁽⁸⁾

Figure 6.1. Normalised four probe dc conductivity measurement as measured for several different single crystals of (TTF)(TCNQ) along the three principle axes of the crystal Room Temperature values $\sigma_a \sim 1 \Omega^{-1}\text{cm}^{-1}$; $\sigma_b \approx 500 \Omega^{-1}\text{cm}^{-1}$; $\sigma_c \approx 5 \Omega^{-1}\text{cm}^{-1}$



The b-Axis Conduction Mechanism

The mechanism of conduction in (TTF)(TCNQ) has been extensively reviewed in a number of recent publications and further information can be found in the papers listed in reference (9). A detailed treatment of the conduction mechanism falls outside the scope of the present work, therefore, the summary given below is of necessity brief and rather superficial.

The mechanism of conduction in (TTF)(TCNQ) which finds general acceptance is based upon ideas originally developed by Peierls,⁽¹⁰⁾ Fröhlich⁽¹¹⁾ and Kuper⁽¹²⁾. As a result of electron coupling to the intramolecular vibrational modes⁽¹³⁾ of TTF and TCNQ a periodic distortion known as the Peierls distortion⁽¹⁰⁾ is introduced into the 1-d lattice causing a gap of magnitude 2Δ in the electronic spectrum. Above the metal-insulator transition temperature this distortion of the lattice is dynamic. Coupling to phonons causes the conduction electrons to move through the lattice and a charge density wave (CDW) of wavevector $0.295b^*$ is established, where b^* is the reciprocal lattice vector along the chain direction.

Bardeen⁽⁶⁾ proposed that the conductivity peak in (TTF)(TCNQ) resulted from fluctuations towards Fröhlich (1-d) superconductivity,⁽¹¹⁾ i.e., from a sliding CDW of finite correlation length. Qualitatively the metal to insulator transition can be considered to arise as a result of a transformation from a dynamic to a static distortion. However, because a 1-d chain is theoretically prevented from undergoing a phase transition,⁽¹⁴⁾ this is not the complete picture. In order to account for the observed properties of (TTF)(TCNQ), Lee et al.⁽¹⁵⁾ included in their model the contribution of an interchain interaction between neighbouring CDWs, which increases as the wavelength of the CDW grows. At the transition this interaction causes the phase of the

CDWs on neighbouring chains to adjust so that a static distortion in three dimensions becomes energetically favourable, leading to the insulating state. Work on organic alloys⁽¹⁶⁾ in which a proportion of the TTF molecules in (TTF)(TCNQ) are replaced by the selenium analogue TSeF has established that the metal-insulator transition in the complex is driven mainly by the CDW on the TCNQ chain.

Anisotropy of the Conductivity

The band width along the b-axis (stacking) has been estimated⁽¹⁷⁾ to be of the order 0.5 eV for both the TTF and TCNQ stacks, whereas in the a-axis direction it has a value of only 0.01 eV.⁽¹⁸⁾ The b-axis (σ_b) conductivity is, therefore, several hundred times greater than that along the a-axis (σ_a) at room temperature, with the ratio $\frac{\sigma_b}{\sigma_a}$ increasing to as much as 3000 at low temperatures. The temperature dependence of the conductivity along the three principle axis is compared in Figure (6.1). In contrast to the 'metallic' properties of the b-axis, transport perpendicular to the stacking axis is diffusive, being severely limited by phonon thermal disorder.⁽¹⁹⁾ This view is supported by the estimate of the mean free path ($\Lambda < 0.01\text{\AA}$)⁽²⁰⁾ for the a and c directions.

A simplistic view of conduction in (TTF)(TCNQ), therefore, is one in which electrons (holes) are able to travel with relative ease in the 'b' direction i.e. within segregated stacks, but on meeting a defect or impurity must hop to an adjacent chain. This transverse hopping is limited by the weak interchain coupling and by a strong intrachain electron phonon interaction.

An important aim of the present study of (TTF)(TCNQ) was to investigate the role of substrate temperature in determining the measured electrical properties of thin films. Because of the anisotropy of (TTF)(TCNQ) it is an ideal material for this purpose. Its

pronounced preference for growth in the crystallographic b-direction coupled with highly anisotropic electrical and optical properties, would, it was hoped, greatly facilitate the experimental correlation of film topography and electrical properties.

In Chapter 4 it was shown that the direction of rapid crystallite growth relative to the film plane was a sensitive function of substrate temperature during deposition. Because of the marked difference in conductivity of the b-axis compared to the a and c axis' these changes in crystallite orientation as a function of substrate temperature should result in a change in the film resistance, in a given direction. In principle, therefore, resistance measurements can provide information about the influence of substrate temperature on film topography. Unfortunately this simple picture is complicated by extrinsic processes and in particular carrier scattering at grain boundaries, which as mentioned in Chapter 1 can profoundly effect the electrical properties of polycrystalline samples. Some information about grain boundary scattering is available from previous conductivity studies on (TTF)(TCNQ) films and this will be reviewed prior to the presentation of the results of the present study.

6.1.2 Electrical Properties of (TTF)(TCNQ) Films

Chaudari et al.⁽²¹⁾ measured the in-plane electrical conductivity of both their singly and doubly positioned (TTF)(TCNQ) films (see Section 4.3.1) as a function of temperature. They observed room temperature conductivities (σ_{300K}) of 30 and 1 ($\Omega.cm.$)⁻¹, respectively, with the former exhibiting metallic-like conductivity, i.e. a negative temperature coefficient of resistance (TCR) down to a broad maximum centred at 125°K. Below this temperature conductivity was activated. In contrast their bi-oriented films displayed

activated behaviour over the whole temperature range. Below 100K both types of film had activation energies for conduction of ≈ 0.02 eV, which is similar to that observed for single crystal samples in the insulating phase. Chen and Schectman,⁽²²⁾ and Reinhardt⁽²³⁾ et al. found similar activation energies in their films, but somewhat higher conductivities with values of σ_{300} between 16 and 26 ($\Omega\cdot\text{cm.}$)⁻¹ and 5 and 65 ($\Omega\cdot\text{cm.}$)⁻¹, respectively. Unlike Chaudari et al. neither group observed metallic conductivity behaviour in their films at higher temperatures, but this perhaps is to be expected in view of the fact that their films were bioriented.

Chen and Schectman noted that a value of 0.01 eV for the intergranular activation barrier could only account for a reduction in σ_{300} to $2/3$ of the single crystal b axis value, whereas the observed film/crystal ratio is of the order of 1:100. They proposed a simple model based upon a random orientation of crystallites. For those films in which the ab plane was parallel to the substrate they assumed a weighted average of the a and b-axis conductivities, such that the current path flowed, on average, 50% along the a axis and 50% along the b-axis. Crystallites in films can thus be considered as resistors in series, the observed conductivity being given by

$$\sigma_{\text{obs}} = \frac{2\sigma_b}{(1 + \sigma_b/\sigma_a)} \quad (6.1)$$

No allowance was made for the influence of grain boundary contributions to the conduction process.

Reinhardt et al. considered a situation in which transport of carriers within grains occurs preferentially along the b direction, and assumed that transport between grain requires excitation across

grain boundaries, $b \parallel b$ or $b \perp b$. Assuming a linear hopping model between grains, in which the carriers are in high concentration on both sides of the boundary, they derived an effective carrier mobility (μ_{eff}) given by

$$\mu_{eff} = \mu_{gb} \frac{1}{S/L + \mu_g/\mu_{gb}} \quad (6.2)$$

Where μ_{gb} is the carrier mobility in the barrier region and μ_g that within crystallites. S is the barrier width and L the average dimension (b-axis) of the crystallites. A constant carrier concentration and a temperature dependent μ_{eff} , was assumed such that,

$$d(\ln \mu_{eff})/d(1/T) = E_{cond}/k \quad (6.3)$$

here E_{cond} is the measured activation energy for conduction, obtained by plotting $\ln \sigma(T)$ vs $1/T$. They derived an expression relating the actual barrier due to grain boundaries (E_b) with the measured activation energy (E_{cond}) viz:

$$E_{gb} = E_{cond} + kT + k \frac{d(\ln v)}{d(1/T)} \quad (6.4)$$

In deriving this expression it was assumed that $\mu_{eff} \ll \mu_g$. v is the mean electron velocity in the crystallites. Since the third term in equation (6.4) varies between 0 and $-\frac{kT}{2}$, E_{gb} is between $\frac{kT}{2}$ and kT higher than E_{cond} . It follows from equation (6.4) that if E_{gb} is of the same order as kT the apparent or measured activation energy may be temperature dependent. In this event curvature in the $\ln \sigma$ vs $1/T$ curve should be observed, as was the case for the singly positioned epitaxial films prepared by Chaudari et al., although not for their bioriented films, or for those prepared by Chen and Schectman and Reinhardt et al. In deriving equation (6.4) Reinhardt et al.

assumed that the temperature dependence of the mobility within grain is negligible when compared to that within grain boundary regions of a film.

To summarise, the results of previous studies of the electrical conductivity of (TTF)(TCNQ) films, have established the following:

- a) The value of E_{cond} is relatively insensitive to deposition temperature and has a magnitude of the order of 0.01 to 0.02 eV.
- b) The magnitude of the measured film resistance is on the other hand, a sensitive function of deposition temperature and it is the high resistivity axis which dominates the measured resistance in a given direction.
- c) Grain boundary scattering begins to influence the measured resistance of a film when $E_b \approx kT$.

Although some electrical measurements have been made on low temperature deposits of (TTF)(TCNQ), the emphasis of previous work was on films prepared at room temperature and above. The present study was concerned for the most part with the properties of films deposited below room temperature, with particular attention being paid to the so-called optimum substrate temperature (OST) region around 215K. The main objective of this work was to correlate film topography and electrical resistance in an attempt to separate out the contribution made by grain boundaries from crystallite orientation effects. The results of this study are described in Section 6.2.5.

Annealing of Films

It is known from Vand's work⁽²⁴⁾ on metal films that the process of annealing can be followed very effectively by monitoring the change in the electrical resistance of films as a function of temperature. The infrared study of the previous chapter showed very

convincingly that the annealing of films deposited at low temperatures causes a considerable change in the electronic properties of (TTF) (TCNQ) films. Since these changes were thought to reflect a change in the fundamental character of the conduction process within films, further information about the nature of these changes was sought with the aid of annealing experiments. The results of this study are presented in Section (6.2.1). Analysis of these results was based largely upon the treatment used by Vand. Since this has already been fully documented only the final equations used in the analysis of the results are given in Section (6.2.1). However, it is worthwhile remarking at this stage that the more recent studies of Primak⁽²⁵⁾ and Kimmel and Uhlmann⁽²⁶⁾ have concluded that Vand's treatment of annealing in metal films was essentially correct and furthermore it is applicable to other than first order kinetic processes.

6.2 Results of Electrical Resistivity Measurements on (TTF) (TCNQ)

Films

Sample Preparation

Deposition of (TTF) (TCNQ) films was carried out using the vacuum equipment described in Chapter 2. Substrate temperature was controlled with the CF104 cryostat described in Section 2.1.3. Details of the type of source used, source/substrate configuration etc., were given in Section 2.1.2.

Electrical measurements were carried out on films grown on fused silica discs at a deposition rate of $1\text{\AA}/\text{sec} \pm 10\%$. A quartz crystal microbalance (QCM) was used to monitor film thickness and deposition rate. Film thickness was also determined independently using the optical absorbance technique described in Appendix 2.

The four probe conductivity measuring circuit used for electrical measurements on (TTF)(TCNQ) films was described in Section 2.2.1. Deposition was carried out with the current supply in the grounded position and the electrometer switched off to eliminate the effects of charge build up. The aforementioned is known⁽²⁷⁾ to cause changes in both the nucleation and growth behaviour of thin films. The dimensions of the (TTF)(TCNQ) films used for electrical measurements are given in Figure 2.8 (Chapter 2), which also shows the configuration of the electrodes. Annealed films were invariably ohmic up to a current of 10 mA. As discussed in Section 2.1.3, water condensation was unavoidable below 150K. However, it had little apparent effect upon electrical measurements on annealed films, although there was usually a small increase in signal noise when water began subliming above 170K.

Samples were kept in a vacuum of less than 10^{-5} torr. after deposition, to avoid contamination prior to electrical measurements being carried out, although there was no apparent change in their room temperature conductivity after exposure to air for short periods. When determining the temperature dependence of the resistivity (TDR) of films, heating and cooling rates of less than $2^{\circ} \text{ min}^{-1}$ were used above 100K. This minimised hysteresis effects due to poor thermal contact between the cryostat and the substrate. Below 100K the (TDR) was usually determined by first cooling to the base temperature of the cryostat and then allowing the cryostat to warm up naturally at a rate which was less than 0.2 K min^{-1} . Changes in film resistance were steepest in this temperature region and the slow rate of heating resulted in better measurement resolution.

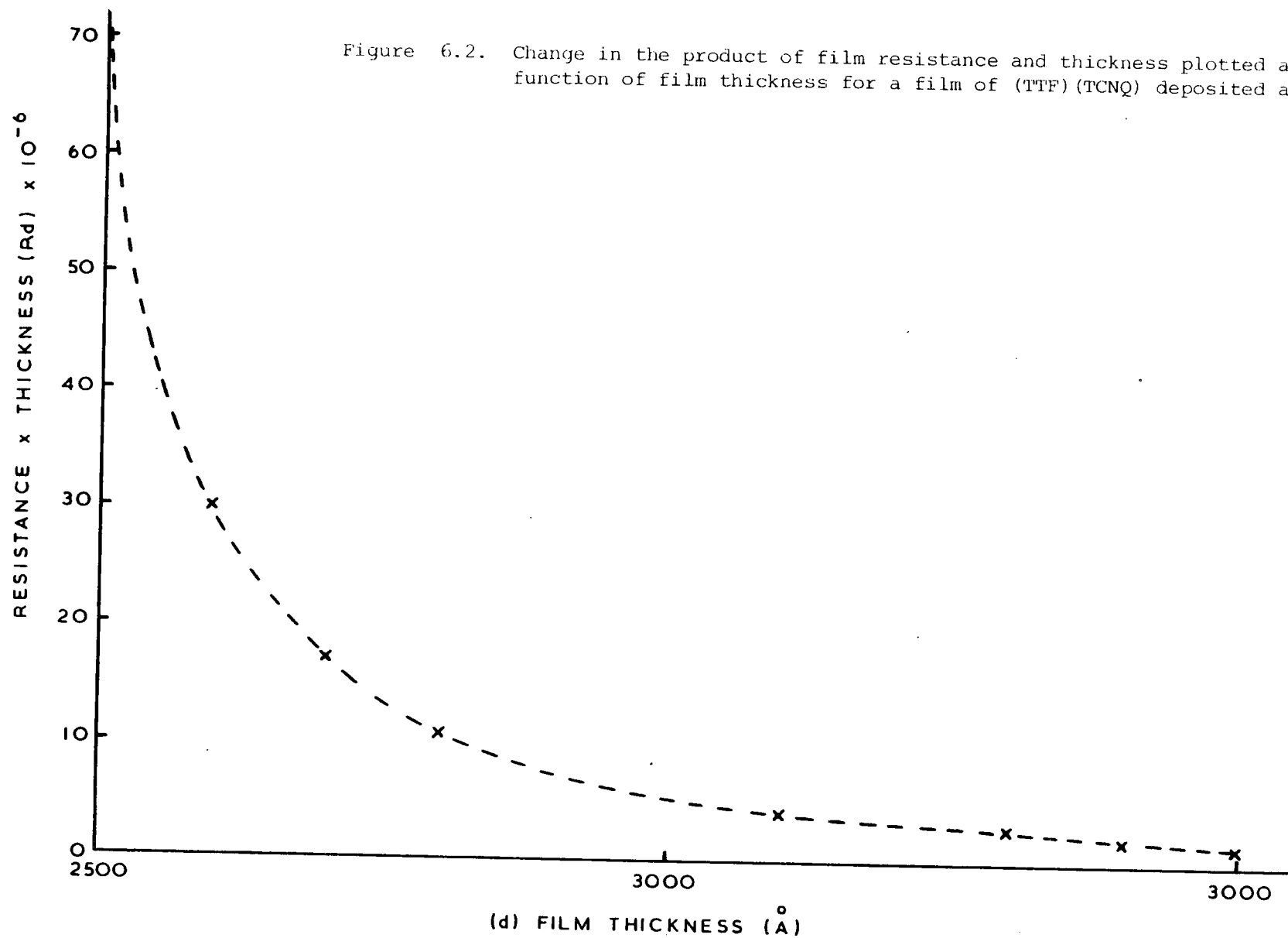
6.2.1 Annealing Behaviour

As-Deposited Films

Films deposited at substrate temperatures below 220K generally had conductances of $10^{-7} \text{ (ohm.cm)}^{-1}$, or less, in the as-deposited state and could not be examined using the four probe method. Two probe resistance measurements in the film plane, using the electrometer in the ohmmeter mode, failed to give reproducible results at temperatures below 150K because of changing effects and spurious voltages induced by the cryostat heater. Between 200K and 270K the resistance of many films deposited below about 235K were almost independent of temperature. Although the TDR of films were routinely examined in the as-deposited state, because of the poor quality of the results obtained and the apparent lack of any consistent pattern of behaviour they have not been included as part of the present study.

Reproducible results were obtained from as-deposited films prepared at substrate temperatures of 235K and above. Curve a in Figure (6.7) was obtained by plotting $\log_{10} \rho$ vs $1/T$ for a film deposited at 235K and shows that the conductivity of the film was activated.

The in-plane resistance (2 probe) of this film was monitored as a function of the thickness, which was measured during deposition with a QCM. The product of resistance and thickness, which is proportional to the resistivity, is plotted against film thickness in Figure (6.2). Measurement of film resistance was only made above 900Å in order to reduce the effect of the applied field during the

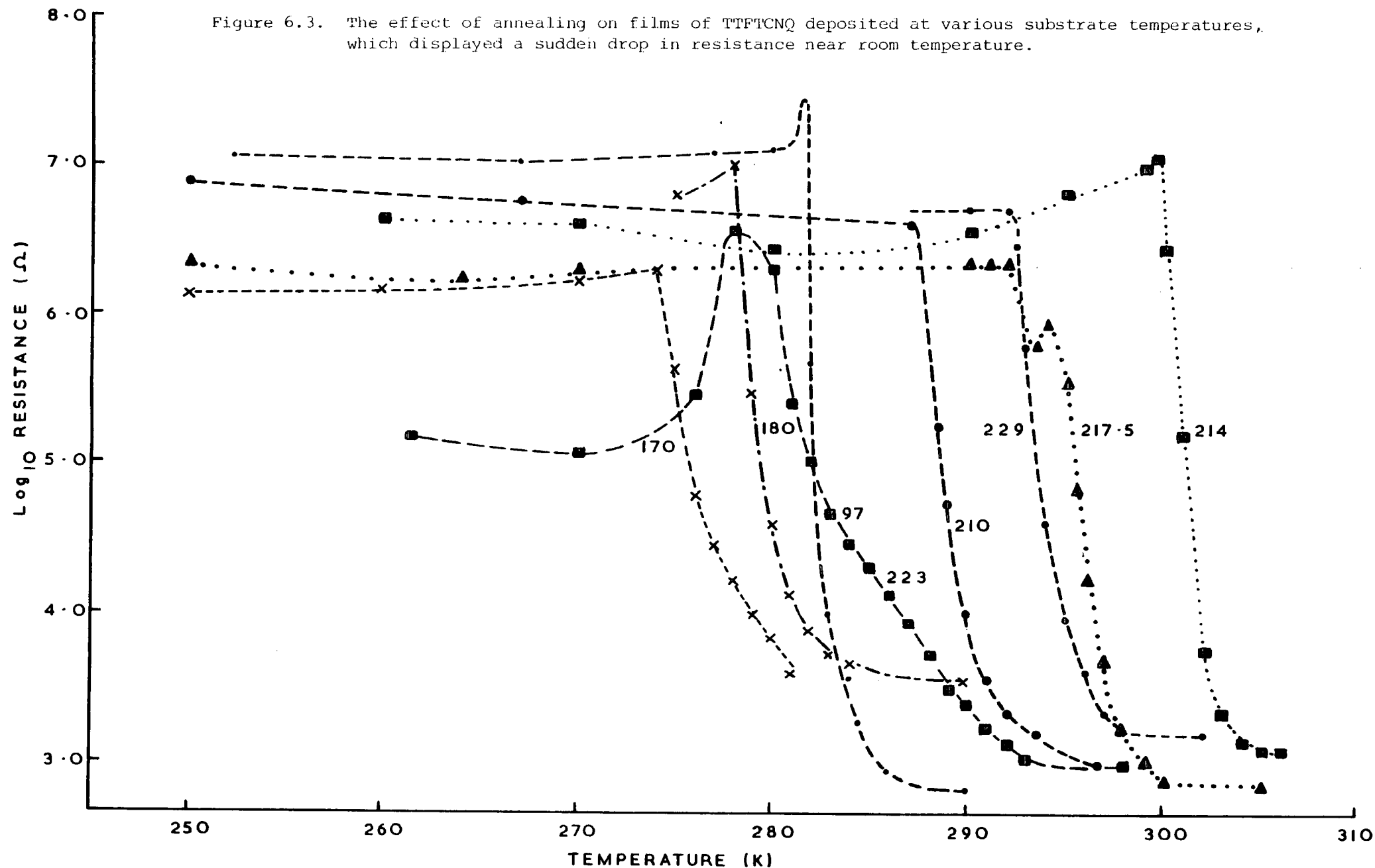


early stages of nucleation and growth. Between $900\text{\AA}$ and $2200\text{\AA}$ the measured resistance remained above 10^8 ohms, but above $2200\text{\AA}$ the resistance dropped by three orders of magnitude from a value of 1.3×10^8 to 3×10^5 ohms. Figure (6.2) only includes data obtained for a film thickness of greater than $2500\text{\AA}$. It shows quite clearly the marked dependence of resistivity upon film thickness for thin samples. Above $3500\text{\AA}$ the resistivity tended toward a constant value. It was for this reason that film thickness of greater than $4000\text{\AA}$ were deposited in subsequent studies.

6.2.2 Tempering experiments

The change in measured resistance of (TTF) (TCNQ) films, annealed at a constant rate of temperature increase of between 1 and 2°C min^{-1} , is plotted as a function of temperature in Figure (6.3). The data show the effect of substrate temperature during deposition, upon the annealing behaviour of films. The most remarkable feature of the annealing curves is that they all exhibit a sudden and irreversible decrease in resistance, of between two and four orders of magnitude in the vicinity of 280K . Films deposited at 223 and 197K exhibited a sharp increase in resistance immediately prior to T_t , whilst others (214 , 180 and 170K deposits) displayed a more gradual but nonetheless significant upward trend. Not all curves showed this increase. Films deposited at 210 and 229K , for example, possessed a very weak temperature dependence below T_t . It was generally true that above 200K films exhibited an essentially temperature independent resistance at temperatures up to the transformation. With the exception of films deposited at 170 and 223K the resistance decayed at approximately the same rate above T_t and in each case the transition was more than 99% completed within

Figure 6.3. The effect of annealing on films of TTFTCNQ deposited at various substrate temperatures, which displayed a sudden drop in resistance near room temperature.



3 to 4K. The final room temperature resistance of films deposited at 170K and 180K was approximately a factor of five greater than that of the other samples for the same nominal thickness of 4400Å (as measured by quartz crystal oscillator). The data in Figure (6.3) were not normalised for film thickness.

The temperature at which the transition from the high to the low resistance state occurred was characteristic of the temperature of the substrate during deposition. This is shown in Figure (6.4), where the temperature ($T_{\max}$) at which maximum rate of change in resistance occurred, is plotted as a function of the temperature of the substrate during deposition. $T_{\max}$ increased to a maximum at a substrate temperature of 214K and then decreased. A further increase in $T_{\max}$ was observed in going from 222K to 229K.

Films deposited between 220 and 240K showed two patterns of annealing behaviour. For example, Figure (6.5) shows two further annealing curves for films deposited at 222 and 235K, which are unlike those shown earlier in Figure (6.3). In this case the resistance of both films began to decay immediately the deposition temperature was exceeded, but the decrease was much more gradual than was observed previously. The difference between the high and low resistivity states for both films was approximately the same as for the corresponding curve in Figure (6.3) i.e. four orders of magnitude. The other curves in Figure (6.5) were obtained for films deposited at 245K and 273K. In both cases the decrease in resistance followed a smooth curve and again unlike films included in Figure (6.3) no discontinuity was observed. The difference between the high and low resistance states for both films was less than an order of magnitude.

Figure 6.4. The temperature at which the transition from the high to the low resistance state occurred for the samples included in Figure 6.3, plotted at a function of their temperature of deposition.

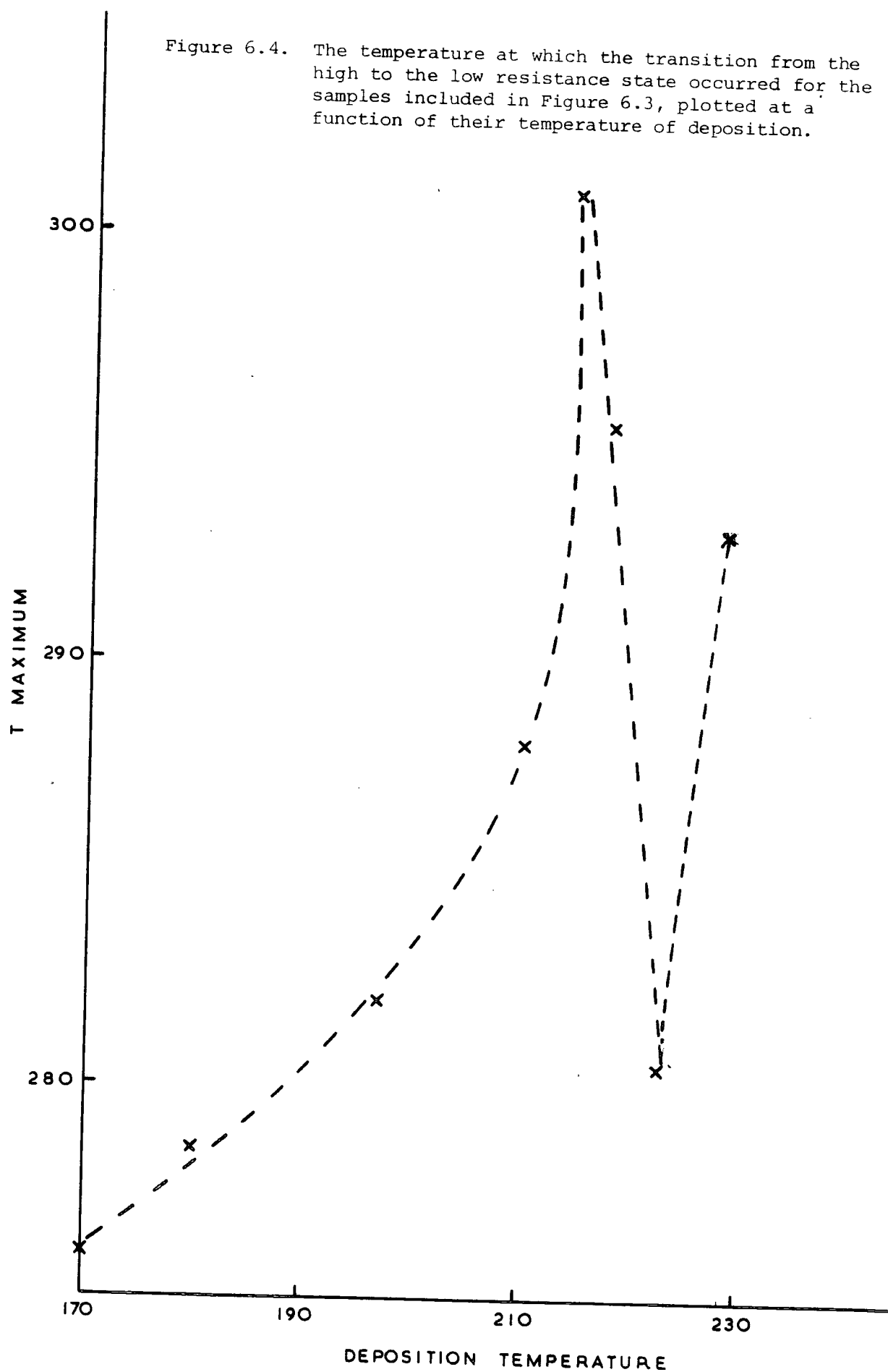
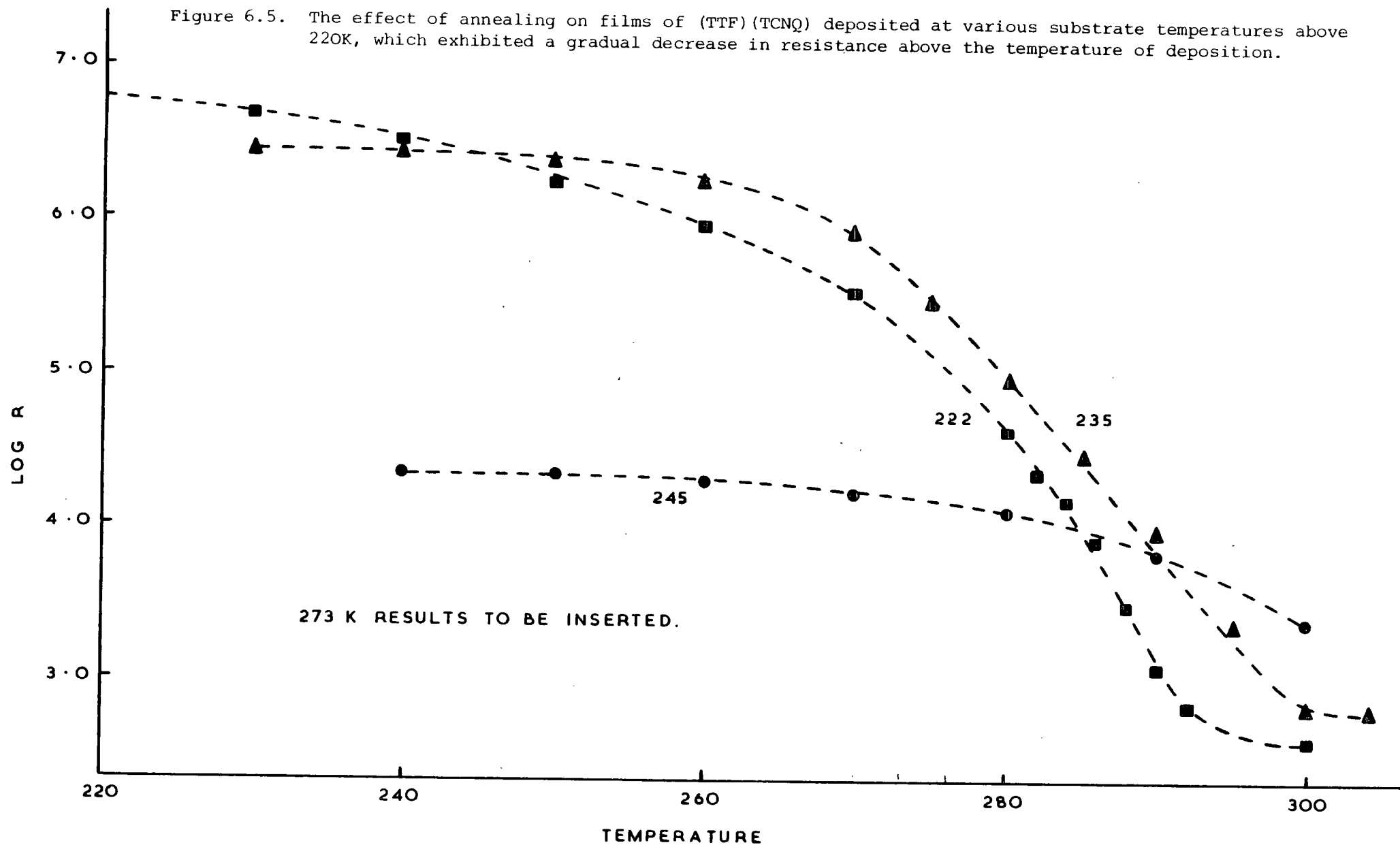


Figure 6.5. The effect of annealing on films of (TTF)(TCNQ) deposited at various substrate temperatures above 220K, which exhibited a gradual decrease in resistance above the temperature of deposition.



6.2.3 Stepwise annealing

The data plotted in Figure (6.6) were obtained by annealing a film deposited at 235K in a stepwise manner at 270, 280 and 285K. After each step in the annealing procedure the film was cooled in order to determine the temperature dependence of the resistivity (TDR). The TDR data are plotted as $\log_{10} \rho$ vs $1/T$ in Figure (6.6) for the film in the as-deposited state (235K), and after annealing at 270, 280, 285K and room temperature (298K).

Between 235K and 286K the resistivity of the film decreased irreversibly by a factor of 25 and yet the slope of the TDR curves remained essentially constant over this temperature range. Each $\log \rho$ vs $1/T$ plot displayed a definite curvature at high temperatures, but approximated a straight line at low temperatures. The activation energy for conduction determined from the slope of these straight line portions varied between 0.0127 and 0.0143 eV. All curves departed from straight line behaviour at higher temperatures, particularly after annealing at room temperature, when the film resistivity was almost independent of temperature above 200K.

The stepwise annealing behaviour of this film is contained in Figure (6.7), in which $\log_{10} R$ is plotted against time, where R is the measured film resistance. The resistance decreased only slowly at 235K (curve a) and below 270K, and approached a constant value for a given annealing temperature. At 280K (curve b) there was an increase in the rate of change of R with $d \log R/dt$ decreasing slowly with time. By 285K (curve c) the rate of change had slowed significantly and also remained constant for much of the time interval studied. At longer times and higher annealing temperatures the resistance approached a constant value as the transformation neared completion.

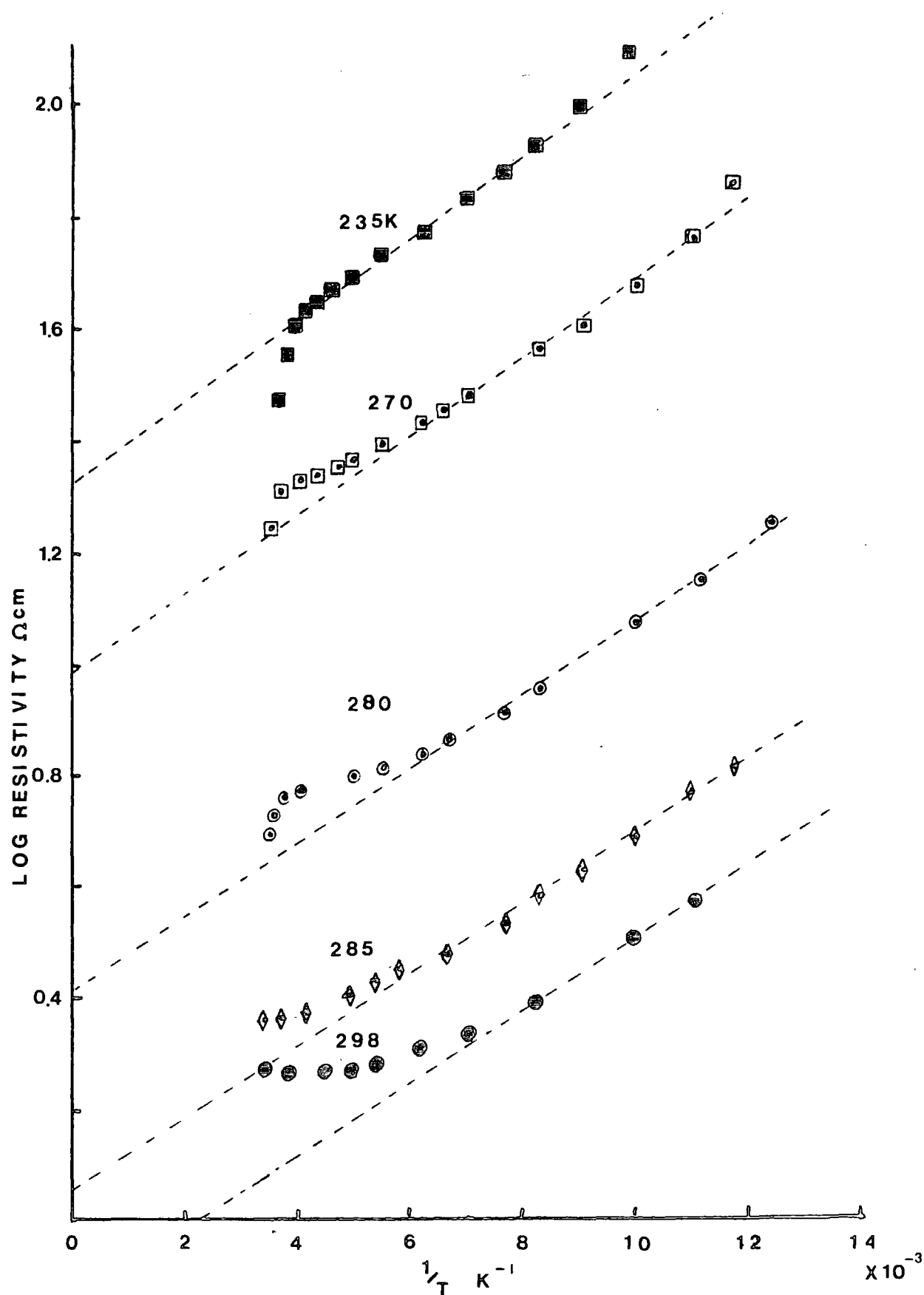
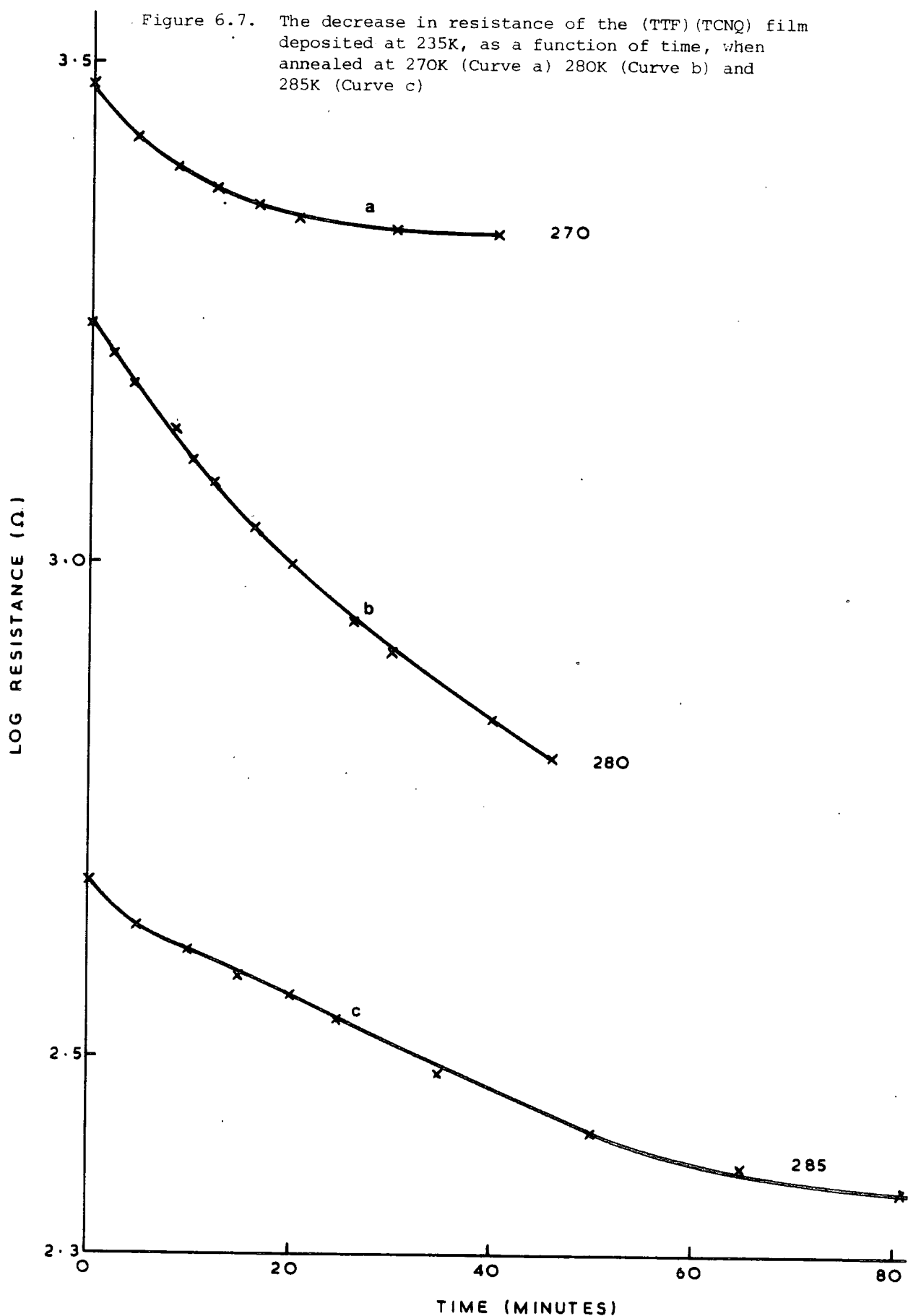


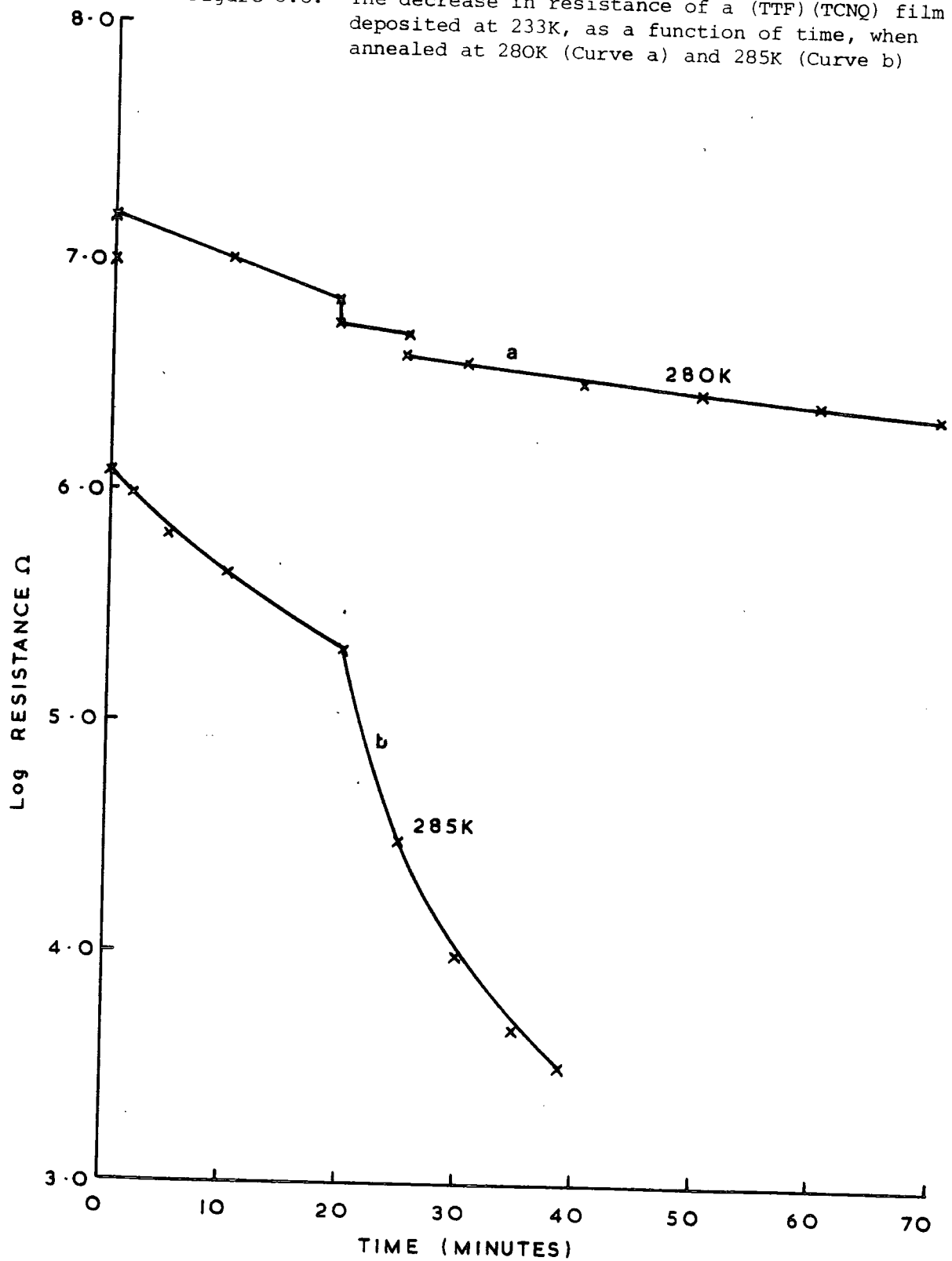
FIGURE 6.6. TDR OF A TTF TCNQ FILM DEPOSITED AT 235K AND ANNEALED IN STEPS

Figure 6.7. The decrease in resistance of the (TTF)(TCNQ) film deposited at 235K, as a function of time, when annealed at 270K (Curve a) 280K (Curve b) and 285K (Curve c)



DEPOSITED AT 233K

Figure 6.8. The decrease in resistance of a (TTF)(TCNQ) film deposited at 233K, as a function of time, when annealed at 280K (Curve a) and 285K (Curve b)



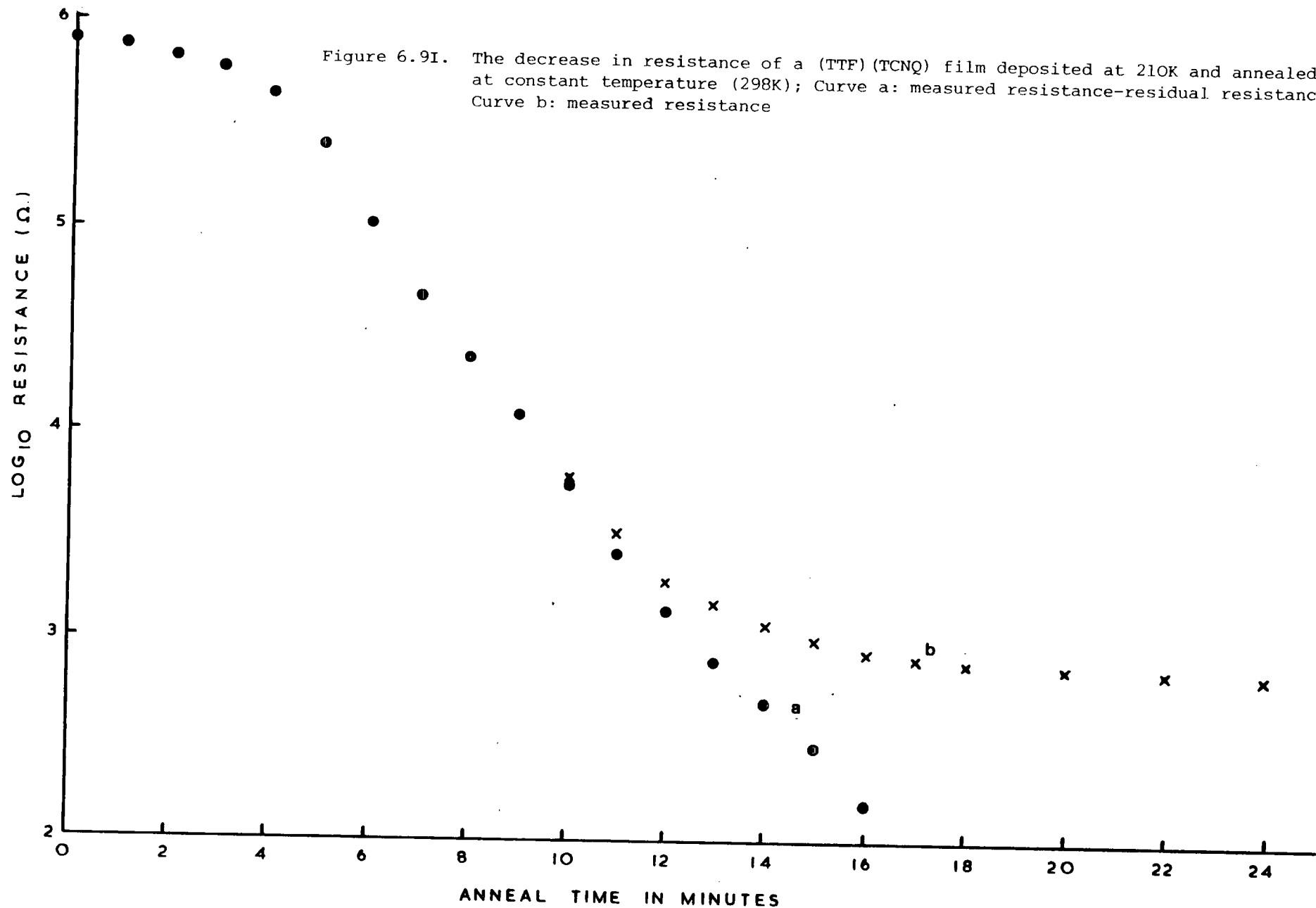
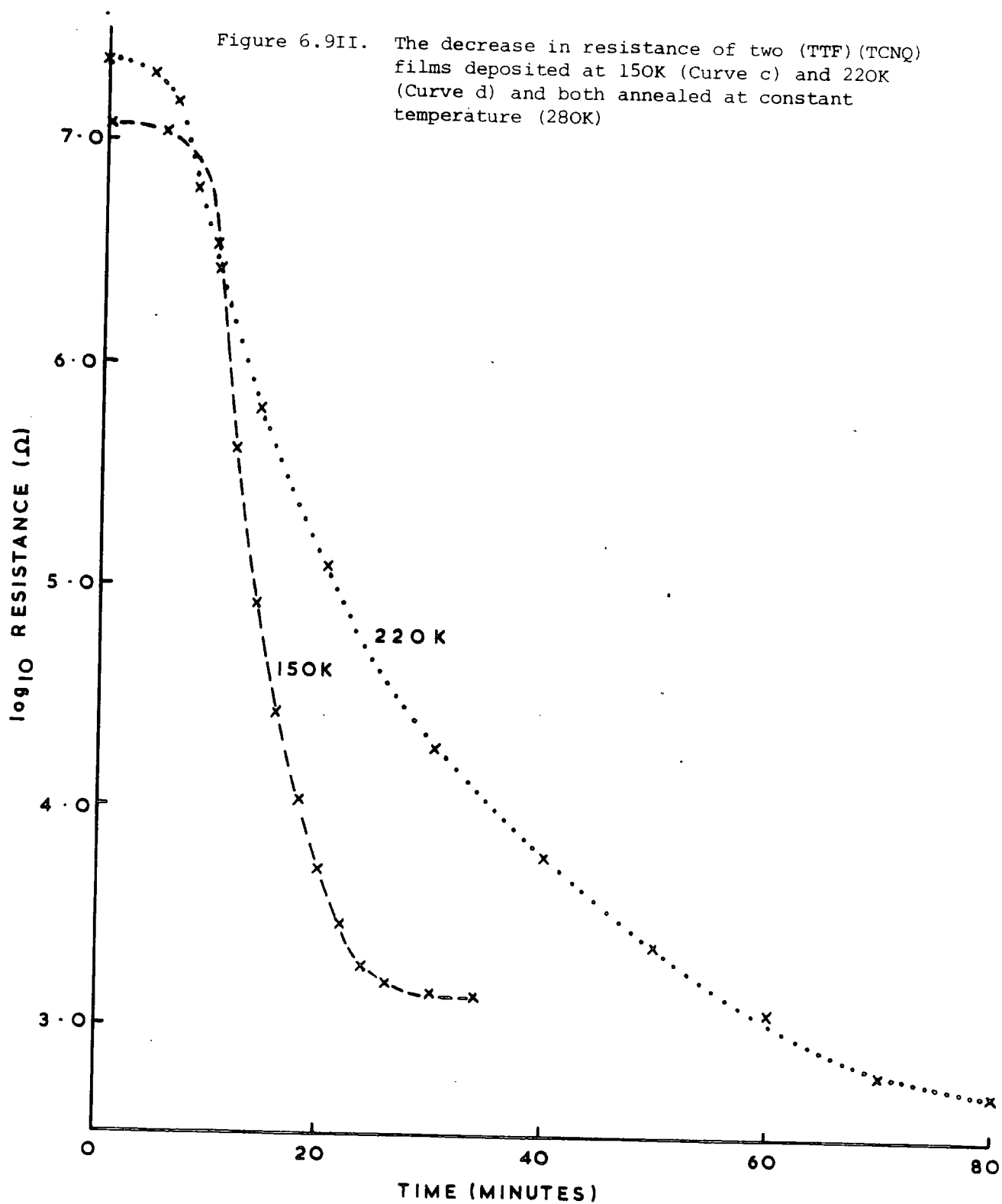


Figure 6.9II. The decrease in resistance of two (TTF)(TCNQ) films deposited at 150K (Curve c) and 220K (Curve d) and both annealed at constant temperature (280K)



The data presented in Figure (6.7) was obtained from a film whose conductivity was monitored during deposition and it is possible that the applied current was responsible for initiating the transformation in this film at lower temperatures. The data shown in Figure (6.8) for a film deposited at 233K is perhaps more representative of films deposited below 235K in the absence of an applied current.

Annealing at a constant temperature of 280K (curve a) resulted in a very slow decrease in the resistance of the film. Over the first 90 mins. at 280K, which is not shown, the film resistance hardly changed and then dropped suddenly by almost an order of magnitude from 10^8 ohms to 2×10^7 . The decrease in $\log R$ was then linear with time for the next 20 mins, when a further sharp but smaller decrease occurred. $\log R$ continued to decrease in a linear fashion for a further 70 mins. at 280K. On increasing the annealing temperature to 285K, (curve b) the resistance decreased at a faster rate, $\log R$ vs t becoming linear after about 5 mins. After 20 mins. at 285K there was a sudden increase in $d \log_{10} R/dt$, which signified the formation of the highly conducting phase of the complex.

The result of annealing a film deposited at 210K, at a constant temperature of 298K is shown in Figure (6.9I). The residual resistivity was allowed for by plotting $\log R_i$ vs t , where R_i is the measured resistance (R) of the film at time t minus the residual resistance after fully annealing the film at 298K. After an initial induction period, the rate of decrease of $\log R_i$ remained constant (curve a). A plot of $\log R$ (curve b) is also given in Figure (6.9I) which shows that measured rate of change decreased to zero after about 24 mins. indicating that the transformation to the conducting phase was

essentially complete. After the initial period $\log R_i$ vs t was a reasonable approximation to a straight line which suggests that the transformation was occurring with constant activation energy over much of its range.

Similar behaviour was observed for two other films deposited at 150K and 220K respectively, and annealed at 280K. The annealing curves are given in Figure (6.9II) (Curves c and d) for which $\log R$ rather than $\log R_i$ is plotted against t .

6.2.4 Determination of the Activation Energy of the Annealing Process

Constant Temperature Annealing

According to Vand's treatment⁽²⁴⁾, if $\log R_i$ vs t can be fitted to a straight line, as the data in Figure 6.7, for the film deposited at 235K and annealed at 285K can, over a large proportion of the time interval studied, the process is occurring with a single activation energy E_{ann} . The value of E_{ann} was obtained from the slope of the line, which is equal to $1/t_0$, where t_0 is given by equation (6.5), that is

$$1/t_0 = C \exp (-E_{\text{ann}}/kT) \quad (6.5)$$

Assuming a value of 10^{12} for the frequency factor (C), the slope of the line gives a value of 0.395 eV (38.17 kJ mole⁻¹) for the activation energy. The error introduced by the assumed value of C is of the order of 0.05 eV (4.81 kJ mole⁻¹), for every two orders of magnitude, as shown in Table 6.1.

Table 6.1

C	E _{ann} (eV)
10 ¹⁴	0.445 (42.89 kJ mole ⁻¹)
10 ¹²	0.395 (38.17 kJ mole ⁻¹)
10 ¹⁰	0.347 (33.45 kJ mole ⁻¹)

(TTF) (TCNQ) has a Debye temperature⁽²⁸⁾ of about 100K, which corresponds to frequency (f) of about 2×10^{11} sec. Since $C = 4fn$, a value of 10^{12} for C is reasonable if an average distortion is composed of only a small number of molecules.

Vand defined a function F_0 which is characteristic of the number of defects N_0 with decay energy E, and the contribution r each makes to the film resistivity. Thus

$$F_0 = r(E) N_0 (E) \quad (6.6)$$

$F_0(E)$ can be obtained from the experimental data using the following equation

$$F_0(E, t) = - \frac{dR_i}{dt} \cdot \frac{t}{kT} \quad (6.7)$$

Applying Vand's analytical procedure to the constant temperature annealing results of Figure (6.9), produces the curves shown in Figure (6.10). The function $F_0(E)$ is plotted against annealing time and in each case gives an almost Gaussian curve, which represents the distribution in activation energies for defect decay within the respective film. In the case of the film deposited at 210K the maximum value of E_0 occurs after approximately 5 mins at 298K with a full width at half the peak maximum (FWHM) of ± 0.7 mins. The position of

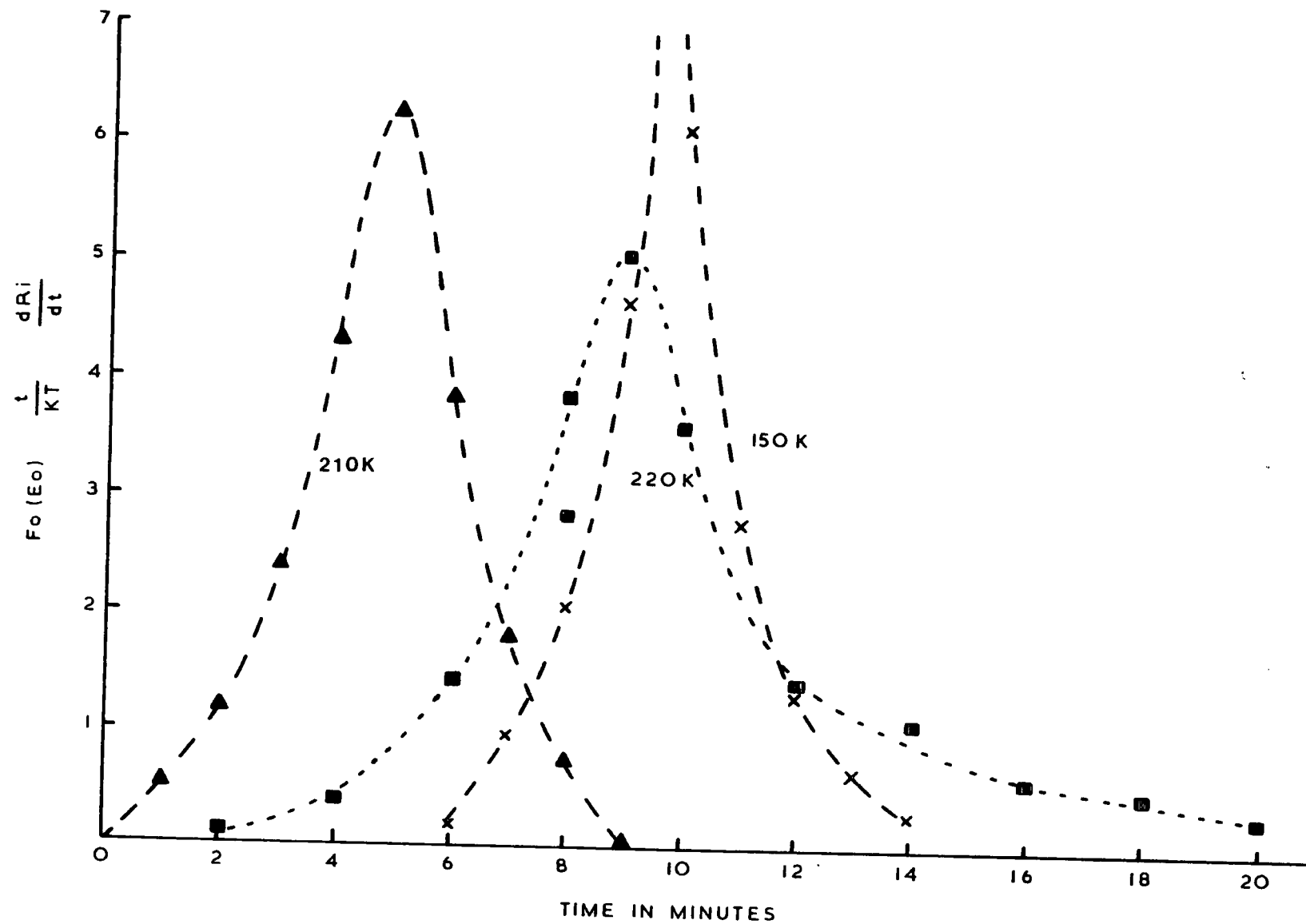


Figure 6.10. Constant temperature annealing data from Figures 6.9I and II replotted as the function $F_o = - \frac{dR_i}{dt} \cdot \frac{t}{KT}$ against time.

the other two curves is given in Table 6.2 below, along with the corresponding value of the activation energy calculated from equation (6.8) (again assuming $C = 10^{12}$) which is,

$$E_0 = kT \log C_t \quad (6.8)$$

Table 6.2

Deposition Temperature K	Annealing Temperature K	Time to F_0 (max) secs	E_0 eV
150	280	530 ± 30	$0.355 \pm .001$
210	298	300 ± 40	$0.372 \pm .001$
220	280	510 ± 70	$0.355 \pm .002$

From the value of E_0 , for each of the three curves, it is apparent that the transformation was occurring with virtually a single activation energy. The FWHM was only of the order of .002 to .004 eV which is well within the error introduced by Vand's approximations. The values of E_0 were somewhat lower than the 0.396 eV estimated from the slope of the line of curve c in Figure 6.5, for the film deposited at 233K.

From a qualitative point of view the distribution in activation energies as judged from the width of the three peaks for the film deposited at 220K appears to be greater than for either of the films deposited at 210K and 155K respectively. This observation is also supported by the more gradual decay in resistance noted for the film deposited at 223K which is given in Figure (6.2) and again for the 222K deposit in Figure (6.2). In general, however, the decay in film resistance, as shown in Figure (6.1), occurred at approximately the

same rate, once initiated, for most of the films studied. This indicates that the width of the distribution in the activation energy of defects was not a particularly sensitive function of the substrate temperature during deposition.

Constant Rate Annealing

The constant temperature or 'ageing' experiments demonstrated that at the point of the insulator to conductor transition the decay of defects was occurring with an activation energy which was effectively constant during the transformation. In analysing the data from 'tempering' experiments it is, therefore, reasonable to expect that the treatment of Vand for this case, with a constant value of E , is appropriate. With the exception of the film deposited at 223K the steepness of the slopes of curves in Figure (6.3) implies that the error introduced by assuming E to be constant will be $\ll kT$. To a good approximation, the transition to the conducting phase is taken to be a step function with a point of inflexion whose coordinate on the energy axis is given by

$$E/kat = ct \exp (-E/kat) \quad (6.9)$$

$$(E/kat) + \log(E/kat) = \log Ct$$

from which the activation energy can be determined, where a is the rate of heating. In calculating the activation energy from equation (6.9), zero k was taken as the starting point and t was the time taken to reach the point of inflexion at a heating rate of 1.5 k/min. The results for the series of curves shown in Figure (6.3) are listed in the last column of Table 6.3. The variation in activation energy was very small, there being a difference of only 0.033 eV (3.2 kJ mole^{-1}) between the films deposited at 214K and 170K. This corresponded to a

Table 6.3

Deposition Temperature K	T inflexion K	T x 30 = t secs x 10 ³	log Ct	E _{ann} (eV)
170	276	8.28	15.92	0.351
180	278.5	8.36	15.922	0.354
197	282	8.46	15.927	0.359
210	288	8.64	15.937	0.367
214	301	9.03	15.956	0.384
217.5	295.5	8.87	15.947	0.376
223	280.5	8.41	15.925	0.357
229	293	8.79	15.944	0.373

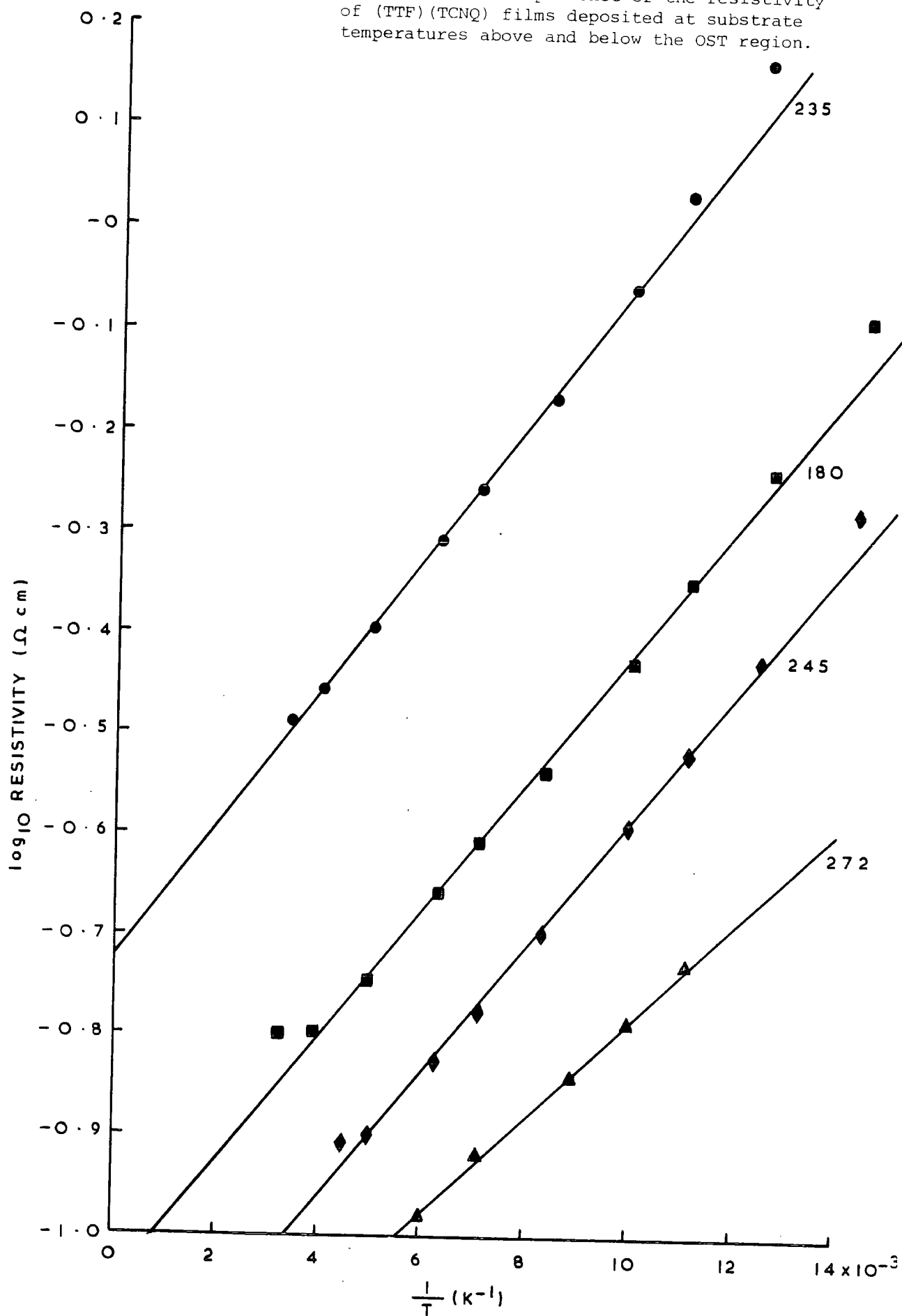
difference in transition temperature of approximately 25°C for these two films. The maximum activation energy for the transformation was observed for the film deposited at 214K.

The activation energy estimated using the three different sets of data are reasonably self consistent in that approximately the same value was obtained in each case. The slightly higher value (0.396) calculated from the log R vs t data, in Figure (6.7) reflects the activation energy when the transformation is nearing completion, whereas the results obtained using the tempering method, correspond to the early stages of growth of the conducting phase.

6.2.5 The Temperature Dependence of the Resistivity of Annealed Films

The variation in resistance as a function of temperature of films annealed at room temperature for 24 hrs. is given in Figure (6.11) and (6.12). Samples were deposited at the substrate temperatures shown alongside each set of data. In both Figures the

Figure 6.11. The temperature dependence of the resistivity of (TTF)(TCNQ) films deposited at substrate temperatures above and below the OST region.



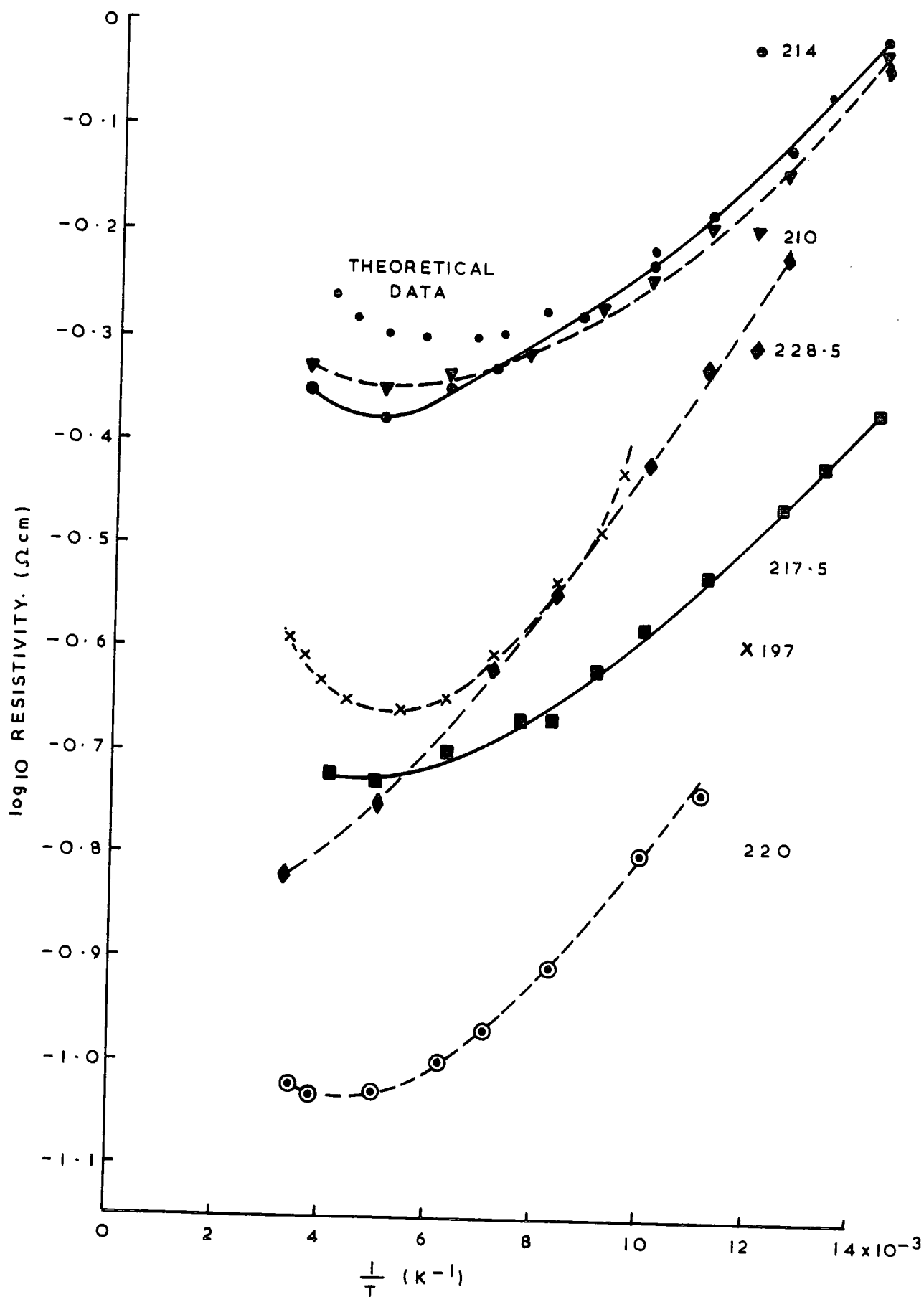


Figure 6.12. The temperature dependence of the resistivity of (TTF)(TCNQ) films deposited at substrate temperatures in the vicinity of the OST region.

logarithm of the resistivity is plotted against the reciprocal temperature. The data shown were taken from continuous curves, since the voltage generated across the two inner probes by a constant current of 10 μ A, was automatically monitored using an x-y or and x-t recorder.

The data are well fitted by the usual expression (6.10) for conduction involving excitation of charge carriers over an energy barrier. (29)

$$\rho = \rho_o \cdot \exp \frac{E_{\text{cond}}}{kT}$$

and

(6.10)

$$\log_{10} \rho = \log_{10} \rho_o + E_A / 2.3 kT$$

ρ_o is a sample dependent constant, and is the resistivity as $T \rightarrow \infty$, i.e. the intercept on the y axis; E_{cond} is the activation energy for conduction. The activation energy was obtained from the slope of the $\log_{10}$ resistivity vs. reciprocal temperature plot which is equal to $E_{\text{cond}}/2.3k$. Three of the films, deposited at 180, 235 and 245K, had virtually the same activation energy at 0.0135 eV, whilst that for the 272K sample was slightly lower at 0.0125 eV.

Table 6.4

Deposition Temperature K	E_{cond} (eV)	ρ_o (ohm.cm.)
180	0.0135	0.089
235	0.0135	0.19
245	0.0135	0.062
272	0.0125	0.055

For films deposited between 197K and 230K pronounced non-linear behaviour was observed for the $\log_{10}$ resistivity vs. reciprocal temperature data, as can be seen in Figure (6.12). The data for the 228.5K deposit is tending toward straight line behaviour with an activation energy similar to those films given in Figure (6.11), but the remaining samples displayed a definite curvature, and in each case the resistance actually increased with temperature above 250K. This is most clearly seen for the film deposited at 197K. Films deposited in the vicinity of 215K showed a similar temperature dependence, but the resistivity of the 217.5K deposit was about half that of the 210K and 214K samples.

The Variation in Film Thickness with Substrate Temperature

An estimate of film thickness was obtained from the extinction coefficient for the 845 nm absorption band, as described in Appendix 2, assuming a density of 1.7g/cm^3 (22) and a film surface area of 2 cm^2 . Table 6.5 lists the thickness (column 2) of a series of films which were used for conductivity measurements. The film thickness measured during deposition, using the quartz crystal oscillator (QCM) was $4400\text{\AA}$ ($3600\text{\AA}$ in the case of the higher resistivity 235K film). However, the (QCM) was maintained at room temperature during deposition and not at the temperature of the substrate. The thickness measured using the optical absorbance method should, therefore, reflect the variation in sticking coefficient with substrate temperature, as the (QCM) was located at precisely the same position for each film deposited.

The variation in film thickness with substrate temperature is given by curve a in Figure (6.13). Although the thickness increases between 270K and 235K, to a maximum value of about $10,000\text{\AA}$, it then decreases again to a value of $4,500\text{\AA}$ at 170K. Between 235K and 210K,

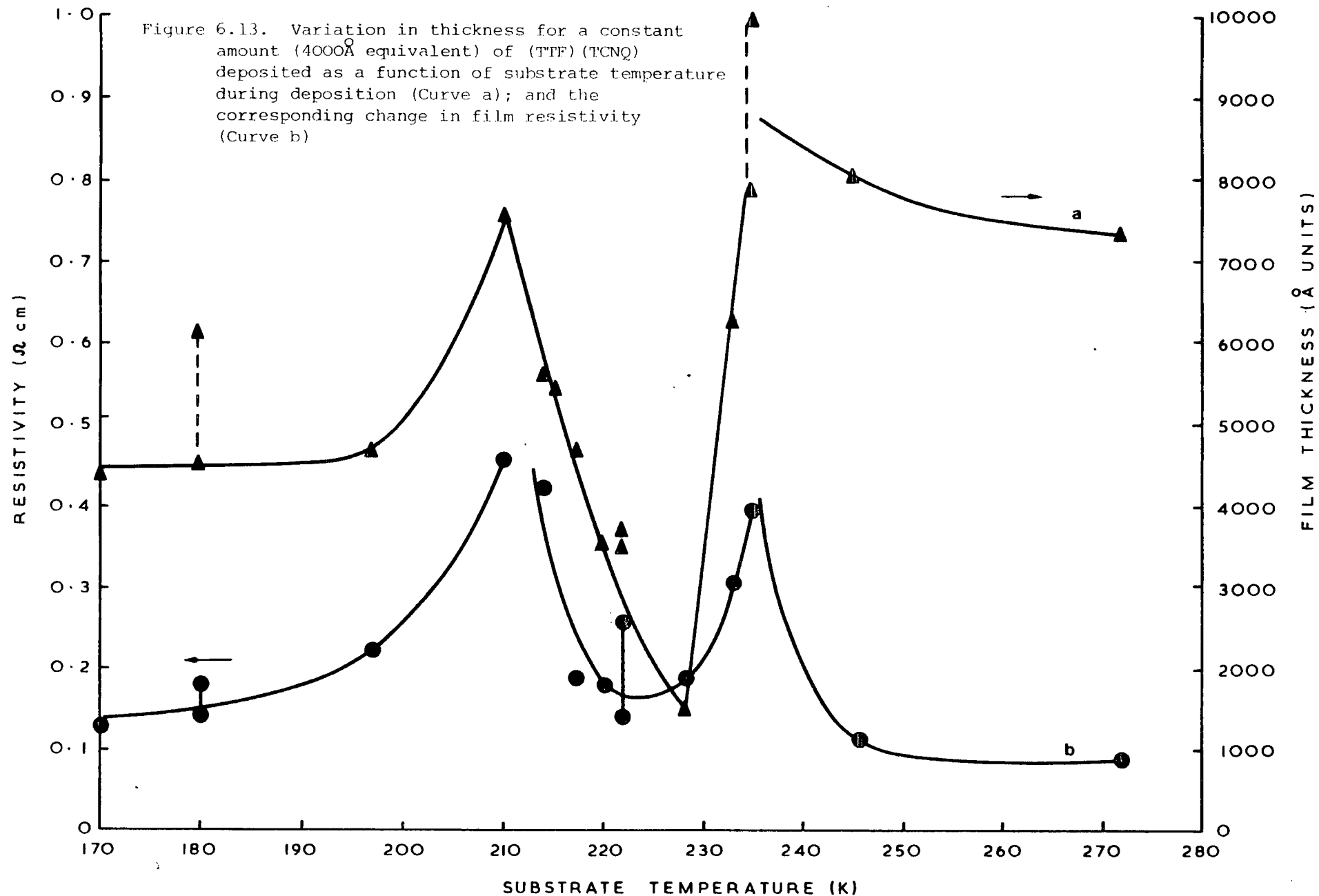


Table 6.5

The Variation in Resistivity and Film Thickness
with Deposition Temperature

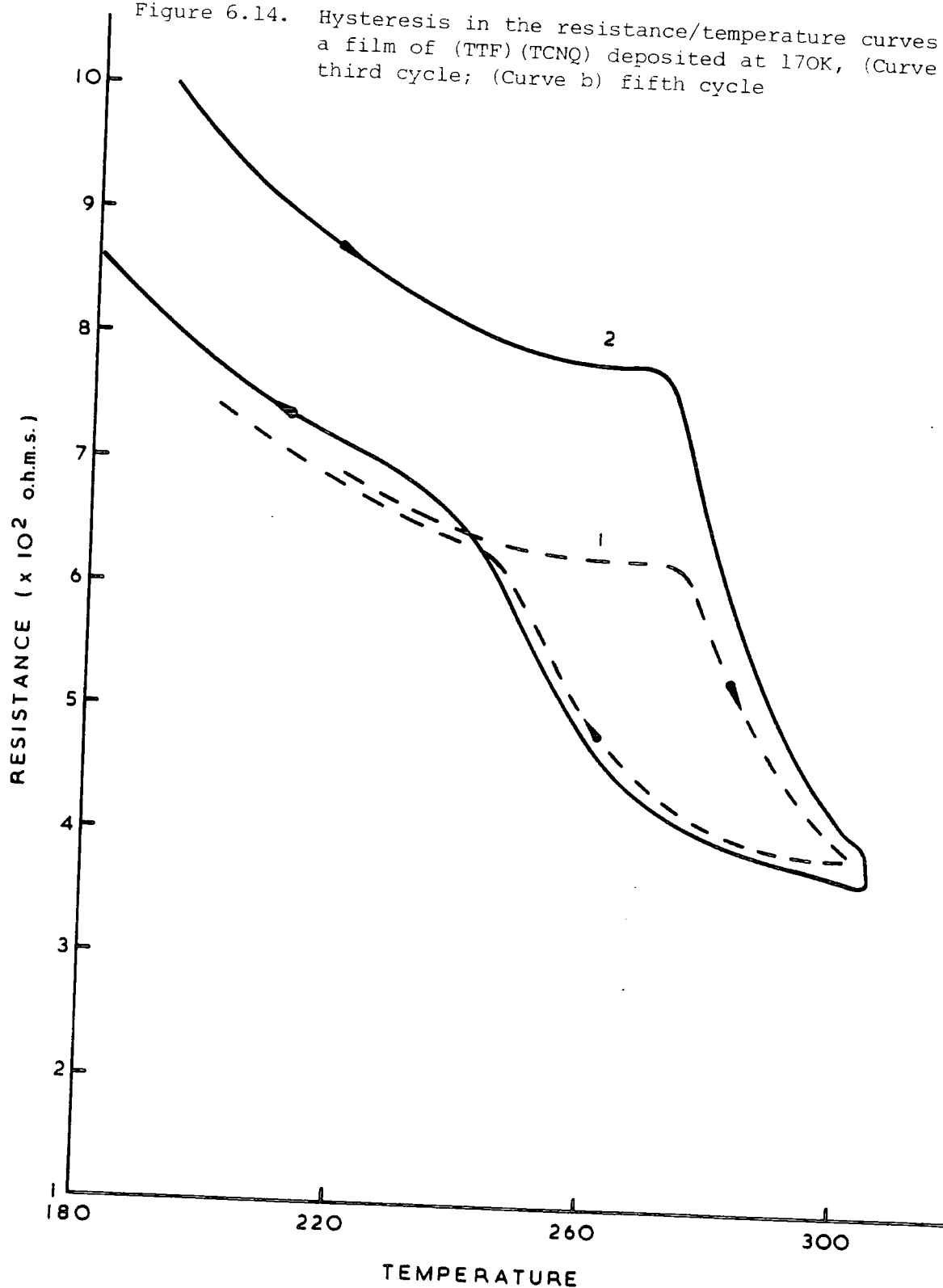
Film Deposition Temperature K	Film Thickness Å	Resistance/Resistivity at 200K	
		Ω	Ω.cm.
150	?	7.3×10^4	
170	4300	5.8×10^2	0.13
180	4500	6.4×10^2	0.144
180	6140	5.7×10^3	0.175
197	4650	9.4×10^2	0.218
210	7600	1.2×10^3	0.456
214	5600	1.5×10^3	0.42
215	5376		
217.5	4700	7.9×10^2	0.185
220	3550	1×10^3	0.18
222	3700	1.4×10^3	0.259
222	3650	7.5×10^2	0.136
228.5	1440	2.5×10^3	0.175
233	6240	1×10^3	0.31
235	8000	1×10^3	0.4
235	10,000	1.8×10^3	0.9
245.5	8060	2.88×10^2	0.115
272	7300	2.57×10^2	0.092

the thickness decreased considerably, to about $1500\text{\AA}$ at 228K , and then increased to a second maximum at 210K . Although some variation in thickness was observed between films deposited at nominally the same substrate temperature, as shown by the vertical lines in Figure (6.13), this cannot account for the observed behaviour, and particularly the very large decrease in thickness between 220 and 230K .

Hysteresis Effects in Annealed Films

A large proportion of the annealed samples examined displayed hysteresis effects which were not connected with poor heat transfer between the sample and cryostat heat exchanger. The effect was particularly marked in, although not confined to, samples deposited at substrate temperatures below 200K , but was less pronounced in samples deposited in the vicinity of T_{opt} . In all cases in which hysteresis was observed, the resistance of the sample measured during the heating cycle was higher than that observed at the same temperature on cooling down. The effect is illustrated in Figure (6.14) which was obtained for a film deposited at 170K . The curves shown were obtained by subjecting the sample to several temperature cycles, whilst measuring the resistance of the film continuously at a current of $10\mu\text{A}$. A hysteresis was obtained on each occasion. Curve 1 was obtained on the third cycle, during which, the film was cooled from room temperature to 200K and then returned to room temperature. On the fifth cycle (curve 2) the sample was cooled to 80K and then returned to 300K . A heating rate of $1^\circ/\text{min}$ was used for both cycles.

Figure 6.14. Hysteresis in the resistance/temperature curves for a film of (TTF)(TCNQ) deposited at 170K, (Curve a) third cycle; (Curve b) fifth cycle



Some of the more important results obtained from a study of the electrical properties of (TTF)(TCNQ) films are summarised below

- a) Films deposited at low temperatures have resistivities of the order of 10^{-7} ohm.cm. and undergo a transformation to the normally highly conducting phase of the complex around room temperature.
- b) The activation energy E_{ann} for the transformation from the low to the high conductivity state was highest for films deposited in the vicinity of 215K.
- c) Two different patterns of annealing behaviour were observed for films deposited above and below 220K, respectively.
- d) There was an apparent reduction in the activation energy for conduction for films deposited between 197K and 220K. For films deposited outside this substrate temperature regime the activation energy appeared to be independent of temperature and had a value between 0.012 and 0.014 eV.
- e) Maxima in film resistivity were observed for film prepared at deposition temperatures of about 215K and 235K, which coincided with maxima in film thickness.
- f) There was a deep minimum in film resistivity for films deposited between 220K and 235K which coincided with a decrease in film resistivity.
- g) Resistance versus temperature curves exhibited hysteresis effects in the vicinity of room temperature.

6.3 Discussion

6.3.1 The Annealing Behaviour of Films

The lack of structural information and the difficulties encountered in making reproducible electrical measurements have prevented a detailed characterisation of films in the as-deposited state. However, it is a reasonable supposition, at least in the case of films deposited below 220K, that in the as-deposited state they no longer possess the regular quasi-1-dimensional metallic lattice of the conducting complex. This supposition is based largely upon the infrared evidence of the previous chapter, although it is supported to some extent by electrical measurements. Thus, films were shown to have a high resistance in the as-deposited state, which as Figure (6.3) reveals was only weakly temperature dependent between 200 and 260K.

The structure envisaged for films deposited below 220K is, therefore, one which lacks LRO and consists of isolated molecules (or dimers) held together by short range van der Waals forces. Although requiring further confirmation it is probable that electrical conduction in these films occurs by localised, possibly phonon assisted, ⁽³⁰⁾ hopping rather than by a band ⁽¹⁷⁾ or charge density wave mechanism. ⁽⁶⁾

Above a deposition temperature of 220K there appears to be a change in the nature of the as-deposited state which manifests itself in two ways, i.e. a decrease in film resistivity, particularly above 235K, and by a change in the pattern of annealing behaviour. These differences can be readily discerned by comparing the experimental data in Figures (6.3) and (6.5). In films deposited above 235K, Figure (6.5), the decrease in resistance began immediately above the

temperature of deposition and continued until the annealing process was completed near room temperature. In contrast, the resistance of films deposited below 230K, Figure (6.3) remained high until near room temperature, when an almost discontinuous decrease occurred, which was completed within a few degrees. Films deposited at nominally the same substrate temperature in the interval 220K and 235K exhibited both patterns of behaviour.

This contrasting annealing behaviour points to a fundamental difference in the structure of deposits formed above and below 220K, and provides further evidence of the anomalous properties of films prepared between 190K and 220K. An explanation of the annealing results is provided within the framework of nucleation theory by postulating the existence of a boundary region between 220K and 235K, above which, nucleation of the conducting phase occurs during deposition of a film, and below which nucleation does not occur until films are annealed above some characteristic temperature (T_m). A further distinction can also be made between films deposited below 220K, which relax to give a metastable structure, and those deposited above 235K, which are thermodynamically unstable toward the growth of the conducting phase of the complex.

Metastability and Instability

A schematic illustration of the difference between the terms metastable and unstable, as used in the present context, is given in Figure (6.15). Considering the metastable case first, which is represented by the upper diagram in Figure (6.15). A (TTF) (TCNQ) film which is deposited at low temperatures (<190K) with a disordered

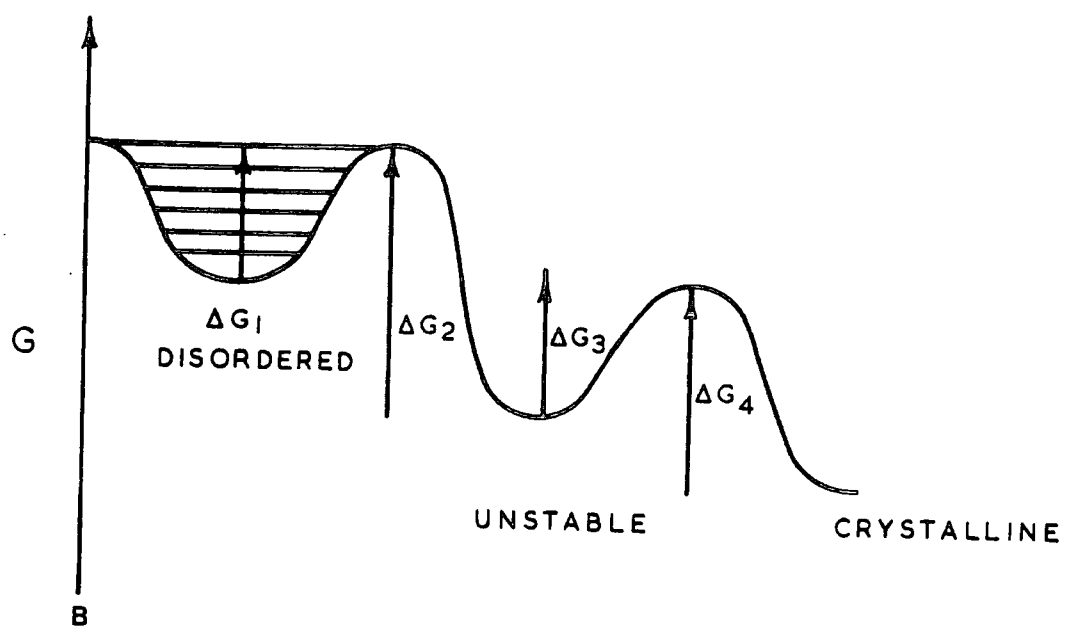
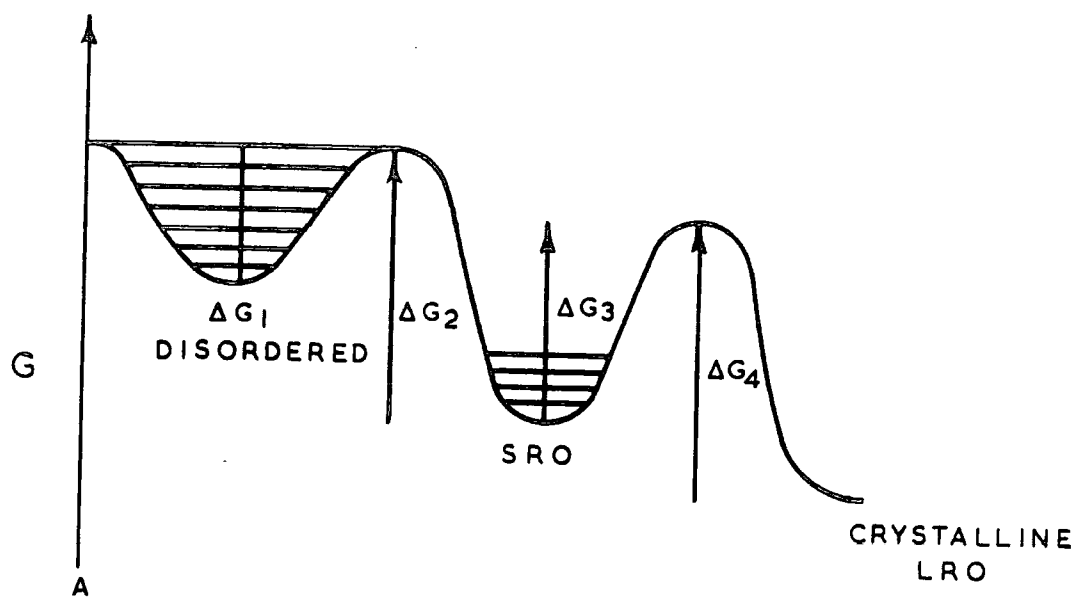


Figure 6.15. Schematic of the difference between a film with a metastable structure (A) and one with an unstable structure (B)

structure will, when annealed above a temperature (ca. 200K), corresponding to the activation free energy ΔG_2 undergo a relaxation process to a lower energy state designated as SRO. In this state the film is assumed to possess a high degree of short range order. Subsequent relaxation to the LRO state is prevented by a second activation energy barrier ΔG_3 , but only if $\Delta G_3 > \Delta G_1$. In this event the metastable state will exist over a temperature interval determined by $\Delta G_3 - \Delta G_1$. If, however, $\Delta G_1 \geq \Delta G_3$, then molecules which have sufficient energy to overcome the first barrier ΔG_1 can also overcome the second barrier ΔG_3 and consequently the intermediate SRO or metastable state is no longer viable. This is the situation depicted by the lower diagram of Figure (6.15).

Although at first sight there is no distinction between a film which is deposited with a disordered structure and one which possesses SRO, in that they both appear to be metastable, in fact they differ in one important respect. Disordered films deposited below 190K are thermodynamically unstable and are only prevented from relaxing to a more stable state by a purely steric or kinetic barrier to diffusion. On the other hand the structure of those films prepared between 190K and 220K is stabilised by virtue of short range inter-molecular forces and is thermodynamically the most stable phase under the conditions prevailing during deposition. Now according to Ostwald's rule of stages,⁽³¹⁾ the relaxation mechanism for the disordered state proceeds via states of intermediate stability i.e., the SRO state, rather than transforming directly to the LRO or crystalline form of the complex on annealing. This explains why films deposited below 190K exhibit the same pattern of annealing behaviour as those deposited between 190K and 220K. Incidentally, it

is also the reason why the intensity of ag vibrational modes, which are characteristic of disordered films, is reduced to zero before electronic-excitation effects become noticeable in their infrared spectra. Electronic transition are, as discussed in Chapter 5, a characteristic feature of the LRO or crystalline state.

When discussing the annealing of films deposited above 190K it is necessary to consider only the second activation energy barrier ΔG_3 . The problem then becomes one of explaining why it is that films deposited between 190K and 220K have a metastable structure, whilst those prepared above 220K are apparently unstable toward the formation of the crystalline phase of the complex.

The Formation of Metastable Films

The infrared spectra of films deposited between 195K and 230K were shown in Section (5.3.3) to be consistent with a neutral van der Waals lattice. It was pointed out in the earlier discussion of these results that a combination of a number of factors, all of which depend for their existence upon LRO being established, are thought to be responsible for stabilising the normal structure of the complex. In the absence of LRO therefore, it is short range forces which are responsible for film stability and which determine the depth of the potential well ΔG_3 in Figure (6.15).

As outlined in Chapter 1, theory predicts that the rate of nucleation goes through a maximum and then decreases because of a reduction in the surface diffusion coefficient of adsorbed molecules at low temperatures. From the SEM results of section (4.2.2), it was concluded that in the case of (TTF)(TCNQ) films the maximum rate

of nucleation occurred in the vicinity of 235K and underwent a rapid reduction below this temperature. Clearly at some lower deposition temperature the rate of nucleation will be reduced below the limit of detection and short range forces will determine film stability. At this point individual molecules may become part of a condensed film without being incorporated into growing nuclei of the conducting phase. Once formed, precipitation of a new phase, within this condensed film, can only take place if molecules are able to diffuse together to form stable nuclei, which as discussed in Chapter 1, have to achieve a certain critical size, r_n .

The diffusion coefficient D normally follows an Arrhenius type of behaviour⁽³²⁾

$$D = D_0 \exp (-E_{\text{diff}}/kT) \quad (6.11)$$

hence if the growth of the conducting phase within films of (TTF)(TCNQ) is solely determined by the rate of molecular diffusion one would expect to observe a similar exponential temperature dependence for the rate of transformation. The results of Figure (6.3), however, show convincingly that the transition is practically discontinuous for films deposited below 220K and is usually preceded by an increase in resistivity. At first sight this behaviour implies that some additional factor may be responsible for preventing nucleation in these films, even in the presence of molecular diffusion. A view supported by the isothermal and stepwise annealing results in Figures (6.9) and (6.8), respectively, which are typical of the behaviour of films deposited below 220K. They show that within a given film the transformation to the highly conducting form of the complex only takes place above some critical temperature T_m . The transformation

rate is several orders of magnitude slower, only a few degrees below T_m .

Similar behaviour has been reported previously for annealing experiments on 'amorphous' films of water,⁽³³⁾ and the organic compounds dichloroethane and chloroform, which were prepared by vacuum deposition onto liquid nitrogen cooled substrates. The phenomenon is referred to as shock crystallisation⁽³⁴⁾ and it occurs when the growth of crystallisation centres is retarded because of the high viscosity of the parent phase. Because of the high viscosity the number of nuclei of critical size r_n increases very rapidly with time, favouring the manifestation of non-stationary nucleation at small heating rates. According to Skripov,⁽³⁴⁾ in order to observe shock crystallisation it is necessary to create an amorphous layer with the smallest possible number of active centres or nuclei and it is proposed that nuclei are also absent from films of (TTF) (TCNQ) in the metastable state.

Non-stationary Nucleation in Metastable Films

The non-stationary nucleation rate $J'(t)$ at time t , for isothermal annealing is given approximately⁽³⁵⁾ by

$$J'(t) = J \exp (-\tau_0/t) \quad (6.12)$$

where J is the stationary nucleation rate and τ_0 is the time lag for the establishment of the stationary nucleation rate. A value for τ_0 of 500 secs was obtained from the infrared study of annealing of a film deposited at 160K and annealed at 265K, by extrapolating the straight line portion of the curve in Figure (5.21) to intersect the t axis.⁽³⁶⁾ Since τ_0 is itself exponentially dependent on temperature,⁽³⁵⁾

$$\tau_0 = \frac{1}{4} n_*^{4/3} \theta \exp (E/kT) \quad (6.13)$$

where n_* is the number of molecules in the critical nucleus and θ the lattice frequency (2×10^{-11} sec for (TTF)(TCNQ)),⁽²⁸⁾ there is a very rapid change in J' with temperature. The number of nucleation centres increases by a factor of 10^4 in a temperature interval $\Delta T = 0.5K$,⁽³⁴⁾ which would cause the transformation to appear to be discontinuous in a non-isothermal annealing experiment.

A value for n_* of approximately 10^5 molecules was obtained by substituting the experimental values of $\tau_0 = 500$ secs and $E_{\text{exp}} \sim 0.37$ eV in equation (6.13). This is some two or three orders of magnitude higher than value of n_* typically encountered. Although a number of simplifying assumption were made in deriving equation (6.13) it is known⁽³⁴⁾ to give estimates of τ_0 accurate to an order of magnitude.

Nucleation in 1-Dimensional Systems

A possible explanation for the unusually large value of n_* is provided by the 1-dimensional nature of the (TTF)(TCNQ) lattice. Thermodynamics determines that a truly 1-dimensional lattice cannot possess long range order at finite temperatures⁽³⁷⁾ and, as a consequence, does not undergo a phase transition. Because of fluctuations it is energetically favourable for the chain to break up into domains, whose characteristic length l is given, in the Mean Field Approximation, by⁽³⁸⁾

$$l(T) = a e^{2A/kT} \quad (6.14)$$

where a is the molecular spacing and A the interaction energy between nearest neighbours. At finite temperatures domains are formed in which there is strong SRO, but molecules separated by distances

greater than 1 are uncorrelated and hence there is no long range order.

Now, although there is an interchain interaction A' between molecular stacks in (TTF)(TCNQ), this is much weaker than the intermolecular interaction energy A , consequently the structure is more susceptible to thermal fluctuations than a lattice which interacts strongly in three dimensions. As a result, above a critical temperature T_c , the structure behaves essentially as an incoherent assembly of independent strands. On the other hand, if the interchain interaction is included, the mean field approach⁽³⁸⁾ predicts a transition temperature at

$$k_1 T_c \sim |l(T_c)/a| A' \quad (6.15)$$

i.e. the interaction between neighbouring stacks is proportional to the coherence length. This implies that, in the metastable state, which may consist of randomly oriented stacks of molecules, fluctuations of some critical length l_n , which corresponds to r_n for 3-dimensional nucleation, must occur on several stacks simultaneously, before nucleation of the conducting phase can occur. Thus nucleation within a metastable film of weakly interacting 1-dimensional stacks of molecules, is likely to occur with lower probability than in an equivalent 3-dimensional structure, where the intermolecular interaction A is isotropic.

A decrease in the probability of nucleation would be reflected in a higher apparent value of τ_0 . This proposal is consistent with the Ising⁽³⁹⁾ model of phase transitions in 2-dimensions, which shows that the transition temperature, compared to an equivalent 3-dimensional structure, is depressed by an amount which is proportional

to the interchain interaction A'

$$\text{i.e.} \quad k T_C = 2A/\ln(2A/A') \quad (6.16)$$

The Nature of the Metastable $\rightarrow$ SRO Transition

Since the correlation length l and hence the probability of nucleation increases with decreasing temperature, according to equation (6.16), presumably at low temperatures the formation of nuclei of the crystalline phase of the complex is prevented by an activation energy barrier associated with the motion of molecules in the low temperature or metastable phase. Furthermore, as emphasised by Landau and Lifshitz⁽⁴⁰⁾ the metastable state is one of partial equilibrium which is characterised by a certain relaxation time τ , and within the framework of equilibrium statistical mechanics, the effect of thermodynamic fluctuations⁽⁴¹⁾ is always such as to drive a system from a state of possible metastability to one of absolute stability. However, apparently there is no thermodynamic boundary (spinodal) with respect to continuous changes of state within a one component metastable phase.⁽³⁴⁾ Hence the metastable phase does not exhibit a tendency toward a reduction in stability, with respect to continuous long wavelength perturbations, i.e. phase transitions of second order. The lack of a spinodal implies that the transition from the metastable to the crystalline phase is in fact discontinuous, i.e. first order, such as that between a liquid and a crystal. Continuity of energy flow at a first order phase transition necessarily⁽³⁴⁾ implies a nucleation process which begins at isolated points within the metastable phase.

The terms first and second order mentioned above are used according to the Ehrenfest Classification⁽⁴²⁾ and refer to discontinuities in entropy ($\frac{\partial G}{\partial T}$), and heat capacity ($\frac{\partial^2 G}{\partial T^2}$), respectively, at the transition. They should not be confused with the kinetic order of reaction which was referred to in Chapter 5.

Hysteresis in Annealed Films

In view of the apparently discontinuous nature of the transition, observed when films deposited below 220K were annealed, it is concluded on the basis of the above discussion that these films were initially obtained in a metastable state and underwent a non-equilibrium first-order phase transition to the highly conducting crystalline form of the complex near room temperature. Further support for this conclusion was provided by the observation of a hysteresis in the conductivity of annealed films, when plotted as a function of temperature as in Figure (6.14). According to Landau's⁽⁴¹⁾ treatment, hysteresis effects of this type are characteristic of a first-order phase transition between an ordered and a disordered state.

Similar hysteresis effects have been reported to occur in single crystals of other TCNQ salts.⁽⁴³⁾ n-Propyl thiazolium (NPTh) (TCNQ)_x, for example, undergoes a metal to insulator transition at 402K, on heating, which is accompanied by a crystallographic phase change. On cooling the reverse transition occurred at 330K. The resistivity changed by a factor of 200 on the first cycle.

Yoshimura and Murakami⁽⁴³⁾ (Y & M) have shown that the hysteresis effect in (NPTh) (TCNQ)_x and other TCNQ salts is caused by a rate determining nucleation step in the solid state phase transformation.

They (Y & M) proposed that the high temperature form was metastable below a temperature T_H , because the increased surface energy σ created at the interface between both phases acted as a barrier to nucleation.

An estimate of σ can be obtained from the following expression ⁽⁴⁴⁾

$$\Delta T^3 - T_H (\Delta T)^2 + \frac{16 \pi v^2 \sigma^3 T_H^2}{3k (\Delta H)^2 (\Delta T)^2} = 0 \quad (6.17)$$

ΔH is the latent heat accompanying the transition, T_H the temperature of the transition on the heating cycle and T_C that for the cooling cycle. $\Delta T = T_H - T_C$ and v is the molecular volume. (Y & M) obtained a value for σ of 1.8 erg cm^{-2} for $(\text{NPTh})(\text{TCNQ})_x$. Values of σ of similar magnitude were obtained for other TCNQ complexes.

A value of 0.8 erg cm^{-2} for the surface energy created at the interface between the resistive and conducting forms of $(\text{TTF})(\text{TCNQ})$ was estimated using equation (6.17). The molecular volume was calculated assuming a density of 1.6 g/cm^3 . ΔH was taken as $1.6 \text{ Kcal mole}^{-1}$, based upon the results of Y & M, who found experimentally that ΔH for their materials were all of similar magnitude T_H and ΔT were obtained from Figure (6.14) and taken to be 280K and 25K, respectively.

The magnitude of the hysteresis effect in $(\text{TTF})(\text{TCNQ})$ films was much smaller than observed by (Y & M) in their single crystal studies. This suggests that it is not associated with a bulk transformation, but that it originates in grain boundary or defected regions of the film. It is presumably caused by a transition within small isolated groups of molecules which for statistical or steric reasons have not been incorporated into crystallites during growth. Its very

observation points to the importance of LRO in stabilising the high temperature form of (TTF)(TCNQ).

Since the hysteresis occurs in the same temperature regime as the irreversible transformation it is natural to assume that both involve similar molecular processes. However, unlike the hysteresis effect, the irreversible change in conductivity observed during annealing was almost certainly associated with a bulk process and was not confined to grain boundaries. This is borne out by infrared spectroscopy which established that films initially containing only neutral molecules are totally converted to the complex on annealing. Further information about the kinetic barrier to nucleation and its dependence upon substrate temperature within metastable films was provided by the magnitude of the experimentally determined activation energy for the metastable $\rightarrow$ SRO transformation.

Activation Energy of the Metastable $\rightarrow$ SRO Transition

As discussed earlier in connection with the infrared study of annealing in the lower temperature regime, the magnitude of an activation energy is a good indicator of the elementary ordering process responsible for a phase transition. From the annealing data on metastable films deposited below 230K, see for example Table (6.3), the transformation within these films takes place with an activation energy of the order of 0.35 to 0.4 eV. It is probable, therefore, that like the disorder $\rightarrow$ SRO relaxation process observed in the vicinity of 215K, the high temperature transformation to the crystalline phase also involves rotational diffusion about an axis perpendicular to the molecular plane. Since bulk and grain boundary translational diffusion, as well as out of plane rotation, require substantially higher activation energies it appears that these are not viable alternative processes even at room temperature. The

reasons for adopting this view have already been discussed in Chapter 5.

It is reasonable to expect that an elementary ordering process involving molecular re-orientation should be sensitive to the magnitude of the nearest neighbour interaction potentials and hence to the details of sub-microscopic structure. The pronounced influence of substrate temperature upon film topography, particularly within the region 190K to 230K, was very apparent in the SEM studies on annealed films. Moreover, a link between topography and anisotropic molecular interaction potentials was clearly established in Chapter 4. Thus, it is probable that the observed changes in topography reflect changes in the underlying structure of films at a molecular level, and that these in their turn will influence annealing behaviour.

Numerous studies of annealing in amorphous thin films, some of which were referred to in Chapter 1 have shown that experimentally determined activation energies for the transformation (E_{ann}) to a more ordered phase are very much a function of deposition temperature. Although there is a spread of only 0.03 eV ($\sim 3 \text{ kJ mole}^{-1}$) in the experimentally determined activation energies listed in Table (6.3) there is a definite trend toward higher activation energies as the optimum substrate temperature is approached. This trend is very convincingly shown in Figure (6.4), where the temperature T_m at which the maximum rate of change in conductivity occurred on annealing, for a given film, is plotted against substrate temperature. T_m is related to E_{ann} by equation (6.8), consequently there is a pronounced maximum in E_{ann} for a substrate temperature of 215K. Normally it would be unwise to have absolute confidence that such

small changes in annealing activation energy were meaningful. However, because of the discontinuous nature of the transition it was possible to locate it in each case to within a few degrees; a change in the rate of heating by an order of magnitude⁽³⁴⁾ is expected to cause a shift of only a few degrees in the experimental values of T_m . Since the heating rate used in the present tempering experiments was nominally $1^{\circ}\text{C min}^{-1}$ and was accurate to $\pm 10\%$, it appears probable that the trend observed in Figure (6.4) is a real effect. Furthermore, in view of the overwhelming evidence for an optimum at 215K, it is proposed that the value of $E_{\text{ann}}(T_m)$ is determined by the conditions prevailing during film deposition and particularly by substrate temperature.

In the absence of quantitative measurements of, for example, molecular relaxation rate and average film density, it is only possible to speculate about the cause of the maximum in E_{ann} . The conductivity/thickness data given in Table (6.5) and plotted in Figure (6.13) have a possible bearing on this question. Although the calculation of conductivity data was based upon film thickness, the visible absorption method used to determine the average thickness of films actually measured mass. Figure (6.13) shows that the mass of material deposited in unit time for precisely the same rate of deposition goes through a maximum at 210K to 215K. An alternative interpretation of this data is that this maximum in the mass of material deposited is due to a denser rather than a thicker deposit. This interpretation is supported by the SEM results of Chapter 4, Figures (4.13) and (4.14), which provide visual evidence that films

deposited at 210K to 215K have fewer grain boundaries and have dense, well packed structures compared to those produced at substrate temperature either side of this optimum.

Free Volume and its Effect on Diffusion

The influence of film density on the rate of rotational diffusion of molecules may be explained qualitatively by an analogy with the free volume model of diffusion, developed by Cohen and Turnbull⁽⁴⁵⁾ and others⁽⁴⁶⁾ in connection with molecular transport in liquids and glasses. The following equation (6.18) relates the diffusion coefficient D to the average free volume V_f

$$D = g a^* u \exp \left| -yV^*/\bar{V}_f \right| \quad (6.18)$$

where $\bar{V}_f = V_f/N$, V_f is the total free volume and N the number of molecules, g is a geometric factor, $U = \left(\frac{3kT}{m}\right)^{1/2}$ and y is a numerical factor with a value of between $1/2$ and 1, introduced to correct for overlap of free volume. V^* is a critical volume, such that $D(V)$ is zero unless V exceeds V^* . $\bar{V}_f$ increases as a function of temperature according to

$$\bar{V}_f = \alpha \bar{V}_m (T - T_0), \quad (6.19)$$

where α is the mean coefficient of thermal expansion and $\bar{V}_m$ is the mean molecular volume and T_0 is the temperature at which the free volume disappears. T_0 may be identified approximately with the glass transition temperature T_g , which for simple van der Waals liquids is usually $1/4$ to $1/3$ of the absolute normal boiling. In Chapter 3 it was pointed out that the optimum temperature may in fact correspond to T_g in hydrocarbon films and this may also be the case for (TTF)(TCNQ). Infrared experiments certainly establish that molecular rotation does not begin until near T_{opt} , in films of (TTF)(TCNQ) deposited below 190K, which were also shown to have a disordered structure.

At constant pressure, combining equations (6.18) and (6.19) gives

$$D = g a^* u \exp \left| - T V^* / \alpha \bar{V}_m (T - T_0) \right| \quad (6.20)$$

It is apparent from equation (6.20) that an increase in average film density, which corresponds to a decrease in $\bar{V}_m$, will cause a reduction in the diffusion coefficient D , for a given temperature. Thus, when annealing, the film with the greatest density should undergo the transition with the highest activation energy, other things being equal.

Comparing equations (6.11) and (6.20) it is possible to write

$$\left| T V^* / \alpha \bar{V}_m (T - T_0) \right| = \frac{E_{\text{exp}}}{kT} \quad (6.21)$$

If T_0 is taken to be 215K and a transition temperature of 301K for the film deposited at 215K is used, then from Table (6.3), E_{exp} for this film is 0.384 eV. An approximate value for α of $1.4 \times 10^{-4} \text{ cm K}^{-1}$ was obtained from the b-axis thermal expansion measurements of Schaffer⁽⁴⁷⁾. Substituting into (6.21) gives a value of 0.18 for the term $T \frac{V^*}{\bar{V}_m}$. Turnbull and Cohen⁽⁴⁵⁾ obtained estimates for this term of the order of 0.5 to 0.75 for several simple liquids. The free volume model predicts that $T V^*$ must be near the molar volume, however, their model was derived assuming translational rather than rotational diffusion and, as pointed out earlier, it is probable that in the case of (TTF) (TCNQ) molecular anisotropy plays an important part in determining the preferred axis of re-orientation. In-plane molecular rotation for example might require a significantly smaller re-distribution of free volume than rotation about the other two principal axis'.

The Formation of Unstable Films

When discussing the process of nucleation within metastable films, in order to explain the absence of a continuous transition, the metastable state was considered to consist of a single component, a sort of orientationally disordered precursor state. The formation of this precursor state within a film with a disordered structure, must of course involve segregation of TTF and TCNQ molecules into separate 1-dimensional stacks, which clearly involves molecular diffusion. In a binary solution at constant temperature and pressure the diffusion coefficient (D) of a component mole fraction x and mobility μ_x may be written as⁽⁴⁸⁾

$$D = \frac{\mu_x}{N_A} x(1 - x) \frac{\partial^2 G}{\partial x^2} \quad (6.22)$$

Since both μ_x and N_A are positive the sign of D is determined by $\frac{\partial^2 G}{\partial x^2}$. When $\frac{\partial^2 G}{\partial x^2} > 0$ then D is positive and diffusion can only take place in the direction of the concentration gradient. This corresponds to the metastable situation since small composition fluctuation decrease with time due to the barrier to nucleation. On the other hand, when $\frac{\partial^2 G}{\partial x^2} < 0$, from equation (6.22), D is positive and diffusion can occur from regions of low to those of high concentration. In this event the nucleation barrier to growth of the new phase is removed, and in the presence of nuclei all fluctuations result in the decomposition of the parent phase. In the absence of nuclei it is known⁽⁴⁹⁾ that only those fluctuations above a critical size are stable, even when $\frac{\partial^2 G}{\partial x^2} < 0$, because of the need to take into account the strain energy generated at the interface between the parent and precipitating phase.

Once nuclei are formed within a condensed film, continued crystallisation can occur by either of two competing processes, i.e. growth of those nucleation centres already present, or secondary

nucleation. This is the situation envisaged for all films deposited above 235K and for some of those formed between 220K and 235K. It is proposed that nuclei of the crystalline phase of (TTF)(TCNQ) are produced during the deposition stage, which removes the necessity of nucleus formation within the condensed film. The proposal is consistent with the view outlined in Chapter 1 that nucleation occurs more readily during deposition as a result of a reduced activation energy for diffusion. Because the activation energy associated with the barrier to nucleation is removed the growth rate of the crystalline phase is then determined simply by the activation energy for diffusion within the condensed phase, at least at low temperatures. This explains why, in these films, changes in both the resistivity, Figure (6.5) and the infrared absorption spectra, Figure (5.20) begin immediately above the deposition temperature. However, it poses the question; If diffusion can occur in these films, why does it not occur at the same temperature in metastable films deposited below 220K?

In order to answer this question it must be remembered that infrared spectroscopy showed that molecular relaxation occurs to give the metastable state when films deposited below 190K were annealed above about 200K, but that further relaxation was prevented until near room temperature. This implies that once molecules have achieved a minimum energy configuration with respect to nearest neighbours, and SRO is established, further movement requires the destruction of this SRO, which involves an additional activation energy. In the case of films deposited above 220K, however, the intercrystalline regions presumably contain molecules in a disordered

phase which must undergo relaxation into a more stable configuration, otherwise they would be lost from the film by re-evaporation. As already discussed in Chapter 5, molecular relaxation is likely to occur with a distribution of activation energies which is determined by the existence of a spectrum of local intermolecular interactions. Thus molecules located close to nuclei may be incorporated with low activation energy and undergo relaxation immediately above the film deposition temperature. The crystalline phase will continue to extend itself in this way until, at sufficiently high temperatures, secondary nucleation can occur within the bulk of the film. This activation energy distribution distinguishes films which initially contain nuclei and are unstable from those which do not and are, therefore, metastable.

Although the annealing results for films deposited above 235K can be satisfactorily explained within the framework of the above arguments, the behaviour of those prepared between 220K and 235K needs further clarification.

The Boundary Region between 220K and 235K

The observation of both types of annealing behaviour in this region is not entirely unexpected since it evidently defines the boundary between two states of different thermodynamic stability. As such, the formation of nuclei may be particularly sensitive to changes in the experimental conditions employed during film formation. It does not, however, explain the marked reduction in T_m , which is apparent in Figure (6.4), for films deposited between 215K and 235K. A similar reduction in T_m was also observed in the data obtained from infrared annealing experiments, (Figure 5.20), It appears to be associated with minima in both the mass of material deposited and the resistivity, which are a prominent feature of the results obtained

from annealed films, shown in Figure (6.3). These minima apparently have a common cause, which is considered in detail in Section (6.3.2). Their observation indicates that films formed within this substrate temperature regime are disordered in the as-deposited state with a maximum in the amount of disorder occurring between 220 and 230K. This increased disorder is thought to be associated with intergranular regions of the film and is responsible for the observed decrease in the activation energy for the annealing process E_{ann} and also for the wider distribution in the magnitude of E_{ann} , apparent in the F_0 vs E plot of Figure (6.10). Further discussion of this point is deferred until Section (6.3.2).

Before proceeding to a discussion of the electrical measurements obtained from the study of annealed films, it is worthwhile summarising the more important conclusions derived from annealing experiments.

- a) Below a deposition temperature of 235K nucleation of the conducting form of the complex gives way to formation of a metastable SRO phase between 220K and 190K.
- b) Growth of the normal crystalline phase of the complex within this metastable phase involves a first order transition and does not take place until near room temperature.
- c) The metastable $\rightarrow$ LRO transformation took place with a single activation energy which was a maximum for films deposited in the vicinity of T_{opt} , because of their higher average density.
- d) Films deposited above 220K were spontaneously unstable toward the formation of the conducting phase. Growth of the crystalline phase within these films occurred with a distribution of activation energies.

6.3.2 The Electrical Properties of Annealed Samples

Temperature Dependence of the Resistivity (TDR)

The results of the present study of the electrical properties of annealed films differ in one important respect from those reported previously. For example, Chen and Schectman⁽²²⁾ and Reinhardt et al.⁽²³⁾ found that the resistance of their films was exponentially dependent upon temperature and that their data were well fitted by an equation of the form of equation (6.10).

$$\rho(T) = \rho_0 \exp \left(-\frac{E_{\text{cond}}}{kT} \right)$$

or

$$\ln \rho(T) = \ln \rho_0 + \left(-\frac{E_{\text{cond}}}{kT} \right) \quad (6.10)$$

Although this simple behaviour was displayed by those samples included in Figure (6.11), a more complex TDR was observed in the case of films deposited between 197K and 230K, Figure (6.12). The $\log \rho$ vs $1/T$ data for these latter films exhibited non-linear behaviour, particularly at temperatures above 200K, and in several cases had a negative temperature coefficient of resistance. Moreover, the slope of the TDR for those films deposited in the vicinity of 210K also apparently decreased at low temperatures indicating a reduced activation energy for conduction (E_{cond}). Other things being equal, a reduction in E_{cond} should have resulted in a smaller resistivity. However, from Figure (6.12), it appears that the opposite is true, i.e. there is a maximum in film resistivity coincident with a deposition temperature of 210 - 215K.

The values of E_{cond} and ρ_0 , in Table (6.4), which were determined from the experimental data of Figure (6.11), also support the observation that it is the magnitude of the resistivity and not the

activation energy which is sensitive to deposition temperature. Furthermore, the results of Chaudari⁽²¹⁾ et al. show that E_{cond} is constant at (0.02 eV) i.e. independent of film structure when measured in the linear region at low temperatures, even for films showing a negative temperature coefficient of resistance. Had the measurement of conductivity in the present study been extended to low temperatures it is possible that linear behaviour would also have been observed for the data plotted in Figure (6.12). Others referred to earlier have also measured E_{cond} for films of (TTF) (TCNQ) produced over a wide range of substrate temperatures and find values of between 0.01 and 0.02 eV, again suggesting that activation energy for conduction is insensitive to film structure.

Grain Boundary Scattering

Activated behaviour of the type exemplified in Figure (6.11) is commonly observed in thin films and polycrystalline samples of semiconductors and is usually associated with scattering of charge carriers within grain boundary regions.⁽²⁹⁾ A grain boundary scattering mechanism as the origin of E_{cond} appears to be appropriate in the case of (TTF) (TCNQ) films, because measurements on single crystals have shown that conductivity is metallic-like along the three principal axis of a crystal. On the other hand, if grain boundary scattering is responsible for the activated behaviour observed it is difficult to appreciate, in view of the marked effect that substrate temperature has on film topography, why the value of E_{cond} does not also change. One possibility is that the energy barrier associated with grain boundary scattering is the result of multiple trapping⁽⁵⁰⁾ at molecular sites within the barrier region, rather than a simple direct thermal activation of carriers between neighbouring crystals

Such a mechanism has been proposed⁽⁵¹⁾ to explain the insensitivity of the activation energy for the mobility of carriers in anthracene to naphthacene impurities.

Further evidence for a 'multiple' trapping mechanism was obtained from the stepwise annealing of a film deposited at 235K. The results of Figure (6.6) show that the value of E_{cond} remained constant on annealing despite a 35-fold decrease in film resistivity. Since this increase conductivity has been shown to be associated with a transition from a disordered to a more ordered state it may be considered to be analogous to the solid to liquid transition of compounds such as benzene. In this latter case E_{cond} was found⁽⁵¹⁾ to remain constant on melting, although the resistivity decreased by a factor of ten. It was concluded that E_{cond} was associated with the nature of molecules i.e. short range order of the system, rather their arrangement or the structure of the system. It is proposed, therefore, that in (TTF)(TCNQ) films, the activation energy for conduction arises as a result of thermal activation over the potential energy barrier between molecules rather than that between crystallites. If correct this proposal implies that the perceived change in the E_{cond} is only apparent rather than a real effect. Since VBR considered that the OSTE may be associated with a minimum in the grain boundary scattering coefficient, it is important to determine the reason for the anomalous behaviour of (TTF)(TCNQ) films deposited in the vicinity of 210 - 215K.

Model for Conduction in Polycrystalline Films of (TTF)(TCNQ)

Since the value of the activation energy determined from Figure (6.11) was approximately 0.013 eV and the value of kT at room temperature is 0.026 eV, it is important to consider if a simple relationship, such as equation (6.10), is appropriate for films of

(TTF) (TCNQ). Using Maxwell-Boltzmann statistics the number of carriers (n) excited over the activation barrier is given by⁽⁵²⁾

$$n = (2\pi m_e kT/\hbar^2)^{3/2} \exp \{ (E_f - E_c)/kT \} \quad (6.23)$$

where m_e is the effective electron mass and $E_f - E_c$ are the energies of the Fermi level and the bottom of the conduction band, respectively. In order for Maxwell-Boltzmann statistics to be applicable, $E_f - E_c > 5kT$. This is clearly not the case for (TTF) (TCNQ) films prepared in the present study, and an accurate determination of n would normally require the use of Fermi-Dirac statistics.⁽⁵³⁾ In which case,

$$n = \int_{E_c}^{\infty} \frac{G(E) (E - E_c)^{1/2} dE}{1 + \exp \{ (E_c - E_f)/kT \}}$$

where $G(E) = A(E - E_c)^{1/2}$ and $A = (4\pi/h^3) (2m_e)^{1/2}$. As a consequence, at sufficiently high temperature ($kT \sim (E_f - E_c)$) the energy gap $E_g = (E_c - E_v)$ is itself a linear function of temperature for most materials, and varies according to the equation

$$E_g = E_g^0 - \alpha T$$

where E_g^0 is the value of E_g at $T \rightarrow 0$ and α is a constant.

A reduction of the energy barrier associated with grain boundaries is a possible cause of the observed change from a positive to a negative temperature coefficient of resistance with increasing temperature. However, the measured activation energy of 0.013 eV also applies to films which show a well defined linear $\log_{10}$ vs $1/T$ plot. This suggests that the reduction in the activation barrier is not sufficient to cause the intrinsic properties of crystallites to dominate the conduction process in these films.

Departure from linear behaviour was observed but only around room temperature, for those films included in Figure (6.11) equation (6.10) would thus appear to be reasonable. An alternative explanation for non-linear behaviour is that, the barrier to conduction, introduced by grain boundaries, may be associated with an activated charge carrier mobility, rather than an activated charge carrier concentration, since

$$\sigma = n e \mu$$

where μ is the charge carrier mobility.

In the absence of impurities the mobility of many organic molecular solids depends on temperature as T^{-n} , where $0 < n < 3$. In such cases it is the lattice vibrations which limit the mean free time between collisions (τ). Mobility is related to τ by the equation (6.24)

$$\mu = e \tau / m^* \quad (6.24)$$

Imperfections and impurities can also dominate carrier scattering and if present in reasonable concentrations, scattering theory⁽⁵⁴⁾ gives

$$\tau \propto m^* E^{3/2}$$

where E is the energy of an electron (or hole). Consequently for charged impurity scattering τ varies as $T^{3/2}$, and since the temperature dependence of τ will determine the way in which carrier mobility varies with temperature, μ will scale as T^m , where m ($-3 \leq m \leq 3/2$) is dependent on scattering mechanism. Additional factors such as phonon assisted transport may also make a contribution, causing a reduction in the temperature dependence of μ from its value of $T^{3/2}$ for lattice scattering at higher temperatures. A detailed review of the temperature dependence of charge carrier mobility in molecular crystals is given in reference (55), from which it transpires that any one, or indeed,

a combination of a number of scattering mechanisms may be operating in the films of (TTF) (TCNQ) under examination.

Neglecting surface processes, the total cross section for carrier scattering in polycrystalline films is given by the sum of the reciprocal mean free paths⁽⁵⁶⁾

$$\frac{1}{\tau_{\text{obs}}} = \frac{1}{\tau_g} + \frac{1}{\tau_{gb}}$$

where τ_g and τ_{gb} are the mean free paths between collisions within crystallites and grain boundary regions, respectively. Therefore, in order to explain the departure from linearity in the $\log \rho$ vs $\frac{1}{T}$ plots, for films deposited near the optimum substrate temperature, it is necessary to define expressions for the temperature dependence of both τ_g and τ_{gb} . Since $\frac{1}{\rho} = n e \mu$, the temperature dependence of n must also be determined to give the complete expression for ρ . Alternatively as the total concentration of charge carriers is derived solely from within the crystalline regions of a film, it is unnecessary to derive separate theoretical expressions for n or τ_{grain} , since the temperature dependence of the resistance of grains can be approximated by experimental data obtained from single crystal measurements. This was the procedure adopted in developing a model for conduction in the (TTF) (TCNQ) films examined in the present study.

As mobility is determined by scattering, it is usually assumed that different scattering modes are additive,⁽⁵⁷⁾ so that

$$\frac{1}{\mu} = \frac{1}{\mu_g} + \frac{1}{\mu_{gb}}$$

where μ_g and μ_{gb} are carrier mobilities within the grain and grain boundary regions, respectively. Since $\sigma = n e \mu$

$$\frac{1}{\sigma_{\text{obs}}} = \frac{1}{n_g e \mu_g} + \frac{1}{n_{gb} e \mu_{gb}}$$

the measured film resistance will be given by the sum of the resistances of both regions of the film i.e.

$$\rho_{\text{obs}} = \rho_g + \rho_{\text{gb}} \quad (6.25)$$

It should be possible, therefore, to reproduce the experimental TDR of films by superimposing the grain boundary contribution to the TDR upon the intrinsic TDR of a crystal.

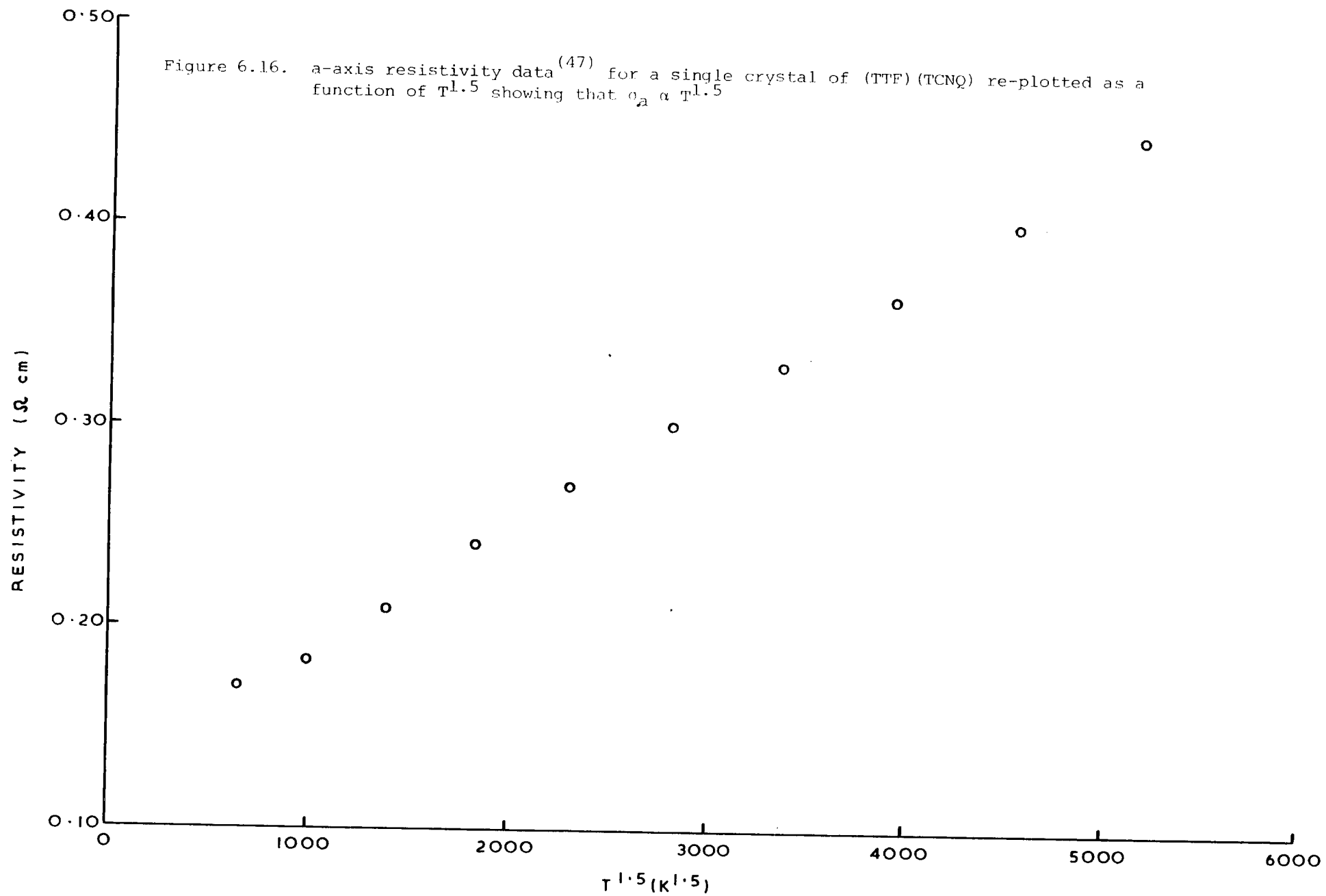
Previous measurements⁽⁵⁸⁾ have shown that the temperature dependence of the intrinsic resistivity (ρ_g) of a large number of (TTF) (TCNQ) crystals is fitted by a simple relationship of the form⁽⁶¹⁾

$$\rho_g = \rho_2 + \rho_1 T^\alpha \quad (6.26)$$

where ρ_1 and α are sample independent constants and ρ_2 is a sample dependent constant. The exponent α is a function of the crystal direction and is 2.33 for conduction along the b-axis.⁽⁵⁸⁾ A value for α of 1.5 for conduction along the a-axis was obtained by replotting a-axis resistivity data taken from the literature⁽⁴⁷⁾ as shown in Figure (6.16) from which it can be seen that ρ vs $T^{3/2}$ is well fitted to a straight line between 75K and 325K. The measured value of resistivity at a given temperature will thus depend upon the average crystallite orientation within a film.

In the region of the optimum substrate temperature for (TTF) (TCNQ) (210-214K) the structural evidence discussed in Section 4.3 is consistent with an alignment of the b-axis of the crystallites perpendicular to the plane of the film, with the a and c axis' parallel. Conduction in the plane for films deposited at this temperature should, therefore, be dominated by the resistance in the direction of the 'a' and 'c' axis' of individual crystallites. In a film consisting of crystallites the film resistivity, to a first

Figure 6.16. a-axis resistivity data⁽⁴⁷⁾ for a single crystal of (TTF)(TCNQ) re-plotted as a function of $T^{1.5}$ showing that $\rho_a \propto T^{1.5}$



approximation the grain resistivity (ρ_g) will be given by addition of the individual a and c axis resistivities.

$$\rho_g = (\rho_a + \rho_c) 0.5$$

Since ρ_a is approximately $10 \times \rho_c$, ρ_g will be dominated by former and should exhibit a temperature dependence similar to that of the 'a' axis i.e. $T^{3/2}$.

If conduction within grain boundary regions of the film is assumed to be limited by a thermal activation of carriers over a barrier of height E_b , then the grain boundary resistivity is given by,

$$\rho_{gb} = \rho_0 \exp \frac{E_b}{kT} \quad (6.27)$$

where ρ_0 is the value of ρ as $\frac{1}{T} \rightarrow 0$. The use of this expression is suggested by the simple exponential dependence upon temperature for the resistivity of films given in Figure (6.11).

Combining equations (6.25), (6.26) and (6.27) and setting $\alpha = 3/2$ gives

$$\rho_{obs} = (\rho_2 + \rho_1 T^{3/2}) + (\rho_0 \exp^{E_b/kT}) \quad (6.28)$$

An equation of similar form was used by Feldman⁽⁵⁹⁾ to describe conduction in thin metal films. At low temperature ($kT \leq E_b$) the term associated with the activation of carriers across grain boundaries predominates but gives way to the normal temperature coefficient of crystalline material at high temperatures i.e. $kT \gg E_b$. Since both terms exhibit opposite temperature dependent behaviour a maximum in the conductivity is expected.

A Comparison with the Experimental Results

Equation (6.28) was used to simulate the TDR of (TTF) (TCNQ) films for a series of values of activation energy E_{gb} between 0.0025 and 0.025 eV, and values of ρ_0 from 0.01 to 0.5 ohm cm. The values of ρ_g were obtained from the temperature dependence of the a-axis single crystal conductivity data plotted in Figure (6.16), which was derived from data in the thesis of Schafer.⁽⁴⁷⁾ An APL⁽⁶⁰⁾ computer routine was used to produce a series of curves of the logarithm of the calculated film resistivity as a function the reciprocal of the absolute temperature. The data reproduced in Figures (6.17) and (6.18), are respectively; the effect of changing E_b whilst keeping ρ_∞ constant at 0.1 ohm cm; (6.17) and changing ρ_∞ whilst keeping E_b constant at 0.01 eV (6.18).

A change in either E_{gb} or ρ_0 caused the shape of the $\log \rho$ vs $\frac{1}{T}$ plot to change, making it impossible to assign a unique value to either E_{gb} or ρ_0 for any of the films examined which did not show straight line behaviour. However, the simple model does provide a reasonable, qualitative description of the observed electrical behaviour, in that the departure from straight line behaviour becomes more pronounced as the magnitude of E_{gb} decreases. At a value of E_{gb} similar to that observed experimentally the model also correctly predicts that the resistivity will exhibit a minimum, which occurs at a temperature which varies with activation energy. A theoretical curve for a value of ρ_0 of 0.1 ohm cm and E_b equal to 0.0125 eV is replotted in Figure (6.12) for comparison with the experimental results. In view of the assumptions made, there is excellent agreement

Figure 6.17. Simulated resistivity curves obtained using equation (6.28) showing the effect of changing E_D whilst keeping ρ_w constant at 0.1 ohm.cm.

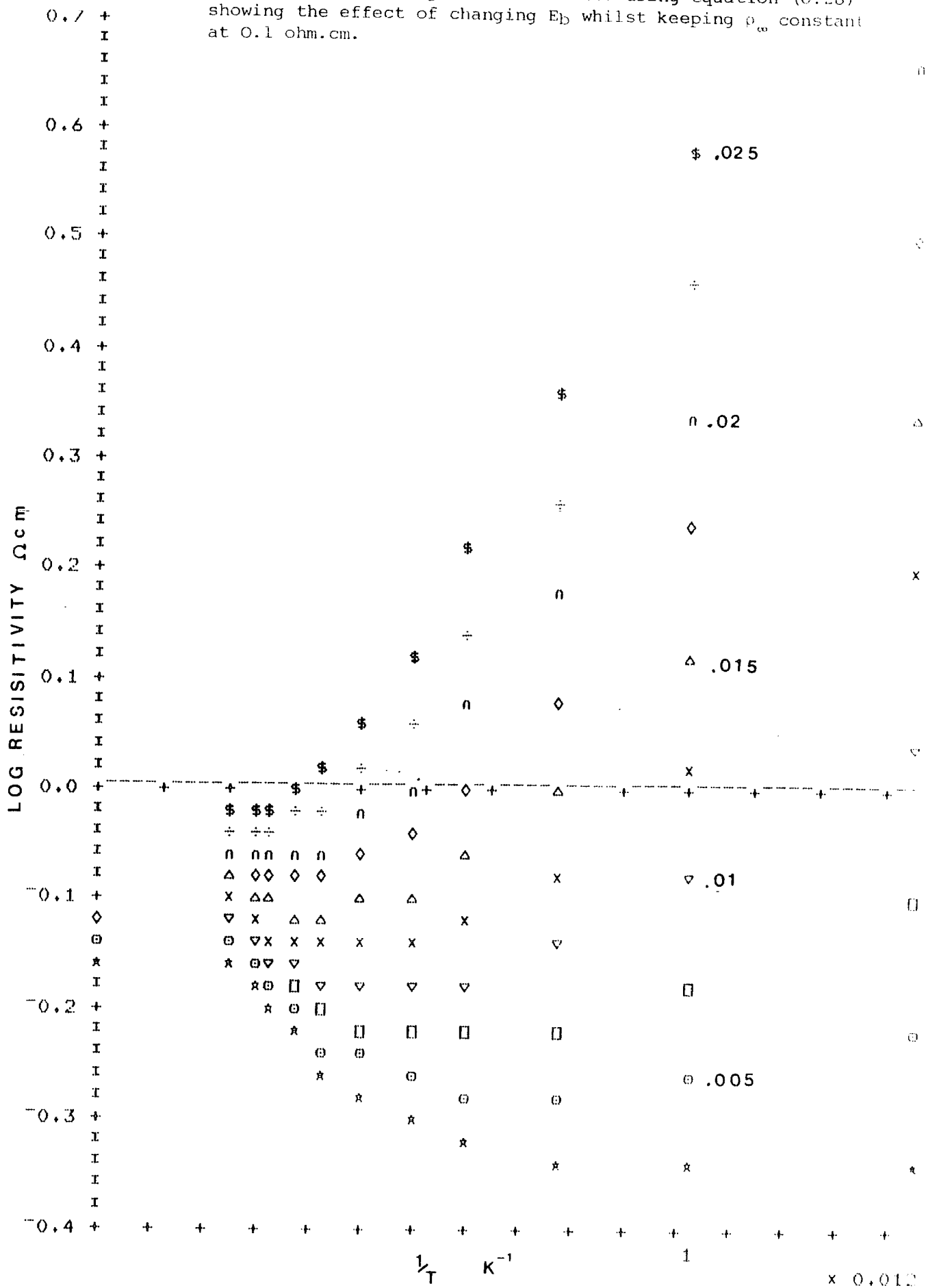
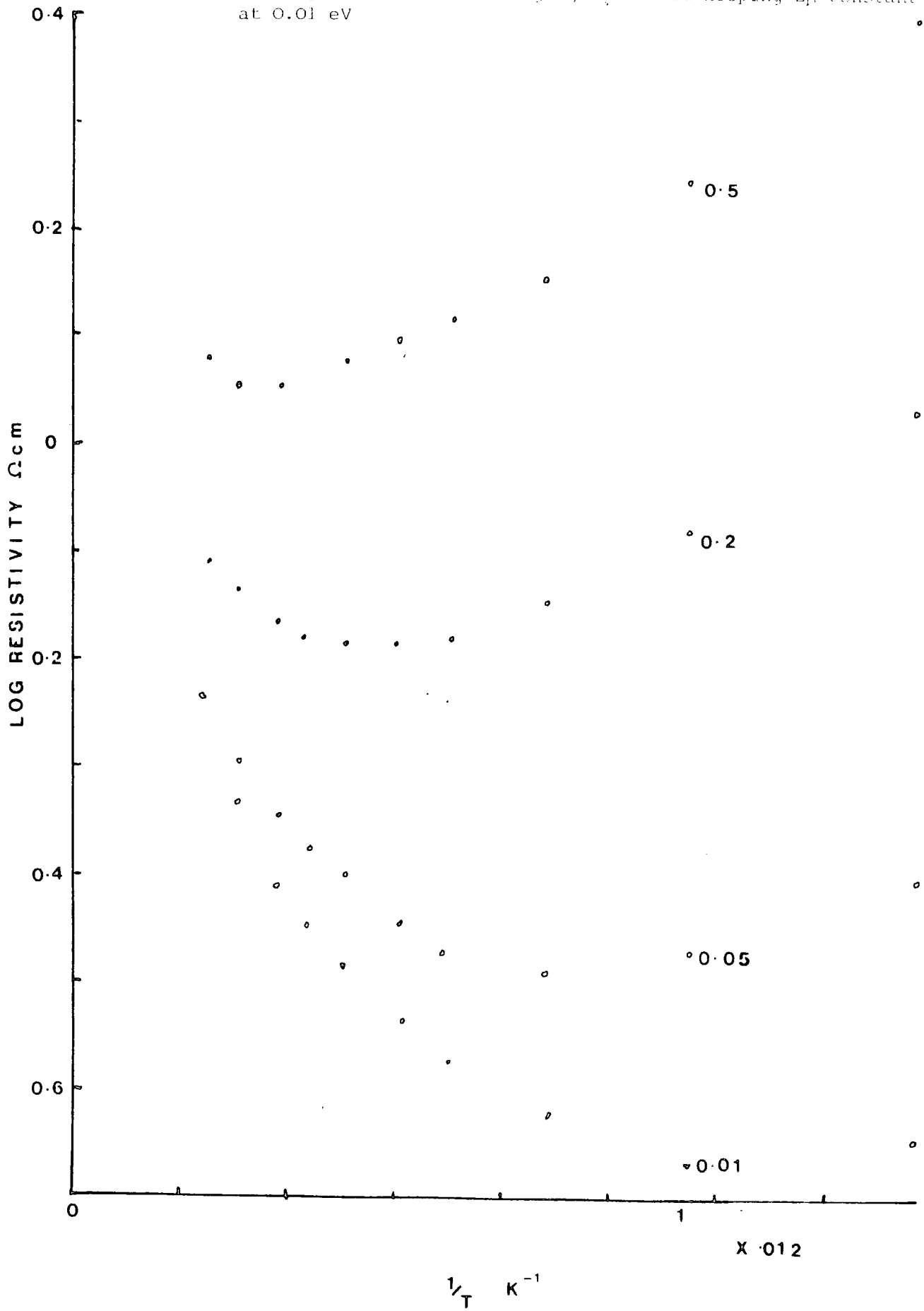


Figure 6.18. Simulated resistivity curves obtained using equation (6.28) showing the effect of changing μ_v whilst keeping E_F constant at 0.01 eV



with the experimental curves for the two films deposited at substrate temperatures of 210 and 214K. In addition to reproducing a curve of very similar shape the model also successfully predicts the actual magnitude of the measured film resistivity. The predicted resistivity minimum, however, occurs 25K lower than the observed minimum and the fit to the experimental data is less satisfactory at high temperatures. A better fit might have been achieved had values of E_{gb} intermediate between .0125 eV and .01 eV been used to simulate film behaviour. However, no attempt was made to find the optimum value of E_{gb} .

At substrate temperatures away from T_{opt} agreement with the experimental results is not as good, the main difference being that the resistivity was significantly lower than predicted by Equation (6.28). Also, a linear dependence of the experimental $\log \rho_{obs}$ vs $1/T$ data was observed over a much wider temperature range than was expected from the model results. The latter exhibited curvature below room temperature, even for activation energies as high as 0.025 eV, and particularly at lower values of ρ_0 . These differences probably arise because the a-axis conductivity doesn't properly reflect the intrinsic resistivity of crystallites which make up the film, i.e. there will also be a contribution from the b and c-axis of crystallites to the in-plane resistivity of the film.

Whatever the orientation of crystallites the exponential temperature dependence of the resistivity of films deposited at substrate temperatures away from T_{opt} is consistent with a grain boundary dominated conduction process. The model used also indicates that the value of E_b for films deposited at T_{opt} (0.0125 eV) is virtually the same as for those prepared at other substrate temperatures,

which suggests that the pronounced curvature observed is primarily due to a crystallite orientation effect and not to a reduction in (E_{gb}) .

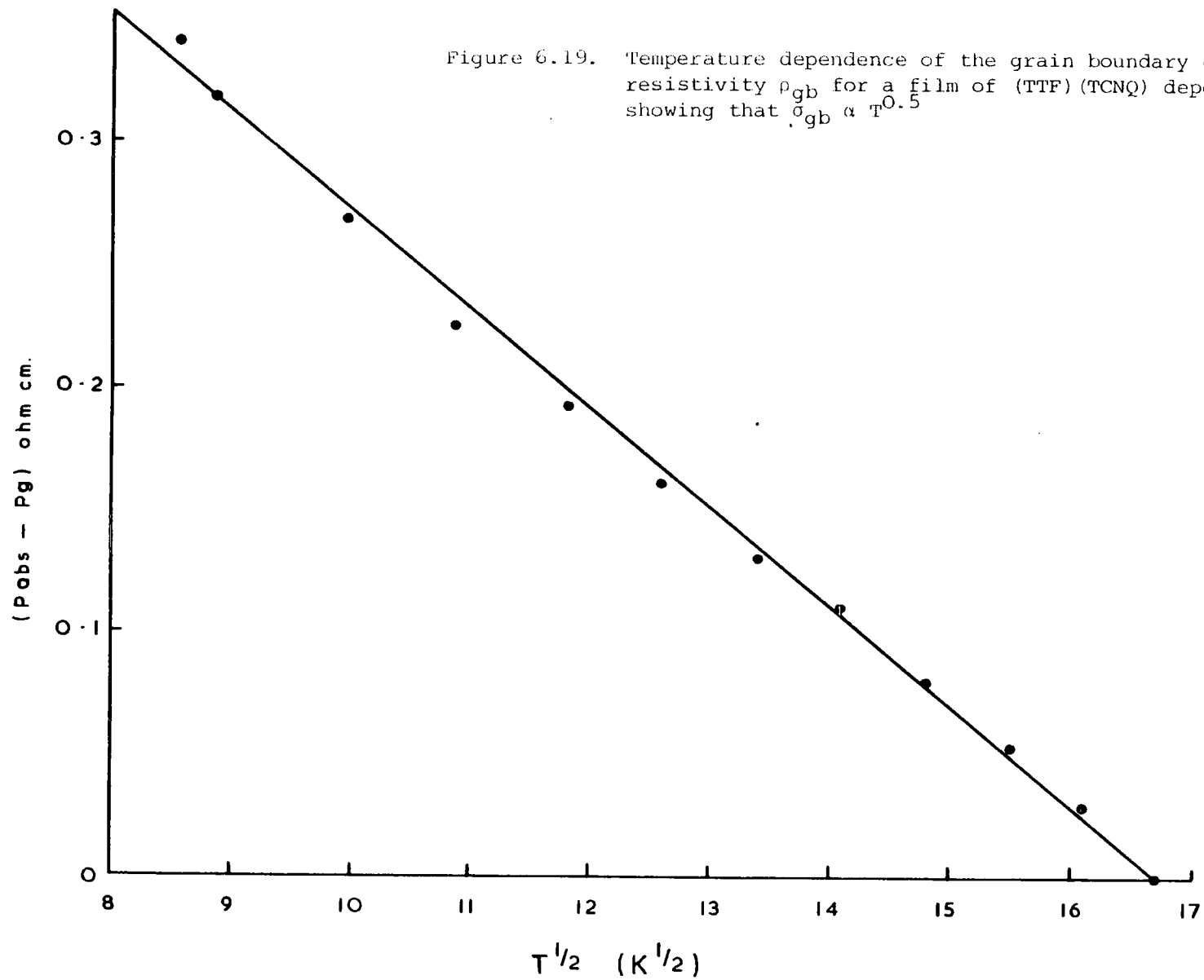
If the assumption that ρ_g and ρ_{gb} are the only two contributions to ρ_{obs} is correct, and Equation (6.28) is valid, then

$$(\rho_{obs} - \rho_g) = \rho_{gb}$$

and $\log(\rho_{obs} - \rho_g)$ vs $1/T$ should give a straight line of slope E_{gb}/K , where E_{gb} is the barrier activation energy. This was found not to be the case for films deposited at T_{opt} , when ρ_g was taken to be the temperature dependent 'a'-axis resistivity. However, a straight line fit was obtained for $1/(\rho_{obs} - \rho_g) = \sigma_{gb}$ vs $T^{0.5}$ over a wide temperature range (70K - 300K), as shown in Figure (6.19). This suggests that the assumed activated process is not appropriate for film deposited at T_{opt} . As discussed earlier films deposited at T_{opt} contain the largest a-axis contribution and should have provided the clearest test of the validity of Equation (6.28).

From the earlier discussion of the temperature dependence of charge carrier mobilities, a $T^{0.5}$ result suggests the possibility of a phonon assisted transport mechanism in the grain boundary region. Viljan⁽⁶¹⁾, for example has shown that mobility in the 'c' direction for anthracene is determined by an electron transfer integral which is sensitive to rotations in the molecular plane. In this case the phonon assisted current was large and increased with temperature as $T^{1.3}$.

A similar approach to that outlined above was adopted by Epstein et al.,⁽⁵⁸⁾ in their analysis of the temperature dependence



of the intrinsic conductivity of a number of TCNQ salts, including the N methyl phenazinium (NMP) and quinolinium compounds. They assumed a temperature dependent charge carrier mobility, $\mu \propto T^{-\alpha}$ and an energy gap 2Δ associated with the generation of charge carriers. The concentration of charge carriers (n) at temperature T being given by the usual expression

$$n \propto \exp (-\Delta/T)$$

Since $\sigma = ne\mu$, they obtained the following expression

$$\sigma(T) = A T^{-\alpha} \exp(-\Delta/T) \quad (6.29)$$

Where A is a constant. Equation (6.29) predicts a maximum in the conductivity at $T_m = \Delta/\alpha$, since μ is a monotonically decreasing function of temperature while n is a monotonically increasing function of temperature.

Epstein et al. interpreted their results on the basis of a scattering mechanism involving optical phonons which they associated with the totally symmetric (a_g) or intramolecular modes of TCNQ. Similar ideas were applied to scattering within crystals of (TTF)(TCNQ) and may also be appropriate to scattering of charge carriers by molecules of TTF and TCNQ present in grain boundary regions of films. The infrared results of Section (5.2.1) certainly established the existence of strong coupling to the a_g vibrational modes of charge transfer dimer species, in as deposited films of the complex, prepared below 190K. However, values of the exponent α were found by Epstein et al. to be much larger (2 to 4) and opposite in sign to that obtained for grain boundary scattering (T_m^{-1}) in films deposited near T_{opt} . It is possible that the observed temperature dependence of

ρ_{gb} i.e. $\rho_{gb} \propto T^{\frac{1}{2}}$ may be related to an activated carrier generation mechanism.

The 'a'-axis conductivity scales as $T^{-3/2}$ for (TTF)(TCNQ), and the number of charge carriers per unit chain length for a 1-d tight binding band is given by, ⁽⁶¹⁾

$$n = C T^{\frac{1}{2}} \exp \{ (E_f - E_c) / kT \} \quad (6.30)$$

where $C = (2/a) (K_B / \pi \epsilon_0)^{\frac{1}{2}}$, E_f the Fermi energy and E_c that of the conduction band. a is the spacing between adjacent molecules along the b axis of a 1-d stack. Since $\sigma = n e \mu \propto T^{-3/2}$ and $\mu \propto T^m$, the following expression may be written for σ ,

$$\sigma \propto \{ T^{-3/2} = T^{\frac{1}{2}} \exp \{ (E_f - E_c) / kT \} \cdot T^m \} \quad (6.31)$$

In (TTF)(TCNQ) above 60K $E_f - E_c = 0$, ⁽⁵⁴⁾ therefore Equation (6.31) reduces to

$$\sigma \propto \{ T^{\frac{1}{2}}, T^m \text{ and } T^{-3/2} \}$$

and $m = -2$.

Now, since it was shown that for films deposited at T_{opt} ,

$$\sigma_{gb} \propto T^{\frac{1}{2}}$$

if carrier generation occurs within crystallites rather than grain boundary regions, we can also write

$$\sigma_{gb} \propto \{ T^{\frac{1}{2}} = T^{\frac{1}{2}} \exp \{ (E_f - E_c) / kT \} T^n \} \quad (6.32)$$

and therefore,

$$\{ T^{\frac{1}{2}} = T^{\frac{1}{2}} \cdot T^n \}$$

If as before $(E_f - E_c)$ is assumed to be zero then

$$n = 0$$

This result implies that in films deposited at T_{opt} the grain boundary contribution to the resistivity is associated with the $T^{\frac{1}{2}}$ factor required for the generation of charge carriers, and that the mobility in the grain boundary region is essentially temperature independent. Such weakly temperature dependent mobilities have been reported for several aromatic hydrocarbons including naphthalene.⁽⁶²⁾ and p-terphenyl⁽⁶³⁾ and are thought to be associated with phonon assisted currents which cancel out the contribution due to acoustic (lattice) modes.

It is also possible, indeed probable, that a $\sigma_{gb} \propto T^{\frac{1}{2}}$ dependence is entirely fortuitous and is the result of an inadequate assumption that conduction in the film plane is dominated by the 'a axis' resistivity. Clearly a larger contribution from the higher conductivity b or c axis introduces different values of ρ_0 and α in equation (6.28), and in the model would cause a reduction in the importance of carrier scattering within grains relative to that within grain boundary regions of a film. On balance the experimental results are consistent with this latter suggestion and support the view that conduction in the barrier region is exponentially dependent, irrespective of film deposition temperature.

The Effect of Substrate Temperature upon Film Resistivity

The magnitude of the resistivity of films provides additional information about the orientation of crystallites within deposits and also about the mechanism of growth. The temperature dependence of the conductivity in the direction of the three principle axis' was given in Figure 6.1. The room temperature conductivities of the a, b and c axis, scale approximately as 1 : 500 : 10. The analysis of Chen and Schectmann,⁽²²⁾ presented in the introduction to this

Chapter established that the lowest rather than the highest conductivity axis determines resistance, because current is carried in series by the grains within a film. In the absence of grain boundaries the value of the in plane film resistivity is obtained using equation (6.33)

$$\frac{1}{\rho_{\text{obs}}} = \sigma_{\text{film}} = 1/\sigma_x + 1/\sigma_y = \frac{\sigma_x \times \sigma_y}{\sigma_x + \sigma_y} \quad (6.33)$$

where x and y denote the crystal direction. This equation assumes a particular crystallite orientation, with one of the principle axis directed out of the plane, the other two axis being equally distributed in the film plane. The following conductivity values were obtained for the orientations shown, using the ratio of the room temperature conductivities given above, assuming a crystal aspect ratio of unity and a random distribution of crystals in the film plane

Orientation		$\sigma_{\text{RT}} = (\Omega \text{ cm})^{-1}$
$\perp$	=	
a	bc	~ 10
b	ac	~ 1
c	ab	~ 1

These figures will of course increase as the crystallite aspect ratio increases in favour of the higher conductivity axis.

From the measured in plane conductivity it should be possible to distinguish between crystallite orientations in which the a axis is perpendicular or parallel to the surface of the film. Neglecting the crystallite boundary contribution to the resistivity should not significantly alter the relative values of σ_{RT} because equation (6.34)

shows that ρ_{gb} is directly related to ρ_g , if the mobility of carriers in the grain boundary region (μ_{gb}) is insensitive to deposition temperature.

$$\rho_{gb} = \frac{1}{n_g \mu_{gb} e} \quad (6.34)$$

The value of ρ at 200K is tabulated, along with the measured thickness, for a number of films deposited at the substrate temperature indicated in column 1 of Table (6.5). Data were obtained for films previously annealed at 300K and the measurement temperature of 200K was arbitrarily chosen. Film resistivity is plotted as a function of the substrate temperature during film deposition (curve b) in Figure (6.13). There is a remarkable correlation between film resistivity and thickness, (curve a), i.e. the resistivity increases with film thickness. Other things being equal film resistivity should of course remain constant with increasing film thickness. The two resistivity maxima at 235K and 210K coincide exactly with the maxima in film thickness. There is also a resistivity minimum between 220K and 230K which corresponds to the minimum in film thickness.

It is known⁽²¹⁾ from X-ray data that (TTF)(TCNQ) crystallites are oriented with their OOn i.e. their ab planes parallel to the plane in films deposited at 310K. This is confirmed by the study presented in Section 4.2.4 for films deposited at room temperature. However, films deposited between 273K and 245K would appear (Figure 6.11) to have a different orientation, since the low value of resistivity observed is consistent with a large contribution from the bc plane of crystallites to the in plane resistivity. The a-axis contribution is clearly largest at 235K and (210-214K), and the SEM evidence suggests that in the region of 210K crystallites are aligned

with their b-axis perpendicular to the film surface. A similar orientation effect, with the strong growth axis perpendicular to the film plane was also observed (Figure 4.10) for films deposited in the vicinity of 235K. The effect of substrate temperature upon the morphology of films is discussed in detail in Chapter 4.

It appears, therefore, that high values of resistivity are associated with strong orientational effects of crystallites, implying a large contribution from the a axis in the film plane.

At low deposition temperatures (<200K) the resistivity once more returns to a low value, probably because crystallites adopt a random orientation in these films. The increase in conductance coincides with a decrease in film thickness. This type of behaviour was also observed between 220 and 230K. In this latter case, however, the low resistivity was accompanied by a very sharp drop in film thickness. SEM micrographs of films deposited at this temperature (Figure 4.10) revealed an unusual growth pattern, with large gaps between crystallites which were oriented with their strong growth axis out of the film plane. These crystallites grew out of an underlying film in which crystallites were apparently randomly oriented.

The observed variation in both film thickness and resistivity, with substrate temperature, is consistent with the Periodic Bonding Chain⁽⁶²⁾ (PBC) model of crystallite growth, which was discussed in Chapter 4. This model predicts that the growth rate in a particular crystal direction, under equilibrium conditions, is determined by the relative bond strengths between adjacent molecules along the three principal axis. Since the attractive interaction between adjacent molecules in crystals of (TTF)(TCNQ) scales as $b > a > c$, the

b axis is the strongest bonding direction, i.e. the direction of fastest growth.

A detailed account of the way in which the anisotropic bonding properties of molecules determine film morphology was given in Chapter 4. In the earlier discussion it was mentioned that there is a correlation between, the orientation of molecules relative to the substrate, and film thickness. Thus, if the molecular b-axis is perpendicular to the film plane molecules require a higher activation energy for desorption, than they would if the a or c axis were perpendicular, and under identical conditions of growth the former situation would result in thicker films. However, with the b-axis being the high conductivity axis of crystallites this will result in a low resistance perpendicular to the film plane, but a high resistance in the parallel direction.

In cases where the b-axis adopts an orientation parallel to the film surface the activation energy for desorption of ad-molecules is determined by either the a or c axis bond strength and is therefore smaller, which results in an increase in the number of molecules possessing sufficient energy to desorb and consequently to thinner films. Since the b-axis lies in the plane of the film the measured resistance is decreased, particularly if the a axis has a perpendicular orientation.

In conclusion, electrical measurements on annealed films of (TTF) (TCNQ) show that it is unnecessary to assume a reduction in the influence of grain boundary scattering for films deposited in the vicinity of T_{opt} . On the contrary the reduction in activation energy is only apparent and is due to a pronounced alignment of

crystallites with their b-axis perpendicular to the film plane.

Put differently, it is the orientation of crystallites which changes with deposition temperature not the activation energy associated with grain boundary scattering. Non-linear behaviour in the $\log \rho$ vs $1/T$ data occurs when scattering within grains begins to dominate the conduction process at higher temperatures. Scattering within grains, in a direction parallel to the film plane, reaches a maximum at 215K and 235K when the out of plane b-axis alignment is most pronounced. In view of the maxima in film thickness observed at both 215K and 235K it appears that the optimum temperature effect in (TTF) (TCNQ) is associated with the molecular anisotropy, and in particular with the strongest bonding direction, i.e. the b-axis of crystallites.

References for Chapter 6

1. Bloch, A.N., Ferraris, J.P., Cowan, D.O., and Poehler, T.O., Sol. State Commun., 13, 753 (1973).
2. Coleman, L.B., Ann. New York, Acad. Sci., 313, 316 (1978).
3. Coleman, L.B., Cohen, M.J., Sandman, D.J., Yamagishi, F.G., Garito, A.F. and Heegar, A.J., Sol. State Commun., 12, 1125 (1973).
4. Coleman, L.B., Cohen, J.A., Garito, A.F. and Heegar, A.J., Phys. Rev. B7, 2122 (1973).
5. Cohen, M.J., Coleman, L.B., Garito, A.F. and Heegar, A.J., Phys. Rev., B10, 1298 (1974).
6. Bardeen, J., Sol. State Commun., 13, 357 (1973).
7. Thomas, G.A., et.al., Phys. Rev. B13, 5105 (1976).
8. Warmack, R.J., Callicott, T.A. and Schweinler, H.C., Appl. Physics Lett., 24, 635 (1974).
9. Keller, H.J., 'Low Dimensional Cooperative Phenomena' (1975), Plenum - New York; Chemistry and Physics of One-dimensional metals (1977), Plenum - New York; 'Synthesis and Properties of Low-Dimensional Materials', Ann. New York Acad. Sci., 313 (1978), Ed. Miller, J.S. and Epstein, A.J.; see also reference (14).
10. Peierls, R.E., Quantum Theory of Solids (1955) Oxford Univ. Press.
11. Fröhlich, H., Proc. Roy. Soc., A233, 296 (1954).
12. Kuper, C.G., Proc. Roy. Soc., A227, 214 (1955).
13. Rice, M.J., Duke, C.B. and Lipari, N.O., Sol. State Commun., 17, 1089 (1975).
14. Berlinsky, A.J., Rep. Prog. Phys. 42, 1243 (1979).
15. Lee, P.A., Rice, T.M. and Anderson, P.W., Phys. Rev. Lett., 31, 462 (1973).

16. Schultz, T.D. and Craven, R.A., 'Highly Conducting One-dimensional Solids', Ed. Devreese, J.T., (1979) (Plenum: New York).
17. Bright, A.A., Garito, A.F. and Heegar, A.J., Phys. Rev. B10, 1328 (1974).
18. Berlinsky, A.J., Carolan, J.F. and Weiler, L., Solid State Commun., 15, 795 (1974).
19. Heegar, A.J. and Garito, A.F., in 'Low Dimensional Cooperative Phenomena', p.89, Ed. Keller, H.J., (Plenum: New York) 1974.
20. in reference (47) p.19.
21. Chaudhari, P., Scott, B.A., Laibowitz, R.B., Tomkiewicz, Y., and Torrance, J.P., Appl. Phys. Lett., 24, 439 (1974).
22. Chen, T.H. and Schectman, B.H., Thin Sol. Films, 30, 1973 (1975).
23. Reinhardt, C., Vollman, W., Hamann, C., Libera, L., Trompler, S., Kristall Technik., 15, 243 (1980).
24. Vand, V., Proc. Phys. Soc. (London) A55, 222 (1943).
25. Primak, W., J. Appl. Phys., 31, 1524 (1960).
26. Kimmel, R.M. and Uhlmann, D.R., J. Appl. Phys., 40, 4254 (1969);
ibid., 41, 592 (1970).
27. Chopra, K.L., J. Appl. Phys., 37, 2249 (1966).
28. Wei, T., Etemad, S., Garito, A.F. and Heegar, A.J., Phys. Lett., 45A, 269 (1973).
29. Roberts, G.G., J. Phys., CA, 3167 (1971).
30. Gosar, P., and Vilfan, I., Mol. Phys., 18, 49 (1970).
31. see Gutzow, I. and Avrimov, I., J. Non-Cryst. Solids, 16, 128 (1974).
32. Weaver, C., in Phys. Thin Films, 6, 301 (1971), Ed. Francombe, M.H., and Hoffmann, R.W., Academic Press.
33. Koverda, V.P., Skripov, V.P. and Bogdanov, N.M., Sov. Phys. Crystallogr., 19, 379 (1974).

34. Skripov, V.P. in 'Crystal Growth and Materials', North Holland, 1976, p.328, Ed. Kaldis, E. and Scheel, H.J.
35. Zeldovich, Ya.B., Zh. Eksp. Teor. Fiz. 12, 525 (1942).
36. in reference (34) p.335.
37. Sato, H., in reference (48) p.591.
38. Pincus, P. in 'Low Dimensional Cooperative Phenomena', p.1, Ed. Keller, H.J., Plenum - New York.
39. The Ising model has been treated by Stout, J.W. and Chisholm, R.C., J. Chem. Phys., 36, 979 (1962).
40. Landau, L.D. and Lifshitz, E.M., 'Statistical Physics', 2nd ed., Pergamon Press, Oxford (1970).
41. Kozak, J.J. in 'Adv. in Chem. Physics', 40, 229 (1979), Ed. Prigogine, I. and Rice, S.A., John Wiley & Sons.
42. Ehrenfest, P., Proc. K. ned. Acad. Wet. Science section 36, 153 (1933).
43. Yoshimura, S. and Murakami, M., Ann. New York Acad. Sci., 313, 269 (1978).
44. Dunning, W.J., in Phys. and Chem. Org. Sol. State, 1, 411 (1963). Ed., Fox, D., Labes, M.M., and Weissberger, A., Interscience.
45. Cohen, M.H. and Turnbull, D., J. Chem. Phys., 31, 1164 (1959).
46. Doolittle, A.K., J. Appl. Phys., 22, 1471 (1951).
47. Schafer, D.E., Ph.D. Thesis, Univ. Of Rochester, New York (1975).
48. Kallweit, M., in Physical Chemistry and Advanced Treatise, Vol.10, 719 (1970). Ed. Jost, W., Academic Press.
49. Rundman, K.B. and Hilliard, J.E., Acta Met., 15, 1025 (1967).
50. Sharp, J.H. and Smith, M., in reference (48), p.491.
51. Hoesterey, P.C. and Letson, G.M., J. Phys. Chem. Solids, 24, 1609 (1963).

52. p.63 in reference (55).
53. p.63 in reference (55).
54. Conwell, E.M. and Weisskopf, V.F., Phys. Rev., 77, 388 (1950).
55. Roberts, G.G., Apsley, N. and Munn, R.W., Physics Rep. 60, 59 (1980).
56. Coutts, T.J., in 'Electrical Conduction in Thin Metal Films', p.158 (1974), Elsevier - Amsterdam.
57. Azaroff, L.V. and Brophy, J.J., 'Electronic Processes in Materials', McGraw-Hill, New York, (1963) p.217; also in reference (55) p.66.
58. Etemad, S., Penney, T., Engler, E.M., Scott, B.A., Seiden, P.E., Phys. Rev. Lett., 34, 741 (1975).
59. Feldman, C., J. Appl. Phys., 34, 1710 (1963).
60. A Programming Language (APL).
61. Epstein, A.J. and Conwell, E.M., Sol. State Commun., 24, 627 (1977).
62. Kepler, R.G., 'Organic Semiconductors', p.1 (1962).
Ed. Brophy, J.J. and Buttrey, J.W., Macmillan - New York.
63. Mark, P. and Helfrich, W., J. Appl. Phys., 33, 205 (1962).
64. Hartman, P. and Perdock, W.G., Acta Cryst., 8, 49 (1955);
ibid, p.521; ibid, p.525.

CHAPTER 7

SUMMARY, CONCLUSIONS AND THE DIRECTION OF FUTURE WORK

Although the important conclusions derived from each part of the experimental programme were summarised at the end of the appropriate section, in this final chapter the various facets of the work are collected together to emphasise the importance of the metastable state and its role in the observation of the OST effect.

The thesis is concluded with a brief account of an investigation currently in progress into the effects of substrate temperature upon the structure and electrical properties of very thin (ca. 20Å) metal films on oxide supports. This latter section is included to demonstrate the usefulness of the combined techniques of vacuum deposition, electrical conductivity and electron microscopy in studying important technological problems associated with the de-activation of heterogeneous catalysts.

7.1 The Optimum Substrate Temperature Effect and the Formation of a Metastable State

Topographical studies of (TTF)(TCNQ) have shown that a pronounced alignment of the b-axis of crystallites occurs in films deposited at a substrate temperature of 235K. This structural singularity is thought to coincide with the boundary between the crystalline and a disordered phase of (TTF)(TCNQ) and is, therefore, consistent with VBR's proposals concerning the cause of the OST effect. However, a second region was identified with similar characteristics at substrate temperatures in vicinity of 213K. The available evidence suggests that it is this low temperature singularity which is the OST for (TTF)(TCNQ). This conclusion is based primarily upon the observation that a metastable phase is formed at the OST, which provides a natural explanation for the relationship between film topography and normal boiling point (or critical temperature), in terms of fundamental dispersion

forces which exist between molecules, and is entirely consistent with the Ostwald Rule of Stages (Chapter 6). The following evidence is cited as providing support for the idea of a metastable state at the OST in films of (TTF)(TCNQ) and the aromatic hydrocarbons, anthracene, pyrene and perylene.

- i) Infrared spectroscopy confirmed the existence of a neutral lattice in (TTF)(TCNQ) films deposited between 195K and 220K. Since charge transfer between (TTF) and (TCNQ) molecules is energetically unfavourable in the absence of LRO, this observation is consistent with the idea that films deposited at the OST only possess SRO.
- ii) Crystallisation of films deposited between 195K and 230K was only observed above some critical temperature which was determined by the temperature of the substrate during deposition; unlike films deposited above 220K, which displayed a continuous increase in conductivity on annealing above the deposition temperature. This behaviour suggests that the SRO $\rightarrow$ LRO transition within 'metastable' films was quasi-first order and involved a nucleation step.
- iii) Changes in fluorescence lifetime and intensity were observed when films of the aromatic hydrocarbons anthracene, pyrene and perylene were annealed in the vicinity of their respective OST's. These changes suggest that the activation barrier to the formation of the crystalline state, within disordered films deposited at low substrate temperatures, is associated with an increased repulsive interaction between molecules in the ground state. However, having overcome this barrier, crystallisation does not proceed until much higher temperatures suggesting that

the intermediate state is metastable as in (TTF)(TCNQ).

The structural singularity observed in (TTF)(TCNQ) at 213K and by VBR in anthracene and pyrene is therefore a consequence of the thermodynamic requirement that short range interaction forces are minimised at equilibrium. It must be emphasised that films either deposited at the OST, or deposited at low temperature and then annealed at the OST, are metastable and possess SRO. They are not disordered in the accepted sense of the term, neither do they contain nuclei of the crystalline phase, otherwise they would be thermodynamically unstable, as were films of (TTF)(TCNQ) deposited above 220K. Thus it was shown in the case of (TTF)(TCNQ) that introduction of disorder into films causes enforced dimerisation, resulting in anomalous infrared activity. The lack of such activity in film deposited above 190K defines the upper limit of the low temperature disordered phase.

It was proposed that molecules deposited onto substrates at the OST have sufficient kinetic energy to overcome the activation barrier which prevents them from minimising short range interaction forces but insufficient kinetic energy to overcome the barrier to nucleation. This, it is believed, produces a minimum in molecular volume which is responsible for the observed structural singularity; a proposal which is supported by the observation of a maximum in the activation energy for crystallisation of films of (TTF)(TCNQ) deposited at 213K.

The step change increase in conductivity observed when films deposited below 220K were annealed near room temperature, indicates that shock crystallisation was occurring in these films and that there were very few if any nuclei of the crystalline phase present in the as-deposited state. In view of this observation it is necessary to distinguish between those materials in Table 1.1 which have OST's

below room temperature, viz. anthracene and pyrene, and which subsequently crystallise on annealing, and the remainder whose OST's are higher than room temperature. Clearly, if the latter are cooled to room temperature, after deposition and without being annealed, they should still retain their metastable form, which having a glass or liquid like structure will contain few, if any, grain boundaries. Furthermore, if like (TTF)(TCNQ), films of these materials deposited immediately above and below the OST have disordered structures, then it is possible to explain why the electrical and electro-optical properties of films deposited at $0.33 T_B$ are optimised. Because the metastable phase possesses SRO a modified electronic energy band description is still appropriate⁽¹⁾, in that there are gaps in the density of states distribution. If, however, as Makinson and Roberts⁽²⁾ show, short range order is disrupted, eventually these gaps will disappear and electronic states will become localised, leading to a reduction in carrier mobility either side of the OST.

It is possible then to explain why the electrical properties and in particular the activation energy for conduction of (TTF)(TCNQ) films were only weakly influenced by substrate temperature during deposition. Annealing experiments demonstrated that (TTF)(TCNQ) films crystallised on annealing at room temperature and were, therefore, no longer in the metastable state. If, as discussed in Section 6.3.2 the activation barrier to conduction in polycrystalline materials is associated with multiple scattering at molecular sites then there is no reason to expect a marked variation in E_{cond} even when the concentration of scattering sites within the grain boundary region changes with deposition conditions employed, i.e. it is the nature of the

scattering site not the number which determines E_{cond} . Thus in annealed films of (TTF)(TCNQ) the topographical parameter which most influenced the electrical properties was crystallite orientation because of the extremely anisotropic properties of crystallites.

In conclusion, this examination of the influence which substrate temperature has upon the structure and properties of vacuum deposited films has confirmed many of the essential features of the proposed explanation of the OST effect. In addition it has been established that the most important single criteria for the observation of a singularity, in both the structure and properties of vacuum deposited films at $0.33 T_B$, is the formation of a metastable, liquid or glassy, phase under quasi-equilibrium conditions, in the absence of nuclei of the crystalline phase. The lower and upper limits of existence of this metastable phase are defined by the temperature at which films become disordered and the activation energy for nucleation of the crystalline phase, respectively.

Although the experimental programme was restricted to a study of planar aromatic molecules for which the intermolecular interaction is dominated by Van der Waals forces the above criteria should be universally applicable. Thus provided conditions of substrate temperature and rate of deposition can be identified which guarantee the existence of metastable state at the phase boundary between the liquid and vapour phase all materials should exhibit an OST effect, but not necessarily at $0.33 T_B$.

7.2 Future Work

7.2.1 Introduction

Many important large scale chemical processes employ metal catalysts to increase the rate of reaction. Since the activity of these catalysts is determined by the surface area available for the adsorption of reactants it is necessary to maintain a high dispersion (surface area/mass) of the metal phase. This is normally achieved by dispersing the metal phase as small particles (ca. 100Å diameter) on an 'inert' support, which is usually an oxide such as silica or alumina. Under reaction conditions these small particles of metal are able to grow either by migration and coalescence⁽³⁾, or by a thermodynamically driven process known as Ostwald ripening⁽⁴⁾. This process, which is normally referred to as sintering, causes a reduction of the metal dispersion and a consequent loss of activity and is a major cause of catalyst de-activation. The rate at which a catalyst loses activity determines its effective operating lifetime, which is a significant factor in determining the economics of a chemical process. It is important, therefore, to increase our knowledge of the mechanism of metal particle sintering and to discover ways of preventing its occurrence.

Transmission electron microscopy (TEM) is a very powerful technique for studying supported metal catalysts⁽⁵⁾ and has been used extensively⁽⁶⁾ to study their sintering behaviour. However, because of the particulate nature of supports used for commercial catalysts it is usually a difficult problem to distinguish between particles of the support and those of the active metal phase, or even to detect smaller particles with diameters of 30Å or less. Since a detailed understanding of the mechanism of sintering depends upon being able to make a quantitative analysis of the metal particle size distribution,

particulate supports are far from ideal substrates for this purpose. On the other hand, in recent years thin films of oxides prepared by techniques ranging from, electrolytic anodisation of metals, to vacuum evaporation have been used very successfully to study heterogeneous nucleation and growth of metal particles deposited from the vapour phase. The use of thin films enables high resolution TEM to be used to study the structure of these metal particles, and furthermore, since all particles are in the same plane, a quantitative determination of particle size distribution becomes routine.

Stimulated largely by results described in the main body of the report, which demonstrate that it is possible to produce materials with a very wide range of structures (Chapter 4) in a reproducible way, techniques were developed for producing thin films of metal oxides and other refractory materials which are of interest as catalyst supports. The main technique used for this purpose was Electron Beam Reactive Evaporation (EBRE). A description of the equipment, which was developed by the author as part of this programme, and a brief outline of the (EBRE) technique were given in Chapter 2, Section (2.1.4). When thin films of metals ($<60\text{\AA}$ thick) are deposited onto these supports they break up to give small metal islands with diameters of the order of $100\text{\AA}$ or less which can be used as realistic models for studying sintering of supported metal catalysts.

As a first step in the study of particle migration and sintering, TEM and electrical conductivity measurements have been used to study discontinuous films of silver and gold on amorphous alumina. Some preliminary results obtained from this work will now be described.

7.2.2 The Preparation of Films for TEM and Electrical Conductivity Measurements

Alumina (Al_2O_3) films ($<300\text{\AA}$ thick) were deposited by (EBRE) in an atmosphere of 10^{-4} Torr of oxygen, onto a freshly cleaved mica substrate previously covered with $100\text{\AA}$ of carbon from an arc source. A rate of deposition of approximately $1\text{\AA sec}^{-1}$ was employed and a high purity source (99.99%) of Al_2O_3 was used. Electron diffraction has shown that films of alumina deposited at room temperature, in this way, are amorphous. They were not observed to crystallise on annealing to temperatures in excess of 600°C and their lack of structure makes them ideal for TEM purposes.

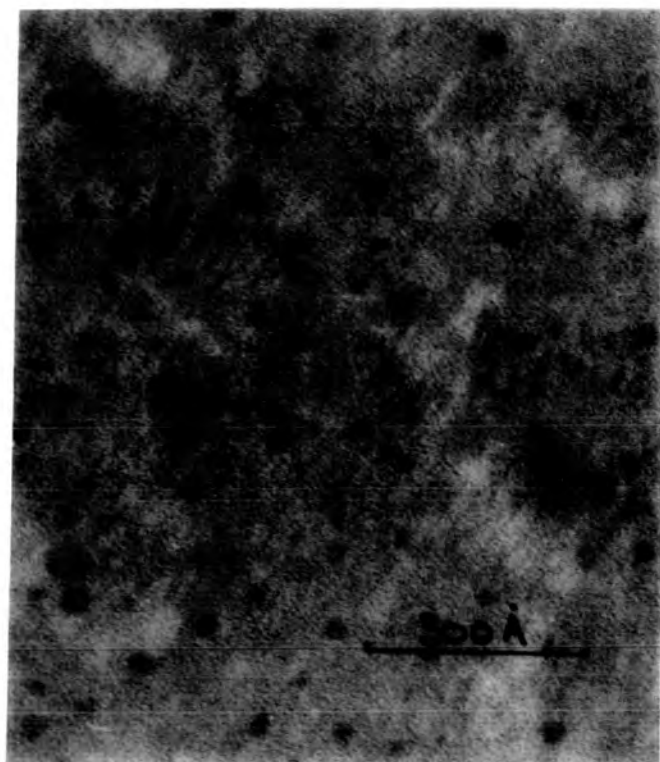
Silver (99.99%) was deposited onto these composite substrates under different conditions of rate and substrate temperature using the evaporator described in Section (2.1.1). After deposition of the metal the film was removed from the mica substrate by immersion in distilled water, the carbon film acting as a release layer for the alumina/silver film. This latter film was picked up from the surface of the water on an electron microscope grid and examined using the Phillip SEM 300 described in Section (2.4.2).

When carrying out conductivity measurements the oxide film was prepared as described above on a silica substrate and silver electrodes were then deposited in the same pump down cycle as described in Section (2.2.2). The sample was transferred to the birvac evaporator for deposition of the discontinuous metal film, which was carried out with the silica substrate cemented to the Oxford Instruments Cryostat, as discussed in section (2.2.2).

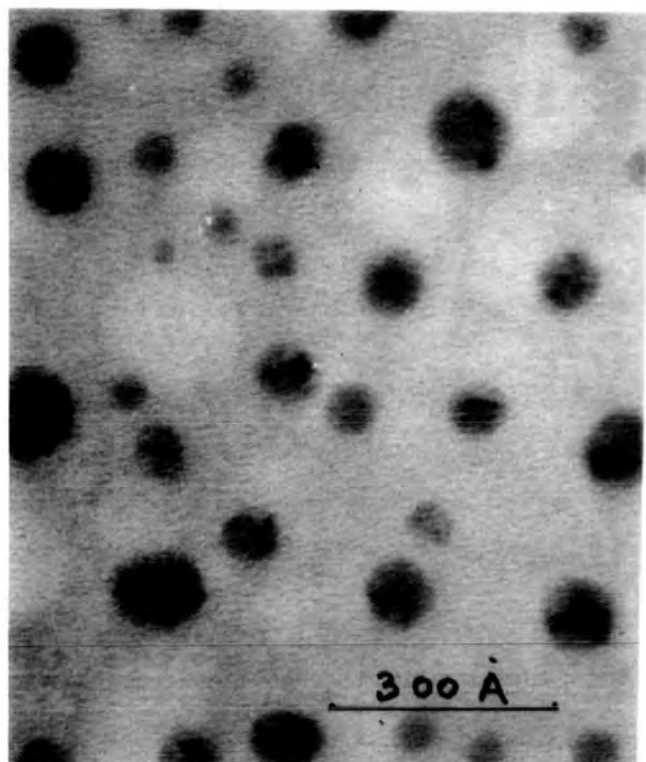
7.2.3 TEM of Discontinuous Metal Films

As the four micrographs in Figure (7.1) show thin films of metal when deposited onto a surface break up to give an island structure. The average diameter of these islands was observed to increase in size with increasing film thickness. Metal films were deposited at $1\text{\AA min}^{-1}$ at room temperature and had the thicknesses indicated in Figure (7.1), as measured by quartz crystal oscillator. The particle size distribution was generated from a number of micrographs taken of the same sample, using the image analyser described in Section (2.4.2). Figure (7.2) shows two such distributions for films deposited at $1\text{\AA sec}^{-1}$ (Figure 7.2(a)) and $1\text{\AA min}^{-1}$ (Figure 7.2(b)), respectively. In both cases the width of the distribution was relatively narrow for the $1\text{\AA}$ thick films. The distribution broadened with increasing film thickness and became bimodal and eventually trimodal at $20\text{\AA}$. An interesting feature, which is most clearly seen in the $1\text{\AA sec}^{-1}$ film, is the reduced concentration of small particles ($<40\text{\AA}$) at a film thickness of $10\text{\AA}$ and yet the relative proportion of these particles has increased again in the $20\text{\AA}$ thick film.

The effect of substrate temperature during deposition of the silver films ($10\text{\AA}$ thick) is shown in Figure (7.3) for two series of films deposited at $1\text{\AA sec}^{-1}$ (Figure 7.3(a)) and $1\text{\AA min}^{-1}$ (Figure 7.3(b)), respectively. A marked decrease in the concentration of silver particles was observed on increasing the substrate temperature during deposition of the silver film from 20°C to 40°C . Above 40°C the particle size increased to a maximum at 100°C and then decreased again above this temperature. The increase in particle concentration was accompanied by a decrease in mean particle size and vice versa.



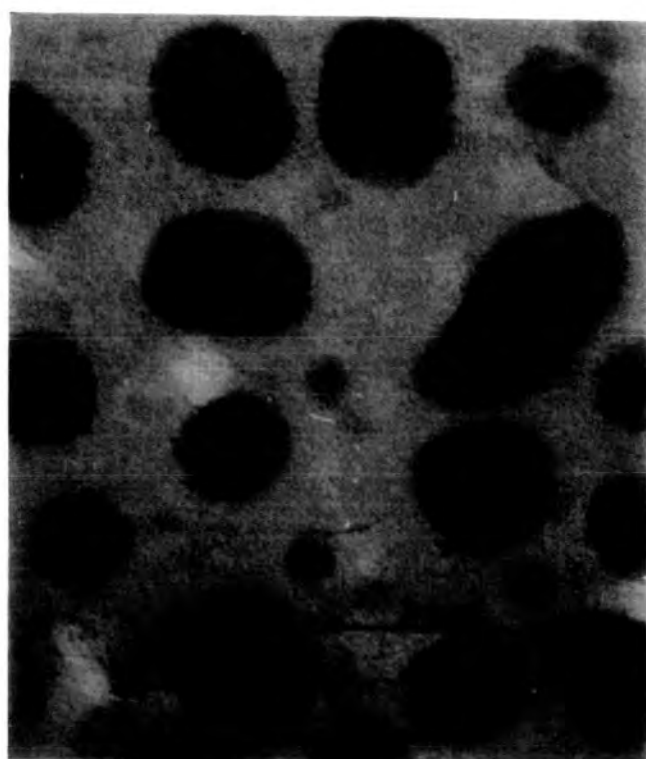
A



B



C



D

Figure 7.1. Micrographs of silver deposited at $1\text{Å}/\text{min}$ rate onto a 150Å Alumina substrate at 20°C . A) 1Å , B) 5Å , C) 10Å and D) 20Å thick.

Figure 7.2. Particle size distributions for silver films of thicknesses 1, 5, 10 and 20Å deposited out on alumina film at $1\text{\AA sec}^{-1}$ (7.2a) and $1\text{\AA min}^{-1}$ (7.2b)

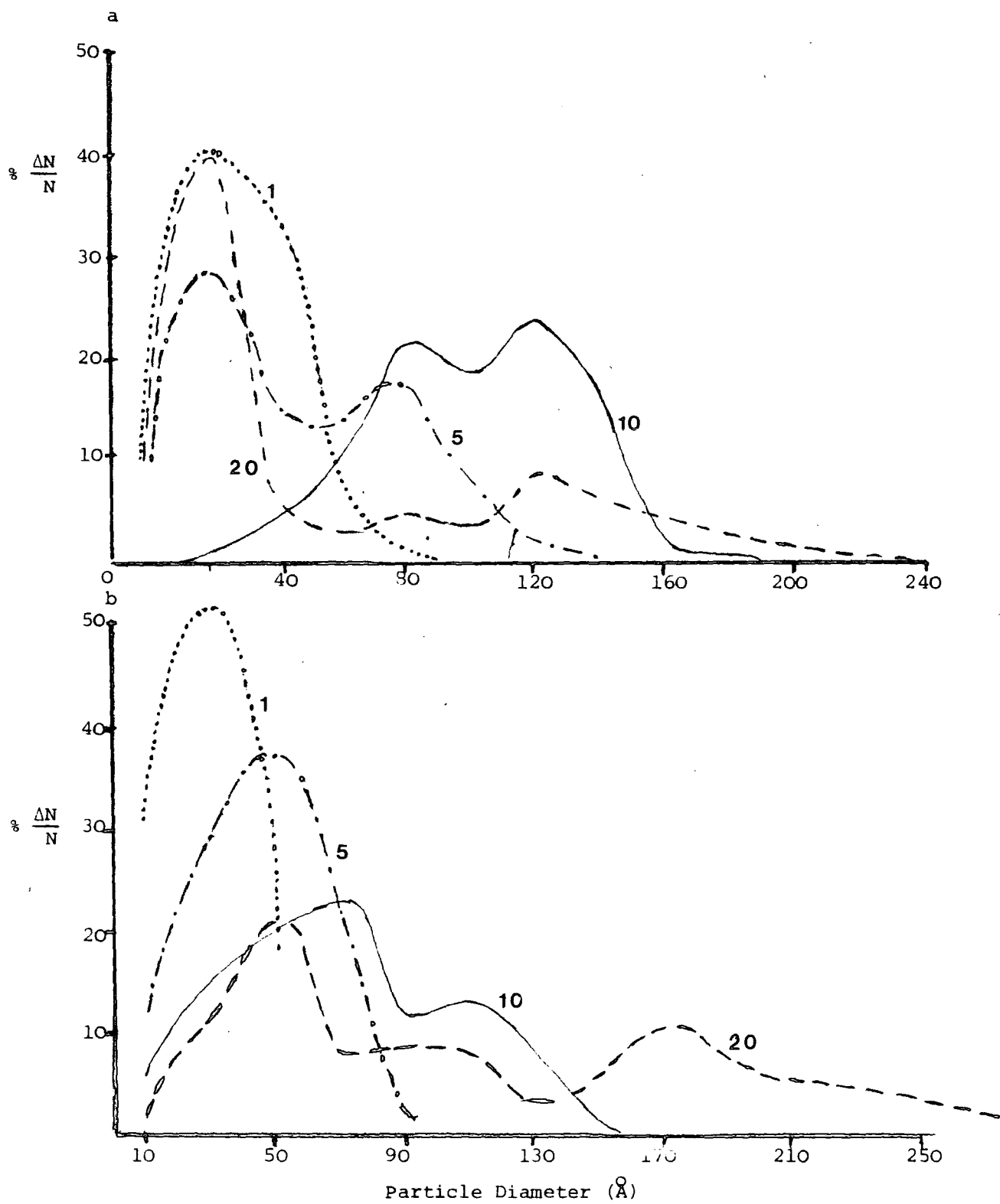
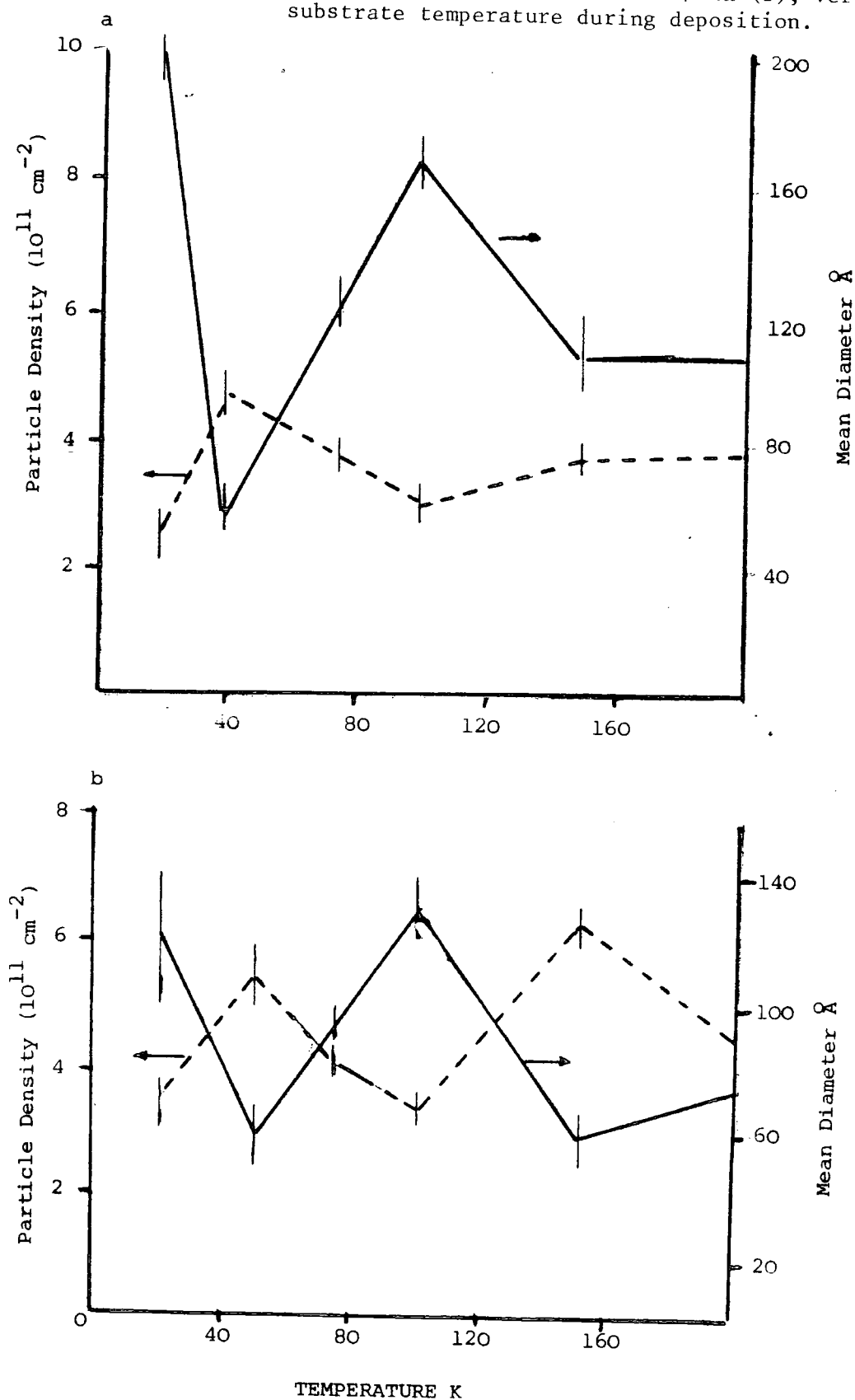


Figure 7.3. Particle density and mean diameter for two films deposited at 1Å/sec (a) and 1Å/min (b), versus substrate temperature during deposition.

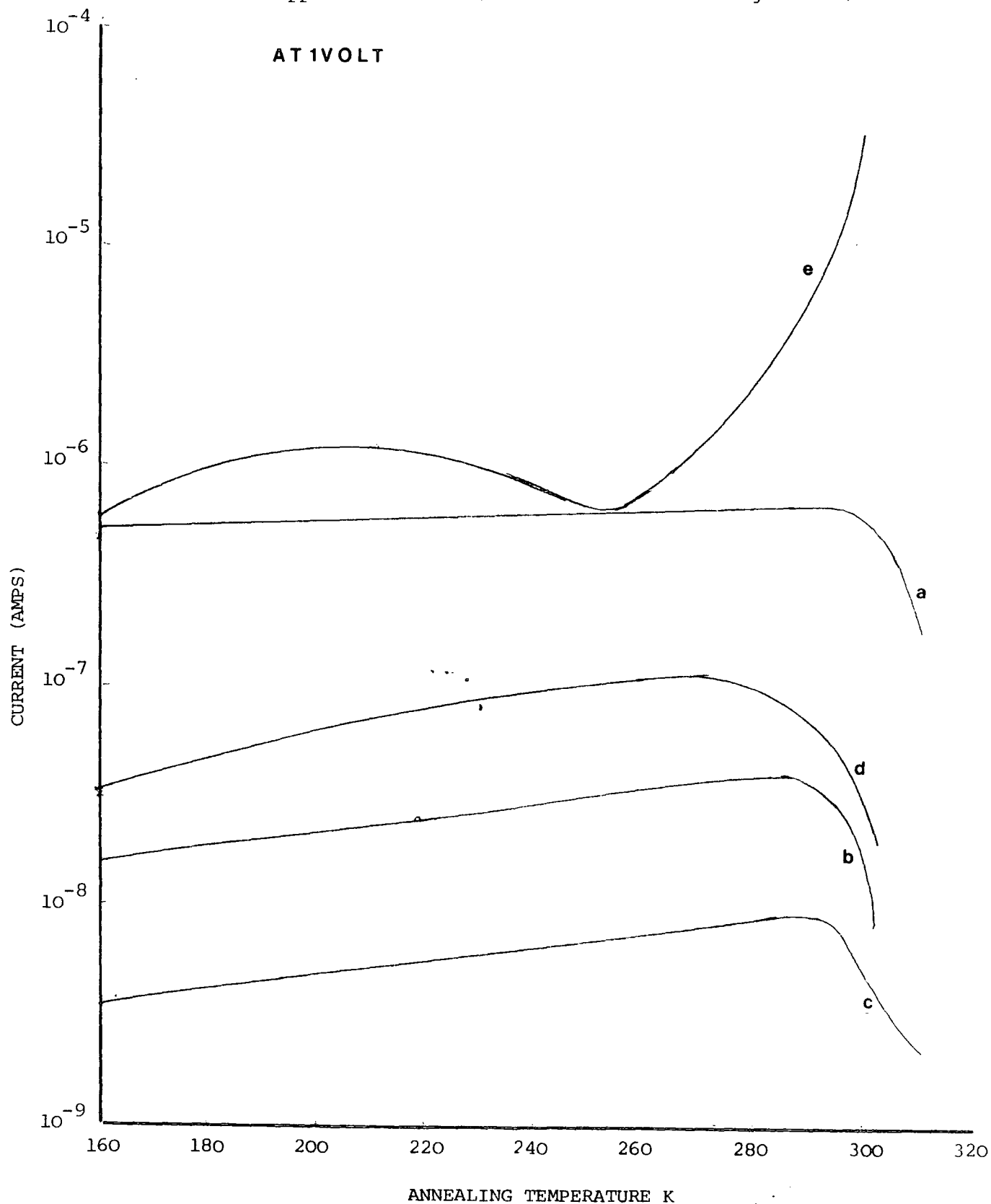


7.2.4 Electrical Conductivity Measurement on Discontinuous Metal Films

Electrical conductivity measurements were carried out on discontinuous metal films deposited at low substrate temperatures onto oxide coated silica slides using the equipment described in Section (2.2.2). The results in Figure (7.4) were obtained for gold deposited onto alumina. Curve (a) was obtained for a gold film $20\text{\AA}$ thick deposited at 200K. The film was cooled to 160K after deposition and the current generated by an applied voltage of IV was monitored as a function temperature on the re-heating cycle (heating rate 1.25K min^{-1}). A rapid decrease in conductance was observed near 300K. Curve (b) was recorded on the second heating cycle after the film had been re-cooled to 160K. The decreased conductance on the second heating cycle suggests that an irreversible change in the particle distribution had taken place. Curves (c) to (e) were obtained after further successive depositions of gold of $5\text{\AA}$, $10\text{\AA}$ and $15\text{\AA}$. The sample was cooled to 200K prior to each deposition. Attention is drawn to the fact that the conductance of the sample remained lower after the second and third depositions than it was after the initial deposit of $20\text{\AA}$. Furthermore, the conductance decreased irreversibly above about 200K in both cases. After the fourth deposit of $15\text{\AA}$ the conductance at low temperatures was only slightly higher than that of the first $20\text{\AA}$ deposit, although it did increase very rapidly above 250K.

The results shown in Figure (7.5) were obtained for a discontinuous film of silver on alumina. Curve (a) shows the conductance change on annealing a $30\text{\AA}$ thick film, deposited at 200K, to 220K.

Figure 7.4. Effect of annealing upon the electrical conductance of a discontinuous gold film, deposited onto an alumina support at 200K. (see text for curve designations)



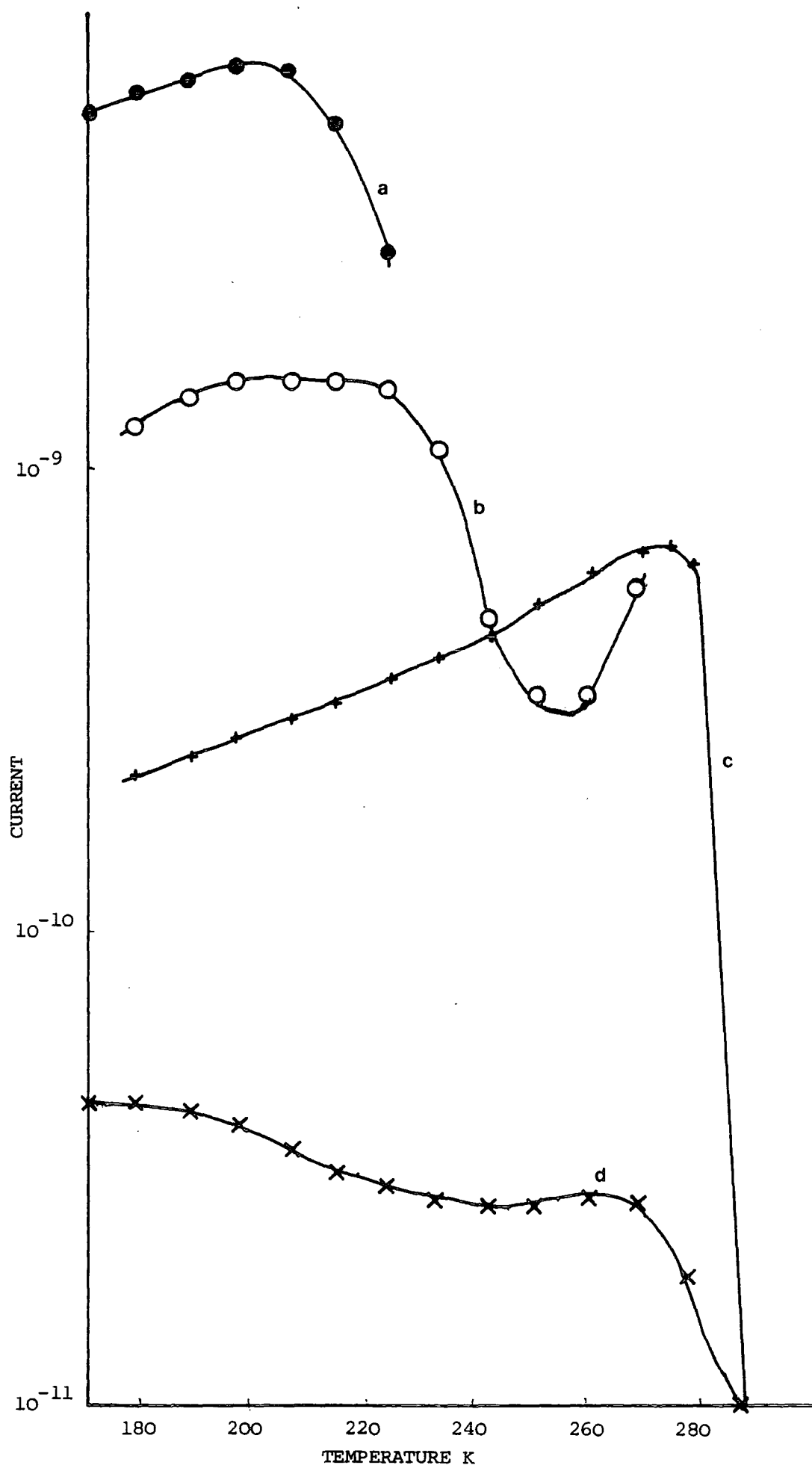


Figure 7.5. Effect of annealing upon the electrical conductance of a discontinuous silver film, deposited onto an alumina support at 200K. (see text for curve designations)

Curve (b) is the conductance of the same sample after cooling to about 170K and the re-heating to 268K. The sample was then cooled a second time to 180K and gave curve (c) on re-heating. The conductance of the film decreased very rapidly above 280K. Curve (d) was obtained after depositing a further 20Å of silver onto the sample at 200K. As with gold on alumina the conductance of the film after the second silver deposition of 20Å was much lower than that obtained after the first deposit of 30Å.

7.2.5 Discussion of the Results Obtained from the Study of Discontinuous Metal Films

Theoretical treatments of nucleation and growth of metal films such as the classical model outlined in Chapter 1 assume that nucleation is a homogeneous process. However, a great deal of experimental work with metals deposited onto freshly cleaved surfaces⁽⁷⁾ has shown that nucleation probably occurs preferentially at kink sites and steps. Furthermore, electron bombardment, which causes an increase in the density of defects on surfaces is known⁽⁸⁾ to increase the rate of nucleation. Thus, it is probable that nucleation on defected surfaces occurs heterogeneously rather than homogeneously. This appears to provide a basis for explaining the results described in the previous section.

It is proposed that ad-atoms impinging on a surface diffuse to defects where they become trapped if the temperature of the surface is $kT < E_{\text{trap}}$ is a binding energy characteristic of a particular type of defect and is probably distributed. Subsequent ad-atom arrivals will lead to the formation of a stable nucleus and eventually to particle growth, thus in very thin films and for $kT < E_{\text{trap}}$ the site of attachment of ad-atoms on the surface is determined by the defect distribution on that surface. This is the situation which is

thought to be represented by micrograph (a) in Figure (7.1) resulting in the mono-modal distribution of particle size shown in Figure (7.2), for the $1\text{\AA}$ thick film.

As the amount of material deposited increases so to does the particle size, causing a reduction in the binding energy per atom at a defect site. Once a particle has grown beyond a certain size, random thermal fluctuation⁽⁹⁾ may give it sufficient kinetic energy to overcome the potential energy binding it to its nucleation site, allowing it to migrate on the surface and collide with other particles. This would explain the disappearance of small particles in the $10\text{\AA}$ thick film, micrograph (c), Figure (7.1). As further material is deposited ad-atoms are able to fill up the vacated defect sites leading to a second increase in the concentration of small particles as observed for the $20\text{\AA}$ thick deposit micrograph (d). The various stages in this process are represented schematically in Figure (7.6).

The electrical conductivity measurements can also be explained on the basis of the above mechanism. Thus, deposition at a low temperature (T) will lead to defect sites with binding energies less than kT being populated. Now if an island structure is obtained at low temperatures⁽¹⁰⁾, the conduction process is activated and, as shown by Abeles and Sleng⁽¹¹⁾, the magnitude of the activation energy will be proportional to the distance between particles. If, as discussed, on annealing, particles are detached from defect or nucleation sites and are able to migrate and coalesce with other particles, the distance between metal islands will be increased,



(1) nucleation at defects



(2) monomer absorption by nuclei



(3) Thermal dissociation of
nuclei from site of attachment



(4) Migration and coalescence



(5) Stable crystallite absorbs
monomers by surface diffusion



(6) Secondary nucleation

Figure 7.6. Schematic of the early stages of nucleation and growth at surface defect sites

leading to a larger activation energy and an irreversible decrease in conductance, as was observed in both the examples shown in Figures (7.4) and (7.5).

Once the film has been annealed and particles in the initial deposit allowed to grow, during subsequent deposition these particles can compete with defect sites for adsorbed atoms, so that the latter are less effectively populated. This, as shown in Figures (7.5) and (7.6), leads to an initial decrease in the conductance of films as a function of thickness, when deposited in a stepwise fashion. However, when deposition is carried out continuously⁽¹²⁾ this does not occur. The increased conductance recorded after depositing 65Å of gold, curve (e); Figure (7.5), is probably associated with fact that particles have grown to a size where the distance between them has begun to decrease rapidly as the film changes from being discontinuous to become semi-continuous.

The decrease in conductance observed above 280K in the case of silver deposited on alumina, Figure (7.5), is consistent with the observation that the particle concentration decreases rapidly above a deposition temperature of 293K as shown in Figure (7.3). It is not clear why there should be an increase in particle concentration between 313K and 373K, although it may be associated with a decrease in supersaturation.

These preliminary results obtained from the study of discontinuous metal films are the first step in a continuing study of sintering in supported metal catalyst. They have shown that thin film deposition techniques when used in conjunction with TEM and electrical conductivity measurements can furnish detailed information

about changes in particle size distribution, and furthermore provide strong evidence for a support metal interaction. The latter is an important parameter for determining the selectivity of catalysts⁽¹³⁾. Since the strength of this interaction determines the temperature at which migration of particles begins to occur, electrical conductivity measurements may be able to quantify the role of the support in determining selectivity, and lead to an improved understanding of supported metal catalysts.

References for Chapter 7

1. Keller, J. and Ziman, J.M., J. Non-Cryst. Solids, 8-10, 111 (1972).
2. Makinson, R.E.B. and Roberts, A.P., Australian J. Physics, 13, 437 (1960).
3. Pashley, D.W., Stowell, H.J., Jacobs, M.H. and Law, T.J., Phil. Mag. 10, 127 (1964).
4. Ruckenstein, E. and Dadyburjor, D.B., Thin Solid Films, 55, 89 (1978).
5. Baker, R.T.K., Prestridge, E.R. and Garten, R.L., J. Catal., 59, 293 (1979). McVicker, G.B., Baker, R.T.K., Garten, R.L. and Kugler, E.L., J. Catal., 65, 207 (1980).
6. Wanke, S., 'Sintering and Catalysis', Plenum - New York (1975).
7. Basset, G.A., Menter, J.W. and Pashley, D.W., in Structure and Properties of Thin Films, p.11, Ed. Neugebauer, C.A., Newkirk, J.B. and Vermulyea, D.A., John Wiley and Sons (1959).
8. Stirland, D.J., Appl. Phys. Lett., 8, 326 (1966).
9. Flynn, P.C. and Wanke, S.E., J. Catal. 34, 390, 1974; *ibid.*, p.400.
10. Levinstein, H.J., J. App. Phys., 20, 306 (1949); also reference (7).
11. Abeles, B., Sheng, P., Coutts, M.D. and Arie, Y., Adv. Physics, 24, 407 (1975).
12. Neugebauer, C.A. and Webb, M.B., J. Appl. Phys., 33, 74 (1962).
13. Ichikawa, M., Bull. Chem. Soc. Jap., 51, 2273 (1978).

APPENDIX 1

MATERIALS PREPARATION

A.1 Preparation and Purification of Tetrathiofulvalene tetracyano-quinodimethane (TTF) (TCNQ)

At the time the work on TTF TCNQ reported in this thesis was being carried out, a collaborative study of crystal growth with the University of Strathclyde, Chemistry Department⁽¹⁾ was also underway. The combined requirements for TTF/TCNQ were substantial (>40g) and there was at that time no commercial supplier of (TTF), although TCNQ was available. Both are now available from Aldrich Chemicals. (TTF) and (TCNQ) were, therefore, synthesised by several people, including the author on a scale large enough to meet these requirements.

A.1.1 Preparation of (TTF)

(TTF) was prepared using a method similar to that described by Melby et.al⁽²⁾. The reaction scheme is shown in figure A.1. Dimethyl acetylene dicarboxylic ester (I) was reacted with ethylene trithiocarbonate (II) to give 1,3-dithiole-2-thione-4,5-dicarboxylic acid methyl ester (III) in 65% yield. Compound (III) was demethylated in glacial acetic acid and concentrated hydrochloric acid to give 1,3-dithiole-2-thione-4,5-dicarboxylic acid (IV) in almost quantitative yield (95%). Decarboxylation of (IV) using pyridine gave 1,3-dithiole-2-thione (V) in 28% yield. Melby's method for preparing (TTF) involved coupling the hexafluorophosphate salt of V using triethylamine which gave only poor yields. A higher yield of pure product was, however, obtained by coupling 1,3 dithiolium fluoroborate (VIII) with triethylamine. Compound (VIII) was prepared by methylation⁽³⁾ of (V) using methyl iodide, followed by sodium borohydride reduction of 2 methylthio-1,3-dithioloylium iodide (VI), and cleavage of the thio-methyl group

Figure A.1. The Reaction Scheme for the Preparation of (TTF)

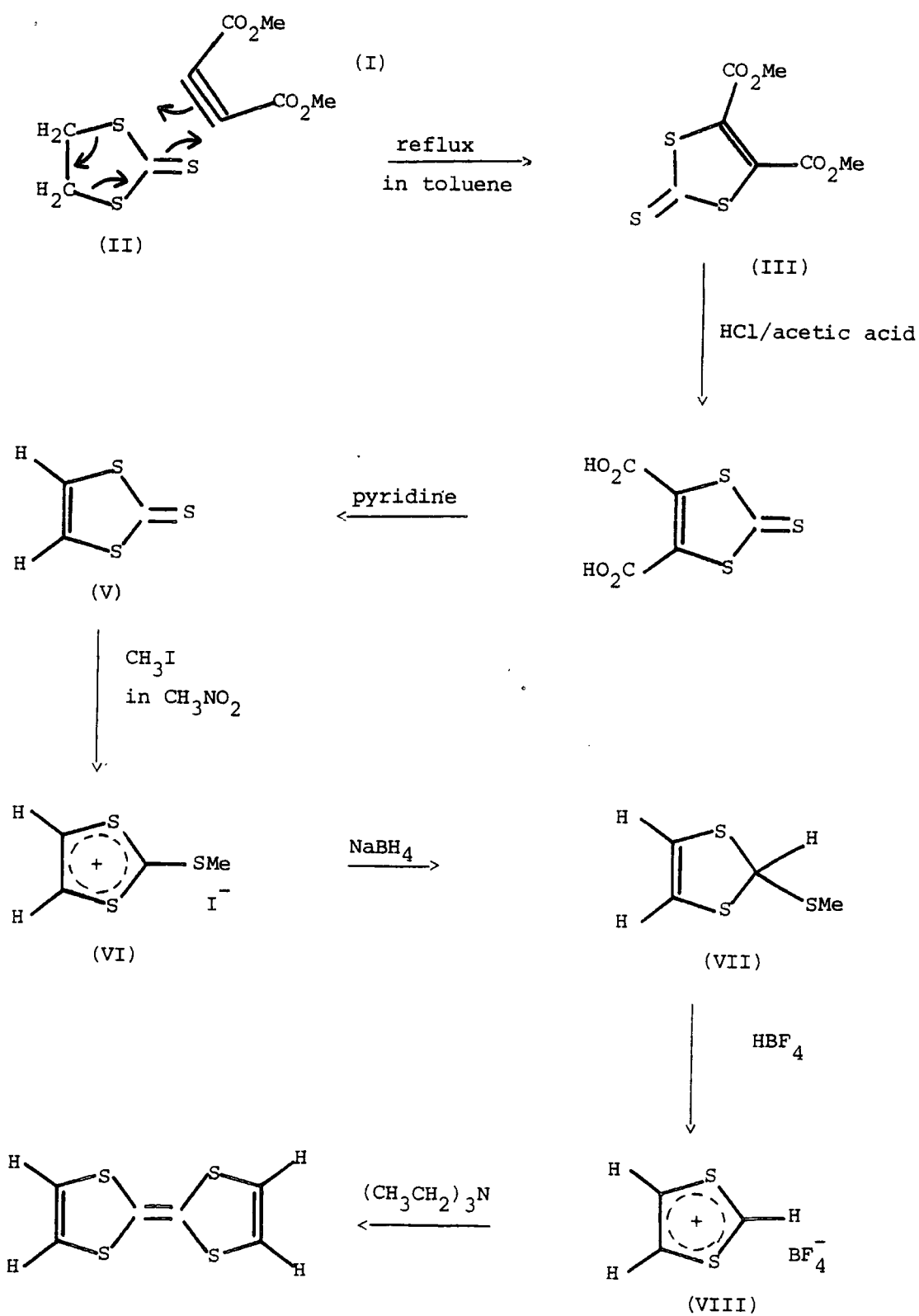
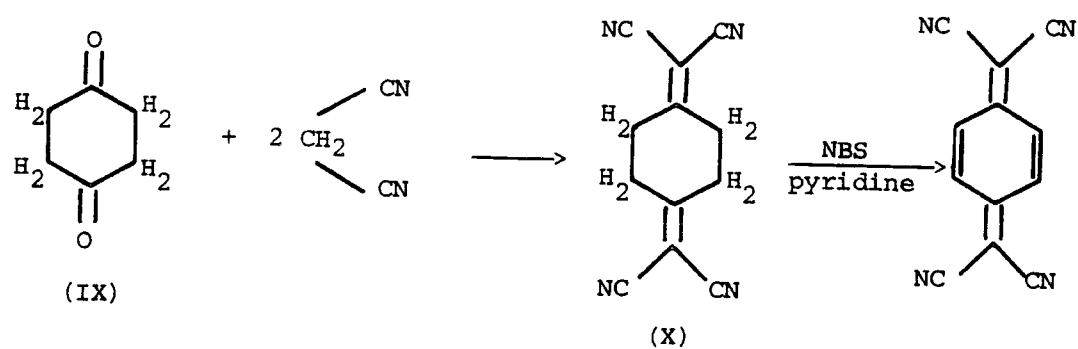


Figure A.2. Reaction Scheme for the Preparation of TCNQ



with fluoroboric acid. The last three reaction steps were carried out without isolating the intermediates.

A.1.2 Preparation of (TCNQ)

(TCNQ) was prepared using the method described by Acker and Hertler⁽⁴⁾, which is shown in the reaction scheme of Figure A.2. 1,4-Cyclohexanedione (IX) and malononitrile were reacted together to give 1,4-bis(dicyanomethylene)cyclohexane (X) which was dehydrogenated with N-bromosuccinimide in pyridine to give the product (TCNQ) (XI).

A.1.3 Preparation of (TTF) (TCNQ) Complex

Starting with the purified precursors, all operations involved in the preparation of the complex were carried out inside a large nitrogen glove box. Immediately prior to use both precursors were purified by double recrystallisation, under nitrogen from dried solvents. (TTF) was recrystallised from a mixture (7.5 to 4.5) of cyclohexane and hexane which had been dried over MgSO_4 for 4 hrs, followed by drying over P_2O_5 for 3 days. The solvent was then distilled from P_2O_5 under nitrogen. TCNQ was recrystallised twice from ethyl acetate which had also previously been dried over MgSO_4 followed by distillation from P_2O_5 . At each stage of the recrystallisation solutions of both materials were boiled with activated charcoal prior to filtering. This was effective in removing the green colouration (due to radical anion) from solutions of (TCNQ). Rust coloured crystals separated from TCNQ solutions. Coleman⁽⁵⁾ et.al, have claimed that pure TCNQ is bright yellow, however, it was found that the rust coloured crystals obtained in the present study gave a bright yellow powder when finely ground. When filtered and dried under vacuum TCNQ, M.pt. 299°C gave the following chemical analysis.

Calculated for $C_{12}H_4N_4$: C, 70.59; H, 1.97; N, 27.44

Found : C, 69.68; H, 2.02; N, 27.13.

TTF was obtained in the form of orange needle crystals, which in certain cases were 4 or 5 cm long, and on drying under vacuum had a M.pt. 120°C and gave the following chemical analysis:

Calculated for C_6S_4H : C, 35.29; H, 1.97; S, 62.74

Found : C, 35.77; H, 1.81; S, 62.30.

The complex was prepared by mixing together hot solutions of the precursors in equimolar amounts in acetonitrile, which was dried by double distillation from P_2O_5 under nitrogen. (TTF) (TCNQ) separated out as microcrystals from the solution and gave a purple almost black solid when dry, which had the chemical analysis shown in Table A.1. All experiments were carried out in pyrex glassware.

A.1.4 Purification of TTF/TCNQ Complex

Studies of TTF/TCNQ reported in the literature have been primarily concerned with its properties when in single crystal form. Because of its poor solubility in most solvents, single crystals of the complex are normally grown by diffusing the two precursors together, either from solution or in the vapour phase. Consequently, most effort has, in the past, been directed toward purification of the precursors rather than trying to purify the complex after precipitation. Workers in a number of Laboratories⁽⁶⁾ have gone to considerable lengths to obtain the precursors in a highly pure form and claim⁽⁷⁾ to have achieved a purity of 99.99% for both materials. However, occluded solvent (acetonitrile) is reported⁽⁸⁾ to be present in crystals of the complex prepared by solution diffusion techniques.

For the present study, absolute levels of purity were not considered to be of paramount importance, as they are, for example, in the study for single crystals, where their electrical properties have been shown to be sensitive to impurity levels and the presence of defects. The controversy which surrounds the conditions used to prepare TTF-TCNQ is primarily concerned with the effect of impurities and defects on the b-axis conductivity of single crystals (see Chapter 6), at and around the metal to insulator transition. In a recent publication⁽⁶⁾ the conductivity of single crystals of TTF-TCNQ prepared in sixteen institutions by different workers, were compared. At room temperature the b-axis conductivities of all but one group fell within the region $2.5 - 7.5 \times 10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$, and values of conductivity observed at the maximum were between $0.3 - 1.5 \times 10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$, indicating that the method of preparation has little effect upon conductivity. It has also been stated⁽⁸⁾, that most of the variation in conductivity among samples of TTF-TCNQ is due to lattice imperfections rather than chemical purity.

The electrical properties of polycrystalline films of TTF-TCNQ have been shown to be effected by the presence of grain boundaries, and are, therefore, expected to be much less sensitive to low concentrations of impurities than are single crystals. Consequently, whilst great care was taken in purifying the precursors TTF and TCNQ, this was restricted to double recrystallisation from pure solvents in a nitrogen glove box as described earlier. Gradient Sublimation of the precursors was not carried out. However, it was particularly important for the present work to confirm reports that the complex sublimed unchanged⁽¹⁰⁾.

A.1.4(i) Gradient Sublimation

Purification of the complex was carried out using a gradient sublimation technique which has been used by other workers^{(8) (11)}, to purify the precursors (TTF) and (TCNQ), although its use for purifying the complex does not appear to have been reported previously. The gradient sublimer used in the present work was similar to that described by McGhie⁽¹¹⁾. It consisted of a thick, brass tube 40 cm long, 4 cm outside diameter, with an observation slit along most of its length. Both ends of the tube were mounted in holes in two square Sandanyo blocks (1 x 15 x 15 cm) which were held rigid with four steel rods. One end of the tube was heated by a coiled heating element, powered by a 50-volt mains operated, regulated power supply, with a maximum current output of 10 amps. The other end was water cooled with a constant flow of water (0.5 litres/min), a copper coil braised to the brass tube. Since the cooling rate was constant, the temperature gradient was determined by the heater current. The gradient was calibrated at atmospheric pressure, using a chromel/alumel thermocouple to determine the temperature at various positions inside the silicon tube, and was found to vary linearly with distance from the heater.

Sublimation was carried out from silica boats capable of holding 3g. of material, inside a 2.8 cm O.D. silica tube, sealed at one end, which was lined internally with a PTFE sheet. The silica tube was located inside the brass tube, the temperature in the region of the heater being high enough to cause the materials to sublime, and was wrapped in a woven glass mat to prevent the development of hot spots. The open end of the silica tube was connected directly to the metal vacuum system with a viton 'O' ring, which enabled it to be evacuated

to a base pressure of less than 10^{-5} Torr prior to carrying out a sublimation. The vacuum system consisted of an air cooled 2" oil diffusion pump (Edwards EO2) backed by an oil trapped mechanical pump which produced a backing pressure of 5×10^{-2} Torr.

Normally gradient sublimation was carried out at a pressure of 10^{-3} Torr of nitrogen. The system was initially evacuated to a pressure of about 10^{-5} Torr, and back filled to a pressure of 10^{-3} Torr with white spot nitrogen, using a needle valve. Evacuation was then continued under a constant leak of nitrogen.

In order to establish that TTFTCNQ complex sublimed unchanged the crude material, prepared by precipitation from solution, was sublimed at a pressure of 10^{-3} Torr at a crucible temperature of $180-200^{\circ}\text{C}$ over a period of about 4 hrs. Sublimed material was deposited as small black shiny crystallites along the length of the PTFE tube, but a large proportion of the deposit occurred in a band which started at about seven cm from the heater and was approximately 4 cm wide. This material was resublimed two further times. A spongy fibrous residue was left in the crucible after the first sublimation which would not sublime even after prolonged heating at temperatures in excess of 220°C . Chemical analysis was carried out after each sublimation and the results are shown in Table A.2.

Analytical Results

The results in Table A.2 show that the composition of TTFTCNQ does not change appreciably upon evaporation at reduced pressure. The observed variation in composition could easily be accounted for as being due to the error involved in the method of chemical analysis.

Table A.2. The Effect of Repeated Sublimation on the
Chemical Analysis of TTFTCNQ

Sample Designation	% C	% H	% N	% S
Calculated for TTFTCNQ	52.92	1.97	13.71	31.39
Crude material precipitated from acetonitrile	53.52	2.02	13.84	30.92
1 x Gradient Sublimed	52.75	1.99	13.82	31.56
2 x Gradient Sublimed	53.18	1.96	13.78	31.46
3 x Gradient Sublimed	52.97	1.96	13.60	31.23
Residue remaining in crucible after 1 x Sublimation	48.06	1.25	10.69	28.28
Pure Single Crystal Data from Reference (12)	52.83	1.94	13.67	31.46

A.2 Purification of Aromatic Hydrocarbons

Three of the four aromatic hydrocarbons used in the fluorescence study described in Chapter 3, anthracene, tetracene and perylene were obtained in the purified form from sources within Imperial Chemical Industries (PLC). Anthracene from a commercial source has been doubly vacuum sublimed⁽¹³⁾. Perylene had been doubly vacuum sublimed and zone refined⁽¹³⁾. Tetracene was prepared synthetically⁽¹⁴⁾ and twice recrystallised from trichlorobenzene followed by vacuum sublimation. Pyrene was obtained from Aldrich Chemicals Ltd, and purified by triple gradient sublimation using the equipment described in the previous section. All four materials gave chemical analyses (C, H) which corresponded within experimental error to those calculated from their respective empirical formulae. Both absorbance and fluorescence spectroscopy of propanol solutions of all four compounds were used to confirm the absence of major impurities.

The purity of samples prepared by vacuum sublimation as shown by elemental analysis also compares favourably with results reported in the literature for TTFTCNQ complex single crystals grown from solution from highly purified precursors⁽¹²⁾.

APPENDIX 2

THICKNESS MEASUREMENT OF TTFTCNQ FILMS

An independent estimate of thickness was obtained by dissolving films in Analar acetone and recording the spectrum of the solution between 350 - 900 nm using a Beckmann Model 25 spectrometer. A typical spectrum is shown in Figure A.3(a). There were three main series of bands which had maxima located at 400, 745 and 845 nm. A solution concentration of approximately 10^{-5} g moles/litre was used, to minimise the formation of dimerised species. As discussed in Chapter 5 dimerisation of the TCNQ radical ion⁽¹⁵⁾ occurs in aqueous solution at room temperature, the concentration of dimer increasing with that of the monomer. TTF radical cations also dimerise in solution, but only at low temperatures⁽¹⁶⁾. Absorption bands characteristic of TCNQ and TTF radical ion dimers occur in the region of 640 nm and 710 nm, respectively. Although a weak absorption was observed in the vicinity of 710 nm it was assigned to the monomer TCNQ^- species. In fact the two series of bands located at 745 and 845 nm are highly characteristic of the TCNQ^- radical ion monomer and the intensity of the latter was used for estimating film thickness.

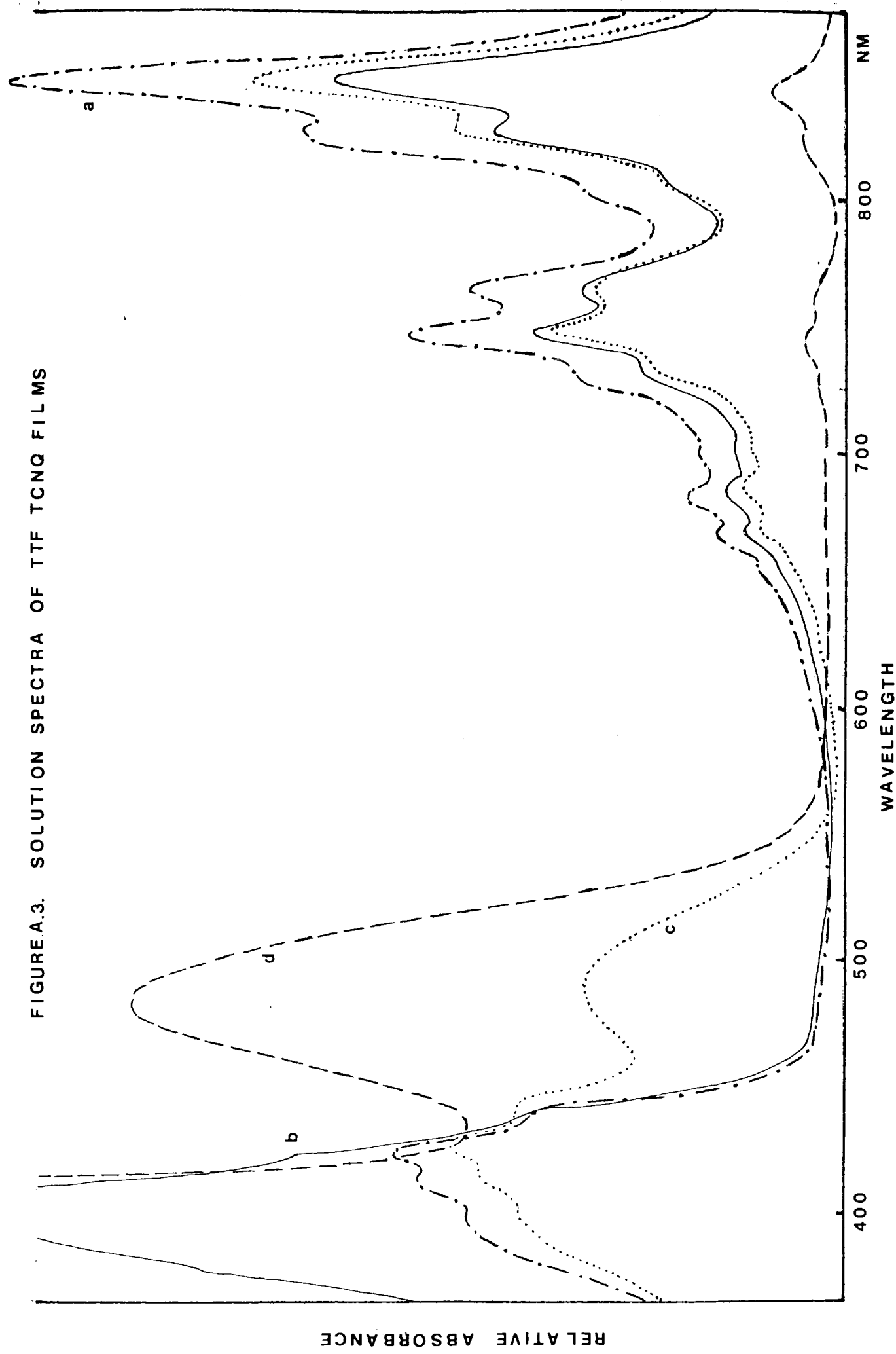
A known amount of the complex was evaporated onto a well defined area (0.12 cm^2) of a quartz crystal mass monitor. It was removed by dissolution in acetone and the spectrum obtained was used to calibrate solutions produced from other films. Time dependent changes in the solution spectra of a type shown in Figure A.3(b), (c) were observed for a number of samples. The initial spectrum (curve b) taken several minutes after dissolution contained an intense band located at 394 nm in addition to bands at 745 and 845 nm due to TCNQ^- . After allowing the sample to stand for a period of 24 hrs the intensity of the band at 394 had decreased considerably whilst those at 745 and 845 nm were observed to increase (curve b). The small shoulder at 488 nm which can be seen in Curve b, increased on

standing for a further 48 hrs, while those at 745 and 845 registered a substantial decrease over this period.

The band at 395 nm is consistent with neutral TCNQ being present in some films prior to dissolution. On standing this may have been converted first to the radical ion monomer, causing an increase in the 745 and 845 nm bands, and then subsequently reduced to the doubly charged TCNQ^{2-} species. This latter species has been generated electrochemically by Jonkmann and Kommandeur⁽¹⁷⁾ and possesses an absorption band at about 500 nm. An alternative explanation of the band at 488 nm is that it may be assigned to the (TTF) (TCNQ) complex, since a band was observed in the same region (580 nm) in spectra of thin film deposits, Figure (5.22). Torrance et.al⁽¹⁸⁾ have shown from single crystal studies that this band is polarised primarily in the molecular plane and can therefore be considered to be intramolecular.

Films which were stored for long periods before dissolution gave a spectrum of the type shown in Figure (A.3), (curve d). The band at 488 nm was in this case the largest in the spectrum and only very weak bands were observed at 745 and 845. Over a period of about 10 mins the band at 488 increased in intensity whilst all the others decreased, until the former was the only one remaining. This change occurred very rapidly compared to those already discussed and indicates that after deposition films continue to age for some considerable time at room temperature. The solution spectra of a number of films were examined weeks or months after deposition. These only gave bands which could be attributed to TCNQ^- , initially there was no band present at all at 488 nm. Those films which gave an initially high intensity 488 nm absorptions in solution had been

FIGURE A.3. SOLUTION SPECTRA OF TTF TCNQ FILMS



stored for 6 months before being dissolved and examined.

In view of the observed changes in the solution spectra of TTF:TCNQ from the thin film deposits, estimates of the concentration of species in solution were from spectra taken obtained immediately upon dissolution. It was assumed that TTF and TCNQ were present in the original film in the ratio of 1:1 although no direct evidence of TTF species was obtained from the solution spectra. When solutions contained species other than TCNQ^- anion, an estimate of their concentration was obtained by comparing the change in the relative intensities of the two bands at 395 (TCNQ^0) and 488 nm (complex) with that at 845 and the total amount of TCNQ in the film was used to compute the film thickness. An extinction coefficient for the band at 845 nm of $5.27 \times 10^4 \text{ litre mole}^{-1} \text{ cm}^{-1}$, was obtained by dissolving the known weight of complex from the quartz crystal.

References for Appendices 1 and 2

1. Begg, I.D., Barang, R.S., Roberts, K.J. and Sherwood, J.N.,
J. Cryst. Growth, 49, 753 (1980).
2. Melby, L.R., Hartzler, H.D. and Sheppard, W.A., J. Org. Chem.,
39, 2456 (1974).
3. Klingsberg, E., J. Amer. Chem. Soc., 86, 5290 (1964).
4. Acker, D.S. and Hertler, W.R., J. Am. Chem. Soc., 84, 3370 (1962).
5. Coleman, L.B., Cohen, J.A., Garito, A.F. and Heegar, A.J.,
Phys. Rev., B7, 2122 (1973).
6. Thomas, G.A. et.al., Phys. Rev. B13, 5105 (1976).
7. McGhie, A.R., Nigrey, P.J., Yamagishi, E.G. and Garito, A.F.,
Ann. New York, Acad. Sci., 313, 301 (1978).
8. Gemmer, R.V., Cowan, D.O., Poehler, T.O., Block, A.N., Pyle, R.E.
and Banks, R.H., J. Org. Chem., 40, 3544 (1975).
9. Chen, T.H. and Schechtman, B.H., Thin Sol. Films, 30, 173
(1975).
10. Chaudhari, P., Scott, B.A., Laibowitz, R.B., Tomikiewicz, Y.
and Torrance, J.B., Appl. Phys. Lett., 24, 439 (1974).
11. McGhie, A.R., Garito, A.F. and Heegar, A.J., J. Cryst. Growth,
22, 295 (1974).
12. Cohen, M.J., Coleman, L.B., Garito, A.F. and Heegar, A.J.,
Phys. Rev., B10, 1298 (1974).
13. Samples of perylene and anthracene were obtained from W.A. Barlow,
Imperial Chemical Industries (PLC), Corporate Laboratory,
The Heath, Runcorn, Cheshire, England.
14. Mitchard, Goodings and Owen., J. C.S. Perkin, 1, 1310 (1972).
15. Boyd, R.H. and Phillips, W.D., J. Chem. Phys., 43, 2927 (1965).
16. Torrance, J.B., Scott, B.A., Welber, B., Kaufman, F.B. and
Seiden, P.E., Phys. Rev. B19, 730 (1979).

17. Jonkman, H.T. and Kommandeur, J., Chem. Phys. Lett., 15, 496 (1972).
18. Torrance, J.B., Scott, B.A. and Kaufman, F.B., Sol. State Comm. 17, 1369 (1975).

APPENDIX 3

'd' SPACINGS FOR (TTF) (TCNQ) SINGLE CRYSTALS,
COMPUTED FROM PUBLISHED DATA (REFERENCE (1) CHAPTER 4)

H	L	L	CLS	CALC	DELTA	DOBS A	DCALC A
0	0	1		0.001876			17.79999
1	0	0		0.004237			11.84276
-1	0	1		0.004709			11.23415
0	0	2	0.007400	0.007503	-0.000103	8.96152	8.80999
1	0	1		0.007517			8.89148
0	0	2	0.008800	0.008932	-0.000132	8.21782	8.15698
1	0	2	0.014300	0.014548	-0.000248	6.44659	6.39136
-2	0	1		0.016017			6.09134
0	0	3	0.016600	0.016881	-0.000281	5.98334	5.93333
-1	0	3		0.016906			5.92895
-2	0	0		0.016949			5.92130
-2	0	2	0.018500	0.018835	-0.000335	5.66777	5.61707
-2	0	1		0.021633			5.24130
-1	0	3		0.025331			4.84367
-2	0	3		0.025406			4.83653
-1	0	4		0.028632			4.55501
0	0	4	0.029700	0.030611	-0.000911	4.07321	4.45009
-2	0	2		0.030066			4.44574
-2	0	4		0.035727			4.07849
-3	0	1		0.035799			4.07439
-3	0	2		0.037214			3.99626
3	0	0		0.038136			3.94759
1	0	4	0.039700	0.039864	-0.000164	3.86903	3.86105
0	1	0		0.042176			3.75400
-2	0	3		0.042255			3.75025
-3	0	3		0.042386			3.74472
0	1	1		0.044046			3.67320
-1	0	5		0.044108			3.67060
3	0	1	0.045200	0.044224	0.000976	3.62601	3.66582
1	1	0		0.046408			3.57852
-1	1	1		0.046679			3.56047
0	0	5		0.046892			3.56000
			0.047900			3.52233	
0	1	2	0.049400	0.049673	-0.000273	3.46844	3.45890
1	1	1		0.049687			3.45840
-2	0	5		0.049800			3.45449
0	1	2		0.051102			3.41019
0	0	4		0.051297			3.40370
3	0	2		0.054063			3.31549
			0.055200			3.28117	
1	1	2	0.057300	0.056719	0.000581	3.22048	3.23695
1	0	5		0.058156			3.19687
-2	1	1		0.058187			3.19584
-2	0	4		0.058193			3.19568
0	1	3		0.059051			3.17236
-1	1	3		0.059076			3.17169
-2	1	0		0.059120			3.17053
-2	1	2		0.061000			3.12113
-1	0	6	0.063100	0.063337	-0.000237	3.06890	3.06310
-2	1	1		0.063503			3.05194
-3	0	5		0.063766			3.04806
0	0	1		0.064056			3.04592
0	0	2		0.064066			3.04567
			0.066200			2.98047	

1	1	3		0.067501		2.96717
0	0	6		0.067524		2.96667
-2	1	3		0.067576		2.96553
-2	0	6		0.067624		2.96447
3	0	3		0.067654		2.96383
4	0	0		0.067797		2.96070
-4	0	3		0.067828		2.96000
			0.068900		2.93680	
-1	1	4		0.070862		2.89718
0	1	4		0.072181		2.86937
2	1	2		0.072239		2.86823
4	0	1		0.075289		2.80953
-4	0	4		0.075342		2.80854
2	0	5		0.077882		2.76236
-2	1	4		0.077897		2.76208
-3	1	1		0.077969		2.76081
-3	1	2		0.079384		2.73610
1	0	6	0.066100	0.080180	-0.000080	2.72384
3	1	0		0.080306		2.72035
-3	0	6		0.080386		2.71899
1	1	4		0.082035		2.69153
2	1	3		0.084425		2.65315
-3	1	3	0.084500	0.084550	-0.000050	2.65198
3	0	4		0.084990		2.64423
-1	1	5		0.086279		2.62450
-1	0	7		0.086310		2.62393
3	1	1		0.086394		2.62275
4	0	2		0.086532		2.62065
-4	0	5		0.086690		2.61953
			0.087400		2.60761	
0	1	5		0.089062		2.58316
-2	0	7		0.089199		2.58117
0	0	7		0.091908		2.54286
-2	1	5		0.091970		2.54199
-3	1	4		0.093467		2.52155
3	1	2		0.096233		2.48505
			0.098500		2.45629	
-5	0	2		0.099394		2.44522
1	1	5		0.100320		2.43391
2	1	4		0.100363		2.43339
-3	0	7		0.100557		2.43104
-5	0	1		0.100787		2.42826
2	0	6		0.101322		2.42184
4	0	3		0.101527		2.41940
-4	0	6		0.101622		2.41826
-5	0	3		0.101752		2.41673
			0.103800		2.39276	
-1	1	6		0.105507		2.37332
5	0	0		0.105932		2.36856
1	0	7		0.105974		2.36809
3	0	5		0.106089		2.36681
-3	1	5		0.106136		2.36628
-4	1	1		0.106226		2.36528
-4	1	2		0.106237		2.36516
-5	0	4	0.107600	0.107861	-0.000261	2.35013
0	1	6		0.109694		2.32759

-2	1	6	0.109794			2.32653
3	1	3	0.109624			2.32621
4	1	0	0.109967			2.32470
-4	1	3	0.109990			2.32436
-1	0	8	0.113047			2.29281
-2	0	8	0.114526			2.27796
5	0	1	0.115000	0.006172	2.27326	2.27490
4	1	1	0.117459			2.24934
-4	1	4	0.117512			2.24883
-5	0	5	0.117721			2.24683
			0.119290		2.23285	
0	0	8	0.120043			2.22500
2	1	5	0.120052			2.22491
4	0	4	0.120273			2.22287
-4	0	7	0.120389			2.22179
1	1	6	0.122356			2.20386
-3	1	6	0.122556			2.20207
-3	0	8	0.124480			2.18498
			0.126100		2.17090	
3	1	4	0.127160			2.16170
5	0	2	0.127476			2.15915
-1	1	7	0.128487			2.15065
2	0	7	0.128514			2.15041
4	1	2	0.128702			2.14884
-4	1	5	0.128776			2.14822
			0.130100		2.13727	
3	0	6	0.130934			2.13046
-5	0	6	0.131333			2.12721
-2	1	7	0.131370			2.12691
0	1	7	0.134076			2.10532
1	0	8	0.135513			2.09415
			0.140300		2.05611	
-5	1	2	0.141564			2.04890
-3	1	7	0.142727			2.04053
4	0	5	0.142770			2.04023
-4	0	6	0.142906			2.03925
-5	1	1	0.142958			2.03889
-6	0	2	0.143196			2.03720
2	1	0	0.143493			2.03509
-1	0	9	0.143529			2.03483
-2	0	9	0.143604			2.03430
4	1	3	0.143697			2.03364
-4	1	6	0.143792			2.03296
5	0	3	0.143875			2.03238
-5	1	3	0.143922			2.03205
-6	0	3	0.144149			2.03045
-6	0	1	0.146400	0.000407	2.01478	2.01758
5	1	0	0.148103			2.00316
1	1	7	0.148144			2.00288
3	1	5	0.148259			2.00211
-5	0	7	0.148696			1.99916
-6	0	4	0.148655			1.99810
-5	1	4	0.150031			1.99025
0	0	9	0.151929			1.97778
-3	0	0	0.152154			1.97632
6	0	0	0.152542			1.97380