STUDY OF THE TEMPERATURE-DEPENDENCE OF THE FAR-INFRARED SPECTRUM OF (TMA)(I)(TCNQ)

by

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Abstract

The temperature-dependence (20-300K) of the far-infrared spectrum (20-1000cm⁻¹) of Trimethylammonium Iodide Tetracyanoquinodimethane (TMA)(I)(TCNQ) in its ordered phase, has been measured for the first time.

Our measurements confirmed the existence of two phase transitions near 150 and 100K. At least three absorption bands are activated below the 150K phase transition. We have assigned two of them to the totally symmetric mode Ag⁹ and Ag¹⁰ of the TCNQ molecule. We have also observed evidence of Brillouin zone splitting, where one band above 150K, split into three, below 150K. Since the conduction band of (TMA)(I)(TCNQ) is 1/3 filled, we have interpreted this result as suggesting that the 150K transition is a Peierls distortion.

We also observe a sharp increased in infrared absorption at 365cm⁻¹ and a weaker one at 100cm⁻¹. Since the D.C. conductivity measurements indicates that a 1000cm⁻¹ band gap is present at all temperatures, we interpret these absorption "edges" in terms of transitions between localised states in the band gap. These localised states would be introduced by either chemical impurities or by some randomness in the potential at each TCNQ site.
Table of Contents

Abstract .............................................................. ii
List of Tables .......................................................... iv
List of Figures ........................................................... v
Acknowledgement ......................................................... vi
I. INTRODUCTION ....................................................... 1
  1.1 The Possibility Of High Temperature Superconductivity ............. 1
  1.2 Applications ..................................................... 3
  1.3 Structural And Physical Properties Of 1-D Conductors ................. 4
      1.3.1 Structural Aspects Of 1-D Conductors .................... 4
      1.3.2 The Concepts Of Charge Transfer .......................... 5
      1.3.3 An Example: The TCNQ Molecule ......................... 5
      1.3.4 The Concept Of Periodic Lattice Distortion ............... 6
      1.3.5 The Concept Of Charge Density Wave ..................... 7
  1.4 Nature Of The Phase Transition In (TMA)(I)(TCNQ) ................... 9
II. PHYSICAL AND STRUCTURAL PROPERTIES OF (TMA)(I)(TCNQ) ............. 12
    2.1 Crystallographic Structure .................................. 12
    2.2 Temperature-dependence Of The Unit-cell Parameters ............... 15
    2.3 Temperature-dependence Of The D.C. Conductivity ................ 16
    2.4 The Thermoelectric Power .................................... 18
    2.5 Optical Measurements ........................................ 19
    2.6 Magnetic Susceptibility ..................................... 22
    2.7 Specific Heat Measurement ................................... 23
    2.8 Conclusions .................................................. 24
III. EXPERIMENTAL METHOD ............................................. 25
    3.1 Experimental Method ........................................... 25
IV. RESULTS AND DISCUSSION ........................................... 28
    4.1 Evidence Of Electron-phonon Interactions ........................ 28
    4.2 Activation Of The Totally Symmetric Modes AgY^9 And AgY^10 ....... 35
    4.3 The Splitting Of The Doublet At 172 And 176cm^-1 ............... 39
    4.4 Detection Of A Second Phase Transition ........................ 39
    4.5 Nature Of The 150K Phase Transition .......................... 40
    4.6 Nature Of The Second Phase Transition ........................ 41
    4.7 Temperature-dependence Of The Integrated Intensity Of The 96, 113 And 135cm^-1 Bands. ......................... 41
    4.8 Evidence Of Hydrogen Bond Stretching ........................ 45
    4.9 Detection Of An Activation Energy Of 365cm^-1 ................ 48
    4.10 Small-particle Scattering .................................... 54
    4.11 Conclusions .................................................. 56
BIBLIOGRAPHY .......................................................... 57
List of Tables

I. Observed frequencies of hydrogen bond stretching modes (21) .........................................................46
II. Force constants for phenol-trimethylamines complexes (21) .........................................................47
List of Figures

1. The TCNQ molecule ............................................. 6
2. Band structure of a 1-D compound ................................. 8
3. Band structure of a 1-D compound after a periodic  
lattice distortion .............................................. 8
4. Temperature-dependence of the D.C. conductivity (6)  
................................................................. 11
5. Temperature-dependence of the D.C. conductivity (7)  
................................................................. 11
6. (TMA)(I)(TCNQ): projection perpendicular to the b axis  
(9) .................................................................. 14
7. (TMA)(I)(TCNQ): projection parallel to the b axis (11)  
................................................................. 14
8. Temperature-dependence of the unit-cell parameters  
(12) .................................................................. 15
9. The thermoelectric power (5) ........................................ 18
10. Frequency-dependent conductivity (15) ............................ 20
11. Dielectric function (15) .............................................. 20
12. Density of states in a 1-D compound ............................. 21
13. Magnetic susceptibility and D.C. conductivity ................. 22
14. Specific heat (16) .................................................. 23
15. F.I.R Spectrum of (TMA)(I)(TCNQ) between 20 and  
400 cm$^{-1}$ ............................................................. 29
16. Temperature-dependence of the 226 cm$^{-1}$ band .......... 32
17. Temperature-dependence of the 313 cm$^{-1}$ band .......... 33
18. Temperature-dependence of the 155, 164, 172 and 176 cm$^{-1}$  
bands ............................................................... 34
19. Temperature-dependence of the integrated intensity of  
the 313 cm$^{-1}$ band ............................................ 37
20. Temperature-dependence of the integrated intensity of  
the 226 cm$^{-1}$ band ............................................ 38
21. Temperature-dependence of the integrated intensity of  
the 155, 164 and 172 bands .................................... 42
22. Brillouin zone splitting ............................................. 43
23. Temperature-dependence of the integrated intensity of  
the 96, 113, 125 and 135 cm$^{-1}$ bands ....................... 44
24. Hydrogen bond ................................................... 45
25. Temperature-dependence of the Background Intensity B .... 51
26. Plot of ln(B) as a function of 1/T ................................. 52
27. Infrared Spectrum of (TMA)(I)(TCNQ) Between 20 and  
1000 cm$^{-1}$ .......................................................... 53
28. Plot of log($I/I$) as a function of log($\lambda$) ....................... 55
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I. INTRODUCTION

1.1 The Possibility Of High Temperature Superconductivity

The search for high temperature superconductivity has been one of the driving forces of the field of one-dimensional organic conductors. Superconductivity in a metal arises when the valence electrons of the atoms forming the lattice condense into pairs, called Cooper pairs. The existence of a bound state between two negatively charge particles is due to a lattice deformation mediated by the electrons as they move in the crystal. An electron passing near two positively charged ions, will pull them together, producing a region with a net positive charge, able to attract a second electron. A Cooper pair is thereby formed.

In a perfect metallic crystal, electrical resistivity is caused by the scattering of conduction electrons by lattice vibrations. Each scattering event reduces the momentum of the electrons, leading to a decaying electrical current and Joule heating. At T=0K its resistance goes to zero.

The electronic energy of a metal in its superconducting state is minimised when all the Cooper pairs have the same momentum. The change in momentum of one pair requires the change in momentum of all the pairs. At the temperature at which the Cooper pairs condense, there is not enough vibrational energy stored in the lattice to achieve such a redistribution of the momentum of the pairs. Thus, they flow in the crystal with a constant momentum.

As the temperature is raised, the thermal agitation of the
ions becomes larger than the lattice distortion induced by the travelling electrons, destroying the superconducting state. This phenomena is thought to become dominant at around 30K and would explain why superconductivity has not been observed at temperatures higher than 22.3K.

In 1964 W.A. Little (1) proposed a new mechanism for the formation of Cooper pairs, by which the attractive potential would be induced by an electronic distortion instead of a lattice distortion, leading to the possibility of high temperature superconductivity. He imagined a molecular crystal formed by a chain of carbon atoms along which the conduction electrons could travel, and highly polarisable organic molecules would be attached to the chain. As an electron travelling along the chain encountered an organic molecule, it would polarise it, and thereby create a region of positive charge near the chain, which would be able to attract a second electron. This type of distortion, induced by the travelling electrons, involves the displacement of light electrons instead of heavy ions. Consequently this former displacement is larger then the latter. Thermal vibrations would not "erase" the distortion as easily and, therefore, the Cooper pairs could exist at high temperatures.

Organic chemistry has not as yet been succesful in producing such a molecular crystal, but it might only be a question of time. Already some of the family of molecular crystals based on the molecule Tetramethyl-tetraselenafulvalene (TMTSF) have become superconducting at low temperatures.
(TMTSF)$_2$ (PF$_6$) becomes a superconductor near 1K, at a pressure of 10 KBar (2). (TMSF)$_2$ (CLO$_A$) becomes a superconductor at 1.2K and atmospheric pressure (3).

Until now, organic superconducting compounds have been one-dimensional. In order to achieve a state of high temperature superconductivity, bridges have been established between the TMTSF columns of TMTSF compounds, in order to enhance the motions of the conducting electrons. The results could be exceptional; three-dimensional organic conductors, resembling in this sense to normal metals, but with a high temperature superconductivity.

1.2 Applications

Organic chemistry has the proven ability of creating compounds with specific architectural structures. Understanding the relationships between physical properties and structural organisations could lead to the design of molecular compounds with specific physical properties. Practical applications could be numerous. These compounds are very sensitive to temperature, pressure, magnetic field and radiation. They could therefore be used in the fabrication of all kinds of detectors. Still in the experimental stages, diodes have been produced by adjoining an organic crystal (TMCLO$_A$) to an non-organic material (GaSb) (1).

Right now the fabrication of integrated circuits (IC) requires the deposition of a polymer film on a semiconducting substrate. Part of the film is then removed, creating valleys that will be filled with a metallic material. The remainder of
the polymer film is then washed away, leaving only the metallic network on the semiconducting substrate. The process could be greatly simplified with the use of organic semiconductors. It has been shown (1) that some molecular crystals can be affected by a beam of electrons. By sending a beam of 20Å in diameter at the surface of an organic semiconductor, it is possible to change the state of the molecules from an insulating state to a metallic one, thereby eliminating the needs for the successive depositions of polymer and metallic films.

In their superconducting state, the results could be even more interesting: high magnetic field for magnetic levitation, ultra-fast electronic devices for computers. All this could be achieved without the use of liquid helium, a rare and expensive fluid.

1.3 Structural And Physical Properties Of 1-D Conductors

1.3.1 Structural Aspects Of 1-D Conductors

There is now a growing number of 1-D organic conductors. Despite this diversity, a careful examination shows that crystals exhibiting high electronic conductivity, all meet specific structural requirements.

First of all, any successful organic conductors must be formed by molecular blocks that fit closely together. The close-packed arrangement allows the conducting electrons to move easily from one molecule to the next.
1.3.2 The Concepts Of Charge Transfer

A second aspect that has proven to be very important is the concept of charge transfer. This effect arises in a crystal which is formed by two types of molecules, one type being electro negative and the other electro positive. These latter molecules will readily give electrons to the former, partly filling a new valence band on the acceptor molecules, while partly emptying the valence band on the donor molecules. This transfer of electrons could therefore lead to a metallic conduction along the stacking direction of the organic molecules. In some cases, the transfer may be completed (each donor atom giving one electron to each acceptor atom), or incompletely (on the averaged each acceptor molecule receiving less than one electron).

1.3.3 An Example: The TCNQ Molecule

The TCNQ molecule (figure-1) exhibits all the characteristics mentioned above. It is large and planar with a substantial electronic affinity. Very little energy is needed to start filling a new valence band. Its planar structure allows a very dense stacking of the molecules on top of each other. The valence orbitals protrude out of the plane of the molecule, permitting a substantial overlap of these orbitals, resulting in a metallic conduction along the stacking direction. In most 1-D compounds involving the TCNQ molecule, the interchain distance is large compared to the interplanar
Therefore, the transverse conductivity is weak, the valence electrons having to hop from one chain to the next, and the one-dimensionality of the electrical conductivity is solely due to the structural organisation of these crystals.

Figure 1 - The TCNQ molecule

![TCNQ molecule diagram]

1.3.4 The Concept Of Periodic Lattice Distortion

In the presence of an external periodic potential, discontinuities appear in the E(k) relationship of a free-electron gas. The first discontinuity appears at the edges of the Brillouin zone. Figure 2 shows the half filled, band structure of a 1-D material with a lattice spacing a. If we assume that a small distortion of the lattice occurs such that

1 Typically, the interplanar distance is 3Å while the interchain distance is 10Å.
2 The shaded area indicates the portion of the E(k) "curve" which is completely filled by electrons.
the periodicity goes from \( a \) to \( 2a \), the first discontinuity will be moved from \( K = \pi/a \) to \( K = \pi/(2a) \), i.e., at the Fermi level. As shown in figure 3, the states just below the Fermi level have been lowered in energy while the states above it have seen their energies increase. Because all the states above \( K_F \) are empty, this new configuration lowers the electronic energy of the system. Obviously, such a distortion increases the potential energy stored in the lattice and will occur only if the electronic energy saved is larger than the mechanical energy spent to create the distortion. It can be shown that this is always the case in 1-D compounds (4).

1.3.5 The Concept Of Charge Density Wave

The distortion of the lattice will modulate the distribution of electrons surrounding it, giving rise to a "CHARGE DENSITY WAVE" (C.D.W). If the periodicity of the C.D.W is not commensurate with the periodicity of the undistorted lattice, it will "slide" along the conducting direction, producing an enhancement of the D.C conductivity. At low temperatures, the C.D.W will be either pinned by Coulomb attraction to an oppositely charged chain, in a multi-chain compound, or by impurities, in a one-chain compound. The pinning will give rise to an absorption band in the far-infrared.
Figure 2 - Band structure of a 1-D compound

Figure 3 - Band structure of a 1-D compound after a periodic lattice distortion
1.4 Nature Of The Phase Transition In (TMA)(I)(TCNQ)

The molecular crystal Trimethylammonium Iodide Tetracyanoquinodimethane (TMA)(I)(TCNQ) has a highly anisotropic D.C. conductivity, the ratio of the conductivity along the conducting axis to the conductivity perpendicular to this axis being ~ 400. Along the conducting axis, the value of the conductivity ranges between 20-40 (mS cm⁻¹) at room temperature (5). It can therefore be considered as a 1-D metal. The temperature-dependence of the D.C. conductivity along this axis exhibit either a semiconducting behavior (6) (figure 4) or has a broad maximum near 240K (7) (figure 5) with a metallic behavior above that temperature and a semiconducting one below it. In every cases a phase transition is observed at 150K. A second transition is also observed at 89K in the Young modulus data (8).

The nature of the phase transition at 150K is still subject to controversy. Two distinct point of view are possible: the transition could be either a metal-semiconductor one or a semiconductor-semiconductor one. In both cases, electron-electrons interactions and electron-phonons interactions could determined the temperature-dependence of the D.C. conductivity.

In this work, we present the first far-infrared powder spectrum of (TMA)(I)(TCNQ) in its ordered phase (section 2.1). The spectra were recorded between 20 and 1000 cm⁻¹, at 9 different temperatures between 20 and 300K. The main goal of this work is to clarify the nature of the phase transitions at 150 and 89K. In chapter II we will review the crystallographic
structure and physical properties of \( (TMA)(I)(TCNQ) \). In chapter III the experimental technique used will be discussed. Finally in chapter IV we will present and discuss the results obtained.
Figure 4 - Temperature-dependence of the D.C. conductivity (6).

Figure 5 - Temperature-dependence of the D.C. conductivity (7).
II. PHYSICAL AND STRUCTURAL PROPERTIES OF (TMA)(I)(TCNQ)

2.1 Crystallographic Structure

In 1976, Cougran et al. (9) reported that Tetracyanoquinodimethane (TCNQ) reacts with Trimethylammonium Iodide (TMA)(I) to form the ternary charge transfer compound (TMA)(I)(TCNQ). Elemental analysis shows that the compound has a 1:1:1 stoichiometry. The presence of the trihalide ion $I^{3-}$ in the crystal has been determined by Raman measurements (5), in which the strong feature observed at 105 cm$^{-1}$ was assigned to the symmetric stretch $\nu_s$ of $I^{3-}$. Therefore the stoichiometry and the conservation of charge suggest the following formulation.

\[
(TMA^+)(TCNQ^{2-})(I^-)_3
\]  

The crystal at room temperature is monoclinic and belongs to the space group C2/m (10) (figure 6). The large planar TCNQ molecules form regular stacks along the $b$ axis with an interplanar distance $b/2$ of 3.23 Å. They are separated by iodine chains along the $a$ axis and by the TMA cations along the $c$ axis. The iodine chains are also parallel to the $b$ axis and presumably non-conducting. All the atoms of a TCNQ molecule are in the plane (AOC). This plane constitutes a mirror plane for the TMA cations. The TCNQ molecules are characterised by a zigzag stacking, two neighbouring TCNQ molecules being related by a screw axis symmetry operation. There is a weak hydrogen bond between the TMA cations and one of the nitrogen atoms of the TCNQ molecule. These cations are therefore linked by the same symmetry operation. The iodine chains constitute an axis
of symmetry $C^2$.

In most cases, X-ray measurements show a strong diffuseness due to an important disorder between the iodine chains. On the other hand, the $I^3-$ ions are well ordered within a chain, with a correlation length of about 100 Å (10).

More recently (11), fully ordered crystals have been obtained by cooling of a solution of acetonitrile at room temperature or below. These crystals are larger than the disordered ones and do not exhibit the diffuse diffraction pattern associated with the disorder of the iodine lattice. By raising the temperature of the acetonitrile solution, various degree of disorder may be obtained. Figure 7 shows a projection of the ordered crystal along the $b$ axis. Columns one, two and three of figure 7 correspond to the columns one, two and three respectively of figure 6.
Figure 6 - (TMA)(I)(TCNQ): projection perpendicular to the b axis (9)

Figure 7 - (TMA)(I)(TCNQ): projection parallel to the b axis (11)
2.2 Temperature-dependence Of The Unit-cell Parameters

The temperature-dependence of the unit-cell parameters have been studied by various authors. Coulon et al. (12) have reported a change in slope at 150K (figure 8), a phenomenon very reminescent of what is observed in TTF-TCNQ at the Peierls transition. Filhol et al. (10) observed a non-linear but continuous variation of the unit-cell parameters.

Figure 8 - Temperature-dependence of the unit-cell parameters (12)
2.3 Temperature-dependence Of The D.C. Conductivity

The room temperature D.C. conductivity along the conducting b axis is \( \sim 20 \, (\text{Acm})^{-1} \) (5). The conductivity is highly anisotropic with \( \sigma_{\parallel}/\sigma_{\perp}=400 \). The temperature-dependence of the D.C. conductivity has been reported as being characteristic of a semiconductor with an activation energy presenting a singularity at 150K (6): Above that temperature, the activation energy was measured to be equal to 0.05 eV (400cm\(^{-1}\)) while below it, to be equal to 0.15 eV (1200cm\(^{-1}\)) (figure 4). In other cases the conductivity exhibited a broad maximum near 240K with a metallic behavior above that temperature (7). An anomaly was also found, but this time at 160K (figure 5).

Abkowitz et al. (7) interpret the metallic behavior in terms of a semiconductor-semiconductor transition. Following the idea of Epstein et al. (13), they argue that the metal-like variation of \( \sigma(T) \) above 240K is due to thermally excited carriers having a strong temperature-dependent mobility. Their results for NMP-TCNQ indicates that the mobility should have a \( T^{-4} \) dependence (13). They have also shown that the scattering of conduction electrons by optical phonons yield the \( T^{-4} \) dependence (13). The gap in the density of states would be induced in the following way:

---

1 The term metallic is used here to describe a material in which the conductivity increases as the temperature is lowered.
The formation of the salt follows the chemical charge transfer reaction:

\[
3(TMA^+I^-) + 3\text{TCNQ} \rightarrow (TMA^+)_3(TCNQ)^2 I_-^-
\]  

(2)

Therefore each TCNQ molecule accepts on the average 2/3 of an electron. In a simple one-electron band model, the number of possible values of the wave vector \( K \) (and therefore the number of states available) is equal to the number of primitive cells \( N \) time the number of spin states \( (2) \). The number of states available is thus \( 4N \). On the other hand, the total number of electrons being transferred is \( (N)(2)(2/3)=4N/3 \). The upper valence band of the TCNQ molecules is therefore 1/3 filled and one would expect the compound to behave like a metal. But the iodine chains, being commensurate with the TCNQ chains, and having a periodicity of \( 3b/2 \), can introduce a gap right at the Fermi level provided that the interaction between the conduction electrons and the iodine chains is strong enough. If this is the case, a gap in the density of states would be present at all temperatures.
2.4 The Thermoelectric Power

The thermoelectric power $S$ of a semiconductor is given by

$$S = -\frac{k_B^2}{e} \left\{ \left( \frac{u_e/m_e - 1}{u_e/m_e + 1} \right) \frac{E_g}{k_B T} + \ln \left( \frac{m_p}{m_e} \right) \right\}.$$  \hspace{1cm} (3)

where $u_e, m_e$ and $u_p, m_p$ denote the mobility and effective mass of the electrons and holes respectively. Above and below the 150K transition, the thermoelectric power varies like $T^{-1}$ suggesting that both regions are semiconducting (5) (figure 9). The change in slope occurring at 150K indicates that the term

$$\frac{u_e/u_p - 1}{u_e/u_p + 1}$$

changes abruptly from a negative value ($u_e < u_p$) to a larger positive value ($u_e > u_p$). It is therefore clear that at least $u_e$ and $u_p$, and presumably $E_g$ change abruptly at 150K.

Figure 9 - The thermoelectric power (5)

![Graph showing the thermoelectric power vs. $1/T$]
2.5 Optical Measurements

Optical measurements made by Tanner et al. (15) indicate the existence of a gap at room temperature. By doing a Kramer-Kronig analysis of their reflectance data, they have evaluated both the frequency-dependent conductivity (figure 10) and the dielectric function (figure 11). Below 200 cm\(^{-1}\), they found a value of \(\sigma(w)\) of 19 cm\(^{-1}\), in good agreement with the room-temperature D.C. value (5). The broad maximum observed in \(\sqrt{\sigma(w)}\) was interpreted as the signature of a gap. The density of states of a truly 1-D conductor varies like \((E - E_c)^{-\gamma_1}\) (and \((E - E_v)^{-\gamma_2}\)) where \(E_c - E_v = E_g\) (see figure 12). 3-D interactions remove the singularity at \(E_v\) and \(E_c\). Because of the high value of \(N(E_c)\) and \(N(E_v)\), the transitions between states of energy \(E_c\) and \(E_v\) are highly favored, giving rise to the strong maximum in \(\sqrt{\sigma(w)}\) at \(E_g = E_c - E_v\). They estimated the room-temperature gap at 0.1 eV.
Figure 10 - Frequency dependent conductivity (15)

![Figure 10](image)

Figure 11 - Dielectric function (15)

![Figure 11](image)
Figure 12 - Density of states in a 1-D compound
2.6 Magnetic Susceptibility

The magnetic susceptibility measurements indicate that (TMA)(I)(TCNQ) is metallic above Tc. The result shown on figure 13 (16) were obtained using the Faraday method. The method gives the total susceptibility of the compound. The diamagnetic contribution is then subtracted to obtain the paramagnetic susceptibility ($\chi$ spin). At high temperatures, the paramagnetism is almost constant, only showing a slight decrease with decreasing temperature. This behavior is typical of a non-magnetic free electron metal (Pauli paramagnetism). The presence of a gap would produce an activated susceptibility that would increase with temperature, that is, the temperature-dependence of $\chi$ spin would be dominated by the temperature dependence of the number of single particle excitations. The data also suggest that $\chi$ spin goes to zero as the temperature goes to zero. (The absence of a linear term in the specific heat (figure 14) confirms that). Thus the low temperatures data of the spin susceptibility exhibit the properties of a non-magnetic small band gap insulator, while the high temperatures data exhibit the features of a metal.

Figure 13 - Magnetic susceptibility and D.C. conductivity
2.7 Specific Heat Measurement

The low temperatures specific heat shows no linear term (16) (figure 14). Thus the electronic contribution is very small. This is indeed expected of a small band gap insulator, since a negligible amount of free carriers are present at low temperatures. The contribution of long wavelength acoustic phonons to the lattice specific heat gives a $T^3$ dependence. The curvature observed implies that low energy optical modes also contribute to the specific heat.

Figure 14 - Specific heat (16)
2.8 Conclusions

The behavior of the D.C. conductivity and magnetic susceptibility above 150K can be seen as indicating that \((\text{TMA})\text{(I)}(\text{TCNQ})\) is metallic. The anomaly observed in the thermoelectric power indicates that the mobility does not vary as a smooth function of temperature \((T^{-4})\) and that a phase transition occurs at 150K. The presence of an inflection point in the thermal variations of the lattice parameters confirms the occurrence of a structural distortion at 150K.
III. EXPERIMENTAL METHOD

3.1 Experimental Method

The measurements were taken using powdered samples of (TMA)(I)(TCNQ) crystals. The crystals were finely ground with a mortar and pestle in a solution of commercial nujol mull. The thick mixture obtained was then spread on a TPX or silicon window. The TPX windows were used in the spectral region between 20 and 400 cm⁻¹, while silicon windows were used for frequencies above 400 cm⁻¹.

Various particle sizes and thickness of mull were tried. In the spectral region covered (20-1000cm⁻¹), no effects related to particle sizes were observed. On the other hand, the spectra were very sensitive to the thickness of the mull. For a thickness larger than ~1mm, only broad and weak features were observed while for a thickness smaller than ~0.25mm no absorption took place and consequently no structures were seen. With a thickness of ~0.5mm and particle diameters ranging between 0.3 and 1.0um, sharp and strong absorption bands were observed. The size of the particles was estimated by comparing the nujol powder with a second powder of known size. Although difficult to evaluate, the leakage through the powder is believed to be smaller than 10 %.

The spectra were recorded using a Michelson interferometer (Beckmann model FS-720). The samples were mounted in a Janis Supervaritemp dewar (model 8 CNDT). The cooling was achieved by vaporizing helium with a heater located beneath the sample. The temperature was measured using a calibrated silicon diode.
embedded in the sample holder. An accuracy of ±1K was achieved for all the measurements using a PAR 152 temperature controller. The instrument controls the current flowing in the heater. A second silicon diode located on the vaporizer arrangement measures the temperature and feeds back the reading to the PAR 152, which adjusts the current accordingly.

The sample and vaporizer arrangement located on the dewar tail were contained within a rectangular cell provided with windows on all sides. For this experiment, mylar windows of 0.75 inch in diameter and 0.025mm thickness were used. Below 100K, the mylar windows were helium tight. Above it, helium started to diffuse through the windows and it was necessary to pump on the sample chamber.

Between 20 and 400 cm\(^{-1}\) a bolometer using a composite germanium element was used as detector. Above 400 cm\(^{-1}\) a Golay detector gave a better signal-to-noise ratio and was used instead.

The long time involved in recording high resolution spectra over a large frequency range, combined with the long time taken by the system to reach high temperatures, forced us to spread the experiment over several days. Care was therefore taken to always repeat some previous measurements before going to any new temperature, allowing consistency in the results from one day to the next. Background measurements were recorded at the same temperatures as the sample measurements, and with identical windows.

All the spectra presented in this work are the logarithm of
the ratio of the background intensity ($I_0$) to the sample intensity ($I$). The transmission through a sample of thickness $d$ is given by:

$$T = \frac{I}{I_0} \times \frac{(1-R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}}$$

(5)

where $R$ is the reflectance and $\alpha$ the absorption coefficient. Neglecting $R$, $\log(I_0/I)$ is then proportional to the absorption coefficient $\alpha$.

The curve showing the temperature-dependence of the integrated intensities of absorption bands are the area of the logarithmic background to sample ratio. The area were measured using a planometer to enlarge spectra. Polynomials of various degrees were then fitted through these experimental data points. The scale used for these graphs is an arbitrary one, 100 refering to the largest intensity measured for a particular band.
IV. RESULTS AND DISCUSSION

4.1 Evidence Of Electron-phonon Interactions

Figure (15) shows a far-infrared spectrum of (TMA)(I)(TCNQ) between 20 and 400 cm\(^{-1}\), obtained at 20 and 300K respectively. The 20K spectrum is the average result of two runs, recorded at a resolution of 2 cm\(^{-1}\), while the 300K spectrum is the average of three runs recorded at a resolution of 4 cm\(^{-1}\). In order to emphasise the differences in the two spectra, we have superposed them on top of each other, using the same scale. The absorption level is therefore arbitrary.

The room temperature spectrum is almost featureless. We observe the presence of two broad absorption bands centered at 120 and 160 cm\(^{-1}\), superimposed on a background which reaches a maximum at 300 cm\(^{-1}\). These broad structures are the room temperature counterparts of the very strong vibrational structures observed in the 20K spectrum, near 113 and 164 cm\(^{-1}\). Another strong rise in absorption is seen at 365 cm\(^{-1}\). Its existence was confirmed by extending the measurements up to 1000 cm\(^{-1}\) (see section 4.9). The nature of these absorption "edges" will be discussed in section 4.9.

The 20K spectrum shows numerous absorption bands. We have indicated the strongest ones. All of the structures have a strong temperature-dependence. We observe at least three bands that do not have counterparts in the 300K spectrum:
Figure 15 - F.I.R Spectrum of (TMA)(I)(TCNQ) between 20 and 400 cm$^{-1}$
- The 226 cm\(^{-1}\) structure is clearly not observed in the 300K spectrum. In figure 16 we show the temperature-dependence of the band between 20 and 180K. The weak structures observed at 230 cm\(^{-1}\) (160K) and 229 cm\(^{-1}\) (180K) cannot be the 226 cm\(^{-1}\) band since they are shifted in the wrong direction.  

-Figure 17 shows the temperature-dependence of the 313 cm\(^{-1}\) band between 20 and 180K. Again the 320 cm\(^{-1}\) feature at 180K cannot be the 313 cm\(^{-1}\) band. On the other hand, the 313 cm\(^{-1}\) is only weakly seen at 140K. We therefore conclude that the broad structure observed in the 160K spectrum is noise.

-Figure 18 shows the temperature-dependence of the bands at 155 and 164 cm\(^{-1}\), and the doublet at 172 and 176 cm\(^{-1}\) (20K values). The 164 band is not observed at 160, 180 and 300K. The broad structures at 153 and 169 cm\(^{-1}\) (160K values) persist up to 300K.

    The intense structure at 113 cm\(^{-1}\) also exhibit a strong temperature-dependence. Nevertheless the band is clearly not activated. The temperature-dependence of its integrated intensity will be discussed in section 4.7 and a preliminary assignment given in section 4.8.

    We attribute these new structures to electron-phonon interactions. More specifically, to the coupling of the conduction electrons with totally symmetric modes of vibration.

    Upon increasing the temperature, the chemical bonds become weaker. One therefore expects the bands to shift to lower frequencies.
It has been shown (18) that this coupling gives rise to a new set of infrared features of frequencies close to the frequency of totally symmetric modes (normally infrared inactive). The coupling may be driven by one of the following mechanism:

1) In dimerised systems, totally symmetric vibrations that are out of phase on the two molecules forming a dimer may drive the radical electron into an oscillatory motion of frequency close to the frequency of the totally symmetric mode. The absorption is electronic in nature and polarised along the dimerised direction.

2) In 1-D Peierls distorted compounds, each component of the incommensurate C.D.W. may couple with a totally symmetric mode, giving rise to infrared activity polarised along the conducting axis.

In figure-15 all the structures of the 20K spectrum appear as absorption bands, indicating that the gap between the valence and conduction band is well above 400cm⁻¹.
Figure 16 - Temperature-dependence of the 226 cm$^{-1}$ band
Figure 17 - Temperature-dependence of the 313 cm$^{-1}$ band
Figure 18 - Temperature-dependence of the 155, 164, 172 and 176 cm$^{-1}$ bands
4.2 Activation Of The Totally Symmetric Modes $\text{Ag}^9$ And $\text{Ag}^{10}$

Among the 10 totally symmetric modes of the TCNQ molecule, only $\text{Ag}^9$ and $\text{Ag}^{10}$ are normally found below 400cm$^{-1}$.

Figure 19 shows the temperature-dependence of the integrated intensity of the 313cm$^{-1}$ band. We have also plotted on the same figure the temperature-dependence of the background absorption measured at the same frequency. The band is clearly activated in the neighbourhood of 140K. We observe a sharp increase between 140 and 120K, followed by a weaker one between 120 and 20K.

This kind of temperature-dependence is typical of what has been observed by Bozio and Pecile (19) (caption of figure 19) and Eldridge and Bates (20), for the activation of $\text{Ag}^9$ and $\text{Ag}^{10}$ in TTF-TCNQ. We tentatively assign the 313cm$^{-1}$ structure to the totally symmetric mode $\text{Ag}^9$. We have also drawn on the figure error bars for typical data points. The error on the intensity axis is ±3 units. This number was reached by calculating the standard deviation of the data points obtained with the planometer. The error on the temperature axis is of the order of ±1K (section 3.1). Using the criteria of Bozio and Pecile (19) for the transition temperature, we find a value of 145±3K.

Figure 20 shows the temperature-dependence of the integrated intensity of the 226cm$^{-1}$ band. Again a sudden enhancement takes place between 140 and 100K. Below 100K, the integrated intensity remains constant. This activated band could be the totally symmetric mode $\text{Ag}^{10}$. Using the criteria
of Bozio and Pecile (19), we find a transition temperature of 159±9K.

Since we have only one data point at every 20K, the determination of the transition temperature by extrapolating the linear portion of the integrated intensity curve on the temperature axis, is rather inaccurate. This inaccuracy is responsible for the two different transition temperatures found (145 and 159K). Nevertheless, from our results (figure 19 and 20), a transition temperature of 150±5K seems to be the most acceptable value.
Intensity of the 313 cm⁻¹ band

Figure 19 - Temperature dependence of the integrated free carrier absorption
Figure 20 - Temperature-dependence of the integrated intensity of the $226\text{cm}^{-1}$ band.

Free carrier absorption.

Temperature measurements at 150K and 167K.
4.3 The Splitting Of The Doublet At 172 And 176cm\(^{-1}\)

Figure 18 shows the temperature-dependence of the group of structures at 155, 164, 172 and 176cm\(^{-1}\) (20K values). Between 300 and 160K, we observe only two weaker bands at 153 and 169cm\(^{-1}\) respectively. Upon reducing the temperature to 140K, a weak shoulder appears at 164cm\(^{-1}\). At 100K two structures are observed at 164 and 172cm\(^{-1}\). A second splitting occurs when the temperature is further reduced: At 100K, the 172cm\(^{-1}\) band does not show any sign of distortion. At 60K it becomes broader than its 100K counterpart and loose its symmetry. Between 60 and 40K, the width of the band still increases and a clear shoulder appears at 175cm\(^{-1}\). At 20K, the two structures are clearly seen at 172 and 176cm\(^{-1}\). Starting with a single band at room-temperature, we therefore end up with a triplet at 20K.

4.4 Detection Of A Second Phase Transition

Figure (21) shows the temperature-dependence of the integrated intensity of the bands at 155, 164cm\(^{-1}\) and the integrated doublet at 172 and 176cm\(^{-1}\) (20K values). Their similarity below 140K is striking. Between 140 and 120K, their intensities are strongly enhanced and remain constant between 120 and 100K. They are then further enhanced between 100 and 60K, and saturate below that temperature. The absence of data points between 60 and 100K does not allow us to precisely determine the onset of this second enhancement but it is clearly related to the anomaly observed in the Young modulus data at 89K (8). We note that this second transition does not show up in
the D.C. conductivity, magnetic susceptibility, thermoelectric power and specific heat measurements. However, our infrared measurements provide good evidence of the existence of the transition.

4.5 Nature Of The 150K Phase Transition

The activation of absorption bands in the infrared spectrum of (TMA)(I)(TCNQ) provides good evidence that a periodic lattice distortion takes place at the 150K transition. The activation of the susceptibility (which goes to zero as the temperature goes to zero) is in agreement with such a possibility, since the susceptibility of a 1-D array of equally spaced electronic spins should remain finite at all finite temperatures. Moreover, the splitting of the 169cm\(^{-1}\) band into three bands suggests that the periodic lattice distortion might be a Peierls distortion. Since the conduction band of (TMA)(I)(TCNQ) is 1/3 filled, such a distortion would push the Brillouin zone from \(\pi/a\) to \(\pi/(3a)\), where \(a\) is the stacking spacing of the conducting TCNQ molecules. The mechanism is indicated in figure 22. This particular zone folding give rise to three branches at \(q=0\) and would explain the formation of triplets as the temperature is reduced below the phase transition temperature. We note that the 313cm\(^{-1}\) band (figure 17 at 20K) also seems to appear as a triplet.

\[\text{The two degenerate lower branches are splitted appart upon interacting with one another.}\]
4.6 Nature Of The Second Phase Transition

Returning to figures 19 and 20, we note that the temperature-dependence of Ag\(^9\) and Ag\(^{10}\) is very weak below 100K. This suggests that the TCNQ chains do not play a major role in the second distortion. This result is in agreement with the interpretation given by Brill et al. (8), who have suggested that the transition is associated with the "freeze out" of the methyl rotation groups.

4.7 Temperature-dependence Of The Integrated Intensity Of The 96, 113 And 135cm\(^{-1}\) Bands.

Figure 23 shows the integrated intensity of the band at 96, 113 and 135 cm\(^{-1}\). No attempt will be made to assign them all. These three bands show an enhancement of their integrated intensity near 140K. The integrated intensity of the 96 cm\(^{-1}\) band shows a second enhancement between 60 and 100K, presumably associated with the onset of the second distortion. For the 113 cm\(^{-1}\) band, the second transition is not clearly observed. Instead the integrated intensity increases at a constant rate as the temperature is reduced from 120 to 60K. The band at 135 cm\(^{-1}\) is the only one for which the onset of the second distortion decreases the value of the integrated intensity of the band.

The complicated temperature-dependence exhibited by these last bands is probably not only determined by the onsets of the first and second distortions, but also by interactions among themselves.
Figure 21 - Temperature-dependence of the integrated intensity of the 155, 164 and 172 bands.
Figure 22 - Brillouin zone splitting
Figure 23 - Temperature-dependence of the integrated intensity of the 96, 113, 125 and 135 cm\(^{-1}\) bands
4.8 Evidence Of Hydrogen Bond Stretching

One of the most interesting features of the spectrum of (TMA)(I)(TCNQ) is the very strong absorption band observed at 113cm\(^{-1}\). In this section we will give it a preliminary assignment.

(TMA)(I)(TCNQ) is a hydrogen bonded compound. The structure of the bond is shown schematically in figure 24.

Figure 24 - Hydrogen bond

The nitrogen atom of the Trimethylammonium ion forms four covalent bonds of the type (SP)\(^3\); Three with the methyl groups and one with the hydrogen atom. The nitrogen atom being more electro-negative than the hydrogen, the pairs of electrons forming the covalent bond will shift toward the former. We therefore have a bare proton sitting at the end of the bond. On the other hand, the nitrogen atom on the TCNQ molecule, being
more electro-negative than the carbon, will be slightly negatively charged. This results in the formation of a weak bound state between the nitrogen atom on the TCNQ molecule and the hydrogen atom on the TMA ion. The binding energy is equivalent to a strong van der Waals interaction (0.4-40 Kj/mole).

The inter-molecular modes of vibration between the TCNQ molecule and the TMA ion will include stretching, bending and torsional motions. The stretching motion normally has the highest frequency (50-200 cm⁻¹).

Because of the large masses involved and the weakness of the bond, one expects the stretching motion to be very large and substantially anharmonic. We also expect it to strongly couple with electromagnetic radiation, since it involves a large vibrating dipole. The end result is the appearance of a strong and broad absorption band in the spectrum of hydrogen bonded compound. In TABLE 1- (21) we list the observed frequencies of hydrogen-bond stretching modes for various phenol-amines complexes.

<table>
<thead>
<tr>
<th>Table I - Observed frequencies of hydrogen bond stretching modes (21)</th>
<th>cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol-pyridine, C₆H₅OH···NC₆H₅</td>
<td>134</td>
</tr>
<tr>
<td>Phenol-d₁-pyridine, C₆H₅OD···NC₆H₅</td>
<td>130</td>
</tr>
<tr>
<td>Phenol-triethylamine</td>
<td>123</td>
</tr>
<tr>
<td>Phenol-d₁-triethylamine</td>
<td>120</td>
</tr>
<tr>
<td>Phenol-trimethylamine in CCl₄ solution</td>
<td>143</td>
</tr>
<tr>
<td>Phenol-d₁-trimethylamine in CCl₄ solution</td>
<td>141</td>
</tr>
<tr>
<td>Phenol in CCl₄ solution</td>
<td>150</td>
</tr>
<tr>
<td>Phenol-d₁ in CCl₄ solution</td>
<td>143</td>
</tr>
</tbody>
</table>
In TABLE 2-(21) we list the structural parameters and force constants for phenol-trimethylamines complexes.

Table II - Force constants for phenol-trimethylamines complexes (21)

<table>
<thead>
<tr>
<th>1:1 Complex</th>
<th>Simplified normal coordinate</th>
<th>O–H···N</th>
<th>PhOH···NR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhOH-trimethylamine</td>
<td>0.27</td>
<td>0.09</td>
<td>0.44</td>
</tr>
<tr>
<td>PhOD-trimethylamine</td>
<td>0.27</td>
<td></td>
<td>0.43</td>
</tr>
<tr>
<td>PhOH-triethylamine</td>
<td>0.24</td>
<td>0.07</td>
<td>0.44</td>
</tr>
<tr>
<td>PhOD-triethylamine</td>
<td>0.22</td>
<td></td>
<td>0.42</td>
</tr>
<tr>
<td>PhOH-pyridine</td>
<td>0.23</td>
<td>0.08</td>
<td>0.45</td>
</tr>
<tr>
<td>PhOD-pyridine</td>
<td>0.23</td>
<td></td>
<td>0.43</td>
</tr>
</tbody>
</table>

We note that the force constant of the hydrogen bond for all the complexes is about 0.3 mdyne/A. Using this value and setting all the other force constants to infinity, we can estimate the frequency of this mode of vibration in (TMA)(I)(TCNQ). The calculation gives 103 cm⁻¹.

The 113 cm⁻¹ band therefore bears all the insinqua (strong intensity, very broad and value of its frequency agreeing with the simplified normal coordinate calculation) of an hydrogen bond stretching mode. The strong temperature-dependence of this mode at the transition temperature is however surprising. On the other hand, one expect that this type of lattice mode will be strongly affected by a structural distortion.
4.9 Detection Of An Activation Energy Of 365cm⁻¹

The optical measurements made by Hoffman et al. (22) indicates the presence of an energy gap of 0.1eV at all temperatures. The measurements of the temperature-dependence of the D.C. conductivity made by Delhaes (6) also show a gap at all temperatures. The temperature-dependence of the D.C. conductivity of some of the crystals studied by Abkowitz et al. (7) had a metallic behavior above 240K, which was explained in terms of a strongly temperature-dependent mobility of excited carriers across a band gap (section 2.3).

All these measurements agree that a gap is present at all temperatures. Whether a crystal exhibits a metallic behavior above 240K or not could be due to the degree of disorder of the iodine chains of the crystals studied (section 2.1). The high value of $\chi$ spin (section 2.6) is an indication that e-e correlations are strong and it is therefore plausible that these interactions are responsible for the gap observed at room temperature. When the temperature is lowered below 150K, we interpret our results as indicating that a structural Peierls distortion takes place. This $2K_\sigma$ distortion would reduce the e-e interaction, and would explain the temperature-dependence of $\chi$ spin. The gap at low temperatures would therefore be a Peierls gap. From the temperature-dependence of our infrared spectra, we have attempted to extract the value of this low temperatures Peierls gap.

Figure 25 shows spectra obtained at 20, 100 and 180K, between 20 and 340 cm⁻¹. We note the strong variation of the
background intensity \((B)\) with temperatures. The background intensity is usually a measure of the contribution of the free carriers to the total absorption \((w)\), and should therefore be proportional to the D.C. conductivity. Figure 26 shows a plot of \(\ln B\) as a function of \(1/T\). The values of \(B\) were measured at 200\,cm\(^{-1}\). The curve can be divided into two regions with activations energies equal to 0.05\,eV (400\,cm\(^{-1}\)) between 150 and 100K, and equal to 0.01\,eV (100\,cm\(^{-1}\)) for temperatures between 100 and 40K. This first value correlates well with the one found in figure 15 (365\,cm\(^{-1}\)). In figure 27 we show a lower resolution spectrum (16\,cm\(^{-1}\)) up to 1000\,cm\(^{-1}\), recorded at room temperature, which confirms the existence of an activation energy of 365\,cm\(^{-1}\).

We note that these results are in agreement with the frequency dependent conductivity obtained by Tanner et al. (15) (figure 10) from their room temperature reflectivity measurements. They observed a rapidly increasing conductivity which peaks near 2000\,cm\(^{-1}\), but interpreted their results as indicating the presence of a 0.1-0.14\,eV (1000\,cm\(^{-1}\)) gap. In our case the temperature-dependence of the background intensity (figure 26) clearly indicates that a 365\,cm\(^{-1}\) activation energy is responsible for the abrupt increase observed in the infrared absorption. We also note that while our measurements were made on powders, the sharp rise in the infrared absorption indicates that the conducting direction dominates the absorption process.

The results of Tanner et al. (15) (figure 10) shows that the absorption along the \(a\) and \(c\) directions is weakly frequency dependent and does not exhibit such a sharp rise with frequency.
This value of activation energy (365 cm\(^{-1}\)) is much smaller than the values found by Delhaes et al. (6) and Abkowitz et al. (7) from their D.C. conductivity measurements, which should detect the smallest gap present in the system. We explain the discrepancy in the following manner:

- The infrared background absorption measured is not caused by free carriers in the conduction band but by electronic transitions between localised states in the band gap. Such transitions would lead to infrared absorption but would not contribute to the D.C. conductivity. These localised states could be introduced by chemical impurities or by some randomness in the potential at each TCNQ site. The gaps measured would represent the energy needed for an electron to hop from one localised state to the next.
Figure 25 - Temperature-dependence of the Background Intensity B

Resolution = 2 cm$^{-1}$
Figure 26 - Plot of ln(B) as a function of 1/T

E_g = 400 cm⁻¹

E_g = 100 cm⁻¹
Figure 27 - Infrared Spectrum of (TMA)(I)(TCNQ) Between 20 and 1000 cm\(^{-1}\)

T = 300 K
 resolution: 16 cm\(^{-1}\)
4.10 Small-particle Scattering

Since the measurements were made on powdered samples, small-particle scattering must be considered. In the limit where the diameter of the particles $d$ is much smaller than the incident wavelength, the scattering can be described by (17):

$$I(\theta) = I_o \left(\frac{a}{2}\right) \pi^\frac{4}{3} \left(\frac{d}{\lambda}\right)^4 \left(\frac{m^2-1}{m^2+1}\right)^2 (1 + \cos^2 \theta)$$  \hspace{1cm} (6)

where $I_o$ is the intensity of the incident beam, $I(\theta)$ the intensity scattered at an angle measured from $I_o$ and $n$ is the refractive index. $d$ and $\lambda$ are the particles diameter and wavelength of the incident beam respectively. The term $\left(\frac{m^2-1}{m^2+1}\right)$ is not strongly frequency-dependent. The results of Tanner et al (15) shows that this term slowly vary from 0.3 to 0.5, between 400 and 1000 cm$^{-1}$. In the case where small-particle scattering dominates, transmission measurements should have a $\lambda^4$ dependence. In figure 28 we have plotted $\lambda \eta (I_o/I)$ as a function of $\lambda \eta \lambda$, using the data shown in figure 27. Between 400 and 800 cm$^{-1}$, the relationship is linear with a slope equal to $2 \pm 0.5$. Above 800 cm$^{-1}$, $\lambda \eta (I_o/I)$ increases at a much faster rate and the tangent to the slope at 900 cm$^{-1}$ is equal to $4 \pm 0.5$. We conclude that above 800 cm$^{-1}$ scattering may be significant. But this is not the case below 400 cm$^{-1}$ and the sharp rise observe at 365 cm$^{-1}$ can be safely attributed to an increased in infrared absorption.
Figure 28 - Plot of $\log(I/I)$ as a function of $\log(\lambda)$
4.11 Conclusions

We have observed the activation of several infrared absorption bands as the temperature is reduced below 150K in (TMA)(I)(TCNQ). We have tentatively assigned two of them to the totally symmetric modes $\text{AgV}^9$ (313 cm$^{-1}$) and $\text{AgV}^{10}$ (226 cm$^{-1}$). We have interpreted these results as indicating that a periodic lattice distortion takes place near 150K.

We have interpreted the splitting of the 169 cm$^{-1}$ band (room temperature value) in term of a Brillouin zone folding effect driven by the periodic lattice distortion, suggesting that the 150K distortion is a Peierls distortion. The activation of $\text{AgV}^9$ and $\text{AgV}^{10}$ would be due to a vibronic effect.

We also have evidence for the existence of a second transition near 100K. Our results indicate that the TCNQ stacks do not play a major role in this transition. This result is in agreement with the interpretation given by Brill et al. (8) that the transition involves the "freeze out" of the methyl rotation groups. Moreover, this interpretation is supported by the results of the D.C. conductivity, thermoelectric power and specific heat measurements, which do not exhibit any anomaly below 150K. A second distortion of the TCNQ stacks would certainly affect these physical properties.

We have detected two absorption edges at 90 and 365 cm$^{-1}$, which we have attributed to transitions between localised states in the band gap.

We have assigned the stong mode at 113 cm$^{-1}$ to the hydrogen bond stretching mode.
BIBLIOGRAPHY


