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FAR-INFRARED PROPERTIES OF TRIMETHYLAMMONIUM IODIDE TETRACYANOQUINODIMETHANE

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Résumé - Nous présentons les spectres d'absorption d'un échantillon en poudre de (TMA)(I)(TCNQ), obtenus dans l'infrarouge lointain, à différentes températures. En-dessous de 160 K , de nouvelles bandes d'absorption apparaissent, alors que l'intensité d'autres bandes augmente. Le comportement est en accord avec les résultats obtenus par diffraction de neutrons et d'électrons, mettant en évidence une distorsion des chaînes de TCNQ à des températures inférieures à 159 K , la température de la première transition de phase (dans les échantillons deutérés.)

Abstract - We present the powder absorption spectrum of (TMA)(I)(TCNQ) in the far-infrared as a function of temperature. Below 160 K new absorption features appear and others increase in intensity. This behaviour supports the electron and neutron diffraction evidence of a distortion on the TCNQ chains below the first phase transition temperature of 159 K (in the deuterated sample).

I. INTRODUCTION

Trimethylammonium iodide tetracyanoquinodimethane (TMA)(I)(TCNQ), where (TMA) is the abbreviation we will use for the partially deuterated form, $N(CH_3)_3D^+$, is a ternary compound composed of TMA cations and separate chains of $TCNQ^{2/3-}$ and $(I_3^-)^{1/3}$ anions. It is an organic conductor, with room-temperature conductivity of around $20(\Omega\ cm)^{-1}$. Upon cooling, the conductivity of some crystals immediately decreases (see for example Cougrand et al. /1/, while for others the conductivity increases slowly to a broad maximum around 240 K and then decreases (see for example Abkowitz et al. /2/. This difference in behaviour may depend on the degree of disorder between the iodine chains /3/, which in turn depends on the method of preparation. The iodine chains contain triodide anions I_3^-, as determined by the very strong resonance at 105 cm^{-1} seen in Raman measurements /2/. These ions are relatively well-ordered within a chain, but there is little correlation between chains in the "disordered" material. All crystals, however, undergo a phase transition at 150 K (T_1) below which they are semiconductors with an activation energy which extrapolates to an estimated value of 1000 K at 0 K /3/. This phase transition is clearly seen in measurements of the d.c. conductivity /1,2/, microwave conductivity /2/, thermoelectric power /2/, e.s.r. linewidth /4/, Youngs modulus /5/, magnetic susceptibility /6/ and the unit-cell parameters /6/. Another phase transition at 89 K (T_2) is seen in the Youngs modulus data (5), microwave dielectric constant (7), and proton-spin-lattice relaxation (8). This latter transition has been associated with the freezing-out of methyl-group rotations (5), and is also the temperature at which the TCNQ molecules develop a tilt so that the $\vec{b}$ axis is no larger normal to the molecular plane /3/.

The present contention centers around the nature of the 150 K phase transition. There are two schools of thought. The authors of references 2, 4, 5, 7 and 8 support the view proposed by Epstein /9/, to explain the behaviour of several similar compounds, that the transition is a semiconductor - semiconductor one, in which there is a gap in the density of states at the Fermi level at all temperatures. This produces an activated number of conduction electrons, and the "metallic" behaviour of the d.c. conductivity above ~240 K (T_M) in the ordered crystals is due to a strongly temperature-dependent mobility, with the mobility decreasing as the temperature rises.

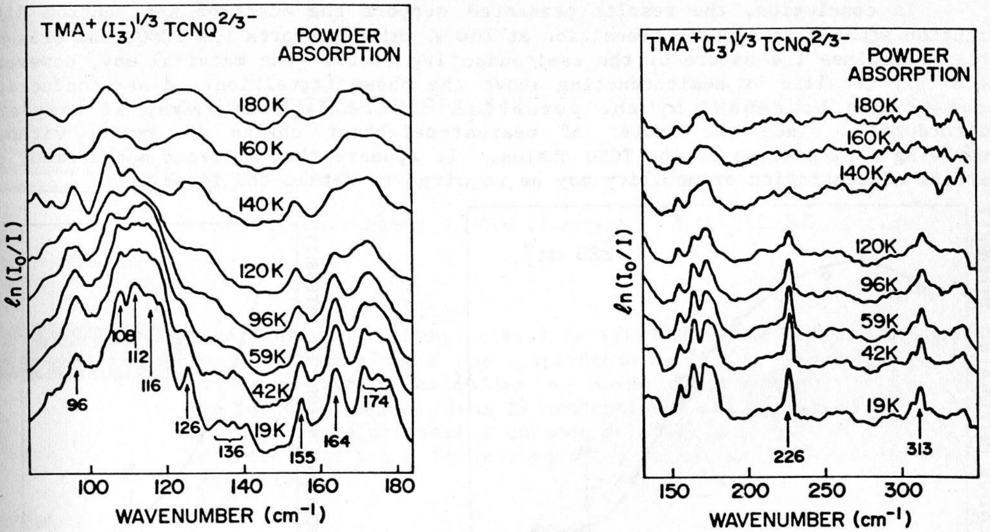
The other school of thought may be found in references 1, 3, and 6. These authors maintain that the phase transition is a Peierls transition, involving the three-dimensional condensation of a charge-density wave, below which a semi-conductor exists due to the Peierls distortion of the conducting TCNQ chain, but above which no distortion exists and the material is metallic. The various measured properties can be accounted for by assuming electron-electron interactions (6). Apart from electron-electron correlations, another factor which may be contributing to the activated behaviour of the d.c. conductivity in the high-temperature phase above 150 K, if it is metallic, is the disorder. A recent N.M.R. study on Qn(TCNQ)$_2$, by Devreux, Nechtschein and Gruner /10/ found that the diffusion constant had the same temperature-dependence as the conductivity. They showed that the carrier concentration was only weakly temperature-dependent, but that the disorder produced a mobility which increased with temperature, due to the thermal surmounting of random potentials and barriers.

The French school therefore investigated the growth of the distortion on the conducting TCNQ chains. A neutron scattering study /3/ and electron-diffraction study /11/ established the existence below 150 K of a distortion of periodicity 3b on these TCNQ chains. This distortion then changes from a reciprocal-lattice vector 0, ± b*/3, 0 to ±(xa*/6, b*/3, 0) with $0 < x < 1/6$ between 100 and 80 K and finally becomes ±(a*/6, b*/3, 0) below 80 K. No distortion was found above 150 K.

In TTF-TCNQ, the effect of the Peierls distortion is evident in the infrared spectra /12,13/. Normally-infrared-inactive modes of vibration, including the totally-symmetric a_g internal modes, become strongly activated as a result of it. Optical studies of (TMA)(I)(TCNQ) /14,15/, identified the strong infrared features as activated a_g modes, and claimed that this supported the view of a distorted TCNQ chain, and semiconducting state at all temperatures. The TCNQ molecules in (TMA)(I)(TCNQ) however, do not sit on inversion centres, and the a_g modes are normally infrared active in this solid. They should be expected at room temperature even though some may be weak. The effect of a distortion on the other hand would be to increase their oscillator strength. The purpose of this paper is to monitor the strength of some low-wavenumber infrared absorption bands as the temperature is lowered through the phase transition at T_1.

II. RESULTS

We have measured the powder spectra of (TMA)(I)(TCNQ) as a function of temperature in the far-infrared. The crystals were grown by one of us (J.S.M.) and were ground in nujol for about 20 minutes. The mull was then spread on a wedged TPX window, which was inserted into a Janis supervaritemp dewar, in which the cooling is accompanied by means of cold helium gas. The results may be seen in Fig.'s 1 and 2, which show an increase in the strength and number of absorption features as the temperature is lowered. "Activated" features in the 19 K spectrum, which are not visible at 180 K, appear at 96, 112, 116, 126 and 164 cm^{-1}. Normally-active modes are at 108, 136 155 and 174 cm^{-1}. The higher-wavenumber modes at 226 and 313 cm^{-1} are much stronger at low temperatures but are still visible at 180 K. The integrated intensities of four of these features are shown as a function of temperature in Fig.'s 3 to 6. The 164 cm^{-1} feature in Fig. 3 shows a clear and strong growth after 159 K , (the phase transition temperature in the deuterated compound). We have assigned it to TCNQ $\nu_{10}(a_g)$ since this is the wavenumber of this mode in TTF-TCNQ /16/. The 313 cm^{-1} feature in Fig. 4 which is probably TCNQ $\nu_9(a_g)$, increases below 150 K, but is still present at room temperature, as we mentioned is possible. The 226 cm^{-1} feature in Fig. 5 also increases abruptly below



Figs. 1 and 2. The absorption spectra, vertically displaced for clarity.

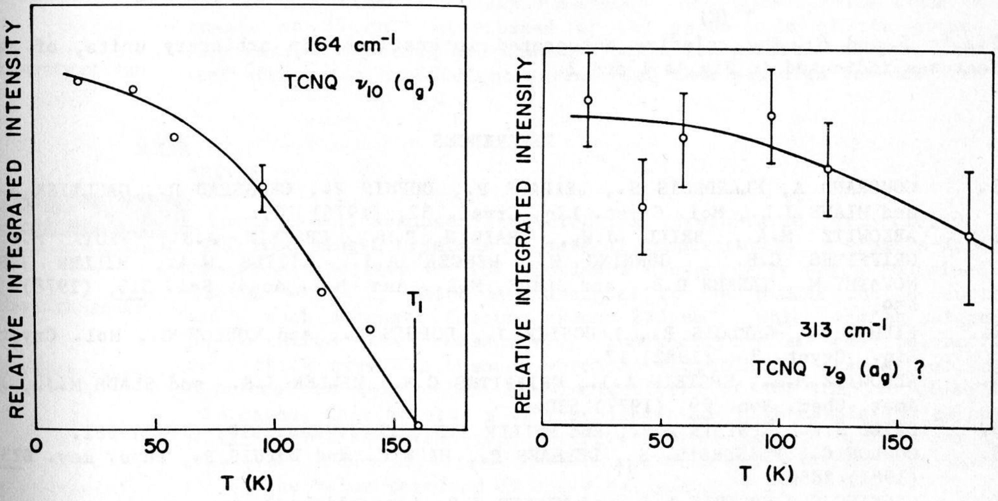


Fig.'s 3 and 4. The relative integrated intensities, in arbitrary units, of two features indicated in Fig.'s 1 and 2.

160 K, while remaining visible but very weak at room temperature. This is probably a non-totally-symmetric intramolecular mode, such as were found in TTF-TCNQ /13/. These results clearly support the electron and neutron-diffraction evidence of a distortion below the phase transition at T_1.

The 126 cm^{-1} feature in Fig. 6 also has a dramatic temperature dependence, but one which seems to follow the second phase transition at 89 K. This could correspond to a torsion of the methyl groups if their rotation is indeed frozen out at this temperature.

Another interesting observation is the apparent appearance of triplets at 136 and 174 cm^{-1}, which may well reflect the Brillouin-zone folding which follows from the b*/3 reciprocal lattice vector.

In conclusion, the results presented support the electron and neutron diffraction studies of a phase transition at 150 K which distorts the TCNQ, and presumably determines the nature of the semiconducting state. The material may, however, be either metallic or semiconducting above the phase transition. A semiconducting state could be caused by the potential of the I_3^- ions, even if they are "disordered", since the number of nearest-neighbour chains is small, without involving a distortion of the TCNQ chains. It appears that a direct measurement of carrier concentration or mobility may be required to settle the issue.

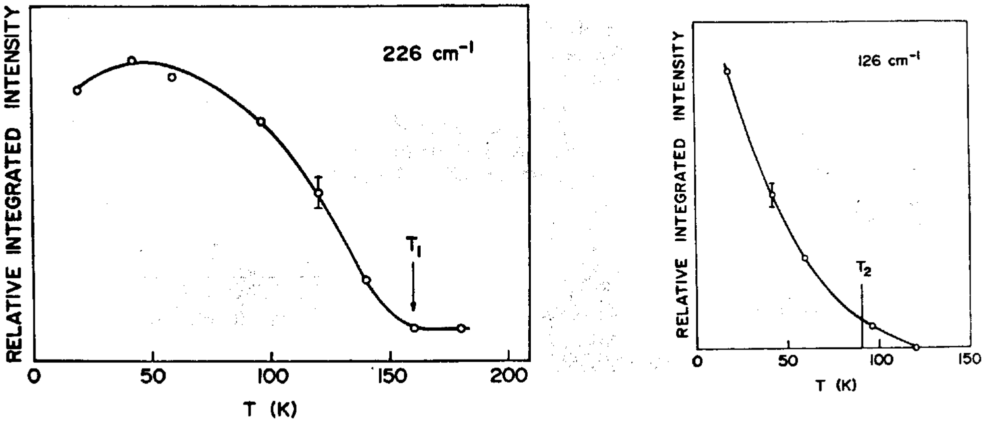


Fig.'s 5 and 6 The relative integrated intensities, in arbitrary units, of two features indicated in Fig.'s 1 and 2.

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