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Evidence for structural transitions in onedimensional organic conductor TMA-TCNQ-I obtained by high voltage electron diffraction at low temperature (*)

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Résumé. — L'utilisation des très hautes tensions accélératrices en microdiffraction électronique a permis, pour la première fois, l'étude du changement de structure en fonction de la température, d'un conducteur organique unidimensionnel, le triméthylammonium tétracyanoquinodiméthane, iode $\text{TMA}^+(\text{TCNQ})^{2/3-}(\text{I}_3^-)_{1/3}$ qui présente une distorsion structurale à basse température. Les composantes du vecteur de distorsion ont pour valeur 0; $\pm 1/3 b^*$; 0 pour $150 \text{ K} > T > 100 \text{ K}$, puis $\pm (xa^*; 1/3 b^*; 0)$ avec $0 < x < 1/6$ de 100 K à 80 K et enfin $\pm (1/6 a^*; 1/3 b^*; 0)$ pour $T < 80 \text{ K}$.

Abstract. — By using a very high accelerating voltage in electron diffraction, it has been possible, for the first time, to study structural change with temperature of a onedimensional organic conductor, the trimethylammonium-iodide-tetracyanoquinodimethane $\text{TMA}^+(\text{TCNQ})^{2/3-}(\text{I}_3^-)_{1/3}$. This exhibits a structural distortion at low temperature. The components of the distortion vector are 0; $\pm 1/3 b^*$; 0 when $150 \text{ K} > T > 100 \text{ K}$, then $\pm (xa^*; 1/3 b^*; 0)$ with $0 < x < 1/6$ on going from 100 K to 80 K and finally $\pm (1/6 a^*; 1/3 b^*; 0)$.

Electron diffraction has been successfully used to study structural transitions in inorganic compounds but has been applied far less to molecular crystals. The main obstacle to the use of this technique is the rapid destruction of the atomic bonds in organic molecules by the electron beam. In practice, one can surmount this difficulty by taking special precautions as specified below. The application described here is concerned with the study of a phenomenon that is especially sensitive to the concentration of defects in the specimen, namely the ordering of charge density waves in a onedimensional (1D) organic conductor. Conductors of this type have produced excellent 1D metals and even 1D superconductors [1-2]. These often exhibit an particular transition of the Peierls type, related to the interchain coupling of charge density waves.

The 1D conductor chosen for our study is the complex salt $\text{TMA}^+(\text{TCNQ})^{2/3-}(\text{I}_3^-)_{1/3}$ or trimethylammonium, tetracyanoquinodimethane, iodine. This exhibits an electric conductivity $\sigma (300 \text{ K}) \sim 30 \Omega^{-1} \cdot \text{cm}^{-1}$, which is quite low compared with that of the best known organic conductors. This choice is justified on the one hand by the fact that the TMA-TCNQ-I metal-

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insulator transition ($T_{MI} \sim 150$ K) [3], can be easily reached by our experimental devices. On the other hand, X-ray and neutron diffraction data can be clarified or complemented by electron diffraction studies.

1. Recapitulation of the physical properties and crystal structure of TMA-TCNQ-I. — Various physical properties of TMA-TCNQ-I have been studied as a function of temperature : electrical conductivity specific heat and paramagnetism for example. Several anomalies have emerged. First, a metal-insulator transition is observed at $T_{MI} \sim 150$ K [3-5]. Around 100 K, the electron paramagnetic resonance (EPR) line width passes through a maximum after which it decreases rapidly [6]. Brill *et al.* [7] found an anomaly in Young's modulus, very weak at 150 K but very marked at 89 K.

The crystal structure of TMA-TCNQ-I has been described by Cougrand *et al.* [3], additional details being given by Filhol *et al.* [8-9]. Figure 1 shows a projection along the **b** axis parallel to the chains of atoms of the monoclinic unit cell ($a = 20.353$ Å ; $b = 6.456$ Å ; $c = 13.922$ Å ;

Fig. 1. — Projection of the TMA-TCNQ-I structure along the **b** axis.

$\beta = 115^\circ 20$). TCNQ⁻ anions that build regular stacks of a « zig-zag » type with an interplanar distance equal to $b/2$ along the **b** axis are responsible for electrical conduction. TMA⁺ cations ($N(CH_3)_3H^+$) are arranged symmetrically about planes parallel to the (**a**, **c**) planes which contain TCNQ⁻ anions. The (I_3)⁻ ions are situated on columns parallel to the **b** axis with a spacing of $a/2$ along **a** and c along **c**. They build a superlattice of the organic lattice and may be either disordered [8] or quasi-ordered [10]. By using neutron diffraction, Filhol *et al.* [5] have shown that, below the transition temperature T_{MI} , a 3D structural distortion occurs, characterized by the wave vector $0; \pm 1/3 b^*; 0$ and attributed to the lattice of organic conduction chains. Below 80 K, a splitting of reciprocal lattice spots has been observed.

By means of electron diffraction, we obtained new information about the relation between the structural behaviour and the physical properties in the temperature range between 300 K and 40 K.

2. Conditions of observation in electron diffraction. — The observation of organic compounds in electron microscopy proves to be difficult. When the electron beam enters the crystal, a considerable part is inelastically scattered and this may cause extensive damage. The inelastic scattering effects depend on the incident electron energy. According to Bethe's relativistic law [11], electrons of 1 MeV cause approximatively three times less damage than electrons of 100 keV; this result has been confirmed by experiment [12-16]. Reimer and Spruth [17] have also shown that the temperature has an influence, notably on radiolysis. Many fewer defects are created at low temperature than at room temperature.

Fig. 2. — Electron diffraction patterns obtained at 2 000 kV and corresponding to the (a^*, b^*) plane of the TMA-TCNQ-I reciprocal lattice, at 300 K and 155 K. The arrows show the spots due to the iodine reciprocal lattice.

Most organic crystals can tolerate only very weak radiation doses, and as they do not dissipate the thermal energy deposited by the electron beam rapidly they are quickly damaged and there is a risk of melting. In the case of 1D organic conductors, Zuppiroli *et al.* [18] have also shown that the coherence between charge density waves is destroyed, which means that the metal-insulator transition disappears when the molecular defect concentration exceeds a few $\%_{\infty}$.

It therefore seemed unlikely that we could observe a lattice distortion at $T_{MI} \sim 150$ K. In fact, thanks to a very high accelerating voltage, a very low intensity beam, and very electron-sensitive films the experiments were successful.

3. Experimental results and discussion. — The microdiffraction experiments have been performed with the 3 MV microscope of this Laboratory equipped with a liquid-helium cooled specimen holder.

Figure 2 shows an example of the results obtained at 2 MV on a TMA-TCNQ-I crystal with an ordered lattice. At 300 K, diffraction spots due to the iodine lattice situated on rows parallel to $\mathbf{a}^*$ and having indices $k = (2n + 1) \pm 1/3$ in the $\mathbf{b}^*$ direction (see arrow), are observed as well as those corresponding to the $(\mathbf{a}^*, \mathbf{b}^*)$ plane of the organic reciprocal lattice C2/m. This micrograph also shows that both the organic and the iodine lattices are commensurate in the $\mathbf{b}^*$ direction. However, it should be noticed that spots due to the iodine lattice are not exactly situated in $(\mathbf{a}^*, \mathbf{b}^*)$ planes since they do not occur in areas close to the zones of intersection of the Ewald sphere and the $(\mathbf{a}^*, \mathbf{b}^*)$ planes, known as « Laue zones », in the diffraction pattern. From our experiments the intensity of these spots does not seem to depend noticeably on temperature, but rather on crystal orientation, which changes slightly with temperature. At 155 K, close to T_{MI} , the diffraction pattern information did not change except for the crystal orientation effects. No 1D precursor effects, such as the diffuse lines perpendicular to $\mathbf{b}^*$ usually associated with Peierls transitions, are seen. However, recent results obtained by X-ray scattering [19] indicate that these effects are extremely weak. It is thus probable that, if they exist, they could only be recorded with prohibitive exposure times.

Below the transition temperature $T_{MI} \sim 150$ K, superlattice spots are observed (see arrow Fig. 3) satellites of organic lattice C2/m spots. These extra spots are similar to those obtained by Filhol *et al.* [5] using neutrons. It is important to notice that spots due to the iodine are not present on this pattern because of a slight change of crystal orientation with respect to figure 2. Experiments performed with other crystal orientations show that these spots are still present at low temperature and they do not coincide with superlattice spots.

At a lower temperature new phenomena appear. The periodic distortion vector remains equal to $0; \pm 1/3 \mathbf{b}^*; 0$ from T_{MI} to 100 K but below 100 K a new component of this vector along $\mathbf{a}$ is found. This component increases up to a maximum value of $1/6 \mathbf{a}^*$ at 80 K; the micrograph illustrates the result obtained at 60 K. From 80 K to 40 K, the lowest temperature reached, the distortion vector remains equal to $\pm (1/6 \mathbf{a}^*; 1/3 \mathbf{b}^*; 0)$.

Thus we have revealed, for the first time by electron diffraction, the existence in TMA-TCNQ-I of an additional component along $\mathbf{a}^*$ of the distortion vector, related to a change in the physical properties of this compound, such as Young's modulus. However, the splitting of spots along $\mathbf{c}^*$ [5] has not been observed. This might be due to the fact that the crystal could not be tilted into the correct orientation for the observation of such an effect.

These results show that electron microscopy can be employed to study the structure of organic compounds despite the very weak electron doses that must be used. At low voltage, below 100 kV for example, the structure is destroyed too rapidly to be observable with present day techniques. Conversely, at very high accelerating voltage, much higher doses can be tolerated. In the case of TMA-TCNQ-I, our measurements show that the limiting dose, for which the structural transition still exists, reaches 3.5×10^{-3} C/cm² (equivalent to 560 mrad. — the method used to convert these units is to be found in [20] for example) at 2 MV at 80 K.

Fig. 3. — Electron diffraction patterns obtained at 2 000 kV and corresponding to the (a^* , b^*) plane of the TMA-TCNQ-I reciprocal lattice, at 100 K and 60 K. The arrows show the superlattice spots, satellites of organic reciprocal lattice spots.

A detailed study of the results obtained by different techniques using X-rays, neutrons or electrons will form the subject of a further paper. Nevertheless it is already clear that high voltage electron microscopy is a valuable means of investigating new organic compounds, of interest on account of particular physical properties.

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