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STRUCTURAL EVIDENCE OF CHARGE DENSITY WAVES IN HMTTF-TCNQ (HEXAMETHYLENE-TETRATHIOFULVALENium- TETRACYANOQUINODIMETHANE)

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Résumé. — Par diffusion diffuse des rayons X, le conducteur unidimensionnel HMTTF-TCNQ présente, dans sa phase haute température ($T > 49$ K), une diffusion unidimensionnelle de vecteur d'onde $0,36 \mathbf{b}^*$, dans la direction des chaînes, assignée à une anomalie $2 \mathbf{k}_F$ à la différence de TTF-TCNQ qui présente des effets précurseurs à $2 \mathbf{k}_F$ et $4 \mathbf{k}_F$. De plus, cette diffusion à $2 \mathbf{k}_F$ est polarisée longitudinalement alors que TTF-TCNQ et TSeF-TCNQ présentent aussi une composante $2 \mathbf{k}_F$ transverse. Autour de 49 K, les ondes de densité de charge se couplent tridimensionnellement, produisant des réflexions satellites correspondant à une période de modulation de $2,38 \mathbf{a} \times 2,78 \mathbf{b} \times \mathbf{xc}$. Aucun changement de cette période n'a été observé jusqu'à 10 K.

Abstract. — X-ray diffuse scattering from the 1-D conductor HMTTF-TCNQ in the high temperature phase ($T > 49$ K) reveals one 1-D scattering at the wave-vector $0.36 \mathbf{b}^*$ in the chain direction, assigned to a $2 \mathbf{k}_F$ anomaly in contrast to the case of TTF-TCNQ where both $2 \mathbf{k}_F$ and $4 \mathbf{k}_F$ precursors have been reported. Furthermore, this $2 \mathbf{k}_F$ scattering was found to have only a longitudinal polarization while in TTF-TCNQ and TSeF-TCNQ a $2 \mathbf{k}_F$ transverse component is also observed. Around 49 K, the charge density waves couple three dimensionally producing satellite reflections corresponding to a modulation period of $2.38 \mathbf{a} \times 2.78 \mathbf{b} \times \mathbf{xc}$. No further change of this modulation period was observed down to 10 K.

1. Introduction. — After the series of recent experimental reports on the structural aspects of the Peierls instabilities in organic 1-D conductors, which mostly

concerned TTF-TCNQ [1, 2, 3], three major features appear to require further study :

(i) the detailed dynamical properties close to the transition temperatures,

(ii) the structure of the distorted low temperature states, or correspondingly the eigenvectors of the precursor anomalies,

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(iii) the origin of the $4\mathbf{k}_F$ scattering (where $\mathbf{k}_F$ is the Fermi-wave-vector). Is it fundamental in these systems, such as electron-electron correlations [4], or due to an accidental or specific effect present only in TTF-TCNQ [5] ?

Clearly one convenient means of exploring these questions is to study other organic 1-D conductors that are comparable to TTF-TCNQ which is the major purpose of current structural studies. For example, it has been suggested that the $4\mathbf{k}_F$ scattering depends directly on the strength of repulsive Coulomb interactions between electrons [4] and among presently available systems related to TTF-TCNQ that apparently exhibit somewhat smaller intrasite Coulomb repulsions are HMTTF-TCNQ and TSeF-TCNQ [6]. TSeF-TCNQ has already been shown to exhibit the usual $2\mathbf{k}_F$ scattering [7, 8] and only one phase transition. These results reported here are the first concerning the structural features of the Peierls transition in HMTTF-TCNQ in which conductivity measurements seem to indicate two phase transitions near 49 and 43 K [9-11].

HMTTF-TCNQ has an orthorhombic unit cell, with segregated HMTTF and TCNQ stacks along the $\mathbf{b}$ direction. The donor and acceptor sites alternate in the $\mathbf{a}$ direction (as in TTF-TCNQ), but also in the $\mathbf{c}$ direction [9, 12].

We have found that HMTTF-TCNQ only shows one 1-D anomaly at the wave-vector $0.36\mathbf{b}^*$ (assumed to be $2\mathbf{k}_F$) which condenses at low temperature at the wave-vector $(0.42\mathbf{a}^*, 0.36\mathbf{b}^*, \mathbf{xc}^*)$ corresponding to the 3-D distortion of the insulating state.

2. Experimental. — The experimental apparatus used in the low temperature X-ray diffuse scattering measurements was similar to that described in earlier work. During all exposures, the crystal was kept in a fixed orientation, but, in addition, an extra rotation of few degrees around the vertical axis ($\mathbf{a}^*$ direction in figure 2) was available in order to bring selected weak superstructure satellite spots, which appear at low temperature, in perfect coincidence with the Ewald sphere. Temperature measurements of the sample, which had raised some problems in the previous studies [1], was however considerably improved by mounting the sample in a separate helium filled container where the temperature could be precisely controlled and measured.

The single crystals of HMTTF-TCNQ came from two different sources. One series was synthesized and grown in Philadelphia (A.F.G.), a second series was synthesized in Montpellier (J.M.F., L.G.) and the crystals grown in Copenhagen (K.B.). Most of the initial work on the high temperature precursor scattering was done with crystals from the first source, the characterization of the low temperature superlattice was done with one crystal of the second source which had a somewhat larger size (about

$5 \times 0.5 \times 0.05$ mm) than all other available samples. No difference could be observed between the samples, which on the whole were considerably smaller than those used for the previous studies on TTF-TCNQ.

3. The 1-D precursor and the Peierls transition. — The 1-D precursor scattering is already weakly observable at room temperature in the form of very broad scattering sheets perpendicular to the chain direction. This scattering increases in intensity and

FIG. 1. — X-ray pattern at 100 K showing the $2\mathbf{k}_F$ satellite diffuse sheets of (a) HMTTF-TCNQ and (b) TSeF-TCNQ. On both patterns, where the $\mathbf{a}^*$ and $\mathbf{b}^*$ directions are indicated, note that the modulation of the diffuse intensity along the $\mathbf{a}^*$ direction has a pseudo period of about $4\mathbf{a}^*$.

sharpens progressively for decreasing temperature; figure 1a shows the X-ray diffuse scattering of HMTTF-TCNQ at 100 K and for comparison figure 1b shows the corresponding scattering observed at the same temperature for TSeF-TCNQ. Other than the difference in contrast, which is due to the stronger scattering from selenium in TSeF-TCNQ, the patterns look similar. As observed in earlier investigations of organic 1-D conductors, the scattering *within each sheet* is strongly wave-vector dependent but follows the variation of the undistorted structure factor, from which it is straight forward to conclude that the main effect is due to translations of rigid molecular units [13]. The most general feature of the scattering within the sheets for each

pattern can be simply accounted for by dominant scattering from the sulphur or selenium atoms of HMTTF and TSeF respectively. Moreover, the scattering within the sheets reveals an intensity modulation with a period approximately $4 a^*$ (see figure 1) related to the separation of about $1/4 a$ between the sulphur (selenium) atoms in HMTTF (TSeF) as already reported in reference [7] for TSeF-TCNQ.

The wave-vector in the chain direction of the single 1-D scattering in HMTTF-TCNQ is found to be $0.36 b^*$ (± 0.01) corresponding to a modulation period of 2.78 lattice spacings. With the assumption that such a single 1-D precursor scattering is due to the $2 k_F$ Kohn anomaly, the modulation period corresponds to a charge transfer of 0.72 electrons. This value is very close to the charge transfer 0.74 reported for the Se analogue : HMTSeF-TCNQ [7].

Further studies of the 1-D precursor scattering of HMTTF-TCNQ, using the procedure given in reference [1], indicate that the polarization of the molecular motion has no measurable transverse component in either a or c directions and is therefore strictly longitudinal. This represents a major difference with TTF-TCNQ and TSeF-TCNQ where both a longitudinal and a transverse (precisely determined to be directly along the c^* direction [1], [8]) component are observed for the $2 k_F$ anomaly.

Around 49 K, short range 3-D coupling between the charge density waves on successive chains becomes visible in the form of broad diffuse spots within the $2 k_F$ sheets (Fig. 2a). At 43 K, these broad spots have condensed into well defined satellite reflections

FIG. 2. — (a) X-ray pattern of HMTTF-TCNQ at 48 K showing the build up of 3-D modulation within the $2 k_F$ satellite diffuse sheets. (b) X-ray pattern of HMTTF-TCNQ at 10 K showing well defined $2 k_F$ superstructure spots.

and besides a rapid increase of intensity no further change is observed down to 10 K as shown in figure 2b. As can be seen in the patterns of figure 2, the transverse wave-vector component in the a^* direction is close, but slightly different from the expected $1/2 a^*$ value. Microdensitometer readings of the photographic patterns, as shown in figure 3, yield a temperature

FIG. 3. — Microdensitometer scans in the $k = 2 + 2 k_F$ plane along the a^* direction and showing the formation of the $(\pm 0.58, 2.36, x)$ satellites indicated by the arrows in the figure 2. The position along the c^* direction is not known because of the experimental set up. Note the temperature independent value of the position of the satellites along the a^* direction.

independent value of $0.42 a^*$ (± 0.03) in the distorted phase. The absolute position of these satellites could not be determined accurately in the c^* direction because of streaking in this direction which is apparently unrelated to the Peierls transition (a tentative value is $0 c^*$). The streaking also occurs on the main Bragg reflections and seems to be due to faults as earlier suggested for HMTSeF-TCNQ where similar effects could be observed [14]. However using a different orientation of the crystal where the c^* direction is directly projected on the photographic film, we have checked that the c^* component is, within experimental errors, also temperature independent.

These features are in agreement with the onset of 3-D short range order at about 49 K and a phase transition to a long range order at 43 K, which corresponds to a 3-D super lattice $2.38 a \times 2.78 b \times xc$.

The behaviour of the a^* component of the $2 k_F$ superstructure satellite reflections of HMTTF-TCNQ differs markedly from that of TTF-TCNQ. The most widely accepted explanation of the $0.5 a^*$ wave-vector component of the distortion in TTF-TCNQ after the first phase transition and between 54 and 49 K, is that only one kind of molecular stack is condensed ;

the decrease of the a^* component below 49 K is attributed to the condensation of the TTF stacks [15]. If we follow the same kind of description for HMTTF-TCNQ, the condensation at $0.42 a^*$ may indicate that the 3-D coupling observed below 49 K already involves both molecular species; this contrasts with the current idea that the 49 K phase transition is driven by the TCNQ stacks and that the lower transition at 43 K involves the HMTTF units [6, 9-11]. Although an incommensurable value of the a^* component can be expected by a simultaneous condensation on both types of stacks [16], its tempe-

rature independence (within experimental errors) is presently not understood. The *simpler* behaviour of HMTTF-TCNQ with respect to the a^* wavevector of the low temperature 3-D distortion may also be directly related to the purely longitudinal polarization observed in the high temperature precursor.

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