0.43 eV/atom $\leq \Delta H \leq$ 0.68 eV/atom between the ordered and disordered states at half-monolayer coverage. This number is, as expected,[12] about 10% of typical A-S binding energies. The uncertainty in the value could probably be reduced by including NNN interactions. Although the measurements were made for half-monolayer coverage, the nature of the disordering of the islands suggests that this lateral-interaction energy should be the same at much lower coverages. Experiments are in progress to check this.

*Research supported in part by the National Science Foundation, Grant No. GH 36354, and in part by the Research Corporation.

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X-Ray-Diffuse-Scattering Evidence for a Phase Transition in Tetrathiafulvalene Tetracyanoquinodimethane (TTF-TCNQ) *

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X-ray-diffuse-scattering measurements of tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) show structural evidence of a phase transition. The low-temperature three dimensional superlattice ($2a \times 3.7b \times Xc$) is found to be preceded above 40 K by one-dimensional fluctuations or a one-dimensional distortion visible up to 55 K.

Earlier studies of the dc, microwave, and optical properties have shown that tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is not a simple metal.[1-9] Above 58 K, there is an energy gap[6] at $\hbar\omega_g = 0.14$ eV and an extremely narrow conductivity mode centered at zero frequency. Near 58 K, TTF-TCNQ undergoes a metal-insulator transition[1,10] to a high-dielectric-constant[3] semiconductor in which the oscillator strength is shifted from zero frequency and pinned in the far infrared.[6]

In an earlier work,[1] it was proposed that above 58 K, the electrical transport in this compound is dominated by superconducting fluctuations associated with a Peierls instability in which a phonon mode is driven soft by the one-dimensional (1D)

divergent response of the electron gas at the wave vector $q = 2k_F$, leading ultimately to the metal-insulator transition near 58 K and a periodic superlattice distortion in the low-temperature semiconducting state.

The extensive experimental studies[1-9] on TTF-TCNQ provide support for such an interpretation which is consistent with theoretical ideas[11] developed by Bardeen[12] and Lee, Rice, and Anderson[13] suggesting that TTF-TCNQ is a Peierls-Fröhlich giant-density-wave superconductor in the 1D fluctuation regime.

The crucial piece of evidence was nevertheless missing; previous x-ray-diffraction studies using conventional structure techniques were unable to show any superlattice distortion[14] in the low-temperature state, leaving little hope for a direct observation of the expected 1D fluctuations.

The present paper reports preliminary results of an x-ray-diffuse-scattering study of TTF-TCNQ using techniques[15] which had been successful in earlier investigations of the Peierls instability in $K_2Pt(CN)_4Br_{0.30} \cdot 3H_2O$ (KCP).[16]

The TTF-TCNQ crystals had typical dimensions of $4 \times 0.3 \times 0.1$ mm^3. The x-ray beam (monochromatic Mo K radiation $\lambda = 0.709$ Å) was perpendicular to the larger-area b-a face as grown from CH_3CN solutions; consequently, no information on changes in the c direction could be obtained. The crystals were cooled using a CTI "cryodine" cryocooler; the temperature was regulated to within 0.5 K. The uncertainty in temperature was ± 2 K from different runs.

The scattering patterns and the sketches of Fig. 1 provide direct evidence for 1D superlattice fluctuations (or a 1D distortion) preceding a lower-temperature 3D superlattice.

The intense layers of fundamental spots, which are perpendicular to the b axis, are due to the undistorted 3D structure and show no remarkable modifications between 300 and 18 K, in agreement with previous x-ray-diffraction studies.[14]

At 20 K [Fig. 1(a)], accompanying the intense layers are well defined arrays of satellite spots which are not visible in similar room-temperature patterns. Taking as reference the undistorted lattice constants, the distance between the arrays of satellites and the fundamental layers indicates a modulation of the structure in the chain direction with a period $3.7b \pm 0.1$, and the distance between satellite spots shows a doubling in the a direction. These data establish that a true phase transition to a larger unit cell ($2a \times 3.7b \times Xc$) has taken place at a higher temperature.

Upon warming, the satellite spots broaden perpendicular to the b direction as shown in Fig. 1(b) (40 K) where arrays of satellite spots are connected by a diffuse line. The simultaneous presence of satellite spots and diffuse lines corresponding to the same modulation in the b direction indicates the existence of a transition region from the low-temperature 3D superstructure to a 1D superstructure; i.e., a progressive loss of trans-

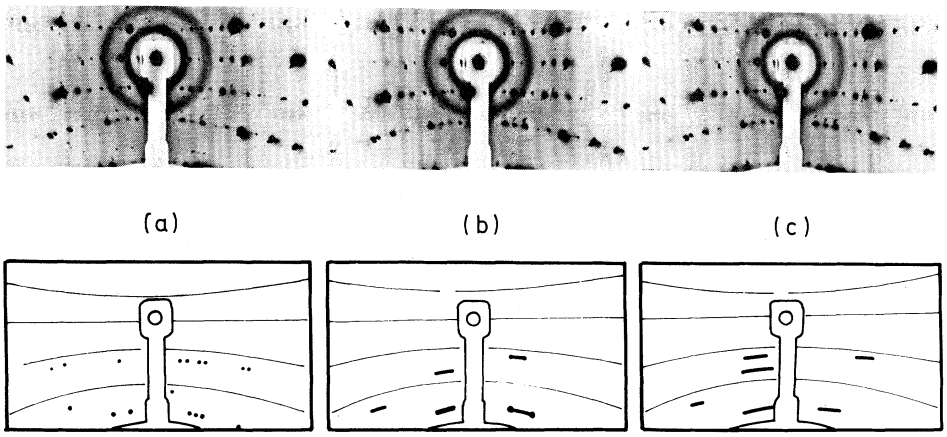

FIG. 1. Diffuse x-ray scattering patterns from TTF-TCNQ and corresponding sketches. (a) ($T = 20$ K). The intense principal spots are due to the 3D structure and the satellite spots to the 3D superstructure at $T < 38$ K. (b) ($T = 40$ K). The 3D superstructure spots broaden into thin continuous lines of the 1D superstructure $T > 38$ K. (c) ($T = 55$ K). Superstructure spots have completely disappeared leaving only sections of continuous diffuse lines. The diffuse rings at the center of the patterns are parasitic and caused by grease deposits on the cold sample.

verse long-range order and only local correlations of the phases of the modulation in adjacent chains.

At 55 K, the spreading of the satellite spots perpendicular to b appears complete, and only weak diffuse lines can be seen in Fig. 1(c); the distortion has become strictly 1D. The diffuse satellite lines are not continuous as in KCP, but this can be explained by the form factor of the relatively large molecules. We conclude that around 55 K the transverse coherence length is less than the interchain distance; the phase of the modulation is uncorrelated between adjacent chains. From an estimate of the width of the satellite lines, the coherence length of the distortion along the chains is at least 50 molecular sites. Above 55 K the diffuse satellite lines become weak and unobservable.

Since the intensity of both the satellite peaks and the higher-temperature 1D scattering increases with increasing scattering vector parallel to the b axis, the corresponding distortion involves sinusoidal displacements of atoms with the main component along the chain direction. There is no evidence for an additional component perpendicular to the chain direction, but as we have no information as far as the c direction is concerned, it cannot be completely ruled out.

If we consider the location of the intensity maxima along one given satellite sheet, they are always found along the most intense Bragg spots (or the acoustic phonon cloud around it) from the fundamental layers of the undistorted 3D structure; in other words, the superstructure spots or diffuse satellite sheets roughly follow the variation of the undistorted structure factor. We can therefore conclude that in first approximation the molecules are displaced as a whole.

The satellite scattering is not symmetric around the main layers in contrast with the scattering earlier observed in KCP. Nonsymmetric satellites are known to be due to correlated displacive and density modulations, but, in such cases, the strongest satellite is always on the same side relative to the fundamental layers.[17] This is not the case in Fig. 1, where there is no such regular asymmetry. With the limited available data, we cannot give a detailed explanation of the asymmetries, but taking into account the form factor of the large molecules of TTF-TCNQ, *patterns* with asymmetric satellites are a normal feature. In fact, the patterns from different runs, which always correspond to small sample alignment variations during cooling, show differences in the observed asymmetry, which can even be reversed.

The existence in TTF-TCNQ of a phase transition related to 1D distortion or to 1D fluctuations (as x-rays cannot distinguish static from dynamic correlations) which appears of the type which was earlier proposed[1] is thus well established. If the driving mechanism of this phase transition is the coupling of the $2k_F$ phonons to the 1D electrons, the first conclusion from the observed superperiod ($3.7b$) is a partially filled band corresponding to a charge transfer of 0.53–0.56 electrons.

The $3.7b$ superperiod along the b axis appears incommensurate with the underlying 3D lattice which satisfies one essential condition for the Peierls-Fröhlich-type mechanism. The values found from a series of patterns are always smaller than 4.

The pinning of the Peierls-Fröhlich distortion is due to weak interchain coupling from 3D band-structure effects or Coulomb interaction.[13] Both have been proposed earlier as being involved in the linear-chain A-15 compounds[18,19] as well as in KCP.[20,21] Finite electronic overlap between chains causes a slight nonplanarity in the 1D Fermi surface. So long as the interchain coupling is not too large, the dominant phonon instability moves from $(0, 2k_F, 0)$ to the zone edge, $(\pi/a, 2k_F, \pi/c)$, leading to a doubling of the unit cell perpendicular to b in agreement with the x-ray results. Coulomb interactions depend on all three q wave-vector components; with two inequivalent cations and anions per unit cell, it is not clear whether the strong Coulomb limit would favor an antiphase ordering of successive chains without doubling the unit cell, or of successive cells resulting in a doubling of the a and c lattice constants.

It has been proposed by Matthias[22] and by Cohen *et al.*[23] that an a-axis ferroelectric distortion would open an energy gap at the Fermi surface resulting in the metal-insulator transition at 58 K. Such a distortion would be internal to the unit cell and would not give rise to a superlattice as experimentally observed. The direct observation of the superlattice structure below 58 K together with complementary structure studies at low temperature[24] rules out such a distortion in TTF-TCNQ.

Koonce[25] has observed that in a donor-acceptor system, interband scattering leads to distortions of wave vector $k_F(\mathrm{TTF}) + k_F(\mathrm{TCNQ}) = \pi/b$, and also of wave vector $|k_F(\mathrm{TTF}) - k_F(\mathrm{TCNQ})|$. The former is ruled out by the $3.7b$ superperiod. Although the interference term is possible, we an-

ticipate that the larger intraband scattering will dominate.

The x-ray diffuse scattering further gives a direct structural observation of a transitional region between roughly 40 and 60 K, dominated by 1D distortions (or eventually 1D fluctuations). This is the same temperature range where distinct changes were previously observed in several measured properties. Near 40 K, there is a second peak in the anisotropy of the dc conductivity,[2] with discontinuities in the b axis thermopower[26] and the slope of dc[27,28] and microwave conductivities.[29] Around 55 K, there is a maximum in the specific heat and a softening in the longitudinal Young's modulus.[31]

In summary, the observation of a superlattice of satellite peaks which broaden into 1D diffuse lines at higher temperatures provides direct evidence of the existence of the Peierls instability in TTF-TCNQ. The incommensurate 1D superlattice together with the earlier observations of the energy gap and the narrow collective-mode conductivity provides further evidence for the possibility of Peierls-Fröhlich giant-density-wave superconductivity in 1D systems.

We are grateful to H. Launois who patiently insisted for this experiment, which looked somewhat hopeless at its beginning, to C. Weyl who participated in its very first steps, to M. Lambert for numerous discussions, to L. Deschamps for his kind technical help, and to P. Nigrey for careful and dedicated sample preparation.

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*Presented in part at the Meeting of the American Physical Society, Denver, Colorado, April 1975.

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‡Work supported in part by the National Science Foundation through the Laboratory for Research on the Structure of Matter, and Grants No. GH-39303 and No. GP-41766X, and by the Advanced Research Projects Agency through Grant No. DAHC-15-72-C-0174.

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Hot Electrons in SiO_2†

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(Received 24 April 1975)

The experimentally determined drift velocity of excess electrons in a-SiO_2 as a function of field is reported. Saturation of the velocity-field curve above 10^7 cm/sec provides evidence for phonon emission by significantly heated electrons. The data provide the first test of, and good agreement with, the Thornber and Feynman theory of electron energy loss in polar materials at high applied fields.

It was pointed out a few years ago by Thornber and Feynman[1] that the anomalously high electron energy loss in thin oxide films on cold cathodes might be due to emission of LO phonons. In this Letter I present the first direct evidence for "hot" electrons in a-SiO_2 in the form of the measured electron drift velocity as a function of field. The drift velocities are stable at fields up to at least 8×10^5 V/cm, which corresponds to a large energy loss of almost 10^{-2} eV/Å. I will also present evidence from pulse-x-ray-induced conductivity measurements on thin SiO_2 films that the drift velocity is stable up to fields of at least 5×10^6 V/cm. The electron drift velocity shows the onset of saturation with field around 8×10^6 cm/sec which can be understood if the energy loss is being dominated by the 0.15-eV LO phonon in SiO_2. However, the energy loss at lower drift velocities (i.e., the low-field mobility) is apparently dominated by the lower-energy LO phonon (0.06 eV) at room temperature because the electron is scattering off the thermal population of phonons rather than emitting phonons. A number of authors have recently discussed the possible effect of hot electrons on electrical phenomena found in thin SiO_2 films [i.e., metal-oxide-semiconductor (MOS) devices] and I will comment on the relevance of the data to the explanations offered.

The drift velocities were obtained by measurement of the transit time of electrons across specimens of Suprasil II fused quartz. The specimen thickness was varied from 0.02 to 0.1 cm. I have reported earlier on measurements of the low-field mobility and its temperature dependence with the data taken in a similar fashion.[2] The electrons are generated in the bulk of the SiO_2 by a 3-nsec pulse of x rays from a Febetron-706 electron-beam machine. Typical wave forms from this kind of experiment are given in Fig. 1, where the integral of the current is given. In Fig. 1(a) the field was held low enough so that very few electrons were swept out during the bulk lifetime of the carriers (in this case about 8 nsec). Figure 1(b) is for a higher field and the effect of the sweepout of electrons is easily seen. The sweepout time t_s was derived from data similar to Fig. 1 and the drift velocity is found from $v_d = d/t_s$, where d is the thickness and t_s is the transit time. To obtain an accuracy of ± 10% it was necessary to fit the experimental curves with simulated transits[2] involving the lifetime and shape of the x-ray pulse. The drift velocity as a function of field for several specimen thicknesses is given in Fig. 2. The sublinear dependence at high fields was checked by comparing the high-field traces with traces from thinner samples at lower fields where the transit times were identical (this is somewhat more accurate than unfolding the effect of the shape of the x-ray pulse). The high-field data were taken with the sample immersed in a special high-voltage chamber filled with Humble x-ray oil, and connected to a Del 120-kV dc power supply by 30 ft of high-voltage cable to prevent reflections. The upper voltage limit was due to arcing around the edge of the sample which, at these energy densities, destroys the sample.

The problem of the behavior of an excess electron in a polar insulator under the influence of an electric field has received a great deal of attention over the last thirty years. A survey of the

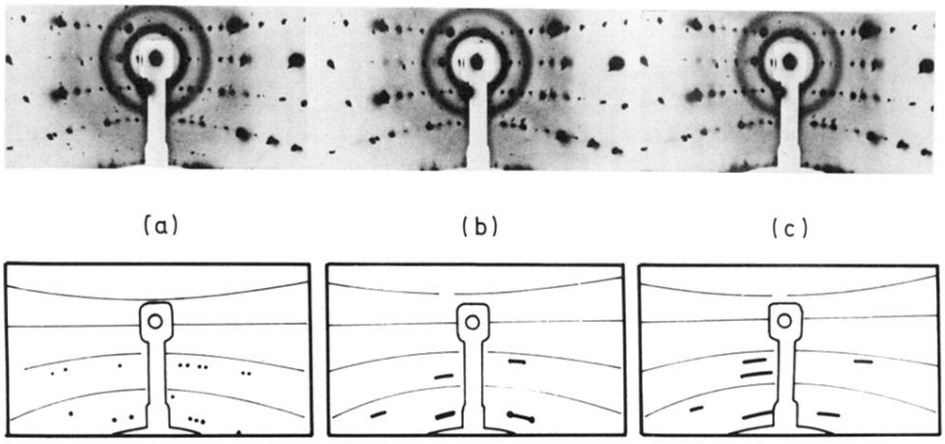

FIG. 1. Diffuse x-ray scattering patterns from TTF-TCNQ and corresponding sketches. (a) ($T = 20$ K). The intense principal spots are due to the 3D structure and the satellite spots to the 3D superstructure at $T < 38$ K. (b) ($T = 40$ K). The 3D superstructure spots broaden into thin continuous lines of the 1D superstructure $T > 38$ K. (c) ($T = 55$ K). Superstructure spots have completely disappeared leaving only sections of continuous diffuse lines. The diffuse rings at the center of the patterns are parasitic and caused by grease deposits on the cold sample.