of freedom. However, his model corresponds to an additional dipolar electronic fluctuation rather than charge fluctuation and consequently he must postulate an attractive direct electron-electron interaction between his supershells.[15]

The model proposed here may also explain the large superconducting transition temperatures found in many of the materials which possess anomalies in their phonon spectrum. The electron-phonon matrix elements are screened by the dielectric function of Eq. (3), and if $S(q)$ becomes large with $V(q)$ negative, the matrix elements for regions of k space coupled by this q will be considerably enhanced. Complete details and implications for superconductivity will be published in the more extended version of this work.

Our conclusion is simply that in metals with a relatively high density of localized states at E_F, anomalies in the phonon spectrum or even lattice instabilities may arise if the q-dependent electron-electron and electron-phonon interactions are favorable for an incipient charge-density wave to couple to the lattice. We have shown this to be true for Nb and NbC and believe the model to be applicable to many other materials. The effective electron-phonon coupling constant may be enhanced by such effects, giving rise to high superconducting transition temperatures. Full details will be published shortly.

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Neutron-Scattering Study of the 38- and 54-K Phase Transitions in Deuterated Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)

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Neutron-elastic-scattering experiments performed on deuterated TTF-TCNQ single crystals reveal two structural transformations at 38 ± 0.5 K and at 54 ± 1.0 K. Below 38 K, a $4\vec{a} \times 3.4\vec{b} \times \vec{c}$ modulation relative to the underlying undistorted lattice is established. At 38 K the modulation period in the $\vec{a}$ direction becomes incommensurate and displays an abrupt decrease from its low-temperature value of $4\vec{a}$ and gradually decreases with increasing temperature to $2\vec{a}$ near 51 K.

Recent x-ray diffuse-scattering experiments performed with photographic patterns, first clearly revealed the existence of a low-temperature long-range-ordered modulated lattice in the one-dimensional (1D) metal tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ),[1] and suggest-

ed a modulation at 20 K corresponding to $2\vec{a}\times 3.7\vec{b}\times\vec{c}$, referring to the underlying monoclinic lattice.[2-4] This work also provided some evidence for a transitional region above 40 K, corresponding to a progressive loss of the transverse order (perpendicular to the chain direction) of the modulation, leading ultimately above 55 K to a typical 1D scattering attributed to the expected Peierls distortion or Kohn anomaly. Such a large anomaly was indeed observed up to room temperature in a subsequent neutron-inelastic-scattering study.[5] Further independent x-ray-scattering work[6] also showed the existence of a high-temperature 1D scattering, and determined, using more precise counter detection, the low-temperature modulation actually to be $4\vec{a}\times 3.7\vec{b}\times\vec{c}$. In light of these results, the transverse modulation period requires further study over the full low-temperature range ($T < 58$ K) with characterization of the transitional region and a precise determination of the structural transition temperature. It is the purpose of the present paper to report elastic-neutron-scattering experiments performed on deuterated TTF-TCNQ in order to study the nature of the low-temperature long-range order and its modification with temperature.

The 3D modulated structure at 25 K is found to be $4\vec{a}\times 3.4\vec{b}\times\vec{c}$ in close agreement with that found by Kagoshima *et al.*[6] A first phase transition is observed at 38 ± 0.5 K, and a second structural transformation at 54 ± 1 K. Between 38 and 54 K, the order remains 3D, possibly only short range in the upper part of this temperature region, but the modulation period along the $\vec{a}$ direction varies continuously from $4\vec{a}$ in the lower phase to a value close to $2\vec{a}$ around 51 K. These results are summarized in Fig. 1 which shows the temperature variation of the strongest satellite peak intensity [Fig. 1(a)] and of its position in reciprocal space [Fig. 1(b)] which reflects the modulation period in the $\vec{a}$ direction.

The deuterated TTF-TCNQ single crystals were grown from acetonitrile solutions and had the usual form of platelets elongated in the [010] chain direction and parallel to the (001) crystallographic plane. Their size was approximately $25\times 2\times 0.05$ mm^3. Several single crystals displaying a very small amount of twinning were studied, but each set of experiments was carried out using only one crystal.[7] The samples were mounted in a cryostat and the temperature measured and controlled by a Pt resistance thermometer to within ± 0.05 K.

The neutron-scattering experiments were performed on a triple-axis spectrometer at the Brookhaven National Laboratory high-flux beam reactor using 13.7-meV incoming neutrons and pyrolytic graphite set for zero energy transfer as an analyzer. By careful selection of collimations, we achieved a background level of 5 counts/min compared to the 150 000-counts/min intensity of the strongest fundamental reflection (013).

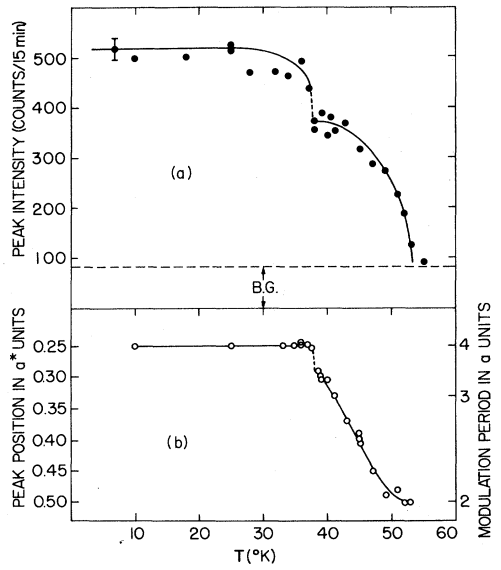

FIG. 1. (a) Temperature-dependent behavior of the satellite peak intensity. Above 38 K the peak intensity may not be directly related to the order parameter because of a varying structure factor accompanying the peak's shift, and because of an eventual broadening of the satellite in the $\vec{a}^*$ direction. (b) Peak position, in units of a^*, and the corresponding modulation period in units of a (right-hand-side scale).

At 25 K, we first surveyed the $[0kl]$, $[hkh]$, $[hk\bar{h}]$, and $[hk0]$ zones. Within the limits of our detectability (1.5 counts/min), we could not observe any satellite peak compatible with $\vec{a}\times n\vec{c}$ (n = integer), $2\vec{a}\times 2\vec{c}$, $\vec{a}\times\vec{c}$, or $2\vec{a}\times\vec{c}$ transverse modulations. However, in the $[hk0]$ zone, which contains only weaker Bragg reflections from the main lattice, several satellite peaks were observed at the positions $(\pm 0.25, \pm 0.295, 0)$ of the reduced Brillouin zone, which correspond to a $4\vec{a}\times 3.4\vec{b}\times\vec{c}$ modulation. The strongest satellite of this zone had a signal of only 5 counts/min. A search for higher intensities motivated the investigation of less usual zones, namely $[hk4h]$ and $[hk12h]$, which contained the appropriate positions close to stronger Bragg reflections of the main lattice.

At 25 K a total of twelve satellites with inten-

sities greater than twice the background were observed and confirmed the $4\vec{a}\times 3.4\vec{b}\times\vec{c}$ modulation. Among them the strongest corresponds to the (0.25, 1.295, 3) position in reciprocal space [Fig. 2(a)] which is close to the strongest (013) reflection of the main lattice. Most of the data shown in Fig. 1 and already mentioned were obtained on this satellite. The intensity relative to the (013) reflection of the main lattice was found to be 2×10^{-4}. We have not collected sufficient satellite data to determine the exact atomic displacements, but we did observe in the present work, as already stated in the earlier x-ray work,[1] that the strongest satellites were always found close to the strongest Bragg peaks of the main lattice; this suggests an acousticlike distortion with TTF and TCNQ molecules modulated as units. If we assume a distortion along $\vec{b}$ (it is impossible to rule out an eventual $\vec{a}$ component with the present data) we can get a rough estimate of the distortion amplitude, namely $\simeq 1\%$ of the lattice spacing.

Let us now examine the linewidth of the satellite peaks below 38 K. This has a particular significance since another 1D electronic system KCP [$K_2Pt(CN)_4Br_{0.30}\cdot 3H_2O$] shows noticeable broadening in its 3D satellites below 100 K.[8] We find that within the limits of our resolution, namely about 0.02 $Å^{-1}$ (corresponding to a lower correlation limit of about 100 Å), no broadening can be observed, and the 3D modulation is long range.

Three satellites were studied as a function of temperature: the (0.25, 1.295, 3), (0.75, 1.295, 3), and (1.25, 2.705, 0) satellites, yielding similar results. Between 7 and 38 K little change in intensity is observed; at about 38 ± 0.5 K the satellite peak intensity shows a sharp decrease of about 20% [Fig. 1(a)] and an abrupt change in position [Fig. 1(b)], possibly indicating a first-order phase transition.

Between 38 and 54 K the satellite position varies continuously as a function of temperature, with a simultaneous decrease of intensity, which ultimately falls to zero above 54 K. Except for the weaker [$hk0$]-zone satellite (1.25, 2.705, 0), which could be followed by normal three-axis spectrometer scans, but only in the lower part of this temperature region where its intensity was still meaningful, a special procedure had to be adopted in order to study the two other satellites, and more particularly, the stronger (0.25, 1.295, 3) satellite.

This reflection was initially brought into the horizontal plane by tilts around the $\vec{b}^*$ axis from the ($0kl$) plane. Below 38 K this corresponds to the [$hk12h$] zone with $h=\frac{1}{4}$. Above 38 K and in the intermediate temperature region, regular scans were first performed at various tilt angles close to the [$hk12h$] zone in order to determine the direction of the satellite's displacement. When the satellite's position was insured to be located along the $\vec{a}^*$ direction, special scans, with a point-by-point adjustment of the tilt angle, were performed along the $\vec{a}^*$ direction. Figure 1(b) shows the variation with temperature of the position of the satellite peak, and Fig. 3 shows typical satellite scans at three different temperatures. Around 51 K and above, when the satel-

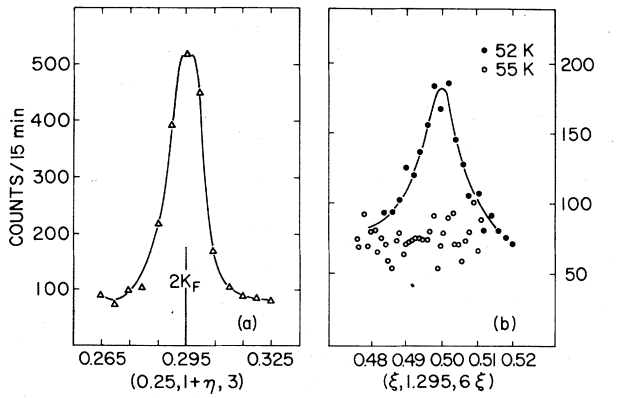

FIG. 2. (a) Scan at 25 K parallel to $\vec{b}^*$, showing the satellite peak at the position (0.25, 1.295, 3). (b) Scans perpendicular to $\vec{b}^*$ (more exactly along a [106] direction) showing the satellite peak at 52 K and its disappearance at 55 K.

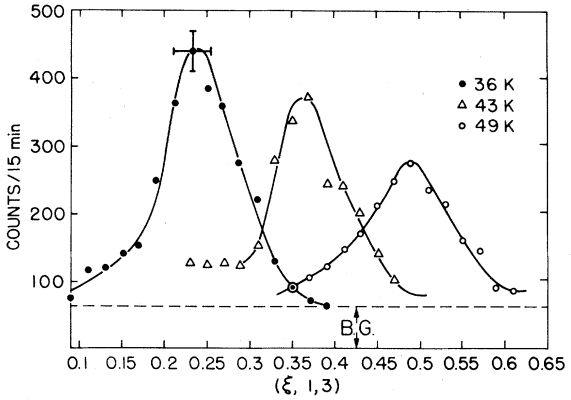

FIG. 3. Scans along $\vec{a}^*$ at three different temperatures. These scans were performed with a manual point-by-point adjustment of the sample tilt and yield therefore a less precise positioning in reciprocal space, as shown with the horizontal error bars.

lite position is close to (0.5, 1.295, 3), corresponding to the $2\vec{a}\times 3.4\vec{b}\times\vec{c}$ modulation, it could be studied in the $[hk6h]$ zone with $h=\frac{1}{2}$; Fig. 2(b) shows two scans perpendicular to $\vec{b}^*$ and recorded in this zone at 52 and 55 K. From this we see that within the limits of our experiment no 3D modulation is observed above 54 K.

If we now consider the line shape of the satellite between 38 and 54 K, as recorded in the $\vec{b}^*$ direction and across $\vec{a}^*$ {namely $[hkx(T)h]$ directions with $6<x(T)<12$} no broadening can be observed relative to the lower-temperature-phase satellites, or the main Bragg peaks; in these directions, and within the limit already mentioned of our horizontal resolution (0.02 Å^{-1}), long-range order is preserved. Along the $\vec{a}^*$ direction, however, some broadening seems to take place above 40 K and can be easily seen in the 49-K scan of Fig. 3. Our resolution along this direction is only 0.05 Å^{-1}, because of poor vertical collimation, and further study is needed for more precise characterization.

The most fascinating result of this study is certainly the observation of a temperature-variable modulation in the $\vec{a}$ direction between 38 and 54 K at which temperatures a variety of experiments had revealed anomalies.[9] The $\vec{a}$ direction in TTF-TCNQ corresponds to alternate sheets of, respectively, TTF and TCNQ molecules, and the modulation along $\vec{a}$ therefore describes the coupling between such sheets. The position along $\vec{b}^*$, at all temperatures, of the satellite peak of the present work yields a $2k_F$ value of $0.295b^*$ which seems slightly outside of the possible errors quoted in the earlier x-ray works.[1,6] This corresponds to a charge transfer of 0.59.

There are several important questions yet to be resolved concerning the unusual phase transitions in TTF-TCNQ. These include the following: (1) Why does the $\vec{a}^*$ periodicity show such a drastic change between 54 and 38 K? (2) How is the diffuse 1D scattering around 54 K, observed by x-ray studies, related to elastic and inelastic scattering? (3) Is there any quasi-elastic 1D scattering well above 54 K similar to the observations in KCP above 100 K? Further experiments are underway with an aggregate of many small single crystals.

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