PHYSICAL REVIEW B VOLUME 16, NUMBER 7 1 OCTOBER 1977

Elastic neutron-scattering study of the three low-temperature transitions in tetrathiafulvalenium-tetracyanoquinodimethanide

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(Received 17 December 1976)

Elastic neutron-scattering measurements of the satellite structure of tetrathiafulvalenium-tetracyanoquinodimethanide show the existence of phase transition points at 38, 48.5, and 54 K. All of the low-temperature phases are incommensurate with a 0.295 component along b^* but differ as to their modulation along the a^* axis. These results are interpreted within the framework of a theory by Bak and Emery. An unusual hysteresis behavior in the intermediate phase between 38.5 and 48.5 K is reported. Measurements on satellites with a component of 0.59 along b^* for the lowest temperature phase are also discussed.

I. INTRODUCTION

The charge-transfer salt tetrathiafulvalenium-tetracyanoquinodimethanide (TTF-TCNQ) has attracted a large amount of interest in the past few years. Since this salt is one of a set of materials which shows quasi-one-dimensional behavior with associated unusual electronic properties, it is important to gain as much information as possible on the structural modifications and dynamics at low temperature. Consequently, a number of x-ray and neutron-scattering measurements have been carried out that have substantially increased the understanding of this system and have in turn led to important theoretical developments. With regard to the structural aspects, this problem has proved to be of considerable theoretical interest as it can be treated as a two-chain system which displays a series of incommensurate phase transitions.

Two independent x-ray scattering measurements[1,2] of TTF-TCNQ first gave direct evidence of a phonon anomaly and transition to a low-temperature modulated phase. Above 54 K, sheets of diffuse scattering attributable to a Kohn anomaly in the phonon dispersion were found along the monoclinic b^* chain axis at $\overline{q} = 0.29b^*$. This value was assumed to be $2k_F$ along the chain direction due to electron-phonon coupling. Ordering with this same b^* modulation period was found below 54 K and interpreted as a Peierls distortion. At about 20 K, both measurements showed satellite spots indicating three-dimensional ordering but differed as to the precise modulation periods. Subsequent neutron-scattering studies[3,4] established the presence of at least two well-defined phase-transition points involving three-dimensional ordering. The transition at 54 K gave rise to Bragg satellites located at positions $(h \pm 0.5,\ k \pm 0.295,\ l \pm 0)$. Here, the h, k, and l indices are defined with respect to the reciprocal-lattice vectors a^*, b^*, c^*, respectively, of the undistorted high-temperature monoclinic cell. At 38 K, a first-order-like transition was observed with a hysteresis of about 1 K with the modulation below this point being characterized by satellite positions of the type $(h \pm 0.25,\ k \pm 0.295,\ l \pm 0)$. These early measurements also indicated an unusual behavior in the temperature dependence of the a^* modulation component which decreased continuously upon cooling from 54 to 38 K and exhibited a discontinuous jump at 38 K to the value of 0.25.

In order to understand these results, a theoretical description of the phase transitions in TTF-TCNQ was developed by Bak and Emery.[5] Starting from a two-chain model and using group theoretical considerations and a Ginzburg-Landau Hamiltonian, it was shown that there should be at least three separate phase-transition points T_1, T_2, and T_3. Each of these phases would be identified by the a^* component of the modulation. At T_1, only one of the sets of chains was expected to order and this would produce a phase with an a^* modulation of 0.5. This modulation would stay constant down to T_2 where the second set of chains would be driven to order. Below T_2, interactions between the two sets of ordered chains would produce a temperature-dependent value for a^*. Finally, at T_3, fourth-order umklapp terms would lead to a lock-in transition to a state characterized by a commensurate a^* modulation of 0.25. These authors[5] reanalyzed part of the earlier neutron-scat-

tering results[3] and concluded that the data fit the description with the well-characterized transitions at 54 and 38 K being T_1 and T_3, respectively, and that T_2 was approximately 47 K. However, as described in Ref. 3, the experimental neutron-scattering data were obtained in a special type of scan requiring manual adjustment of goniometer tilts in order to follow the movement of satellites. In addition, the relatively poor vertical resolution of the instrument caused broadening effects in this type of scan so that it could not be precisely established at which temperature the satellite position broke away from the 0.5 value. To obtain a very accurate determination of the satellite positions as a function of temperature provided the principal motivation for a further series of neutron scattering measurements, and several of these results have been reported in an earlier communication.[6] Details of these and some supplementary measurements will be reported here as well as observations indicating that there can be sample dependent effects. The measurements additionally show a quite unusual thermal hysteresis in the continuous transition region between 38 and 48.5 K.

Another aspect of the scattering in TTF-TCNQ has been the recent observation by x-ray measurements[7,8] of another set of anomalies located at $0.59b^*$. This component along b^* is twice that of the $2k_F$ satellites originally discovered, and the new scattering has been termed as arising from $4k_F$ anomalies. The origin of this scattering is not yet clear as there have been suggestions[7,8] that what has been termed $2k_F$ and $4k_F$ scattering may represent k_F and $2k_F$ instead. For purposes of consistency we will continue to use the $2k_F$ and $4k_F$ terminology in this paper. We report here on the neutron-scattering observations of these new superlattice reflections which were found at positions $(h \pm 0.5,\ k \pm 0.59,\ l \pm 0)$. Unfortunately, intensity considerations limited the amount of new information that could be gained for this new scattering.

Finally, it should be mentioned that extensive measurements on the inelastic spectra have been reported and they give important insights into the transition at 54 K. These aspects of the scattering will not be discussed here but may be found in Refs. 9–11.

II. EXPERIMENTAL

Three different samples, studied in earlier experiments and denoted A, B, and C, were used in these measurements. Sample A was approximately $25 \times 2 \times 0.05$ mm in size and gave a counting rate of 2.5×10^5 counts/min on the most intense reflection (013). This sample was mounted in a strain-free manner by wrapping it loosely in aluminum foil and then affixing this foil to a thin aluminum plate. Samples B and C were larger but somewhat irregular in shape and gave about 1×10^6 counts/min on the (013) reflection. Sample B was mounted similarly to that described above. However, crystal C was directly affixed to an aluminum support plate with a small amount of glue. It is important to note the manner of mounting because differential thermal contraction between sample C and the support plate may have led to an unknown amount of stress being applied to at least part of this sample. The samples were mounted in cryostats with the temperature being measured and controlled by a calibrated platinum resistor to within ±0.05 K. These samples were always slowly cooled to low temperatures over a period of hours to help reduce any temperature induced stress-strain effects.

The neutron-scattering measurements were performed with pyrolytic graphite crystals as monochromator, filter, and analyzer on triple-axis spectrometers at the Brookhaven High Flux Beam Reactor. Collimations were carefully selected to optimize the signal-to-noise ratio. Collimations of 20-20-20-40 and use of the spectrometer in the $E = 0$ analyzing mode with 2.46-Å neutrons gave backgrounds of about 4 counts/min for sample A.

An important feature of the measurements to be described was the choice of the scattering plane and the realization of this plane on the spectrometer. For most single-crystal measurements on triple-axis spectrometers, a scattering plane with high symmetry is selected and the crystal can be easily oriented by aligning on strong Bragg reflections in this plane. This procedure becomes more complicated when working with crystals having incommensurate phases because there may be an absence of strong reflections on which to align. The particular requirements, for example, for the $2k_F$ satellites in TTF-TCNQ were dictated by the fact that these spots occur at positions $(h \pm q(T), k \pm 0.295, l \pm 0)$, where 0.295 along b^* is the $2k_F$ modulation and the a^* modulation is temperature dependent. The temperature dependence of the a^* modulation was the primary quantity of interest making it particularly convenient to have this axis as one of the basis vectors of the measured zone. Earlier studies at low temperature had shown that the satellites at positions (0.25, 1.295, 3) and (0.75, 1.295, 3) were the most intense which led to the choice of the $(h\ 1.29k\ 3k)$ scattering plane in which to perform the bulk of the measurements. This scattering plane is schematically depicted in Fig. 1 where the main and satellite Bragg peaks are indicated. Achievement of this zone on the spectrometer was accomplished by a series of manual rotations of the orientation of the

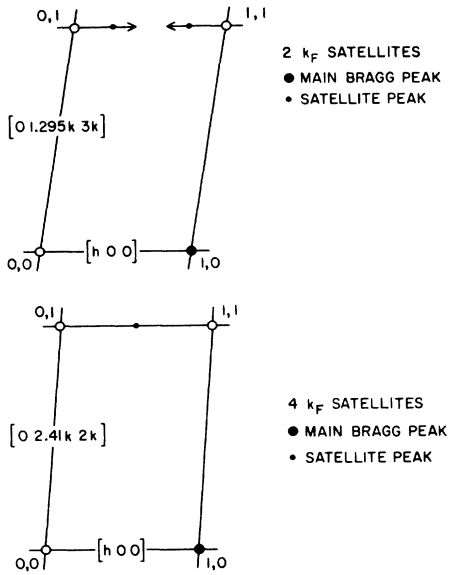

FIG. 1. Typical scattering plane geometries used for TTF-TCNQ measurements on a triple-axis spectrometer. The arrows on the upper diagram indicate the temperature-dependent satellite positions along a^*. Unit-cell parameters were $a^* = 0.532$ Å^{-1}, $b^* = 1.685$ Å^{-1}, $c^* = 0.353$ Å^{-1}, and $\beta^* = 75.5°$.

sample. The sample was initially aligned on Bragg reflections in the $(hk0)$ plane with the orthogonal a^* and b^* axes precisely directed along the tilt axes of the spectrometer goniometer. The sample was then brought into the $(h\,1k\,3k)$ zone by using the proper goniometer tilt to rotate about a^* by a calculated amount. This alignment procedure was checked by observing, for example, the (500) and (013) reflections. A further small rotation about a^* brought the $(h\,1.295k\,3k)$ zone into the scattering plane. The temperature dependence of the a^* modulation could then be followed simply by changing the temperature with no further adjustments of the crystal orientation. A similar procedure was followed for measuring satellites at $4k_F$ positions. One of these zones is also depicted in Fig. 1.

A. $2k_f$ satellites

The greatest part of these measurements was performed in the $(h\,1.295k\,3k)$ zone (Fig. 1). A few consistency checks were also performed in the $(hk0)$ zone. From 10 K up to 38 K, sharp satellite peaks were observed at the constant positions of (0.25, 1.295, 3) and (0.75, 1.295, 3). In direct space, these correspond to a $4a \times 3.4b \times c$ periodicity which is incommensurate only along the b axis. As observed earlier,[4] the integrated intensity of these peaks tended to decrease as the temperature was raised toward 38 K, but there was no detectable increase in the widths. Figure 2 shows scans parallel and perpendicular to a^* taken on sample C at 35 K. Using the collimations and neutron wavelength employed in the measurements, the instrumental resolution widths were calculated, and these are indicated in Fig. 2. For both scan directions, the observed linewidths are completely attributable to the instrumental resolution. An additional check was found by establishing that the primary Bragg peaks which are derived from the high-temperature undistorted lattice also possessed the same widths. This confirms that this incommensurate phase possesses well-defined three-dimensional ordering which can be contrasted to the case of $K_2Pt(Cn)_4Br_{0.3} \cdot 3.2D_2O$ (KCP) (Ref. 12), where complete ordering was not observed even at the lowest temperatures.

Upon warming above 38 K, a first-order-like

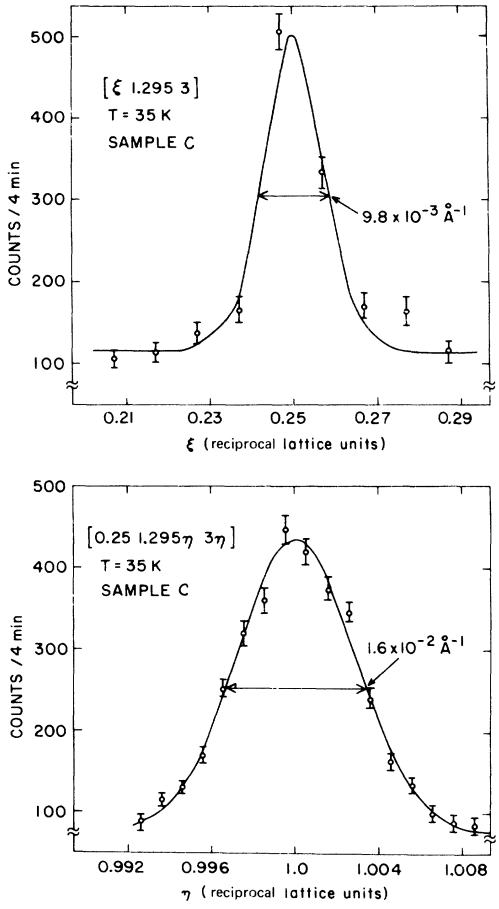

FIG. 2. Scans taken along and perpendicular to a^* for sample C at 35 K. The calculated instrumental widths are indicated by the arrows. Collimations were 20′-20′-20′-40′.

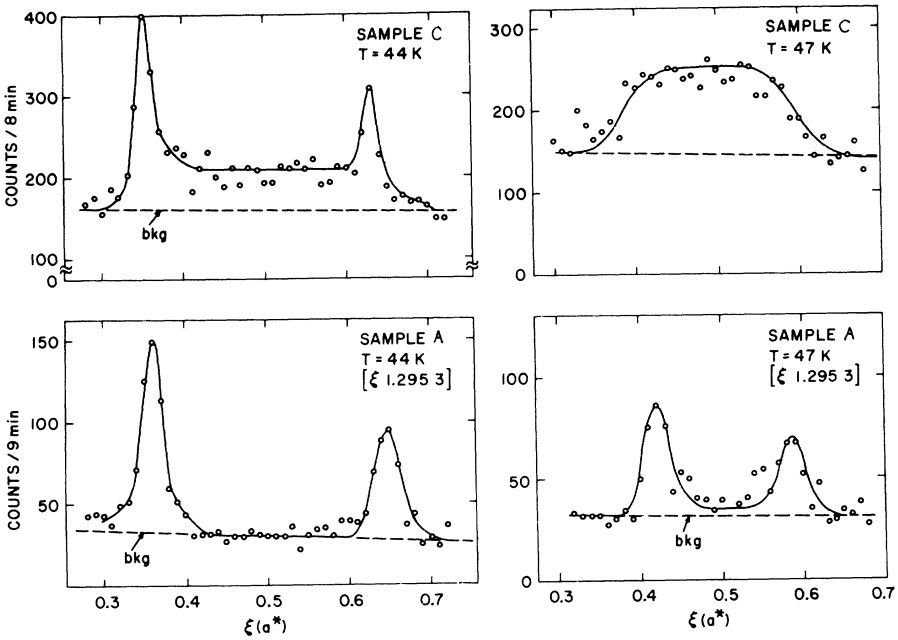

FIG. 3. Scans along a^* for samples C and A at the temperatures 44 and 47 K. Background levels are indicated by dashed lines. Solid lines are only guides to the eye.

transition was observed with the satellite positions shifting discontinuously to incommensurate values along a^*. At 39 K satellite positions could be indexed as $(h \pm 0.32,\ k \pm 0.295,\ l \pm 0)$. As the temperature was further raised, the satellites were observed to shift continuously moving toward the positions $(h \pm 0.5,\ k \pm 0.295,\ l \pm 0)$ which were first established at about 49 K. It is important to note that the spectra in this transitional region showed a sample dependence. Figure 3 shows scans taken at 44 and 47 K for different samples. A scan at 44 K for sample A, which was mounted as strain free as possible, shows two sharp satellites. However, the scan for crystal C, whose manner of mounting could have involved some strain, shows satellite peak maxima at the same points but shows some additional broad flat scattering between the two peaks. As a note, the difference of intensity between the two peaks in each scan can be attributed to differing structure factors. Scans perpendicular to a^* at the peak position for either sample showed no broadening beyond the instrumental resolution. At 47 K, sample A showed two relatively sharp well separated peaks and a small amount of scattering between the peaks. Sample C at this temperature showed instead a broad flat-topped maximum centered at 0.5 along a^*. This type of broad maximum was observed for sample C over the range of 45–49 K. Although no sharp peaks could be identified as at 44 K, the width of this broad scattering did parallel the separation of the two satellites seen in the strain-free mounted crystal A. As it has been recently suggested,[13] strain may play an important role in the phase transitions of this system. These differences of behavior between the two samples might be related to subtle strain effects caused by the different modes of mounting, but it is difficult to quantify these factors. Only a small fraction of sample C should have been affected by the mounting and such a large effect would be unexpected. Alternatively, this may have been an intrinsic effect due to the difference of quality of the crystals. On a visual basis, sample A appeared much more regular with well-defined edges than did sample C. No apparent anomalies in the main Bragg peak intensities or positions were observed for either sample. The energy difference between various ordered arrangements of the chains may be quite small so that strains or sample quality can be of importance to the effects being measured. These results suggest that strain-free mounting of high-quality single crystals would be advisable for other types of measurements as well. A few checks of the satellite positions in the $(hk0)$ zone as a function of temperature were made. The same temperature dependence of satellite position was seen up to about 45 K where intensity considerations became important.

The well-resolved pair of satellites from 39 to 44 K for sample C and 39 to 48 K for sample A allowed the linewidths to be determined with some accuracy. As mentioned above, the satellite peaks were resolution limited below 38 K with a full width at half-maximum of about 0.01 Å^{-1}. In this continuous transitional region, there appeared to

be an apparent systematic broadening for scans along a^* which increased as 49 K was approached, reaching about 0.025 $Å^{-1}$ at the upper end. This broadening might be interpreted as a shortening of the correlation range or smaller particle size, but an explanation which bears consideration for this system is that not all regions of the crystal may maintain precisely the same amount of distortion at a given temperature. These distortions may depend heavily on strain effects or impurity effects, especially at the upper end of the transitional region where the satellite positions shift rapidly with temperature. The broadening was much less pronounced in the crystal mounted strain free but was still present presumably because of residual strains or impurities. The appearance of scattering between the two peaks at higher temperatures in this continuous satellite movement region as seen in Fig. 3 is apparently a closely related phenomenon which could be explained in this way. Scans perpendicular to a^* in the measured zone showed no broadening.

Finally, scans above 49 K showed a sharp component at the position (0.5, 1.295, 3) whose intensity decreased until it disappeared at 54 K. In addition to the sharp component, these scans also showed the presence of an underlying component which was about five times as broad as the instrumental resolution. The intensity was not sufficient to highly parameterize this scattering, but a possible source of this scattering will be mentioned later.

B. Hysteresis effects

The measurements discussed so far were all obtained under conditions in which the temperature of observation had been approached from below. Earlier work[4] had shown that there was a well-defined hysteresis of approximately 1 K about the transition at 38 K. This behavior was again found for sample A by observing the satellite positions as the temperature was cycled. Sample C also showed hysteresis behavior about this point but the width of the loop was larger. The transition region for this sample with decreasing temperature was smeared over about a five degree range. Again, this seemed to show either the effects of strain or inhomogeneities in this sample.

The most surprising behavior was found in the temperature region between 38 and 48.5 K where the continuous variation of the satellite position with temperature was observed. The continuous nature of this transition suggested that no hysteresis would be observed in this region. Several typical spectra, all taken at 44 K, are shown in Fig. 4. Scan a was obtained in the usual way by approaching the observation temperature from far

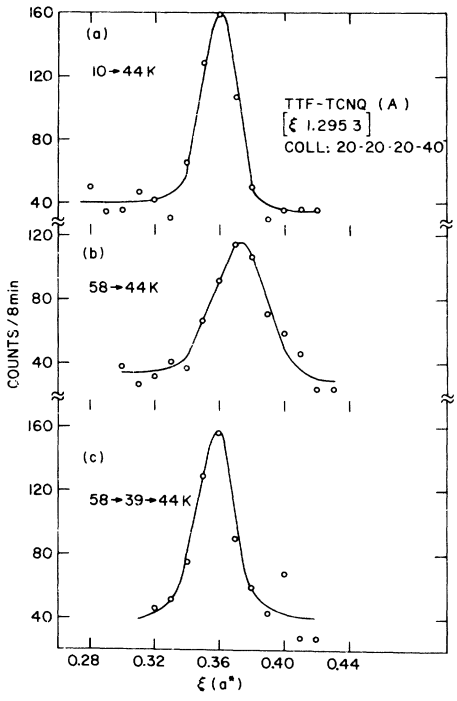

FIG. 4. Three observations of the satellite position at 44 K. The temperature sequences used to obtain 44 K are indicated to the left of each scan.

below. Scan b was obtained by slowly cooling the sample to 44 K from about 60 K. The satellite position is not the same as with the heating cycle and instead lies at a position expected for about 45 K. From here, the sample was cooled by 5 K, staying in the continuous region, and then heated to 44 K where scan c was taken. The satellite position, intensity, and linewidth reproduce that found by heating from very low temperatures. Similar differences between the satellite positions, depending upon whether the fixed temperature was reached by heating or cooling, was observed throughout the temperature region of the intermediate phase. It should be stressed that these effects were not time dependent. In one case, the sample was kept for 48 h at the same temperature after cooling and the spectra were the same at the end of this period as at the beginning. This unusual behavior can be loosely described as a kind of "backlash" effect. Whenever the direction of temperature change, increasing or decreasing, is reversed, the satellite positions stay constant for about a one degree interval and only then begin following the sense of the temperature direction.

III. DISCUSSION

The original motivation for a careful study of the satellite positions as a function of temperature

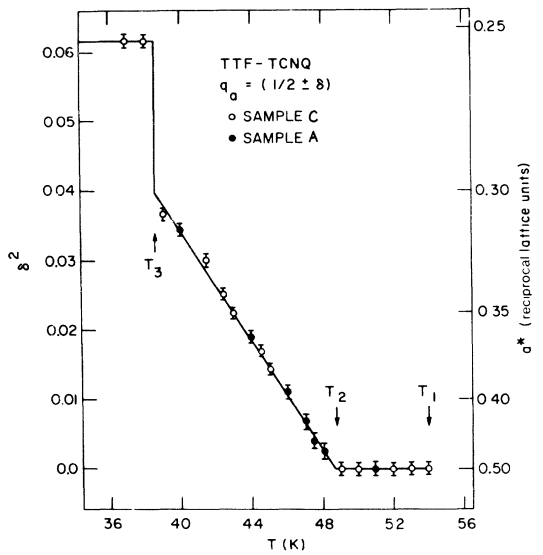

FIG. 5. Plot of satellite positions upon heating along a^* (nonlinear right-hand scale) and derived values of δ^2 (left-hand scale). The functional relationship between δ and q_a is given in the heading. The three transition temperatures are also indicated.

was the development by Bak and Emery[5] of a theory for the phase transitions in the TTF-TCNQ system. As is known from x-ray diffraction results,[14] the structure consists of stacks of TCNQ molecules alternating with stacks of TTF molecules. The b axis of the monoclinic cell is the direction of stacking and is the direction along which the Peierls distortion takes place. Stacks of similar molecules lie in bc planes. These bc sheets then alternate as to the type of molecule along the a direction. The important point is that couplings between the different types of stacks may be reflected in the modulation along the a direction. Bak and Emery began their investigation with the observation that this arrangement of the molecules in segregated stacks of different chemical species allows for the possibility that one of the sets of stacks will tend to undergo a Peierls distortion at a higher temperature than the other set. Symmetry arguments and free-energy expansions suggested that there should be at least three phase-transition points T_1, T_2, and T_3 for the coupled system. The experimentally observed transition at 54 K was assigned as T_1 and interpreted as a Peierls distortion in which only one of the sets of chains orders, either the TCNQ or TTF. This leads to the observed doubling of the cell along the a direction which in reciprocal space produces intensity at $0.5a^*$ points, where a^* still refers to the high-temperature cell. The other set of chains could be expected to independently undergo an analogous type of transition at some lower transition temperature T'. However, interactions with the already ordered set of chains were shown to drive the ordering transition in this second set at a higher temperature T_2. A most interesting result of a free-energy expansion below T_2 was that the a^* modulation would be temperature dependent with $(q_a - \frac{1}{2})^2 \sim T_2 - T$, where q_a is the wave vector associated with the a^* modulation. Finally, at a yet lower temperature T_3 (experimentally 38 K), a lock-in transition where the period along the a axis discontinuously jumped to $4a$ provided a new minimum in the free energy on account of fourth-order umklapp terms. Additional higher-order lock-in transitions at still lower temperatures were shown to be possible but there have been no experimental observations of such effects. With the aim of establishing T_2, an earlier set of neutron-scattering data[3] which had reported the change of a^* modulation with temperature was reanalyzed by the authors.[5] Within the experimental uncertainties of those studies, the new intermediate phase-transition point T_2 could be assigned as coming at about 47 K. The results from the present more precise observations of the a^* modulation are shown in Fig. 5 where the peak maxima values are plotted in terms of $(q_a - \frac{1}{2})^2$, as suggested by the theoretical treatment. This manner of plotting allows a quite accurate determination of T_2 by extrapolation of the linear sloped part of the curve with the result that T_2 is equal to 48.5 ± 0.1 K. Close to this temperature, no deviations from straight-line behavior are seen even though the satellite positions are a quite strong function of temperature in this region. At 48 K, only 0.5 K away from the transition point, the satellites in the strain-free mounted sample are separated and easily resolvable.

As mentioned above, the theoretical treatment of Bak and Emery did not identify which particular set of chains that was first to order. To get this information from x-ray or neutron-diffraction measurements would require precise full structural determinations at a series of temperatures. This would probably be quite difficult because of the number of atoms involved and because the distortions from the high-temperature phase have been suggested to be only on the 1% level.[4] However, a number of other types of measurements[15-17] have now indicated that it is the TCNQ chains which are involved in the 54-K transition and that the TTF chains are highly involved in the 38-K transition. Very recent ^{13}C Knight-shift measurements[17] have also detected a transition at 49 K and it was inferred to be associated with the ordering of the TTF chains.

A comparison of the x-ray and neutron-scatter-

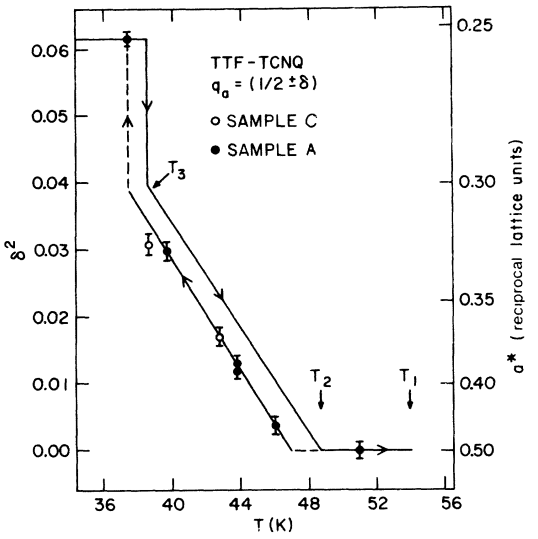

FIG. 6. Satellite positions upon cooling along a^* (right-hand scale) and derived values of δ^2 (left-hand scale). The behavior found with heating is shown as the line with arrows pointing in the temperature increasing direction. The transition temperatures are also from the results upon heating.

ing results in the temperature region between 48.5 and 54 K allows an inferral of the identification of the ordered species over this range. A recent x-ray scattering study[8] was unable to find scattering distinguishable from the background in this temperature region. As mentioned in that paper, this is presumably due to the differing structure factors for x-ray and neutron scattering. The nitrogen nuclei in the TCNQ molecules have the highest scattering strength for neutron measurements, whereas the sulfurs of the TTF molecules are the predominant scatterers for x-ray measurements. This differences of results provides a supplementary piece of evidence that it is the TCNQ molecules which are ordered in this phase. As mentioned in Sec. II, the broad underlying component found in the neutron scattering in this temperature region may then be associated with the incipient ordering of the TTF chains at 48.5 K.

Figure 6 demonstrates the results for the a^* modulation from measurements made upon cooling the sample. For comparison, the curve from the measurements carried out upon warming is also given. The slopes of the lines in the continuous transition region are the same to within experimental accuracy but are displaced from each other by about 1 K along the temperature axis. It can be noted that the hysteresis about the lock-in transition at 38 K has also been found to be about 1 K at least for the unstrained sample. For that case, it has been remarked that this represents a rather large hysteresis at such low temperatures but is quite surprising to find similar behavior in the continuous-transition regime. In the recent description of this region by Bak,[13] this is where the charge density waves can be pictured as uniformly "sliding" with respect to each other and giving rise to the changing a^* modulation. At this time, it is difficult to understand the type of potential energy barriers or pinning effects that must be operative to produce the observed effect. This may be of fundamental importance theoretically and further efforts should be devoted toward understanding it. From an experimental point of view, this effect may lead to problems of reproducibility for other types of measurements also. In this regard, the discussion in the experimental portion of this paper concerning Fig. 4 should be quite relevant.

A. $4k_F$ satellites

The satellites so far discussed in this paper have been those characterized by a b^* modulation of 0.295. Since these satellites correspond to the positions in reciprocal space where one-dimensional-like phonon anomalies have been observed,[9-11] these have been termed $2k_F$ satellites. In addition, scattering has also been detected at low temperatures in a few positions characterized by a modulation of 0.590 along b^* and 0.5 along a^*. To within experimental error, these are exactly twice the modulations found for the $2k_F$ satellites and can be called $4k_F$ scattering. It should be noted that within the reduced zone scheme these satellites appear at 0.410 of b^*, where b^* refers to the high-temperature undistorted lattice. Although a number of positions in reciprocal space with these modulation values were examined at about 20 K, measureable intensities were found at only three points (0.5, 1.41, 2), (−0.5, 1.41, 2), and (2.5, 1.41, 2). The intensity at these points was about 5% of that found for the $2k_F$ scattering and barely above background levels. Figure 7 shows the temperature dependence of the peak intensity for (0.5, 1.41, 2) satellite. The solid line which is drawn through the points is only a guide to the eye but the shape is similar to that which has been found for the variation of the $2k_F$ satellite intensities over the same temperature region.[4] In both cases, there is a substantial drop in intensity as 38 K is approached.

In analogy to the $2k_F$ situation, these satellites would be expected to shift to new positions along a^* above 38 K. A scan along a^* at 40 K was not successful in finding these positions but they could have been missed because of the extremely weak intensity. A recent x-ray study[8] has been somewhat more successful in determining the tempera-

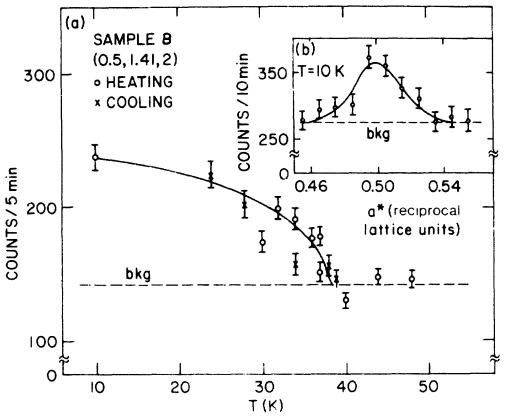

FIG. 7. (a) Temperature variation of the intensity of a $4k_f$ satellite. Background levels are indicated by the dashed line and the solid line is only a guide to the eye for the experimental data. (b) Typical scan for the (0.5, 1.41, 2) satellite at 10 K.

ture evolution of this scattering. In agreement with the studies here, satellites were found below 38 K with positions ($h \pm 0.5$, $k \pm 0.59$, $l \pm 0$). Also some satellites given by ($h \pm 0$, $k \pm 0.59$, $l \pm 0$) were seen. From 39 to 45 K, there was still sufficient intensity to follow the positions shifts along a^*. To within experimental uncertainty, it was found that the a^* modulation was just twice that found for the $2k_F$ satellite at the same temperatures. Although this low-temperature behavior suggests that the $4k_F$ scattering is simply derived from harmonics of the $2k_F$, there are substantial differences in their high-temperature behavior as evidenced by the one-dimensional diffuse x-ray scattering.[7,8] $4k_F$ scattering is clearly visible as high as 220 K, whereas the $2k_F$ scattering is noticeable only below 150 K. These results have led to suggestions[7,8] that what has been termed $2k_F$ and $4k_F$ scattering could instead be scattering at k_F and $2k_F$. Unfortunately, the elastic neutron-scattering measurements here do not shed any new light on this important problem.

ACKNOWLEDGMENTS

We wish to acknowledge helpful discussions with P. Bak, V. J. Emery, A. J. Heeger, and R. Comès. We also thank Paul Nigrey for the growth of the deuterated sampler.

*Work performed under the auspices of the U. S. ERDA.
†Work supported in part by the NSF and Advanced Research Projects Agency.

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