Diffuse x-ray and inelastic neutron scattering study of the spin Peierl's transition in N-methyl-N-ethyl-morpholinium bistetracyanoquinodimethane [MEM(TCNQ)$_2$]

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X-ray and neutron scattering techniques have been used to investigate the spin Peierl's transition in N-methyl-N-ethyl-morpholinium bistetracyanoquinodimethane [MEM(TCNQ)$_2$]. Both techniques reveal a doubling of the c-axis stacking of the TCNQ molecules below the transition. Diffuse x-ray scattering was observed well above the transition at the position of the low-temperature superlattice reflections. The geometry of the scattering showed that the critical scattering related to the structural changes at T_c results from fluctuations of a mainly transverse nature. Neutron scattering measurements revealed no softening of longitudinal-acoustic phonons at the transition. It was impossible to determine the position of the transverse-acoustic phonons, because they have either very low energies or very large linewidths; therefore, we cannot define the fluctuations to be of a static or dynamic character.

INTRODUCTION

The compound N-methyl-N-ethyl-morpholinium bistetracyanoquinodimethane [MEM(TCNQ)$_2$] is a linear chain compound that has phase transitions at 19 and 340 K. According to Sawatzky, Huizinga, and Kommandeur[1] these transitions are of the spin-Peierl's and (electronic) Peierl's type, respectively. For the high-temperature transition the changes in physical properties have been correlated with observed structural changes in the TCNQ chain.[2] Above 340 K the stacks of TCNQ molecules are nearly regular along c with a translation period of 3.29 (1) Å at 348 K as is shown schematically in the first part of Fig. 1. Between the two transitions the stacks are strongly dimerized (distortion period $\lambda_d = 2\pi/4k_F$) as is shown in the second part of Fig. 1. This dimerization results in one electron spin residing on each dimer. In this region the crystals are triclinic with, at 113 K, $a = 7.824(5)$, $b = 15.426(16)$, $c = 6.896(5)$ Å, $\alpha = 113.59(8)$, $\beta = 73.27(7)$, and $\lambda = 112.71(8)°$. Below 19 K another distortion of period $\lambda_d = 2\pi/2k_F$ is expected resulting in a tetramerization of the TCNQ chain such as shown in the third part of Fig. 1. This paper presents scattering results which show that this tetramerization takes place and is preceded by the occurrence of lattice fluctuations (distortions) of a transverse nature.

APPARATUS

The diffuse x-ray scattering experiment was carried out with a single crystal of approximately 12 × 0.6 × 2.0 mm^3. The crystal was mounted in a conduction-type cryostat where its temperature was kept constant within 0.5 K. The measurements were made on a conventional double-circle x-ray spectrometer with Cu $K\alpha$ radiation ($\lambda = 1.54$ Å) from a 12-kW rotating anode generator. Monochromatization and collimation of the primary beam from the spot focus (0.5×0.5 mm^2) was attained by use of a flat pyrolytic-graphite monochromator and slits. The radiation scattered from the sample was measured with a linear-position-sensitive proportional counter provided with an adjustable horizontal slit. Most of the measurements were made with the crystal mounted
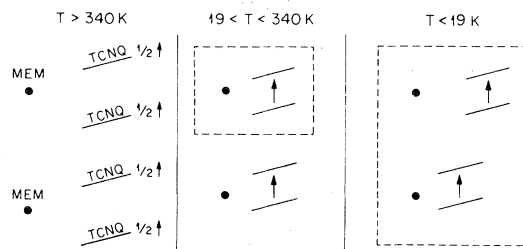

FIG. 1. Schematic diagram showing the stacking of the TCNQ chain at various temperatures. Above 340 K the chain is uniform and the TCNQ molecules have a charge of a half an electron. Between 340 and 19 K the TCNQ chain dimerizes resulting in one electron spin residing on each dimer. The present work shows that below 19 K a further distortion of the chain takes place resulting in a tetramerization of the original TCNQ chain.

with its b^*c^* plane in the horizontal plane of the dif-fractometer with some additional measurements per-formed in the a^*c^* plane.

The inelastic neutron scattering experiments were performed on a conventional triple-axis spectrometer located at the high-flux reactor at Oak Ridge National Laboratory. Pyrolytic-graphite monochromators and analyzers were used and graphite filters were em-ployed to eliminate higher-order contamination. A collimation of 0.6° was used before and after the sample. By using a low-efficiency monitor counter in the incoming neutron beam all measurements were related to a constant incoming intensity to avoid er-rors due to reactor power fluctuations. A single non-deuterated crystal with well-developed (100), (010), and (001) boundary planes and approximate dimen-sions of $12 \times 7 \times 0.8$ mm^3 was mounted in a low-temperature cryostat. Scans were made only in the b^*c^* plane which coincided with the horizontal plane of the diffractometer.

EXPERIMENTAL WORK AND DISCUSSION

The scattering vectors in the (b^*c^*) plane are $\vec{Q} = \vec{H} + \vec{q}$, $\vec{H}$ corresponding to the position of a reciprocal-lattice point and $\vec{q}$ being the wave vector. $\vec{Q}$ was taken more or less parallel to the $\vec{c}^*$ axis, or at ~45° relative to the stacking axis $\vec{c}^*$. In the former case the diffuse scattering is mainly due to atomic displacements parallel to $\vec{c}$ and in the latter case to displacements both parallel to $\vec{c}$ and perpendicular to $\vec{c}$. X-ray scattering measurements were made with the $(0,\bar{7},4.5)$ and $(0,0,4.5)$ reflections centered at the proportional counter. Figures 2 and 3 give data taken at 30 K and 10 K and show that a superlattice peak appears at low temperatures. The superlattice peaks are resolution limited, but show long-range or-der of at least 1000 Å. These peaks show that the expected tetramerization of the TCNQ chain does in fact occur at low temperatures. Since data are accu-mulated in a position-sensitive detector, the scans are not made along symmetry directions but follow a path through the reciprocal lattice determined by the geometry of the detector. The paths of the scans in reciprocal space through the $(0,\bar{7},4.5)$ and $(0,0,4.5)$ reflections are shown in Fig. 4.

We notice that some diffuse scattering remains above the transition. This diffuse scattering is small in the neighborhood of the $(0,0,4.5)$ reflection but easily observable at the position of the $(0,\bar{7},4.5)$ re-flection. This suggests that the fluctuations contri-buting to the diffuse scattering have a transverse na-ture since the momentum transfer for scattering around the $(0,\bar{7},4.5)$ reflection contains a com-ponent perpendicular to the scattering vector Q. On the other hand the fluctuations contributing to the diffuse scattering at the $(0,0,4.5)$ reflections have
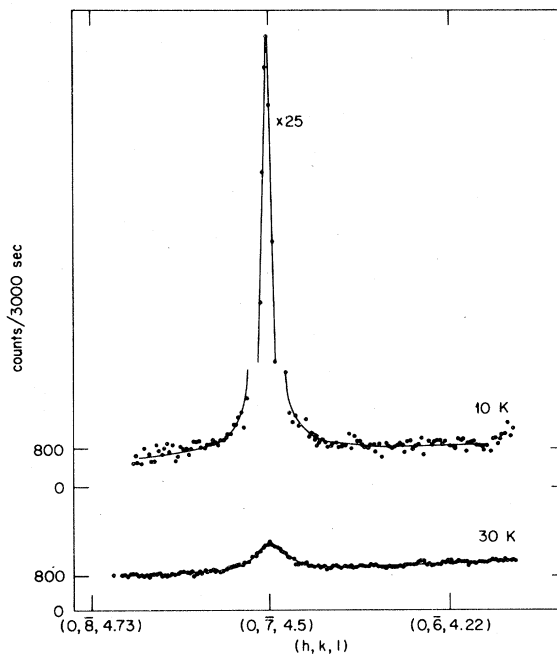

FIG. 2. X-ray scattering near the $(0,\bar{7},4.5)$ position at temperatures above and below the 19-K phase transition. See Fig. 4 for the measurement trace.
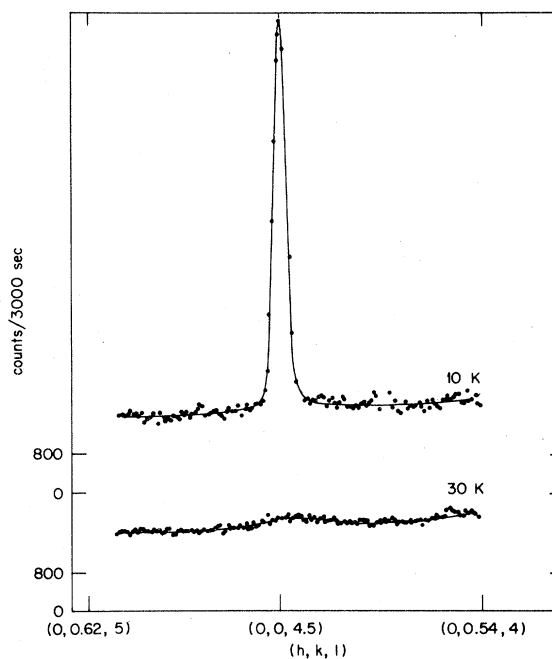

FIG. 3. X-ray scattering near the $(0,0.4.5)$ position at temperatures above and below the 19-K phase transition. See Fig. 4 for the measurement trace.
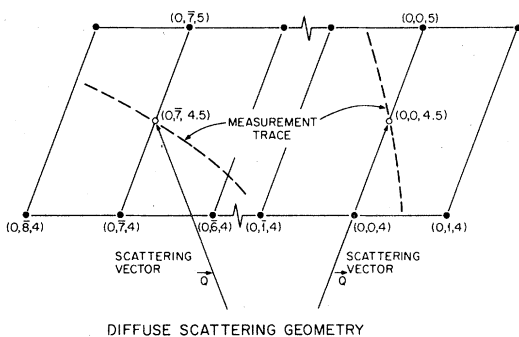
FIG. 4. Reciprocal-space geometry showing the measurement traces for the x-ray scattering in Figs. 2, 3, and 5.

their momentum transfers q parallel to Q and thus are purely longitudinal in nature. We will see that this is consistent with the neutron scattering results that show no change in the longitudinal-acoustic phonons in the neighborhood of the transition.

Figure 5 shows a measurement of the diffuse scattering in the neighborhood of the $(0, \overline{7}, 4.5)$ reflection at various temperatures. We see that the diffuse scattering continues to be visible even up to room temperature. At the highest temperatures, ex-
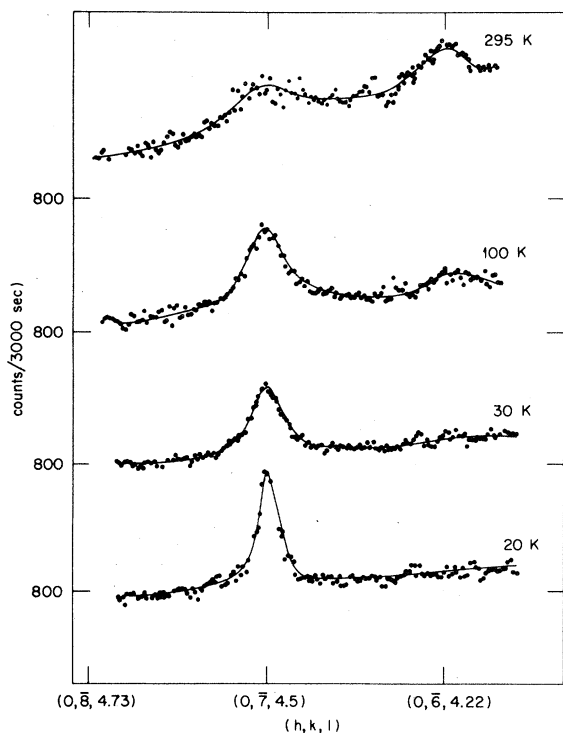

FIG. 5. X-ray scattering near the $(0, \overline{7}, 4.5)$ position as a function of temperature between 295 and 20 K.

tra diffuse scattering is found around $(0, \overline{6}, 4.22)$. Other scans show that diffuse scattering from transverse fluctuations is found at the higher temperatures for positions along the c^* axis. Scattering from the transverse fluctuations along c^* is generally predominant, but becomes particularly strong at the zone-boundary positions as the temperature approaches the 19-K transition. As the temperature nears the transition the scattering is still slightly extended along c^* but is nearly isotropic around the zone-boundary position. This implies that the lattice fluctuations are three dimensional in contrast to the magnetic fluctuations which are expected to be one dimensional. A rather similar result has been obtained for TTF-CuBDT by Moncton et al.[3] However, in the case of TTF-CuBDT the dimerization was not found to be along the molecular stacking axis but in a direction diagonal to this axis. A limited number of x-ray measurements were made with the crystal remounted in the a^*, c^* plane. Results were obtained similar to those in the b^*, c^* plane; however, no doubling of the a^* axis was found at low temperatures.

The reasonably large crystal used in the neutron scattering measurements made it fairly easy to measure the LA-phonon branch along c^*. The LA dispersion curve is shown in Fig. 6. The curve was measured at several temperatures and found to be insensitive to the temperature. Points for 110 and 21 K are shown in Fig. 6.

Difficulty was encountered in measuring the TA-phonon branch and indeed it was not clear that any acoustical phonons of a transverse nature were observed. Of course, it is difficult to make measurements at low-energy transfers because of the large elastic incoherent scattering background from the hydrogen atoms in the sample. Still it is surprising that no TA phonons could be observed, and it is possible that they are at very low energies or highly damped. The diffuse x-ray measurements suggest that if the
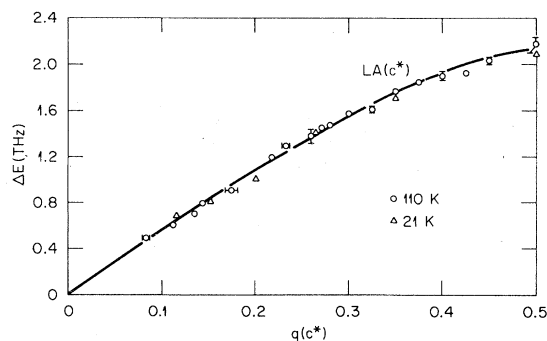

FIG. 6. LA-phonon dispersion relation for $MEM(TCNQ)_2$ for the c^* direction. Points are shown for measurements at 110 and 21 K.

lattice fluctuations are dynamic in nature, the TA phonons may be quite soft. A number of peaks were found in the neutron scattering that remained constant in energy independent of q. These flat modes are reminiscent of the rather flat optic modes with librational and/or translational character calculated for rigid-body molecular crystals such as naphthalene.[4] In the present case these transverse modes may have low frequencies as it is relatively easy to make transverse distortions of the TCNQ stacks. The modes show up strongly in the scattering measurements because of the high incoherent cross section of hydrogen. Raman and infrared (IR) measurements were also made on other sample crystals and confirmed the existence of low-lying flat modes at $q = 0$.[5] Similar flat modes were seen in measurements on nondeuterated samples of TTF-TCNQ.[6] Transverse scans at the zone boundary did show low-lying excitations that appeared to soften as the temperature approached the transition temperature of about 19 K but it is not clear that these are acoustic phonons and the data are not of high quality because of the large hydrogen incoherent scattering.

Below T_c elastic neutron scattering showed the presence of additional reflections $(0,k,l+\frac{1}{2})$ similar to those observed in the x-ray measurements. On the average their intensities were a factor of 10^3 smaller than those of the $(0,k,l)$ reflections. No indication was found for a change in periodicity along b^*. Figure 7 shows the intensity of the $(0,0,\frac{1}{2})$ reflection as a function of temperature where T_c was chosen to be 19 K. Since we do not know what type of distortion is responsible for the superlattice peak we did not try to fit the temperature-dependent intensity to any particular function.

CONCLUSIONS

The present study has revealed the major features of the phase transition at 19 K in MEM(TCNQ)$_2$.
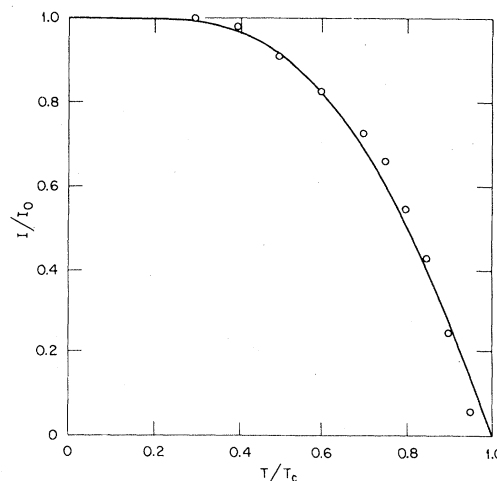

FIG. 7. Neutron scattering intensity of the $(0,0,\frac{1}{2})$ reflection measured as a function of temperature. T_c was chosen to be 19 K.

We find a superlattice along c^* below the transition and diffuse x-ray scattering above the transition indicative of transverse fluctuations. Neutron scattering studies show no change in the LA-phonon dispersion curve at the transition. In order to further characterize the fluctuations in the vicinity of the transition, neutron scattering measurements must be made on deuterated samples. We hope deuterated crystals will be available in the near future.

ACKNOWLEDGMENT

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