

Synchrotron-Radiation Study of the Five-Dimensional Modulated Phase of Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ) at 15 K

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The $2k_F$ modulated structure of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) at 15 K has been analyzed by use of a set of satellite intensities collected at the National Synchrotron Light Source. The analysis in the five-dimensional superspace group $P:P2_1/c:mmm$ shows the largest modulation to be a slip of the TTF molecules with an amplitude of about 0.02 Å, in the direction of the long molecular axis of the molecule. The TCNQ translational modulations are similar, but of much smaller magnitude. Rotations about the long molecular axes of both types of molecules are also observed.

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It is well known that the one-dimensional conductor tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) undergoes a Peierls transition at 53 K and further transformations at 49 and 38 K.^{1,2} Though the modulation vectors have been determined with both x-ray- and neutron-scattering techniques and the average structure is known at 45 K, no direct measurements of the molecular displacements have been reported. Magnetic-susceptibility measurements suggest that the 53-K transition involves only the TCNQ stacks, while at 49 K the TTF molecules also undergo displacement.³

Diffuse scattering patterns give evidence for both $2k_F$ and $4k_F$ lattice distortions. Since $2k_F$ scattering was not found for the $0k0$ reflections, while the $4k_F$ scattering was absent for $00l$, it was concluded that the former is mainly transverse to the molecular stacks and the latter mainly longitudinal.^{2,4} However, weak $2k_F$ scattering has also been observed for the $00l$ reflections.

The scarcity of experimental information is due to the weakness of the satellite intensities which are typically not more than 10^{-4} times the intensities of the main reflections.⁵ With the use of high-intensity synchrotron radiation it is possible, however, to measure at least the first-order satellites with adequate counting statistics.

With the State University of New York (SUNY) X21 beam line at the National Synchrotron Light Source we have measured a total of 1342 reflections, including 1154 satellite reflections with $\sin\theta/\lambda$ in the range of 0.2–0.5 Å⁻¹, using a crystal with dimensions 2.40×0.96×0.52 mm³, mounted in a Displex cryostat. Satellite intensities on an absolute scale were obtained by scaling each of the satellite intensities with the ratio of the main reflection F^2 value calculated with the parameters of the 45-K

structure determination⁶ and the measured intensity of the main reflection. Since the orientation of the crystal is almost the same during the measurement of a main reflection and its associated satellite reflections, and the 45-K data have been absorption corrected, this procedure implies an absorption correction of the synchrotron intensities. After averaging over symmetry-equivalent reflections, and elimination of reflections affected by instrumental instabilities and a number of reflections for which the corresponding main reflection had not been measured, 137 unique satellite intensities with $F^2 > 3\sigma(F^2)$ were obtained which were used as input to the least-squares refinement. No second-order satellites were observed in this study. Though these reflections are even weaker than the first-order satellites, they should be accessible in future experiments if sufficient beam time is available.

The symmetry of the three phases of TTF-TCNQ has been discussed by Bak and Janssen.⁷ The five-dimensional superspace group $P:P2_1/c:mmm$, which is in agreement with all observed absences, was selected for the analysis. Equations for the displacements of symmetry-related atoms in the five-dimensional case were developed and will be given elsewhere. They are incorporated in a new computer program, JANA5. We assumed as in our previous work⁸ that the molecules are displaced by the modulation wave as rigid bodies. This assumption has proven successful in a number of other modulated molecular crystals,⁹ and greatly reduces the number of parameters to be determined. The centrosymmetric site symmetry of the TTF and TCNQ molecules allows only 24 independent parameters describing the harmonic rigid-body displacements:

$$\mathbf{u}_i(\mathbf{q}_1, \mathbf{q}_2) = \sum_{k=1}^2 \{ \mathbf{V}_\alpha^k \sin(2\pi \mathbf{q}_k \cdot \mathbf{r}_\alpha) + [\mathbf{W}_\alpha^k \times (\mathbf{r}_i - \mathbf{r}_\alpha)] \cos(2\pi \mathbf{q}_k \cdot \mathbf{r}_\alpha) \},$$

where \mathbf{u}_i is the displacement of the i th atom, $\mathbf{q}_1, \mathbf{q}_2$ are modulation vectors related by a twofold axis, $\mathbf{V}_\alpha, \mathbf{W}_\alpha$ are translational and rotational molecular displacements ($\alpha = 1, 2$ refer to the TTF and TCNQ molecules, respectively), and $\mathbf{r}_i, \mathbf{r}_\alpha$

TABLE I. Translational and rotational displacement vectors of TTF and TCNQ molecules.

	Phase	Magnitude	Direction cosines with					
			<i>a</i>	<i>b</i>	<i>c</i>	<i>L</i> ^a	<i>M</i>	<i>N</i>
TTF								
Translations (Å)								
q ₁	0°	0.0074(9)	-0.06(8)	0.26(9)	0.96(11)	-0.98(12)	0.09(7)	0.16(12)
q ₂	0°	0.0191(8)	-0.07(3)	-0.55(2)	0.83(8)	0.99(4)	0.05(3)	0.16(6)
Rotations (deg)								
q ₁	90°	0.10(3)	0.34(22)	0.14(20)	-0.93(19)	0.91(24)	-0.31(25)	0.26(59)
q ₂	90°	0.17(3)	-0.29(15)	-0.033(10)	0.89(20)	0.96(15)	0.27(15)	0.07(30)
TCNQ								
Translations (Å)								
q ₁	0°	0.0043(14)	0.12(33)	0.80(13)	-0.59(83)	0.04(3)	-0.14(31)	0.99(14)
q ₂	0°	0.0067(13)	-0.30(18)	-0.09(21)	0.95(13)	-0.74(18)	0.31(20)	-0.60(25)
Rotations (deg)								
q ₁	90°	0.07(4)	-0.621(47)	0.30(40)	0.73(52)	-0.77(58)	0.62(40)	-0.15(92)
q ₂	90°	0.19(4)	0.62(27)	0.65(83)	0.45(17)	-0.72(18)	-0.63(13)	0.28(23)

^aInertial axes in order of increasing moment of inertia.

are the atomic positional vector and the phase reference point of the *ath* molecule, respectively.

Results are summarized in Table I. The least-squares refinement converged rapidly. The final *R* value for 137 satellite reflections is 0.198. In the final cycle the ratio of the shifts to the standard deviations of the parameters was always less than 0.005. Inclusion of the second-harmonic terms in the displacement algorithm did not lead to a significant improvement. The main displacement is a translation of the TTF molecules with amplitude 0.0191(8) Å which is part of the **q**₂ translational wave. The polarization vector for this translational displacement lies within experimental error along the long axis of the molecule, and thus does not affect the interplanar spacings of the molecules. As the phase difference between two adjacent molecules in a stack is $0.295 \times 2\pi$, the relative shift of two adjacent molecules in a stack is about equal to or smaller than the displacement amplitude. In some of the stacks the **q**₁ and **q**₂ displacements combine to give a relative slip of the TTF molecules which can be as large as 0.034 Å; in others the slip is at most 0.015 Å. All translations of TCNQ are smaller than 0.007 Å. Though small, they have a significant component of 0.004 Å along the normal to the TCNQ planes. The combination of the two (**q**₁ and **q**₂) displacement waves leads to a shortening or lengthening of the interplanar spacing with a maximum value of about 0.01 Å (see Fig. 1). All rotations are less than 0.2° and about the long molecular axes. The largest atomic displacements under these rotations are about 0.007 Å. The much larger displacement of the TTF molecules, though somewhat unexpected, is in agreement with theoretical calculations of the TTF and TCNQ dimers which indicate that the energy variation with slip parameter δ is smaller for the dimer composed of two

TTF molecules.¹⁰

It has been suggested that the $2k_F$ transverse anomaly occurs on one set of chains, while the longitudinal anomalies ($2k_F$ and $4k_F$) occur on the other set.¹ The present results show that the $2k_F$ charge-density wave in the low-temperature phase has a significantly larger amplitude on the TTF chains; it has both transverse and longitudinal components as its main feature is a relative slip of the TTF molecules. The possibility that the $4k_F$ distortion is mainly localized on the TCNQ chains requires measurement of the $4k_F$ satellites, which will be

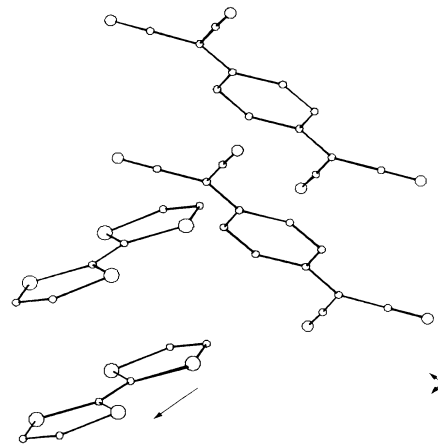


FIG. 1. Relative arrangement of TTF and TCNQ molecules. Arrows represent the amplitudes of the main modulation waves enlarged by a factor of 100. The TCNQ modulation has a component along the molecular normal, while the TTF modulation represents a slip along the long molecular axis.

the subject of future studies.

The modulation geometry determined in this study is to be taken into account in any calculations of the band gap of the low-temperature insulator.

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