

## Neutron and x-ray diffraction evidence for a structural phase transition in the sulfur-based ambient-pressure organic superconductor bis(ethylenedithio)tetrathiafulvalene triiodide

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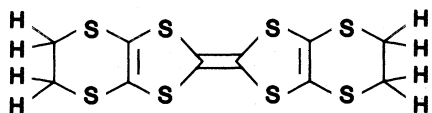
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A low-temperature structural phase transition in the ambient-pressure organic superconductor, bis(ethylenedithio)tetrathiafulvalene triiodide,  $(\text{BEDT-TTF})_2\text{I}_3$ , abbreviated  $(\text{ET})_2\text{I}_3$ , has been observed from single-crystal x-ray diffraction and time-of-flight neutron diffraction data. Superlattice peaks with indices of  $(hkl) \pm q$ , where  $q = (0.08, 0.27, 0.205)$ , appear when crystals are cooled below  $\sim 200$  K. This is the first example of an incommensurate modulated superstructure in the class of sulfur- and selenium-containing organic superconductors of which  $(\text{ET})_2\text{I}_3$  is the first ambient-pressure S-based derivative.

Synthetic metals based on salts of tetramethyltetraselenafulvalene,  $(\text{TMTSF})_2X$ , can undergo phase transitions to insulating or superconducting states at low temperatures.<sup>1</sup> The type of the transition is dependent on the size and symmetry of the particular anion  $X^-$ ,<sup>2</sup> the applied pressure, and in the case of  $X^- = \text{ClO}_4^-$ , on the rate of cooling.<sup>3</sup> The  $\text{ClO}_4^-$  salt is also unique in that the low-temperature phase, with lattice constants of  $a, 2b, c$  relative to the high-temperature phase,<sup>4,5</sup> becomes superconducting ( $T_c \approx 1.3$  K) at ambient pressure, whereas the salts of  $\text{ReO}_4^-$  and  $\text{FSO}_3^-$  require pressures of 5–10 kbar to suppress metal-insulator transitions and attain a low-temperature superconducting state.<sup>1</sup> At ambient pressures, the low-temperature insulating superlattices for  $X^- = \text{ReO}_4^-$  (Ref. 6),  $\text{FSO}_3^-$  (Ref. 7), and  $\text{BF}_4^-$  (Ref. 5) are of the type  $2a, 2b, 2c$ . The salt containing the trigonal planar anion  $\text{NO}_3^-$  has a low-temperature superlattice of the type  $2a, b, c$ .<sup>8</sup> Two important common features of each of these phase transitions is that they all involve an orientational ordering of the anions, which are disordered at room temperature due to crystallographic inversion centers, and that all the low-temperature superlattices are *commensurate* with the high-temperature phases.

In contrast, the tetrahedral anions in the organic metals based on  $(\text{ET})_2X$ ,  $X =$  monovalent anion, are structurally ordered at room temperature.<sup>9,10</sup> ET is bis(ethylenedithio)tetrathiafulvalene



(1)

Superconductivity is observed for  $X^- = \text{ReO}_4^-$  at  $T_c \approx 2$  K and a pressure of 4 kbar.<sup>10</sup> The recent discovery<sup>11</sup> of ambient-pressure superconductivity in  $(\text{ET})_2\text{I}_3$  at  $T_c \approx 1.4$ – $1.5$  K and the determination of its room temperature x-ray structure<sup>12</sup> has led us to study its superconducting properties,<sup>13</sup> and its structure<sup>14</sup> in greater detail. At room temperature, the structure consists of a “corrugated sheet” network of S-S interactions in the plane of the unit cell  $a$  and  $b$  axes (see Fig. 1, bottom). The linear  $\text{I}_3^-$  anions are

encapsulated in a  $-\text{CH}_2$  group H-atom cavity, and form chains with a relatively short intermolecular I-I distance of  $4.211(1)$  Å. The only evidence for structural disorder at room temperature is in the orientation of one set of terminal ethylene groups of an ET cation. In this Rapid Communication we report the observation of *incommensurate* superlattice Bragg peaks, the first of this type for any organic superconductor, in low-temperature neutron and x-ray diffraction studies of  $(\text{ET})_2\text{I}_3$ .

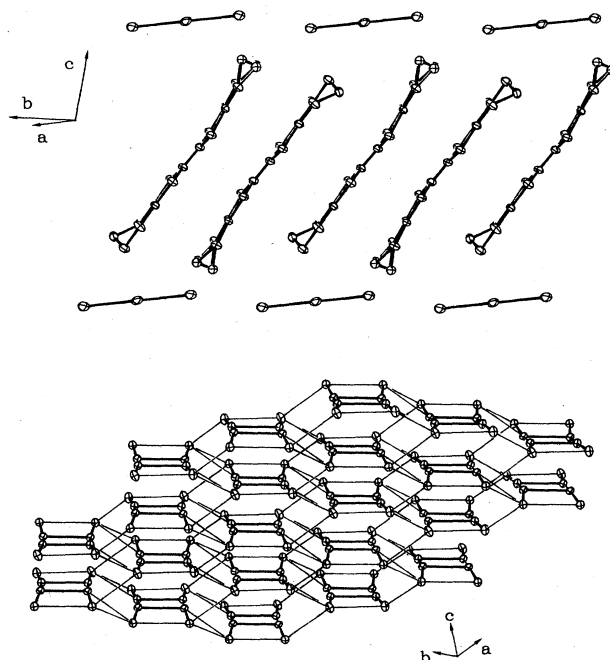


FIG. 1. The loose *intrastack* packing of the ET molecules ( $d_{S-S} > 3.60$  Å) and  $\text{I}_3^-$  anions in  $(\text{ET})_2\text{I}_3$  (top) and the “corrugated sheet network” of short ( $d_{S-S} < 3.60$  Å) *interstack* S-S interactions (bottom—light lines between ET molecules) (Ref. 14). For clarity only the S atoms of the ET molecules are given in the bottom portion of the figure. The modulation vector is  $(1.0a, 1.1b, 0.3c)$ .

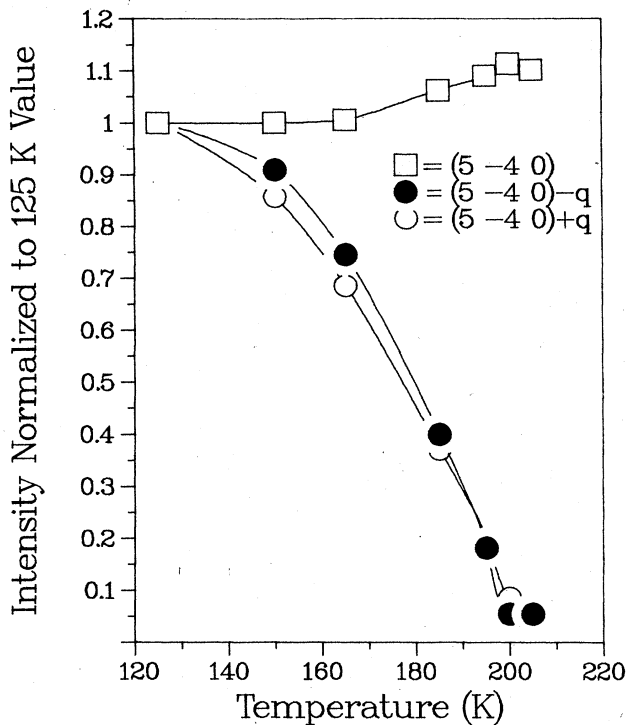


FIG. 2. Plot of the normalized intensities of the (5, 4, 0) Bragg reflection and its two satellites ( $q = 0.08, 0.27, 0.205$ ) vs temperature derived from single-crystal x-ray diffraction data indicating that the phase transition occurs at  $\sim 200(5)$  K.

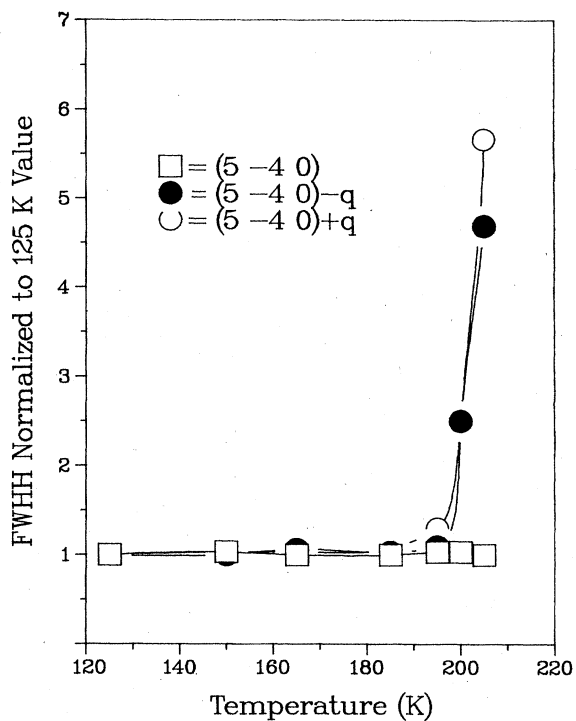


FIG. 3. Plot of the normalized full width at half maximum of the (5, 4, 0) Bragg peak and its two satellites ( $q = 0.08, 0.27, 0.205$ ) vs temperature. At 125 K, the measured full width at half maximum values for all three reflections was  $0.014 \text{ \AA}^{-1}$ .

Single-crystal x-ray diffraction rotation photographs taken at 125 K clearly exhibited satellite peaks which were not present at room temperature. The temperature dependence of the intensities of several of the peaks was measured on an automated diffractometer and the results for one fundamental Bragg reflection, and its two symmetrically placed sa-

tellites, are plotted in Figs. 2 and 3. [The unit-cell parameters at 125 K are  $a = 6.561(1)$ ,  $b = 9.013(1)$ ,  $c = 15.173(2)$  Å,  $\alpha = 95.07(1)$ ,  $\beta = 95.93(1)$ ,  $\gamma = 110.28(1)^\circ$ , and  $\text{Vol.} = 829.7(2) \text{ \AA}^3$ , space group  $P\bar{1}$ .] The transition at 200(5) K is quite sharp and reproducible on cooling and warming and does not appear to depend on the thermal cycling rate.

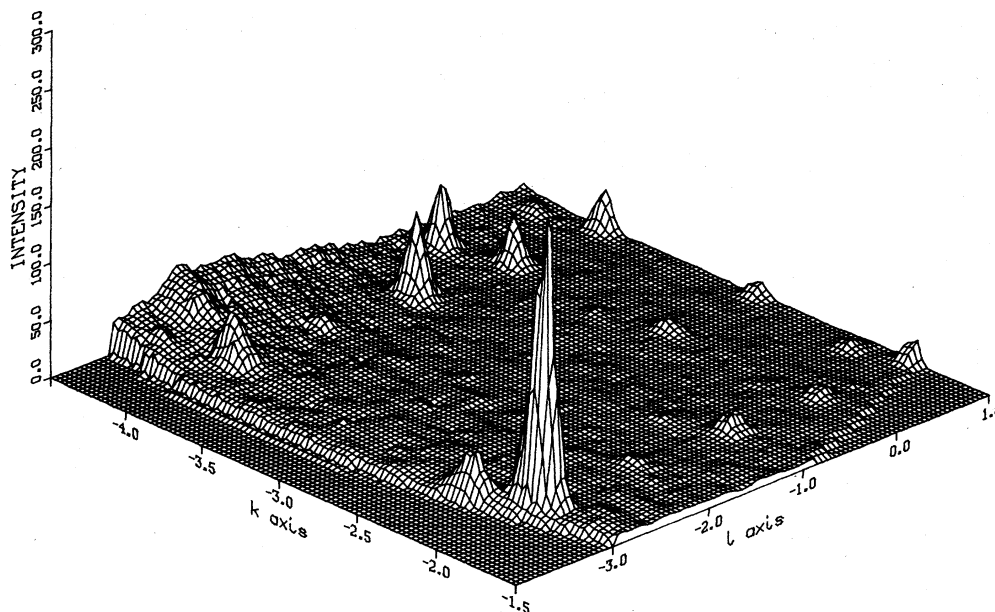


FIG. 4. Plot of the time-of-flight neutron diffraction intensity distribution of the 4.93,  $k, l$  plane of  $(\text{ET})_2\text{I}_3$  at 20 K. Satellite peaks at  $(5, \bar{2}, \bar{3}) - q$ ,  $(5, \bar{2}, 1) - q$ , and  $(5, \bar{4}, 0) - q$  are clearly observable.

The superlattice peak intensities can be several times less than the intensity of its fundamental peak to several times greater.

In order to verify the existence of the superstructure at a temperature much closer to  $T_c$ , we obtained a neutron time-of-flight Laue pattern from a large single crystal of  $(\text{ET})_2\text{I}_3$  at 20 K. The growth of the crystals is described elsewhere.<sup>14</sup> The data were measured with a large-area position-sensitive <sup>6</sup>Li-glass scintillation detector on the single-crystal diffractometer at the Argonne Intense Pulsed Neutron Source (IPNS) in a manner described previously.<sup>5,15</sup> A portion of the time-of-flight Laue histogram is shown in Fig. 4. A complete examination of the data reveals two symmetrically placed satellite peaks, the signature of a modulated structure, around each fundamental peak with satellite indices of  $(hkl) \pm q$ , where  $q = (0.08, 0.27, 0.205)$ . As in the x-ray data, the satellite intensities can be less or more intense than the accompanying fundamental Bragg peaks and each pair is generally nonequivalent in integrated intensity.

The data described above are consistent with a one-dimensional modulated superstructure with a modulation wavelength of 23.1 Å at 125 K which is not commensurate with the fundamental lattice. The modulation is ordered in

three dimensions below  $\sim 200$  K, but we did not observe any evidence for one- or two-dimensional ordering between 200 K and room temperature. The direction of the modulation in real space is  $(1.0a, 1.1b, 0.3c)$ , which is close to the stacking direction of the ET molecules (see Fig. 1), but it is not feasible to describe at this time the exact nature of the structural modulation and which atoms are involved. However, the often high intensity of the satellite peaks, relative to the fundamental Bragg reflection, is a clear sign that the atom positions to be derived for the modulated structure may be considerably different from those one would obtain for the "average structure." It would appear that any future theoretical work on this system must include the possible structural distortions, and resultant changes in orbital overlap, which arise from the structural modulation. Work is presently in progress to fully characterize the nature of the modulated structure.

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