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Neutron-diffraction evidence for ordering in the high-T_c phase of β-di[bis(ethylenedithio)tetrathiafulvalene]triiodide [β^*-(ET)$_2$I$_3$]

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Satellite reflections, which are present in the neutron-diffraction pattern of β-di[bis(ethylenedithio)tetrathiafulvalene]triiodide [β-(ET)$_2$I$_3$] at ambient pressure below 200 K, are absent above a critical pressure of 0.5 kbar applied at room temperature and followed by cooling. The satellite reflections remain absent if the pressure is released while the temperature is maintained at 20 K. The absence of satellite reflections, and therefore the absence of a previously discovered modulated structure, indicates a higher degree of ordering in the high-pressure–high-T_c state in comparison to the ambient-pressure–low-T_c state of β-(ET)$_2$I$_3$.

Recently it has been reported that the superconducting transition temperature T_c for β-(ET)$_2$I$_3$ [ET, or BEDT-TTF, is bis(ethylenedithio)tetrathiafulvalene] rises from ~1.5 K at ambient pressure to 7–8 K with applied pressures above 1.2–1.3 kbar, indicating the existence of a new high-pressure phase of β-(ET)$_2$I$_3$.[1,2] This finding is unusual because in the nearly isostructural ambient pressure superconductors β-(ET)$_2$IBr$_2$ (T_c = 2.8 K)[3,4] and β-(ET)$_2$AuI$_2$ (T_c = 5.0 K),[5,6] T_c *decreases* linearly with increasing *hydrostatic* pressure without any evidence of high-pressure phases.[7] The I$_3^-$ compound also differs from the isostructural IBr$_2^-$ and AuI$_2^-$ compounds in that only β_H-(ET)$_2$I$_3$ has disorder in one of the terminal ethylene groups of the ET molecule[8,9] (Fig. 1) and only β_L-(ET)$_2$I$_3$ exhibits *incommensurate satellite* reflections below 200 K at ambient pressure.[10–12] [β_H and β_L are the high- and low-temperature ambient pressure phases of β-(ET)$_2$I$_3$, respectively.] As described previously,[10–12] the two satellite peaks which surround the Bragg reflections have indices of (hkl) ± q, where $q = 0.076a^* + 0.272b^* + 0.206c^*$, and each pair is generally nonequivalent in integrated intensity. From x-ray diffraction data, the satellite reflections have been shown to be consistent with sinusoidal modulations of the ET molecules and I$_3^-$ anions as rigid bodies, with maximum amplitudes of displacement of 0.11 and 0.27 Å, respectively.[12] In this Rapid Communication we describe the dependence of the satellite reflection intensities on pressure and temperature.

Neutron-diffraction data were obtained at the Argonne Intense Pulsed Neutron Source, using the time of flight single-crystal diffractometer with the 30×30-cm position-sensitive area scintillation detector.[13] With a stationary crystal and detector, each detected neutron is characterized by three coordinates representing its horizontal and vertical detector channels and its time of flight or wavelength. The resulting histogram of intensity data can then be mapped into three-dimensional reciprocal-space coordinates and displayed as shown in Fig. 2. For this experiment, ~1-mm^3 crystals of β-(ET)$_2$I$_3$, prepared by electrocrystallization,[9] were placed in a helium pressure cell which was then mounted on the cold stage of the Displex® helium refrigerator on the diffractometer. All measurements using He were done at pressures and temperatures above its freezing point.

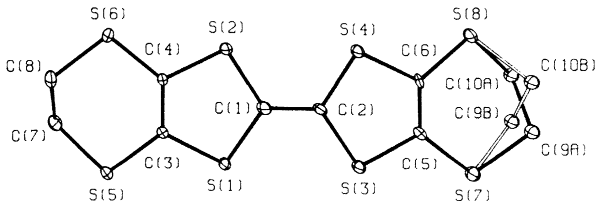

FIG. 1. The molecular geometry of the ET molecule showing the disorder of the terminal ethylene group (—CH$_2$—CH$_2$—). At room temperature and ambient pressure each of the two orientations, C(9*A*)—C(10*A*) and C(9*B*)—C(10*B*), are randomly present.

For the first set of runs (see Table I), a crystal (Xl = 1) was placed in the sample tube on the pressure cell with only a cotton plug to keep it stationary. A pressure of 1.6 kbar, chosen because of previous reports,[1,2] was applied at room temperature, the crystal was cooled to 20 K, and data were collected (run 1). In contrast to the previously reported ambient pressure results,[11] no satellite reflections were observable. We will call this phase β^* (low temperature without satellites) to differentiate it from the β_L phase (low temperature with satellites). The satellite reflections did not appear when the pressure was released while maintaining the temperature at 20 K (run 2).

The data in Fig. 2(a) were obtained after releasing the pressure at 20 K, warming the sample to room temperature, and cooling back down to 20 K under ambient pressure at all times (run 3). Satellite reflections due to the modulated structures are clearly observable in the plot. Next, while maintaining the temperature at 20 K, a pressure of 1.4 kbar was applied to the crystal, and diffraction data were again collected (run 4). As before, there was no change in the observed diffraction pattern and the satellites remained. Finally, while maintaining a pressure of 1.4 kbar, the crystal was subsequently warmed to room temperature and cooled back down to 20 K (run 5). The satellite reflections were again absent, as shown in Fig. 2(b).

These results clearly indicate that either the ambient pressure β_L phase or the high pressure β^* phase of β-(ET)$_2$I$_3$ is frozen in at low temperature depending on the pressure conditions at high temperatures. The application or release of pressure at low temperature does not alter the structural phase. This is consistent with a number of reports of the continued existence of the high-T_c phase after applying and releasing pressure.[14–19]

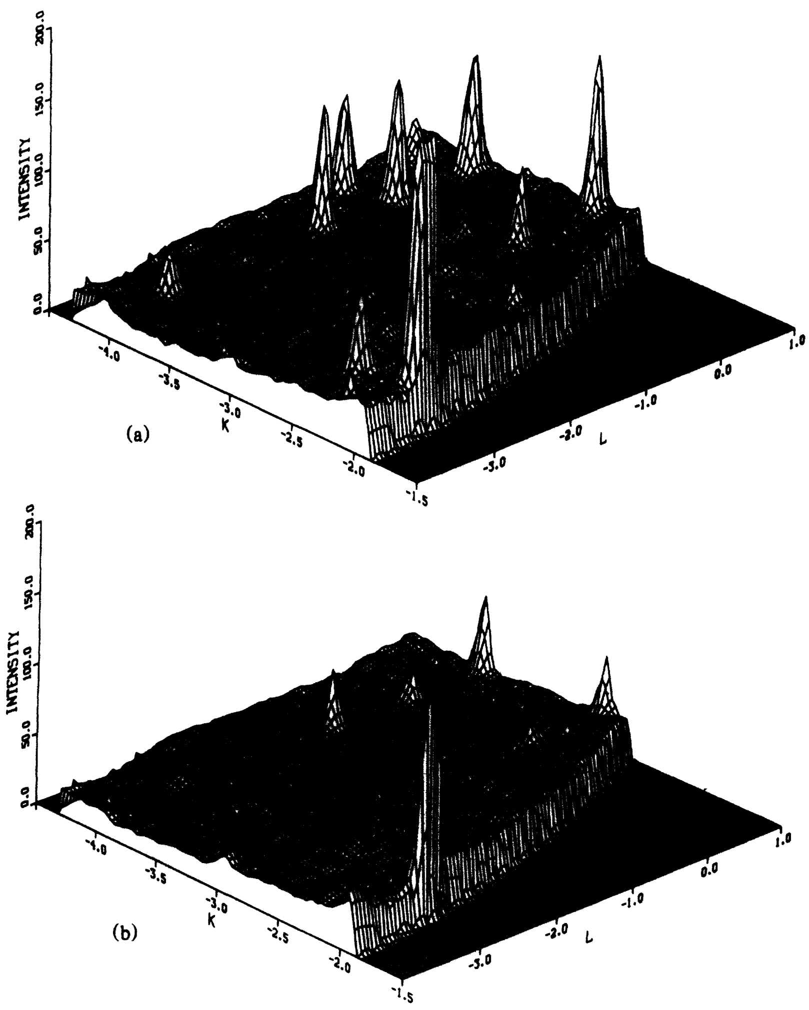

FIG. 2. (a) Plot of the neutron-diffraction intensity distribution in the $h=4.92$ reciprocal lattice plane of β-$(ET)_2I_3$ at 20 K and with zero pressure (run 3). Satellite peaks at $(5,-2,-3)-q$, $(5,-4,0)-q$, and $(5,-4,1)-q$ are clearly observable. (b) The same $h=4.92$ reciprocal lattice plane after applying a pressure of 1.4 kbar at 20 K, warming to room temperature, and cooling back down to 20 K (run 5). There are no observable satellite reflections.

In a second set of runs on the first crystal, to our consternation, the satellite reflections could not be suppressed even with the application of 2.0 kbar of pressure. However, there is now strong evidence[7] that the high-T_c state is only produced under *non*-hydrostatic pressure conditions on crystals in a medium such as ice,[20] or with attached electrical leads which produce anisotropic strain.[7] Although we can only speculate, it is possible that during the first set of runs the crystal was wedged in the sample cylinder in such a manner that strain was produced. Prior to the second run, dismounting and remounting the pressure cell may have shifted the crystal, possibly relieving the strain so that the pressure in the helium gas was purely hydrostatic.

To test this hypothesis, a second crystal ($XI=2$) was placed in the sample tube immersed in the fluorinated hydrocarbon Fluorinert® (3M Company). (The first crystal was destroyed in our first attempt to use Fluorinert.) The satellites were present after cooling to 20 K at ambient pressure (run 6), and were absent after warming to room temperature, applying 1.4 kbar of pressure, and cooling to 20 K (run 7). In order to determine the "critical pressure" for suppression of the satellites, we next lowered the pressure in stages by warming to room temperature under pressure, reducing the pressure to zero, and then immediately increasing to a new pressure level, cooling to 20 K, and collecting the data. In this manner, data were obtained at 1.3, 1.0, and 0.5 kbar (runs 8, 9, and 10). In each case, there were no satellite reflections in the diffraction pattern.

Finally, the crystal was warmed to room temperature, the pressure was released, and the data which were then obtained after cooling to 20 K again contained satellite reflections (run 11). The pressure was then increased in steps by warming to room temperature under pressure, increasing the pressure directly from the existing level to the new level, and then cooling back to 20 K. This time the data contained satellite reflections at 0.5 kbar (run 12), in contrast to the previous 0.5-kbar data (run 10). Thus it appears that there is some hysteresis in the pressure-temperature behavior of β-$(ET)_2I_3$ and the β^* phase is metastable for short periods of time (< 1 h) at room temperature. Runs 10 through 14 appear to demonstrate that the critical pressure required to suppress the appearance of the satellite reflec-

TABLE I. Temperature and pressure history for crystals of β-$(\mathrm{ET})_2\mathrm{I}_3$. Heating and cooling rates were ~3 K/min. In step 2 of runs 8, 9, and 10, releasing pressure and repressurizing were performed in immediate succession. For run 14, the crystal was at $T=300$ and applied $P=0$ for 2–3 h.

Run	Xl	T (K) P (kbar)	Step 1	Step 2	Step 3	Satellites
1	1	T	300	300→ 20		
		P	0→ 1.6	1.6		No
2	1	T	20			
		P	1.6→ 0			No
3	1	T	20→ 300→ 20			
		P	0			Yes
4	1	T	20			
		P	0→ 1.4			Yes
5	1	T	20→ 300→ 20			
		P	1.4			No
6	2	T	300→ 20			
		P	0			Yes
7	2	T	20→ 300	300	300→ 20	
		P	0	0→ 1.4	1.4	No
8	2	T	20→ 300	300	300→ 20	
		P	1.4	1.4→ 0→ 1.3	1.3	No
9	2	T	20→ 300	300	300→ 20	
		P	1.3	1.3→ 0→ 1.0	1.0	No
10	2	T	20→ 300	300	300→ 20	
		P	1.0	1.0→ 0→ 0.5	0.5	No
11	2	T	20→ 300	300	300→ 20	
		P	0.5	0.5→ 0	0	Yes
12	2	T	20→ 300	300	300→ 20	
		P	0	0→ 0.5	0.5	Yes
13	2	T	20→ 300	300	300→ 20	
		P	0.5	0.5→ 0.8	0.8	No
14	2	T	20→ 300	300	300→ 20	
		P	0.8	0.8→ 0→ 0.6	0.6	No

tions is about 0.5 kbar. This differs from the pressure of 1.2 kbar required to produce $T_c \simeq 8$ K in β-$(\mathrm{ET})_2\mathrm{I}_3$.[1,2]

With respect to the structure of β-$(\mathrm{ET})_2\mathrm{I}_3$, we should note that we find no evidence for the existence of a commensurate superstructure which has been reported to occur below 100 K.[21] The unit-cell volume derived from the cell parameters provided in Ref. 16 is exactly three times the normal volume for β-$(\mathrm{ET})_2\mathrm{I}_3$. However, we have not observed any peaks corresponding to this commensurate superlattice in any of our runs.

It has been previously proposed[22] that the ambient pressure phase of β-$(\mathrm{ET})_2\mathrm{I}_3$ has an anomously low T_c due to disorder of one ethylene group (Fig. 1) in the ET molecule, in comparison to β-$(\mathrm{ET})_2\mathrm{IBr}_2$ and β-$(\mathrm{ET})_2\mathrm{AuI}_2$, which contain *ordered* ET molecules. The existence of the long-range modulation at $T < 200$ K (ambient pressure) appears to introduce partial ordering of the ethylene group as a result of the variation in $\mathrm{H} \cdots \mathrm{I}$ contacts from one unit cell to another,[12] but the degree of ordering would still be less than that in the completely ordered β-$(\mathrm{ET})_2\mathrm{IBr}_2$ and β-$(\mathrm{ET})_2\mathrm{AuI}_2$. The sensitivity of these materials to disorder is exemplified by the isostructural β-$(\mathrm{ET})_2\mathrm{I}_2\mathrm{Br}$, where the complete disorder of the anion (both I-I-Br$^-$ and Br-I-I$^-$ orientations exist randomly) apparently prevents the onset of superconductivity and the material remains metallic down to 0.45 K at ambient pressure, and down to 1.07 K at $P=4$ kbar.[23]

Thus, the higher onset temperature for superconductivity in the high pressure phase of β-$(\mathrm{ET})_2\mathrm{I}_3$ is indicative of a more highly ordered structural phase. In addition to the absence of the structural modulation at $P > 0.5$ kbar, it is possible that the ethylene group, which is disordered at ambient pressure, is ordered and completely isostructural with the IBr_2^- and AuI_2^- salts in the high pressure β^* phase. Furthermore, whereas a T_c of 1.5 K for β_L-$(\mathrm{ET})_2\mathrm{I}_3$ appeared anomalously low, a T_c of 8 K for β^*-$(\mathrm{ET})_2\mathrm{I}_3$ is consistent with the variation of T_c with unit cell volume and calculated density of states for the three superconducting ET salts.[22]

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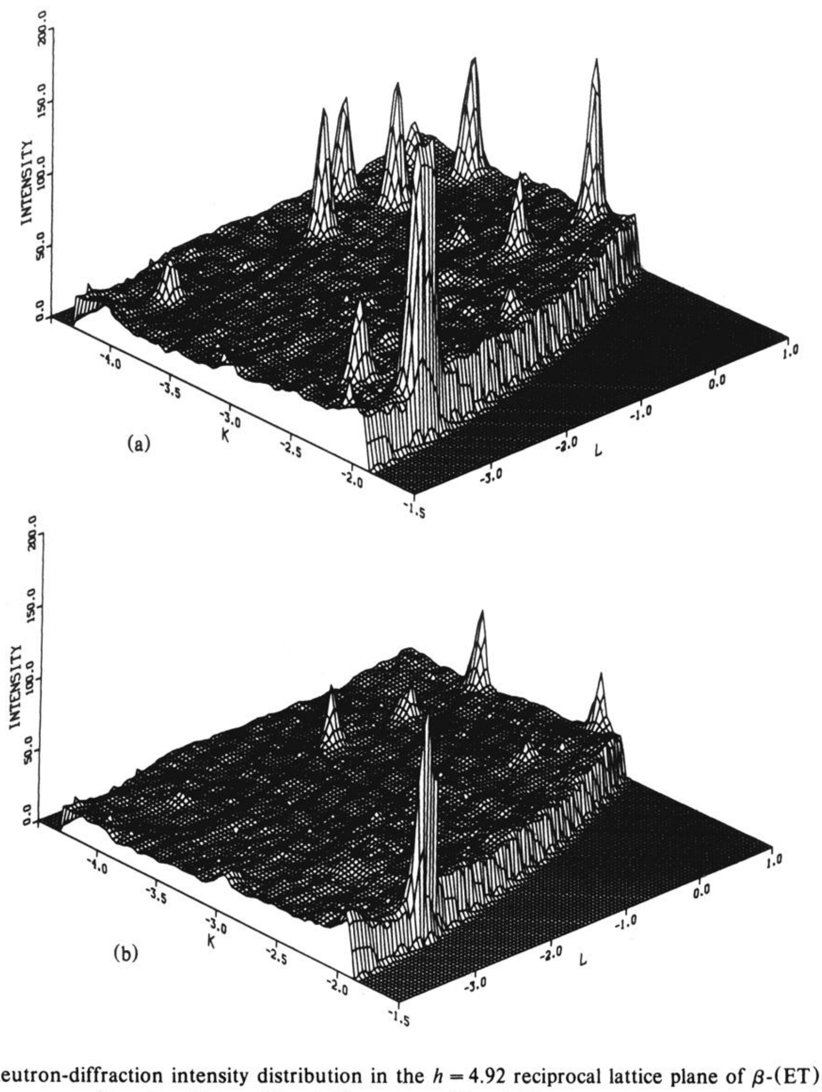

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