Brief Reports

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Shear-induced superconductivity in β-di[bis(ethylenedithio)tetrathiafulvalene]triiodide [β-(BEDT-TTF)$_2$I$_3$]

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We show that the high-T_c (8-K) superconducting state of β-(BEDT-TTF)$_2$I$_3$ [β-($C_{10}H_8S_8$)$_2$I$_3$] is formed by a combination of shear stress and hydrostatic pressure and *cannot* be accessed by pressure alone. Also, measurements of the pressure dependence of T_c in the ambient-pressure superconductors β-(BEDT-TTF)$_2$I$_3$, β-(BEDT-TTF)$_2$IBr$_2$, and β-(BEDT-TTF)$_2$AuI$_2$ show a common pressure derivative of about 1 K/kbar, which is nearly an order of magnitude larger than that of any previously reported superconductor. We present a structural model which is consistent with these observations.

Pressure is an important variable in the study of organic superconductors. Indeed, most of the compounds found to be superconducting to date require pressures of the order of several kilobar in order to suppress the insulating transitions often observed at low temperatures.[1] Both hydrostatic and quasihydrostatic techniques have been found to suppress the metal-insulator transition and induce superconductivity in many systems, but there have been puzzling disparities where superconductivity was not observed under hydrostatic conditions. An example is (BEDT-TTF)$_2$ReO$_4$ where pressures of 4 kbar from frozen oil clamp techniques gave[2] a value of T_c near 2 K but no superconductivity was observed to 8 kbar under hydrostatic conditions in solid He. At the time, different sample sources were blamed for these differences. (Throughout this paper we will denote BEDT-TTF, bis(ethylenedithio)tetrathiafulvalene, or 2,2′-*bi*[5*H*, 6*H*-(1,3,4,7-tetrathia)-indene-2-ylidene] with chemical formula $C_{10}H_8S_8$ as ET.) Recently, Tauklin *et al.*[3] and Murata *et al.*[4] have reported that modest pressures above about 1.3 kbar result in a superconducting transition temperature in β-(ET)$_2$I$_3$ of about 7 K, which is depressed very rapidly with further increase in pressure at a rate of 1 K/kbar. Although we previously detected[5] inductive anomalies near 7 K in a large number of β-(ET)$_2$I$_3$ samples, the reproducibility was poor and it was never unambiguous that the anomalies were associated with superconductivity. We have also detected anomalies in the 7–8 K range by resistive measurements.[6] In this Brief Report we present data which show that the high-T_c superconductivity state in β-(ET)$_2$I$_3$ *cannot* be accessed by truly hydrostatic pressure but requires, in addition, a substantial shear component. A reasonable model of the likely structural changes under pressure based on the length of the I$_3^-$ anion chains, and their accommodation in the structure, is presented.

All the organic superconductors studied to date show a decrease in the superconducting transition temperature, T_c, with increasing pressure. The selenium-based (TMTSF)$_2X$ salts [where tetramethyltetraselenafulvalene is 2,2′-*bi*(4,5-dimethyl-1,3-diselenole-2-ylidene), with the chemical formula $(CH_3)_4C_6Se_4$, with X equal to anions such as PF_6^-, AsF_6^-, ClO_4,$^-$, etc.] all have T_c values which decrease at rates of about 0.1 K/kbar, independent of the pressure generation scheme. Our early data[5] on β-(ET)$_2$I$_3$, and that of Tauklin *et al.*[3] and Murata *et al.*[4] on the same salt indicated a much larger pressure dependence of T_c, of the order of 1 K/kbar. This is surprising because recent compressibility measurements by Murata *et al.*[7] indicate that the pressure dependence of the lattice constants of β-(ET)$_2$I$_3$ is similar to that in the TMTSF salts. Here we present data on the β-(ET)$_2X$ ambient-pressure superconducting compounds where X's are the linear-symmetric anions I_3^-, IBr_2^-, or AuI_2^- and the T_c's are 1.5, 2.8, and 5 K, respectively. It is of interest to ascertain whether this enormous difference in magnitude of the pressure derivative of T_c is true in general for the β-(ET)$_2X$ salts and if these effects can be understood in terms of possible pressure-induced structural changes in these novel anisotropic conductors.

Single-crystal samples were grown by electrocrystallization as described earlier,[8] and characterized by both electron spin resonance (ESR) and x-ray measurements. Low-frequency (30–70 MHz) ESR measurements were made on single crystals as small as ($0.1\times0.25\times1.2$ mm^3) by custom winding coils of 25-μ-Cu wire for each sample.[9] Four terminals were attached to the larger crystals ($0.2\times7\times1.2$ mm^3) with silver epoxy on evaporated Au pads. Both experimental configurations slip into the $\frac{1}{8}$ in. bore of a BeCu pressure vessel. Hydrostatic pressures to 8 kbar were generated by careful isobaric freezing of He^4 about the sample.[10] Nonhydrostatic "pressures" were obtained either by fast quenching of fluid He or more reproducibly by freezing cyclopentane about the sample at various pressures. Pressure magnitude in the latter case was determined from an indium T_c marker. Temperatures were determined from the vapor pressure of the He^4 bath in which the pressure vessel was immersed.

Superconducting transition temperatures were defined as onsets in both the ESR and four-terminal resistance measurements. This definition does not affect the value of the pressure derivative.

Results for the pressure dependence of T_c are shown in Fig. 1 for β-$(ET)_2X$, $X = I_3^-$, IBr_2^-, and AuI_2^-. The striking result obvious from this figure is that the slopes of T_c versus pressure are essentially the same in spite of the variation of the magnitude of T_c from near 1 to 5 K in the different salts. The T_c versus pressure data shown (connected by lines intended to guide the eye) are all taken by careful isobaric freezing of He^4 about the sample resulting in very hydrostatic conditions.

Above about 0.5–7.5 kbar in solid He the $(ET)_2I_3$ remains metallic and nonsuperconducting down to 1.1 K as evidenced by the ESR signal and conductivity data. Shown in the same figure are T_c values for β-$(ET)_2I_3$ obtained under *non*hydrostatic conditions either by fast quenching of fluid He (shown as a cross) or cyclopentane (open circles). Also shown are data (open squares) for deuterated β-$(ET)_2I_3$ which appears to be indistinguishable from the ordinary β-$(ET)_2I_3$. The points are plotted on the pressure axis at values indicated by an In T_c marker which gives the pressure experienced by the In. Surprisingly, only under such nonhydrostatic conditions can these high-T_c values be achieved in β-$(ET)_2I_3$. Previous measurements verify this finding because the pressure techniques used by Tauklin

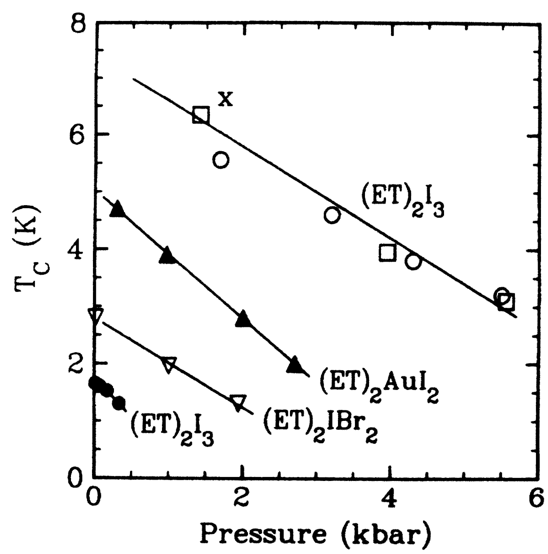

FIG. 1. Superconducting transition temperature vs pressure. ●, β-$(ET)_2I_3$ using solid He; ▽, β-$(ET)_2IBr_2$ using solid He; ▲, β-$(ET)_2AuI_2$ using solid He; ○, β-$(ET)_2I_3$ using frozen cyclopentane; □, deuterated $\beta(ET)_2I_3$ using frozen cyclopentane; ×, β-$(ET)_2I_3$ using fast quenched He; "pressure" is determined by the shift in T_c of an In marker.

et al.[3] and Murata *et al.*[4] are very similar to our cyclopentane experiments. Our attempts to access a higher-T_c state in either β-$(ET)_2IBr_2$ or β-$(ET)_2AuI_2$ have failed with all of these techniques and we believe this is due to the novel crystal structure of β-$(ET)_2I_3$ compared to β-$(ET)_2X$, $X = IBr_2^-$, and AuI_2^-.

Recent work[11] has shown that the β-$(ET)_2I_3$ salt has a modulated structure (onset $T \sim 200$ K) while both the β-$(ET)_2IBr_2$ and the β-$(ET)_2AuI_2$ derivatives do not, down to $T = 9$ and 125 K, respectively. Furthermore, it has been demonstrated[12] that the *asymmetric* anion containing β-$(ET)_2I_2Br$ is not superconducting at all (to $T = 0.45$ K) in spite of its identical structure and very similar lattice dimensions to β-$(ET)_2IBr_2$. This latter finding in the I_2Br^- salt is interpreted as extreme sensitivity to anion or molecular disorder since the β-$(ET)_2I_2Br$ derivative is asymmetric and so the anion can fit into its $-CH_2$ group H-atom cavity in two ways [$(I$-I-$Br)^-$ or $(Br$-I-$I)^-$] at random.

The interplanar spacing in the ET column stacking direction tends to increase with increasing anion size (length) as shown in Table I. Theoretical calculations[13] using the extended Huckel method indicate that the density of states at the Fermi level is most sensitive to these *intra*stack distances, and increases with increasing intrastack spacings for the β-$(ET)_2X$ (X = trihalide or pseudotrihalide anions) materials, and, therefore, the superconducting transition temperature, T_c, is expected to be the highest for β-$(ET)_2I_3$, contrary to previous experimental observations[14] [i.e., $T_c = 1.5$ K in β-$(ET)_2I_3$]. However, such a discrepancy can be explained by the presence of the structural modulation in the triiodide salt which, we believe, depressed the T_c from the $\sim$7–8 (under pressure) to 1.5 K. Now we turn to the likely effects anisotropic pressure might cause in β-$(ET)_2I_3$.

It has been observed[11] from x-ray and neutron diffraction data that the period of the incommensurate structural modulation in β-$(ET)_2I_3$ remains constant from 120 to 8.5 K. This modulated structure of β-$(ET)_2I_3$ under *ambient pressure* can, therefore, likely be considered as the ground state of this material down to the lowest temperatures. Analyses of the x-ray and neutron diffraction intensity data suggested that *only one* of the two ethylene groups in the ET molecule, which is disordered at $T > 195$ K, becomes ordered via the structural modulation. Therefore, partial $-CH_2$ group disorder remains to the lowest temperatures which can reduce T_c. Furthermore, this structural modulation results in a minimization of the energies of the H $\cdots$ I packing interactions resulting from the interactions of the

TABLE I. Intrastack spacing (Å), anion lengths (Å) (all values are obtained from x-ray diffraction data collected at 120 K), and T_c values in β-$(ET)_2X$.

X	I_3	I_2Br	AuI_2	IBr_2
Spacing I[a]	3.91	3.88	3.87	3.85
Spacing II	3.30	3.31	3.29	3.30
Anion length[b]	10.1 Å	9.70 Å	9.36 Å	9.41 Å
T_c	8	0	5	2.8

[a]The two independent intrastack spacings (I and II) alternate along the stacking direction. See Fig. 2 in Ref. 14 for an illustration.
[b]The lengths of the linear anions are estimated from the sum of the two X–X bond distances and the van der Waal radii of the terminal atoms. The uncertainty in this procedure may be substantial.

I_3^- anions with the $-CH_2$ group H atoms. However, under *anisotropic pressure*, some of the energetically less favorable (short) H $\cdots$ I packing interactions may become feasible resulting in a change in the structural modulation. Thus, it is possible that β-$(ET)_2I_3$ may become completely ordered under anisotropic pressure conditions which would, expectedly, increase T_c.

As judged from the magnitudes and the direction of the molecular displacements[15] in the modulated structure of β-$(ET)_2I_3$ (0.28 Å for I_3^- along **a** and 0.12 Å for ET along **a** − **b**) the packing arrangement appears to be most nonrigid or "flexible" on the a-b plane. Hence, the anisotropic shear is expected to occur parallel to this direction in the crystal, resulting in a structure that might be more ordered and therefore would more closely resemble those in the *completely ordered* β-$(ET)_2IBr_2$ and β-$(ET)_2AuI_2$ salts which have T_c's considerably in excess of 1.5 K. At this point, it must be remembered that the β-$(ET)_2X$ structure is *layered* in nature and contains alternating two-dimensional sheets of linear $(X$-X-$X)^-$ anions between which a "corrugated-sheet" network of short S $\cdots$ S interactions (from the ET molecule) is sandwiched.[16] The application of anisotropic pressure probably causes these sheets to shift or "slip" relative to each other because of the relative ease with which the weak $-CH_2 \cdots X$ interactions can be broken. This slippage could have two effects: (i) increased ordering of the ET molecule $-CH_2$ groups, and (ii) change in the *intra*stack distances (see Table I). Both effects would likely change T_c, but without quantitative knowledge of the structural changes we can only speculate on their effects. In the case of (ii), the *intra*stack distances correspond to the [110] direction in the crystal and the (110) plane spacing might be sensitive to anisotropic pressure (and easily measured by x-ray diffraction methods). It is of interest to note in Table I the correlation between the *intra*stack spacing and T_c. If this is indeed the relevant parameter, the large dependence of T_c upon pressure would follow. Furthermore, this is consistent with the band picture of Whangbo.[13]

Thus our model is as follows: The superconducting transition is a very sensitive function of both molecular and anionic disorder, and the relative length of the anion, with respect to the H-atom cavity into which it must fit in the structure. Disorder thus completely destroys superconductivity in β-$(ET)_2I_2Br$, and severely suppresses T_c in β-$(ET)_2I_3$ because the I_3^- ion is too large and introduces an incommensurate structural modulation, a lesser type of partial $-CH_2$ group disorder. We speculate that the shear introduced by fast freezing of the solid He, or by the relative thermal expansivities of the sample and the cyclopentane in cooling from the freezing point of the latter above 200 K, shears the structure allowing better "accommodation" of the I_3^- anion in its cavity, thereby resulting in $-CH_2$ group ordering and a concomitant rise in T_c.

This model nicely accounts for the data to date: (i) the difference between β-$(ET)_2IBr_2$ and $(ET)_2I_2Br$, (ii) the increase with pressure plus shear of T_c in β-$(ET)_2I_3$, and (iii) the lack of a higher-T_c state in β-$(ET)_2IBr_2$ and β-$(ET)_2AuI_2$. The enormous dependence of T_c upon hydrostatic pressure and the common magnitude of the effect for all these materials may be related to the *intra*stack spacing driving the density of states, consistent with recent band calculations. While this model is speculative, it is plausible and is providing a guide for synthesis efforts in our laboratories and elsewhere.

Note added in proof. We have recently learned of work by Creuzet *et al.* [F. Creuzet, G. Creuzet, D. Jerome, D. Schweitzer, and H. J. Keller, J. Phys. (Paris) Lett. (to be published)]. In their study 8-K superconductivity is reported in β-$(ET)_2I_3$ at ambient pressure after pressurization to 1.5 kbar in He gas and subsequent release of the pressure at low temperature. Their work involves electrical leads on the sample which we speculate strain the crystal during pressurization or depressurization. In all our experiments on a number of crystals, with and without electrical leads, shear, in addition to pressure, is *essential* in accessing the 8-K superconducting state.

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