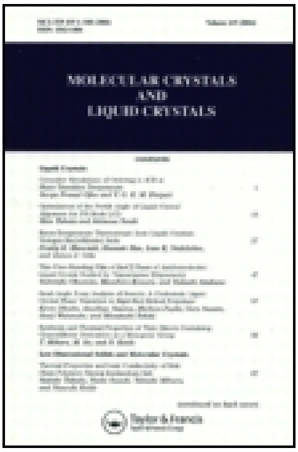

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Ubiquitous Superconductivity Near 4K in Salts of the BEDT-TTF/I System: Is There a Common Source?

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UBIQUITOUS SUPERCONDUCTIVITY NEAR 4 K IN SALTS OF THE BEDT-TTF / I SYSTEM: IS THERE A COMMON SOURCE?

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Abstract An unusually large number of metallic and superconducting phases exist among the organic charge-transfer salts of the BEDT-TTF / I system [BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene]. In addition to the well-known superconducting transitions near 1.4 K and ~ 8 K in β-$(ET)_2I_3$ and β*-$(ET)_2I_3$, respectively, superconductivity near 4 K occurs in three other superconducting salts of this system, frequently in other conventionally synthesized salts, and in the products of thermally processed salts and chemically modified syntheses. A critical review of the literature of this system indicates that the source of superconductivity near 4 K in many cases is a β-like phase of $(ET)_2I_3$ stoichiometry. It is argued that superconductivity in the γ-$(ET)_3(I_3)_{2.5}$ salt (onset $T_c \sim 4$ K) has not been persuasively demonstrated and that the source of superconductivity likely is a β-phase component in α-β mixed-phase crystals.

INTRODUCTION

Charge-transfer salts composed of the organic radical-cation electron-donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) and the homonuclear anionic species of iodine comprise a system of organic electrical conductors which is remarkably large in content and abundant in superconducting phases. This system presently consists of the 14 salts which are listed in Table I. All but one of these salts are metallic conductors at room temperature, most are metallic to low temperatures, and one-half are superconducting at ambient pressure with one notable exception.

The preeminent salt of the ET / I system is β-$(ET)_2I_3$ because its discovery[1] represents a benchmark in the pursuit of new ambient-pressure organic superconductors and because under applied pressure[2] it exhibits a remarkably elevated superconducting transition temperature (T_c). β-$(ET)_2I_3$, which possesses a slightly disordered structure,[3] has a T_c of 1.4 K at ambient pressure. This salt under mild applied pressures (~ 0.5 kbar), where it undergoes a change to an ordered structure[4] (denoted as β* or β_H), has a T_c near 8 K. β-$(ET)_2I_3$ and its high-pressure variant β*-$(ET)_2I_3$ are well-documented volume superconductors.[5,6] The superconducting salt α_t-$(ET)_2I_3$[7] also is a well-established volume superconductor.[8] This salt is a thermally converted (tempered) product of nonsuperconducting α-$(ET)_2I_3$,[9] and depending on its preparation, it exhibits an inhomogeneous distribution of T_c's extending over a range of 2 — 8 K at ambient pressure.[7,8,10] The α_t-phase salt apparently possesses a β-type structure and, because of its elevated T_c, likely some degree of ordering similar to that of the β*-phase salt. However, in contrast to β*-$(ET)_2I_3$, α_t-$(ET)_2I_3$ is stable at ambient pressure and room temperature.[8]

TABLE I Electrical Conductive States, Metal-Insulator Transition Temperatures (T_{MI}), and Superconducting Transition Temperatures (T_c) of the Charge-Transfer Salts of ET and Polyiodide Anions.

Salt	State[a]	T_{MI} (K)	T_c (K)[b]	Ref.[c]
α-$(ET)_2I_3$	M	135		9
α_t-$(ET)_2I_3$	M		2—8	7
β-$(ET)_2I_3$	M		1.4	1
β* (or β_H)-$(ET)_2I_3$	M		8 (0.5 kbar)	2
β_d-$(ET)_2I_3$	M	140		14
β_t-$(ET)_2I_3$	M		4.5	8
γ-$(ET)_3(I_3)_{2.5}$	M		2.5	11
δ-$(ET)(I_3)$	M	130		15
ε-$(ET)_2(I_3)(I_8)_{0.5}$	M[d]			15
ζ-$(ET)_2(I_2)(I_8)$	S			16
η-$(ET)_2(I_3)(I_5)$	M			17
θ-$(ET)_2(I_3)$	M		3.6	12
κ-$(ET)_2(I_3)$	M		3.6	13
λ_d-$(ET)_2I_3$	M	220		14

a Metallic (M) or semiconducting (S) behavior at 300 K.
b At ambient pressure unless specified otherwise.
c See text for additional references.
d Either M or S depending on stoichiometry (see ref. 17).

β_t-$(ET)_2I_3$ ($T_c \approx 4.5$ K) is a thermally converted product of β-$(ET)_2I_3$.[8] Inductive measurements indicate that this product is a bulk superconductor, and its T_c suggests that its structure is intermediate between those of the β-phase salt and the β*-phase or α_t-phase salts. The superconducting salts γ-$(ET)_3(I_3)_{2.5}$,[11] θ-$(ET)_2I_3$,[12] and κ-$(ET)_2I_3$[13] occur as minor constituents in the products of electrocrystallization and, therefore, have been difficult to obtain universally for detailed studies. The evidence for superconductivity in these phases is derived at present only from resistive measurements, so that it is not yet established that these are truly bulk superconductors. The γ-phase salt is reported to have a resistive superconducting onset temperature of ~ 4 K and a rather broad superconducting transition with a midpoint temperature of ~ 2.5 K. The θ- and κ-phase salts have much sharper resistive transitions with midpoints near 3.6 K. The remaining salts[14-17] listed in Table I are not superconducting, but several can be converted by thermal treatment to materials which superconduct considerably above 2 K.

It is now well recognized, and generally understood as a matter of crystallographic order vs. disorder, that 1.4 K and 8 K are significant characteristic temperatures for superconductivity in ambient-pressure β-$(ET)_2I_3$ and pressurized β^*-$(ET)_2I_3$. Thus, it is not particularly surprising that superconductivity at ambient pressure near 8 K occurs in α_t-$(ET)_2I_3$. On the other hand, it is interesting and perhaps significant that four other salts of the ET/ I system are superconducting near 4 K and that 4 K, among other temperatures, also is relevant to superconductivity in α_t-$(ET)_2I_3$. It is a remarkable fact, moreover, that 4 K frequently appears as a characteristic temperature for superconductivity in a variety of conventionally synthesized, thermally processed, and chemically modified salts of the ET / I system, not all of which products can be conveniently tabulated as well-differentiated phases. This poses the question of whether there might be some common source for a characteristic superconducting temperature near 4 K. In this article we review the evidence for superconductivity near 4 K in these salts and consider whether there exists some common, identifiable phase which might account for the experimental observations.

THE β-PHASE SALT

The discovery by Yagubskii et al.[1] of superconductivity in β-$(ET)_2I_3$ at ambient pressure involved resistive measurements of several crystal specimens which exhibited, in addition to the superconducting onset and loss of resistance near 1 K, an accelerated decrease in the resistance near 4 K . This abnormal drop considerably above T_c was considered significant but unexplainable at that time. Subsequent measurements of single-crystal β-$(ET)_2I_3$ at ambient pressure by some of the present authors[18] detected a similar resistive decrease near 4 K and also a very pronounced resistive drop near 8 K, although inductive studies showed an absence of volume superconductivity above 1.4 K. Further measurements in different laboratories have since shown rather commonly the occurrence of similar resistive decreases, suggesting that these anomalies are not instrumental artifacts but instead signatures of the coexistence[19] of other superconducting phases in single crystals of apparent high quality. Resistive drops, of course, are indicators of filamentary electrical shunts rather than bulk superconductivity, but resistivity measurements can be a very sensitive detector of trace quantities of a superconducting phase. With the discovery of superconductivity near 8 K in β^*-$(ET)_2I_3$ and the reports of superconductivity at 2 — 4 K in the γ-phase salt, there appeared to be at least a superficial explanation for the resistive drops in β-$(ET)_2I_3$.

Experiments reported by Ginodman et al.[20] on the thermal cycling of β-$(ET)_2I_3$ crystals between 300 K and ~ 1 K at ambient pressure revealed interesting resistivity behavior. These studies showed that the initial drop in resistivity near 1.5 K progressed to higher temperatures, finally reaching ~ 8 K after 5 cycles. The completion of the superconducting transition, however, remained practically unchanged near 1 K, so that the transition widths became increasingly broader with each cycle and the midpoint transitions progressed from 1.3 K to 4.5 K. In one of the most complete investigations of single-crystal β-$(ET)_2I_3$ at ambient pressure, Buravov et al.[21] described similar thermal cycling effects along with many more details on resistive changes. In this study, three different kinds of β-$(ET)_2I_3$ crystals could be distinguished by their resistive behavior, as illustrated in Figure 1(A): crystals with transitions or resistive drops at (a) 1.5 K and ~ 4 K, (b) 1.5 K and ~ 8 K, and (c) ~ 4 K and ~ 8 K.

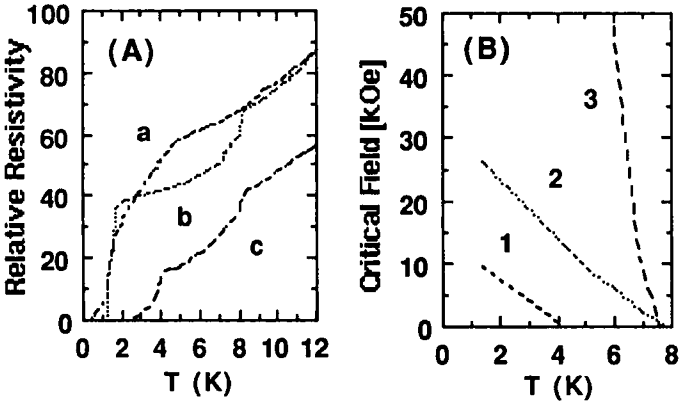

FIGURE 1 (A) The resistive behavior of three different crystals (a,b and c) of β-$(ET)_2I_3$ (from Fig. 1 of ref. 21); (B) H_{c2} for the resistive drops near 4 K and 8 K with magnetic field along *c* (1,2) and *b* (3) (from Fig. 4 of ref. 21).

It was emphasized that x-ray analyses of each crystal showed the presence of only the β phase. Resistive measurements with applied magnetic fields yielded genuine temperature dependencies for upper critical magnetic fields (H_{c2}), as illustrated in Figure 1(B). Thermal cycling between 300 K and low temperatures led to the disappearance of the resistive drop near 4 K but otherwise gave behavior similar to that reported by Ginodman et al.[20] Buravov et al.[21] concluded that their apparent β-phase crystals contained a mixture of different superconducting phases that likely were connected in series, because of the incomplete shunting (incomplete transitions), and likely possessed the same chemical composition, because of the thermal cycling behavior.

THE γ-PHASE SALT

Measurements of the resistive normal-state and superconducting properties of the γ phase were determined and published[11] before its structure was fully identified. There still remains some uncertainty in its structure,[15] and thus in its chemical composition, but the reported structure is very similar to that of another ET-based salt, δ-$(ET)_2AuI_2$.[22] The structural study of this salt indicated the presence of some unidentified contaminant phase which was suggested[15] as a possible alternate source of the superconductivity. These structural and impurity issues, and especially the unusual experimental results described below, make it unclear whether or not any of the resistive properties reported for the γ-phase crystals truly pertain to this phase.

In their investigations of the γ-phase crystals, Yagubskii et al.[11] observed resistive changes with temperature which exhibited "humps" in the region of 100 K. This behavior is illustrated in Figure 2, which shows the resistivity-temperature curves for three of five reported crystal specimens (labeled 1 through 5) having decreasing maxima in their resistivities.

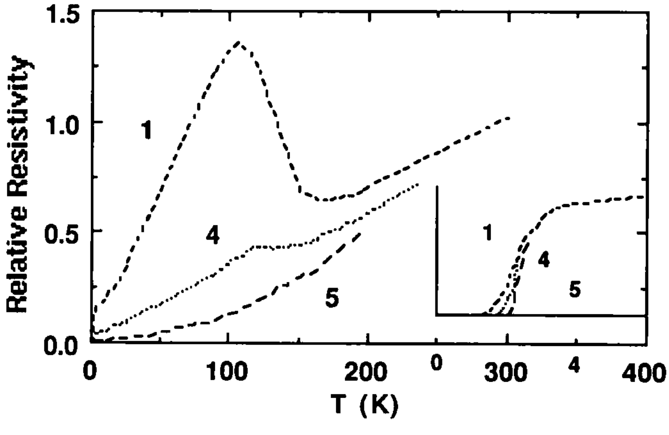

FIGURE 2 Resistive behavior of three γ-phase crystals (specimens 1, 4 and 5); the inset shows the superconducting transitions with onsets near 4 K and completions near 1 — 2 K (from Fig. 1 of ref. 11).

The curves of Figure 2 exhibit metallic conductivity down to ~ 150 K, then semiconductive behavior at lower temperatures followed by a maximum in the resistivity and a return to metallic behavior. For the curve of specimen 1, the resistive maximum (hump) is remarkably pronounced. For the curve of specimen 5, the hump is barely discernible. At low temperatures, the crystals undergo a superconducting transition with an onset near 4 K, completion in the range 1—2 K, and midpoints in the region of 2.5 K. The completion temperatures appear to increase from ~ 1 K to ~ 2 K with decrease in the height of the hump. The onset near 4 K was found to have upper critical magnetic field behavior typical of organic superconductors, thus confirming the presence of a superconducting phase.

In a second article, Yagubskii and associates[19] reported more details on the nature of their γ-phase crystal specimens. First, the appearance of the humps in the resistivity curves was found to be strongly influenced by the positions of the voltage probes on the crystal face. For certain positions the hump was very large, whereas for other positions the hump was almost imperceptible. Second, while the superconducting transition temperatures varied over a range of ~ 1 K from crystal to crystal, these nevertheless were found to be uncorrelated with the height of the resistive maxima. Thus, they concluded that the hump is unrelated to the γ phase and that the apparent single crystals consisted of different phases with considerably different electrical properties. The spread in T_c's was suggested to occur either because of the existence of different T_c properties of the γ phase arising from variations in the iodine content or, alternatively, because of the existence of varying amounts of the γ phase distributed throughout regions of a nonsuperconducting matrix. Although it was not originally proposed by Yagugskii et al.,[19] one now can reasonably suggest that the hump is simply due to a matrix, or at least to the inclusion, of nonsuperconducting α-$(ET)_2I_3$, which undergoes a metal-to-semiconductive transition near 135 K.

THERMAL CONVERSIONS

Numerous articles on the thermal processing of ET-based salts have been published, most of which deal with the iodide derivatives. The heating of iodide salts at temperatures near 400 K apparently produces, in all cases where a transformation occurs, some form (or forms) of the β-$(ET)_2I_3$ phase having an elevated T_c at ambient pressure. The first report[23] of a thermal conversion process concerned the transformation of ε-$(ET)_2(I_3)(I_8)$, which is the most iodine-rich phase of the ET / I system. It is of interest to note that the ε phase was originally reported to be superconducting with a resistive superconducting transition curve very similar to that of the γ phase (midpoint $T_c \cong 2.5$ K).[15] Later it was established that the ε phase is semiconductive but was contaminated in the original studies by the presence of the (superconducting) β phase.[24] Additional studies have shown that the ε phase can be metallic to the lowest temperatures (but not superconducting) as the result of slight changes in the iodine stoichiometry.[17]

Merzhanov et al.[23] and Zvarykina et al.[25] found that ε-phase crystals heated to about 400 K for several hours in vacuum yielded intact crystals which exhibited resistive superconducting transitions with onsets near 7—8 K, completions near 2 K, and midpoints ranging from 2.5 K to 6—7 K. The onset temperatures generally always occurred near 8 K, but the transition widths were found to be dependent on the temperature and duration of the applied heat, with relatively sharper transitions occurring for longer periods of heating at a given temperature. The wide transition widths indicate an inhomogeneous distribution of T_c's, similar to the situation found in the thermal conversion of the α-phase salt. The article by Zvarykina and associates[25] shows figures in which converted crystals exhibit superconducting onsets near 8 K and completions near 4 K for some crystals and near 6 K for others. X-ray analyses of the crystal products indicated the presence of twinned or mosaic crystals having the β-phase structure. Magnetic field effects determined for the 8 K onset showed genuine H_{c2} behavior. The salt ζ-$(ET)_2(I_2)(I_8)$ heated to ~ 400 K in argon has been reported[16] to undergo a conversion to a β-type superconducter having $T_c \cong 6$ K (midpoint?), but no details of this material and its properties have been published.

As previously mentioned, nonsuperconducting α-$(ET)_2I_3$ can be thermally converted to a phase, denoted as α_t-$(ET)_2I_3$, that has a β-type structure and an inhomogeneous distribution of T_c's in the range 2 — 8 K at ambient pressure.[7,8,10] The question of what structural differences distinguish this phase from the ambient-pressure, low-T_c β phase and the pressurized, high-T_c β* phase is yet unanswered. Baram and associates[7] and later Schweitzer et al[8] have shown that with prolonged heating near 400 K for many hours to several days, resistive completion temperatures of 5 — 6.5 K can be obtained for the superconducting transition. Inductive measurements clearly establish that the α_t phase is a volume superconductor,[8,10] but one with an extended distribution of T_c's down to 2 K even for specimens which have much higher resistive completion temperatures. A significant result of these studies is that no trace of the α-phase metal-to-semiconductor transition near 135 K has been detected in the resistive behavior of the tempered product; the α_t phase is metallic at all temperatures below 300 K and apparently metallic considerably above this temperature.

The superconducting β_t-$(ET)_2I_3$ phase is a thermally converted product of β-$(ET)_2I_3$ with a T_c near 4.5 K.[8] This product requires a much more prolonged heating period (about 12 days) at a somewhat higher temperature than does the α phase to produce a superconducting material with a T_c approaching that of the α_t phase. The differences in the thermalization rates suggests that the β phase is kinetically more stable than the α phase, and the T_c of the β_t phase suggests that 4 K or thereabout is a temperature of some intermediate state of kinetic stability relative to a thermodynamically stable superconducting state with T_c near 8 K. θ-$(ET)_2I_3$ is an ambient pressure superconducting phase[12] with a resistive T_c of ~ 3.6 K (midpoint) and with a relatively sharp resistive superconducting transition. Not all crystal specimens have been found to be superconducting, however, and the lack of superconductivity in some specimens has been attributed to the sensitivity of the crystals to lattice imperfections.[26] The present authors have isolated several θ-phase crystals which are metallic to low temperatures but exhibit no evidence of ambient-pressure superconductivity at temperatures as low as ~ 0.5 K. These nonsuperconducting crystals heated to temperatures near 370 K, however, readily convert to an ambient-pressure superconducting phase of apparent β-phase structure with a superconductive onset temperature of ~ 3.8 K as determined by inductive measurements.[27]

CHEMICAL MODIFICATIONS

The normal-state and superconducting properties of α-$(ET)_2I_3$ and β-$(ET)_2I_3$ apparently can be substantially altered by chemical processing and by chemical modifications in the syntheses. An example of chemical processing is that reported by Yagubskii et al.[28] in which the α phase was converted to a superconducting phase by exposing α-phase crystals to saturated I_2 vapor at ambient temperature. The resistive properties of the product crystals were found to be remarkably similar to those reported for the γ phase (see Fig. 2). The resistivity-temperature curves exhibit a metal-to-semiconductive transition near 140 K, a pronounced maximum in the resistivity near 100 K, metallic resistivity below this temperature, and finally a superconducting transition beginning near 4 K. Presumably I_2 could serve the role of increasing the iodide content within certain regions of the α phase, thus producing small quantities of some superconducting non-stoichiometric phase or even producing some quantities of the γ phase superconductor. On the other hand, as demonstrated by the later experiments of Yagubskii et al.,[19] the resistivity behavior of the product may have no relationship to any practical change in the initial α phase but, instead, simply may represent a difference in the placement of the voltage probes in a crystal initially containing a mixture of different phases. In any case, an examination of similarly processed crystals for evidence of a Meissner effect or field-induced diamagnetic shielding currents found no trace of volume superconductivity in the product.[29]

Chemical modifications in the syntheses of ET / I salts involving a change in solvent for the electrocrystallization is a well-known method for altering the relative yields of multiple products, for example, the favorable production of β-$(ET)_2I_3$ at the expense of the α phase. The inclusion of "impurities" — either by accident or by intention in the case of dopants — is another modification of practical importance. The superconducting salts θ-$(ET)_2I_3$ and κ-$(ET)_2I_3$, for example, were discovered in products of electrocrystallization in attempts to alter the modulated structure of β-$(ET)_2I_3$ by the introduction of an impurity anion (AuI_2^-) which produces salts with the same β-type structure.[12,13] In a different attempt to alter the modulated structure in β-$(ET)_2I_3$, Beno et al.[30] included the cationic electron-donor molecule MET [4,5-methylenedithio-4′,5′-ethylenedithio-tetrathiafulvalene] in a mixture with ET to electrocrystallize salts of the type β-$(ET)_{2-x}(MET)_xI_3$. Among the products, crystals with the β*-$(ET)_2I_3$ structure at ambient pressure were obtained and found by rf penetration depth measurements to be superconducting at ambient pressure with an onset T_c of ~ 4.6 K. The prototypical β*-phase structure,[4] which is perfectly ordered and free of the structural modulation, is unstable at ambient pressure and temperature. However, the ambient-pressure β*-phase product of this synthesis was identical in structure to the prototype with the exception that about 2 % of the I_3^- anions were disordered. X-ray analyses gave no indication of the inclusion of MET in the lattice above the limit of detection (~ 10 %), although the disorder in I_3^- may imply the inclusion of a small amount of MET. It is reasonable to assume that the slight I_3^- disorder in this β*-phase product accounts for the reduction in T_c below 8 K and possibly accounts for its stability at ambient conditions. To our knowledge, this phase represents the first documented example of a β*-phase material stable at ambient pressure and temperature.

Another route to the possible disruption of the modulated structure in β-$(ET)_2I_3$ was pursued by Montgomery et al.,[31] who included the donor molecule PT [bis(propylenedithio)tetrathiafulvalene], which is a symmetrical donor in contrast to MET, along with ET in the electrocrystallization of I_3^- salts. The results of this study are remarkably curious, but significant to this article, because the product phases were found to be apparent "single" crystals consisting of a combination of the α and β phases of $(ET)_2I_3$ and possessing ambient-pressure, onset T_c's within the range of ~ 2.5 — 6.9 K, as determined inductively. A crystal derived from a 1:1 ratio of the two donor molecules was shown by x-ray analysis to consist basically of a large α-phase single crystal embedded with smaller crystals and powdered specimens of the β phase. Further investigations of the products of electrocrystallization showed that "single" crystals containing α-β mixtures could be found in conventional syntheses in the absence of PT.

Figure 3 shows the superconducting transition of one such crystal with an onset T_c of ~ 4.5 K as determined by rf penetration depth measurements.

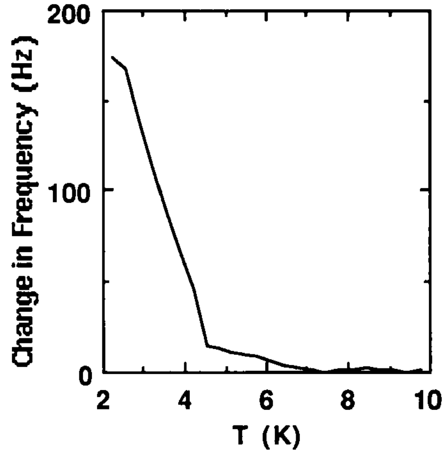

FIGURE 3 Superconducting transition curve, as determined by rf penetration depth measurements, of an apparent single crystal containing a mixture of α and β phases of $(ET)_2I_3$ (from unpublished data of the authors).

In relation to mixed crystal specimens, it is relevant to mention that Zvarykina et al.[32] have found that β-$(ET)_2I_3$ crystals can undergo plastic deformation by twinning accompanied by increases in T_c. It was suggested that the β* (or β_H) structure can be induced and stabilized by local strains arising from such plastic deformations.

DISCUSSION

The preceding review demonstrates that 4 K (and nearby temperatures) frequently occurs as a characteristic temperature for superconducting transitions at ambient pressure in conventionally synthesized crystals of β-$(ET)_2I_3$, in the salts γ-$(ET)_3(I_3)_{2.5}$, θ-$(ET)_2I_3$, and κ-$(ET)_2I_3$, and in the products of thermally processed and chemically modified salts of the ET / I system. Some of the evidence is based solely on resistivity measurements, but viewed in the context of all of the published studies of a similar nature, the results are reasonably definite. In resistive measurements, the appearance of an incomplete resistive drop at 4 K indicates the existence only of some filamentary, incomplete electrical shunt, but the appearance of genuine H_{c2} behavior suggests the existence of at least some amount, perhaps only trace quantities, of a superconducting phase. In inductive measurements, the appearance of superconductivity at 4 K is generally a positive indication of a bulk superconducting phase.

The evidence for a superconducting phase with T_c near 4 K (as well as near 8 K) in conventionally synthesized crystals of β-$(ET)_2I_3$ is rather convincing, especially the detailed evidence reported by Buravov et al.[21]. On the basis of the thermal cycling effects, it seems likely that the contaminant phase responsible for superconductivity near 4 K, as well as near 8 K, is a β-like material of $(ET)_2I_3$ stoichiometry. It is doubtful that the γ phase is the contaminant, partly because of its different stoichiometry and particularly because of its questionable superconducting properties. Other than a β-like contaminant, it would be reasonable to suggest a θ-phase or κ-phase contaminant, either of which has the same stoichiometry but likely has a less stable structure because of its rarity.

All thermally converted products of the ET / I salts seem to be β-like phases, and these have T_c's near 4 K in the case of the tempered θ phase and the β_t product, or T_c's near 4 K within a wide range of other superconducting transition temperatures in α_t and in the thermally converted ε-phase salt. The precise structures of these thermally converted products are unknown, but it is reasonable to suppose that these are very similar, if not identical, to that of the 4 K contaminant of the β phase. As previously mentioned, the phase responsible for superconductivity near 4 K appears to be thermally metastable with respect to the phase superconducting near 8 K, and this could account for the wide range of T_c's observed in the products of some thermally processed salts. Temperatures near 4 K, however, seem to be the most generally favored within the ET / I system.

Finally, superconductivity near 4 K occurs in β-$(ET)_2I_3$ salts synthesized by chemical modifications: in crystals of the type β^*-$(ET/MET)_2I_3$ ($T_c \cong 4.6$ K) and in crystals of the mixed-phase type α/β–$(ET)_2I_3$ ($T_c \cong 2.5$ — 6.9 K). The mixed-phase crystals apparently occur also as products during conventional electrocrystallization reactions, which strongly suggests that mixed phases may be a general phenomenon for salts of this system. The β^* phase of the $(ET/MET)_2I_3$ salt is the only product phase with a definitely known crystal structure. This stucture is a slightly anion-disordered variant of the original ordered β^* structure, apparently stabilized at ambient pressure by the disorder and/or the presence of small amounts of MET. Superficially at least, the disorder accounts for the T_c being lower than 8 K. Superconductivity near 4 K in the mixed α-β salts no doubt occurs from the presence of the β phase, and the elevated T_c may arise from some pressure effect due to encapsulation or, in what amounts to the same thing, from plastic deformations similar to those occurring in twinned crystals.[32] It is not obvious that these various β-like phases with T_c near 4 K are materials with identical structures, but it seems likely that all are variants of the perfectly ordered β^* (or β_H) structure. One speculates that slight disorder, slight nonstoichiometry, and plastic deformations are all possible mechanisms for yielding ambient pressure, lower T_c variants of the β^* phase.

Evidence for superconductivity in the salt γ-$(ET)_3(I_3)_{2.5}$ is not persuasive. In fact, the resistivity data suggest that the measurements attributed to the γ phase apply instead to an α-β mixed crystal because of the appearance of the metal-to-semiconductor transition near 140 K. For similar reasons, superconductivity in the product of α-$(ET)_2I_3$ exposed to I_2 vapor likely pertains to superconductivity in small amounts of the β phase in a mixed α-β crystal. On the other hand, superconductivity near 4 K in θ-$(ET)_2I_3$ and κ-$(ET)_2I_3$ seem to be genuine attributes of these phases, but there is the curious circumstance that not all θ-phase crystals are superconductors. Because of the similarity in stoichiometry, one wonders whether or not a β-phase contaminant might be the source of superconductivity in the θ-phase salt.

Very recent studies have demonstrated that 2 K is another characteristic superconducting temperature of β-$(ET)_2I_3$.[33] The annealing of the conventionally synthesized, low-T_c phase for 20—40 hr near 110 K causes a change in the incommensurate superstructure and an increase in T_c from 1.4 K to 2 K. Magnetization measurements demonstrate that this is a volume superconducting material, and it is suggested again that reduction in the original disorder is the reason for the increase in T_c.[34] The superconducting properties of β-$(ET)_2I_3$ are certainly among the most intriguing of any organic superconductor.

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