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## Competition Between Superconductivity and a New 20 K Phase in $-(\text{BEDT-TTF})_2\text{I}_3$ : Specific Heat Measurements

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## Competition between Superconductivity and a New 20 K Phase in $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>: Specific Heat Measurements

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We present here direct calorimetric evidence for a new transition at  $T^* = 22.25$  K in the metallic state of quasi-2D organic superconductor  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> at ambient pressure, as suggested by our previous measurement of the temperature-dependent Hall coefficient  $R_H(T)$ . The apparent reduction in the effective electronic density of states at  $T^*$  quantitatively explains for the first time the suppression of  $T_c$  from the pressure-stabilized "high- $T_c$ " value of 8 K to the ambient-pressure cooled "low- $T_c$ " value of 1.5 K.

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The quasi-2D (BEDT-TTF)<sub>2</sub>X sulfur-based organic conductors and superconductors exhibit a wide variety of crystal structures and electronic properties [1]. In the case of superconducting  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>, two different low-temperature crystal structures with two different maximum superconducting critical temperatures occur, depending on the exact pressure treatment. At ambient pressure and room temperature, each BEDT-TTF cation in  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> has one orientationally disordered C<sub>2</sub>H<sub>4</sub> ethylene group and one ordered group [2]. Upon cooling to 175 K at ambient pressure, a second-order structural phase transition occurs in which the disordered ethylene groups now undergo long-range orientational order, forming a superlattice that is incommensurate with the underlying crystal structure [2,3]. The wave vector of this superstructure, although incommensurate, is close to a commensurate description [3] and in fact is reported to be indistinguishable from the commensurate wave vector  $\mathbf{q} = (\mathbf{a}^* + 4\mathbf{b}^* + 3\mathbf{c}^*)/14$  at 4.5 K [3,4]. The ordering of the ethylene groups also induces small translational displacements in the BEDT-TTF cations and I<sub>3</sub> anions [2]. In this ambient-pressure "low- $T_c$ " structure, the superconducting critical temperature for  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> is 1.5 K [5].

Cooling under a weak hydrostatic pressure, however, leads to a different low-temperature orientational ordering and a significantly higher  $T_c$ . In this pressure-stabilized "high- $T_c$ " structure, all of the ethylene groups share the same orientation [6]. It is important to note that the pressure can be released at low temperature without any change in the orientational order, as long as the temperature remains below 125 K [7]. The maximum  $T_c$  for this pressure-stabilized structure is 8 K, with increasing pressure leading to a decreasing  $T_c$  [8].

While this difference in crystal structure clearly correlates with the reduction in  $T_c$ , the physical mechanism by which this more than fivefold suppression in  $T_c$  occurs has not been established. We have previously inferred [9]

from the sharp change in the temperature dependence of the Hall coefficient below 20 K that an additional phase transition of apparently electronic origin may occur near 20 K in ambient-pressure low- $T_c$  phase  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>. We present here direct calorimetric evidence for a phase transition at 22.25 K in the ambient-pressure low- $T_c$  phase, in excellent agreement with our Hall-effect measurements. We argue that this new transition suppresses the superconducting critical temperature in the low- $T_c$  phase by reducing the available electronic density of states.

Single crystals of  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> were grown by the standard electrochemical method.  $\beta$ -phase crystals were distinguished from those of the  $\alpha$  phase (which grows under similar conditions) by measuring the electron spin resonance (ESR) linewidth [10]. Preliminary calorimetric measurements were made on a thick 4.75-mg bicrystal; subsequent detailed calorimetric measurements were made on a 117-mm-thin, 0.61-mg single crystal. The heat capacity was measured from 4 to 300 K using an ac calorimeter described elsewhere [11]. Care was taken to ensure that the heat capacity data were taken in the appropriate frequency range for each temperature. The heat capacity of a 105-mm-thin 0.85-mg (99.99%) Cu standard was also measured in the same temperature ranges presented below to check the absolute sensitivity of the calorimeter (in mJ/K) and to verify the absence of spurious peaks and jumps in the specific heat.

In Fig. 1, we show the total specific heat (in relative units) versus temperature passing through the 175-K order-disorder transition for the 4.75-mg sample at ambient pressure. As noted above, the ethylene groups that were disordered at room temperature (and ambient pressure) undergo long-range order at 175 K, forming a superlattice that is incommensurate with the underlying crystal structure. The superstructure persists (with a temperature-dependent wave vector) at all  $T < 175$  K for ambient-pressure cooled  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> [3].

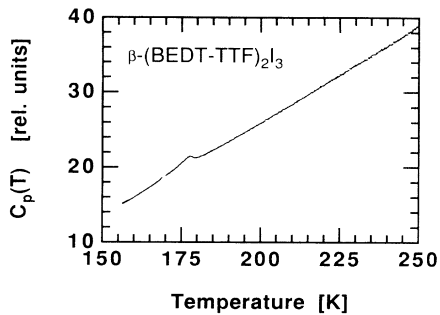


FIG. 1. Specific heat  $C_p(T)$  (in relative units) vs temperature  $T$  through the (second-order) order-disorder phase transition for a 4.75-mg crystal of  $\beta$ -(BEDT-TTF) $_2$ I $_3$  at ambient pressure. Below 175 K, previously disordered ethylene groups on the ends of the BEDT-TTF molecular cations undergo long-range orientational order, forming a superlattice that is incommensurate with the underlying crystal structure.

It is interesting to compare the small jump in the specific heat at this second-order structural phase transition in  $\beta$ -(BEDT-TTF) $_2$ I $_3$  with that observed at 136 K in  $\alpha$ -(BEDT-TTF) $_2$ I $_3$  [11]. In both the  $\alpha$  and the  $\beta$  phase of (BEDT-TTF) $_2$ I $_3$ , the BEDT-TTF molecular cations form parallel stacks along the crystalline  $a$  axis, but in the  $\alpha$  phase, these stacks are crystallographically *inequivalent*, doubling the size of the unit cell. In addition, all the ethylene groups in  $\alpha$ -(BEDT-TTF) $_2$ I $_3$  are ordered at room temperature. These differences in crystal structure lead to a first-order metal-insulator transition at 136 K with a jump in the specific heat  $\Delta C/C \approx 2$  in  $\alpha$ -(BEDT-TTF) $_2$ I $_3$  [11].

The formation of the incommensurate superstructure in ambient-pressure  $\beta$ -(BEDT-TTF) $_2$ I $_3$  leads to a small 8% shift in the magnitude of the Hall coefficient  $R_H(T)$  at 175 K [9,12]. Detailed measurements near 175 K confirm that the change in  $R_H(T)$  is not discontinuous but varies smoothly through the transition, in agreement with the second-order nature of the transition [12]. The metallic nature of  $\beta$ -(BEDT-TTF) $_2$ I $_3$  both above and below the 175-K transition is confirmed by the otherwise nearly temperature-independent Hall coefficient down to approximately 20 K. Below 20 K, however, the magnitude of  $R_H(T)$  abruptly decreases with decreasing temperature [9]. The anomalous low-temperature behavior of  $R_H(T)$  has also been observed in a later measurement at ambient pressure by another group [13]. A relatively sharp change in the temperature-dependent thermopower occurs at this same temperature [14].

While we have suggested that the anomalous temperature dependence of  $R_H(T)$  is indirect evidence for a new electronic phase at 20 K [9], it has also been interpreted in terms of a smooth temperature-dependent change in the dominant electron-scattering mechanism within the same electronic phase [13]. To directly address the nature of the 20-K anomaly, we have measured the low-temperature specific heat of single-crystal  $\beta$ -(BEDT-

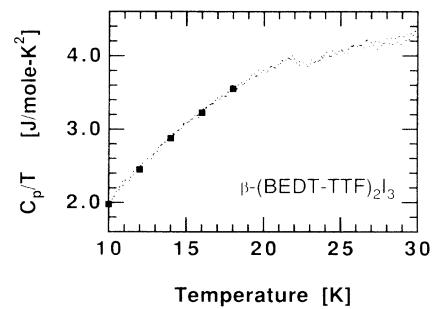


FIG. 2. Specific heat divided by temperature  $C_p/T$  (in J/mole K $^2$ ) vs temperature  $T$  from 10 to 30 K for a 0.61-mg crystal of  $\beta$ -(BEDT-TTF) $_2$ I $_3$  at ambient pressure, after cooling through the 175-K structural ordering transition. The absolute value has been fixed at 18 K to 3.55 J/mole K $^2$  [15]. Measurements of the specific heat above 10 K from Ref. [15] have been plotted as solid squares for comparison. A phase transition occurs just at 22.5 K; a corresponding anomaly occurs in the temperature dependence of the Hall coefficient.

TTF) $_2$ I $_3$  at ambient pressure.

In Fig. 2 we show the total specific heat divided by temperature (in J/mole K $^2$ ) versus temperature from 10 to 30 K for the 0.61-mg single crystal. We have scaled our ac specific heat measurements (in relative units) for the 0.61-mg single crystal to the absolute value of the specific heat at 18 K, as determined in Ref. [15]. Measurements of the specific heat above 10 K from Ref. [15] have been plotted as solid squares in Fig. 2 for comparison. A 4% jump in  $\Delta C/C$  occurs at  $T^* = 22.25$  K ( $\Delta C/T \approx 0.15$  J/mole K $^2$ ), indicating that a phase transition does in fact occur near 20 K. We have also observed a transition in the specific heat at the same temperature for the larger bicrystal. Measurements of the heat capacity (in mJ/K) of a 0.85-mg Cu standard in the same temperature range indicate that the jump in  $\Delta C/C$  is an order of magnitude larger than our sensitivity limit (better than 0.5% in  $\Delta C/C$ ) at the transition temperature.

The sharp changes at  $T^*$  in the temperature dependence of the Hall-effect and thermopower measurements—both of which are directly sensitive to changes in the electronic density of states—and the persistence of the orientational order superstructure down to 4 K suggest that the transition at  $T^*$  is primarily of electronic origin. For a BCS-type second-order electronic phase transition, we expect the change in the specific heat  $\Delta C$  at the transition relative to the total electronic specific heat  $C_{el} = \gamma T$  to be on the order of  $\Delta C/C_{el} \approx 1.43$  [16]. Here, we find that  $\Delta C/C_{el} = \Delta C/(\gamma T^*) \approx 6.25$ , much larger than would be expected. In contrast, we now show that assuming an entropy change  $\Delta S$  due to a reduction in the available electronic density of states below  $T^*$  allows us, for the first time, to quantitatively account for the suppression of the superconductivity in  $\beta$ -(BEDT-TTF) $_2$ I $_3$  from the pressure-stabilized high- $T_c$  value of 8 K to the

ambient-pressure cooled low- $T_c$  value of 1.5 K.

We can estimate the change in entropy by subtracting the temperature-dependent background of  $C/T$  from the measured value and integrating with respect to  $T$ . Arbitrarily fitting the background between 15 and 28 K to a cubic polynomial in  $T$ , we find an approximate entropy removal  $\Delta S_{\text{obs}} \approx 0.2$  J/moleK, corresponding to 40% of  $\gamma T^*$ . If we take  $\Delta S_{\text{obs}}$  to be electronic in origin, then the entropy change is on the order of 40% of that expected for removing all the electronic states at  $T^*$ .

If we assume the applicability of the BCS model to this system, then the electronic density of states  $N(0)$  can be related to the superconducting transition temperature  $T_c$  through the BCS relation

$$T_c = 1.13\Theta_D \exp[-1/N(0)V], \quad (1)$$

where  $\Theta_D$  is the Debye temperature and  $V$  is a measure of the electron-phonon coupling strength [16]. For purposes of illustration, assume a constant  $V$  and  $\Theta_D$ . A suppression of  $T_c$  from 8 to 1.5 K would correspond to a decrease in the electronic density of states  $N(0)$  of 46%, in good agreement with  $\Delta S_{\text{obs}}$ . In organic superconductors such as  $\beta$ -(BEDT-TTF) $_2$ I $_3$ ,  $T_c$  is also expected to depend on the on-site Coulomb repulsion energy  $U$  and the effective intermolecular transfer energy  $t_{\text{eff}}$  [1]. In this "electron-molecular-vibration" model, suppression of  $T_c$  from 8 to 1.5 K would correspond to a slightly larger decrease in the electronic density of states  $N(0)$  of 51% [1,17]. In either model, an entropy change of the magnitude observed can account for the more than fivefold decrease in  $T_c$ .

Could a charge- or spin-density wave nest a large fraction of the Fermi surface at  $T^*$ , removing a substantial fraction of the available electronic density of states? Multiple electronic states, including charge-density waves (CDW), spin-density waves (SDW), and superconductivity are frequently observed in other classes of lower-dimensional organic conductors [1]. The apparent Shubnikov-de Haas (SdH) frequency in the low- $T_c$  state [18] is nearly twice that observed in the high- $T_c$  state [19], consistent with a reduction in the area of the Fermi surface due to partial nesting. The calculated Fermi surface [20], however, does not have a CDW or SDW nesting vector that would remove roughly 40% of the electronic density of states. Further, although ESR [10], NMR [21], and anisotropic susceptibility [22] measurements exhibit some qualitative temperature-dependent changes below 20–30 K, the traditional signatures for CDW or SDW formation (over all or most of the Fermi surface) have not yet been observed.

We now briefly outline two possible modifications that would allow all or part of the Fermi surface to remain metallic below  $T^*$ . The periodic potential created by the superstructure is expected to subdivide the Brillouin zone into new, open Fermi surfaces and smaller closed orbits, as shown in Fig. 3(a). Nesting of some or all of the open Fermi surface sheets [23] at  $T^*$  could reduce the single-

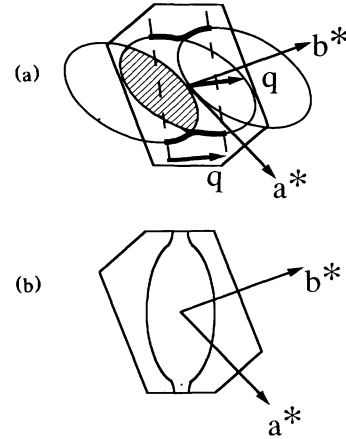


FIG. 3. Two possible modifications of Fermi surface of  $\beta$ -(BEDT-TTF) $_2$ I $_3$  at  $T=T^*$  in the basal plane of the first Brillouin zone. The ellipse (solid curve) is an approximation to the shape of the original Fermi surface [20(a)]. (a) Subdivision of the original first Brillouin zone (dashed lines) by the wave vector  $\mathbf{q}$ , creating new open and closed Fermi surfaces. The open Fermi surface (thick solid curves) is susceptible to nesting at  $T^*$ , but the closed Fermi surface pocket (hatched area) remains metallic. The wave vector  $\mathbf{q}$  is the projection of the 3D superstructure  $\mathbf{q} \approx (\mathbf{a}^* + 4\mathbf{b}^* + 3\mathbf{c}^*)/14$  formed at 175 K [3] into the  $\mathbf{a}^*$ - $\mathbf{b}^*$  plane. (b) Distortion of the Fermi surface [20(b)] at the Brillouin zone boundary to form (nearly closed) open orbits below  $T^*$ .

particle density of states available for superconductivity but allow un-nested closed metallic orbits to remain below  $T^*$ . This model requires the contribution from the un-nested metallic regions to the total ESR and NMR signals below  $T^*$  to dominate the contribution from the nested regions.

Alternatively, the closeness of the calculated Fermi surface—which resembles an eccentric ellipse [20]—to the Brillouin zone boundary suggests that a transition from a closed-orbit to open-orbit metal could occur at  $T^*$ . As the Fermi level shifts with temperature-dependent changes in the intermolecular transfer energies, it could become energetically favorable for the surface to transform from a closed-orbit to a (nearly closed) open-orbit metal [17], as shown in Fig. 3(b). This closed-to-open orbit metal transition model would explain the abrupt drop in  $R_H(T)$  [24] and the predominantly metallic nature of  $\beta$ -(BEDT-TTF) $_2$ I $_3$  below  $T^*$ , but the change in state density alone at  $T^*$  may not be sufficiently large to explain the fivefold suppression of  $T_c$ . In this case changes must also occur in  $U$  and  $t_{\text{eff}}$  [1]. To our knowledge, the presence or absence of open orbits in the low- $T_c$  phase of ambient pressure  $\beta$ -(BEDT-TTF) $_2$ I $_3$  has not yet been determined. SdH oscillations do not rule out this model, since they could arise from magnetic breakdown across the very small energy gap at the Brillouin zone boundary.

In conclusion, we have presented direct calorimetric evidence for a new phase transition at  $T^* = 22.25$  K, below the 175 K orientational order-disorder transition and above the 1.5-K superconducting transition in ambient pressure  $\beta$ -(BEDT-TTF) $_2$ I $_3$ . The transition at  $T^*$  provides a direct mechanism for the previously explained suppression of  $T_c$  in the low- $T_c$  phase by reducing the effective electronic density of states below  $T^*$ . Pressure stabilization changes the crystal structure, suppressing  $T^*$  and enhancing  $T_c$ , by altering both the strength of coupling of the Fermi surface to the Brillouin zone and the possibilities for nesting. A definitive answer regarding the nature of the  $T^*$  transition will require careful calculations and measurements of the temperature and pressure dependence of the electronic band structure and Fermi surface of  $\beta$ -(BEDT-TTF) $_2$ I $_3$  and related (BEDT-TTF) $_2$ X superconductors.

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