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Enhanced Critical Temperature in a Dual-Layered Molecular Superconductor

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Abstract: Single-crystal X-ray diffraction has shown that the high-critical-temperature (T_c) phase of the filamentary molecular superconductor (BEDT-TTF)$_2$Ag(CF$_3$)$_4$(1,1,2-trichloroethane) [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene] contains layers of BEDT-TTF radical cations with alternating κ- and α'-type packing motifs. This molecule-based superconductor with dual BEDT-TTF packing motifs has a T_c five times higher than that of its polymorph that contains only κ-type packing.

The crystal structure of the high-critical-temperature (T_c) phase of the filamentary molecular superconductor (BEDT-TTF)$_2$Ag(CF$_3$)$_4$(TCE) [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene; TCE = 1,1,2-trichloroethane] has been determined by single-crystal X-ray diffraction. Superconductivity was discovered in this material over a decade ago with a T_c of 11.1 K,[1] which is within 0.5 K of the record for cation radical salts at ambient pressure. We now report that this material has a dual-layer structure that is unique among BEDT-TTF superconductors and reminiscent of the multilayer structure in the high-T_c cuprates.

Due in part to competition for intermolecular S···S and hydrogen-bonding interactions during the crystallization process, BEDT-TTF salts are susceptible to polymorphism. For example, we previously reported that the κ- and κ'-phases of (BEDT-TTF)$_2$Cu(CF$_3$)$_4$(1,2-dibromo-1-chloroethane) differ by the tilt pattern of the BEDT-TTF layers.[2] The packing motif of the electron donor molecules is critical for defining the electronic properties of these materials. The crystallization of kinetic phases provides a route to new structural motifs with potential for novel functionality.

In 1994, we introduced the use of organometallic anions as components of molecular superconductors with the discovery of the κ_L-(BEDT-TTF)$_2$M(CF$_3$)$_4$(solvent) (M = Cu, Ag, Au; solvent =1,1,2-trihaloethane) family, which has 15 members with T_c ranging from 2.1 to 5.8 K.[3] Among these plate-like crystals of the κ_L-phase, fibrous crystals with a higher T_c (7.2−11.1 K) were occasionally observed. Based on the normal-state resistivity behavior[4] and preliminary crystallographic data, this phase was denoted κ_H.[5]

The κ-type packing motif, which is characterized by an orthogonal arrangement of BEDT-TTF molecules,[6] frequently yields superconducting salts. κ-(BEDT-TTF)$_2$Cu(NCS)$_2$[7] and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br[8] are examples of κ-phase salts with T_c > 10 K. In contrast, the α'-motif is characterized by stacks of molecules that are alternately twisted with respect to the stacking axis.[9] The α'-(BEDT-TTF)$_2$X [X = Au(CN)$_2$, CuCl$_2$, AuBr$_2$] salts are Mott−Hubbard insulators with narrow bandwidth and weak antiferromagnetic coupling.[10,11] Of the hundreds of TTF-based cation radical salts that have been structurally characterized, only a handful possesses alternating layers with different packing motifs. Examples of dual-layered conductors include α-κ-(BEDT-TTF)$_2$Hg(SCN)$_3$,[12] β'-θ-(BEDT-TTF)$_2$C(SO$_2$CF$_3$)$_3$,[13] α-β''-(BEDT-TTF)$_4$[(NH$_4$)M(C$_2$O$_4$)$_3$]·(solvent),[14,15] (EDO-TTF)$_2$X (EDO-TTF = ethylenedioxytetrathiafulvalene; X = GaCl$_4$ and ReO$_4$),[16] and (TMET-STF)$_2$X (TMET-STF = trimethylene(ethylenedithio)diselenadithiafulvalene; X = ClO$_4$ and BF$_4$).[17,18] Of these, only (TMET-STF)$_2$BF$_4$ is a superconductor (T_c = 4.1 K).[18]

We report that κ_H-(BEDT-TTF)$_2$Ag(CF$_3$)$_4$(TCE) is the first example of a dual-layered BEDT-TTF superconductor and is more accurately described as κ-α'-(BEDT-TTF)$_2$Ag(CF$_3$)$_4$(TCE) (**1**). This material is also unique because a low-T_c polymorph exists in which all the BEDT-TTF layers exhibit κ-type packing. The current interest in multiband superconductors, such as MgB$_2$,[19] renders this finding especially intriguing. It is now clear that, for many families of superconductors, the antiferromagnetic and superconducting regions of the phase diagram lie in close proximity to each other.[20] It is therefore of interest to study the electronic coupling in systems with interleaved antiferromagnetic and superconducting layers.

Crystals of **1** were grown electrochemically, as previously reported.[1] We have found that a higher initial current density of 1.5 μA/cm^2 results in preferential growth of **1**. The κ_L-phase typically begins to grow several days later and frequently nucleates on crystals of **1**. This suggests that the higher T_c phase is a kinetic product and that the search for high-T_c superconductors may benefit from efforts to trap metastable phases through the use of novel crystallization methods, including the use of high pressure, temperature, current, etc. To date, it has not been possible to grow phase-pure crystals of **1** for bulk measurements, and mechanical separation is necessary to yield phase-enriched samples.

A filamentary crystal of **1** was separated from a bundle of needles. X-ray diffraction data from this crystal were collected with an Oxford Xcalibur3 diffractometer equipped with a Sapphire3 CCD. **1** crystallizes in the triclinic space group $P\bar{1}$, with a = 8.4136(6) Å, b = 13.2172(7) Å, c = 37.7991(16) Å, α = 90.220(4)°, β = 91.244(5)°, γ = 90.444(5)°, V = 4202.3(4) Å^3, Z = 4, T = 110 K, ρ_{calcd} = 2.034 g cm^{-3}, $R(F_0)$ = 0.0645 for 7164 reflections with $F_0 > 4\sigma$. These results were confirmed through use of the microcrystallography facility (ChemMatCARS, Sector 15) at the Advanced Photon Source.

As illustrated in Figure 1, the packing motif of the BEDT-TTF radical cations in the layer centered at z = 0 possesses a κ-type motif of orthogonal dimers. The packing in this layer is quite similar

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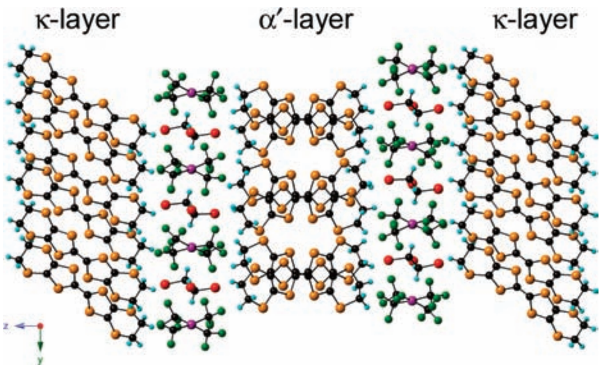

Figure 1. Dual-layer packing motif of **1**. The BEDT-TTF molecules in the layer centered at $z = 0$ possess a κ-type packing motif, while those in the layer centered at $z = 0.5$ possess an α′-type packing motif. The anionic layers contain $[Ag(CF_3)_4]^-$ and TCE solvent molecules.

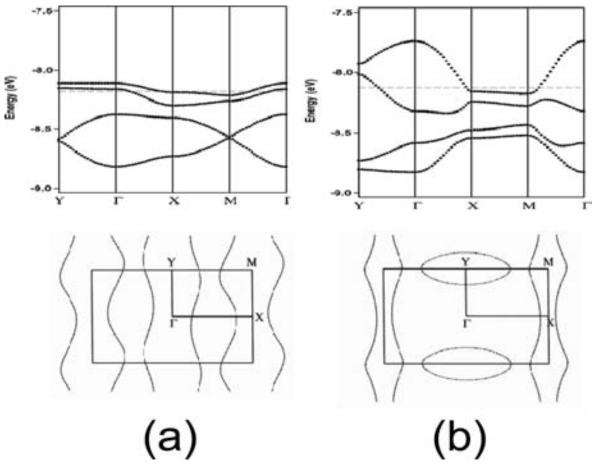

Figure 2. Band dispersion (above) and Fermi surface (below) obtained for the (a) α′-type and (b) κ-type layers of **1** from EHTB calculations, which include effects of charge separation in the α′-type layer.

to that present in the κ_L-(BEDT-TTF)$_2$Ag(CF$_3$)$_4$(TCE) salt that has a T_c of 2.4 K. The BEDT-TTF layer centered at $z = 0.5$ possesses an α′-type packing motif with twisted stacks of BEDT-TTF radical cations. Between these layers reside $[Ag(CF_3)_4]^-$ anions and TCE solvent molecules, which, in contrast to the κ_L-phase, are both crystallographically ordered.

Using the established empirical correlation between the C−S and C═S bond lengths and the donor charges in the BEDT-TTF salts,[21] the oxidation states of the BEDT-TTF molecules in **1** have been calculated. All molecules in the κ-type layer have an oxidation state of about +0.5(1), providing a uniform charge distribution within this layer. Within the α′-type layer, half of the molecules are nearly fully oxidized to +1.0(2), while the other half are close to neutral, resulting in a possible charge-ordered insulating layer. A highly 2D superconductor would thus be expected. This is different from the case of the dual-layered (TMET-STF)$_2$BF$_4$ superconductor, where the TMET-STF molecules in both layers have a formal charge of approximately +0.5.

The electronic structures obtained for isolated α′-type and κ-type layers from extended Hückel tight-binding (EHTB) calculations[22] are summarized in Figure 2, where the dispersion relations are shown only for the four bands arising largely from the HOMOs of four BEDT-TTF molecules per unit cell. The HOMO bands are narrower for the α′-type than for the κ-type layer. In addition, the α′-type layer has one-dimensional (1D) Fermi surfaces, while the κ-type layer has both 1D and two-dimensional (2D) Fermi surfaces.

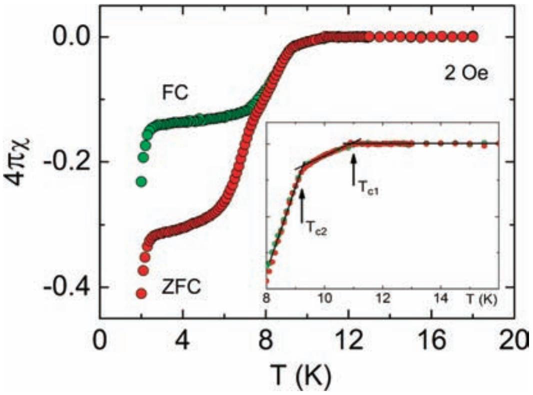

Figure 3. Magnetic susceptibility for **1** taken in ZFC and FC measurements as described in the main text. Inset: Cut-out of the data around the two-step superconducting transition. T_{c1} and T_{c2} correspond to the crossing points of the linear extrapolations.

These aspects are the same as found for the α′- and κ-type salts of BEDT-TTF. Each α′-type layer adopts a magnetic insulating state rather than a metallic state because its partially occupied bands are narrow.[23]

The magnetic susceptibility of the specimens was measured using a SQUID magnetometer (Quantum Design MPMS). The measurements were taken on a set of randomly orientated microcrystals, with a total mass of 3.00 mg, according to the following protocol: after cooling the specimens to 2 K at zero field (a small remanent field of about 7.6 Oe was compensated by applying a correspondingly large offset field), a magnetic field of 2 Oe was applied, and the dc magnetization was measured upon warming to 18 K (Figure 3, zero-field-cooled (ZFC) curve). After this run, measurements were taken on cooling at 2 Oe (field-cooled (FC) curve). While the ZFC signal can be assigned to the shielding effect, the FC signal provides only a lower bound for the Meissner effect due to the material's potentially small and anisotropic lower critical field H_{c1} and corresponding effects of trapped vortices. The shielding effect lacks any sign of saturation even at 2 K, the lowest temperature of our experiment, but rather shows a further decrease with an onset around 2.5 K. This may indicate that some portion of the crystals contain an admixture of the κ_L-phase. The ratio of the FC to the ZFC signal of ∼48% at 2 Oe decreases to ∼28% and ∼23% by increasing the field to 5 and 10 Oe, respectively. This indicates that flux trapping is still active and gives rise to a reduced FC signal. An extrapolation to vanishingly small field yields a FC/ZFC fraction of over 70%, consistent with bulk superconductivity. As illustrated in the inset of Figure 3, the data reveal two transition temperatures with $T_{c1} \approx 9.2$ K and $T_{c2} \approx 11.1$ K,[1] defined by the intercepts of linear extrapolations from temperatures below and above. These features, which have been reproduced in detail on all crystals from four batches investigated, confirm the previously observed two-step superconducting transition in this material.[1]

It will be important to understand why the T_c of **1** is nearly five times higher than that of its κ_L-(BEDT-TTF)$_2$Ag(CF$_3$)$_4$(TCE) polymorph, in which every (rather than every other) layer has κ-packing. It is tempting to suggest that this may be a result of either the ordered arrangement of the anions and solvent molecules in the charge-compensating layers of **1** or some kind of electronic coupling between the "superconducting" and "antiferromagnetic" subsystems. Likewise, the nature of the two-step superconducting transition and its relation to the two subsystems will need to be clarified.

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Supporting Information Available: Crystallographic information file for **1**; thermal ellipsoid plots of the molecular components with atomic numbering scheme, calculated partial oxidation states, and packing diagrams of the BEDT-TTF and anionic layers; complete refs 1 and 4. This materials is available free of charge via the Internet at http://pubs.acs.org.

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