80 K anomaly and its effect on the superconducting and magnetic transition in deuterated \( \kappa-(\text{BEDT-TTF})_2\text{Cu}[\text{N(CN)}_2]\)Br

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In this paper, we report careful transport and magnetic measurements on single crystals of deuterated \( \kappa-(\text{ET})_2\text{Cu}[\text{N(CN)}_2]\)Br. By cooling the sample at different rates, it is found that cooling through 80 K has a dramatic effect on the normal state metal-insulator transition and the superconducting transition temperatures. In-plane resistivity depends strongly on the cooling rate for temperatures below 80 K, above which all resistivity curves cooled at different rates converge. By comparing it with the nondeuterated salt and the quasi-1D Bechgaard salt, we speculate that 80 K corresponds to a structural phase transition in the anion chain. Fast cooling through 80 K will freeze the high temperature magnetic phase to low temperatures and the presence of local magnetic moments suppresses the superconducting \( T_c \).

The low temperature ground state of the organic \( \kappa-(\text{BEDT-TTF})_2\text{X} \) [BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene, abbreviated as ET] is known to depend on the anion, \( \text{X} \), and the pressure.\(^1\text{-}\text{4,7}\) At ambient pressure, \( \kappa-(\text{ET})_2\text{Cu}[\text{N(CN)}_2]\)Cl is an insulator with an antiferromagnetic ground state with a Néel temperature of 27 K. Under a pressure of 0.3 kbar, it superconducts at the highest transition temperature, 13 K, in the ET family. \( \kappa-(\text{ET})_2\text{Cu(NCS)}_2 \) and \( \kappa-(\text{ET})_2\text{Cu}[\text{N(CN)}_2] \)Br, on the other hand, have superconducting ground states with \( T_c \) of 10 K and 11.6 K, respectively. \( T_c \) decreases with increasing pressure at a typical rate of \( \sim 3 \text{ K/kbar} \). Deuterated \( \kappa-(\text{ET})_2\text{Cu}[\text{N(CN)}_2] \)Br, however, is presumably at the boundary between the magnetic and superconducting phases, with both superconducting and magnetic transitions.\(^4,5\)

The anion and pressure dependence are very similar to the quasi-one-dimensional Bechgaard salts \( \text{TMTSF}_2\text{X} \), where TMTSF denotes tetramethyltetraselenafulvalenium; \( \text{X} = \text{ClO}_4, \text{PF}_6 \) with a ground state bordering the superconducting state and magnetic spin-density-wave state.\(^3,8\text{-}11\) Furthermore, in \( \text{TMTSF}_2\text{ClO}_4 \), the ground state is also found to depend strongly on the cooling rate with a superconducting ground state when slowly cooled and an insulating magnetic state when cooled rapidly. X-ray diffraction and neutron scattering measurements reveal that the thermal history dependence of the ground state arises from a structural phase transition in the one-dimensional (1D) molecular stacks of anions.\(^10,11\) The presence of the polymeric anion chain in the quasi-two-dimensional \( \kappa-(\text{ET})_2\text{X} \) system, especially the deuterated \( \kappa-(\text{ET})_2\text{Cu}[\text{N(CN)}_2] \)Br, calls for a close examination of possible ordering of the chains.

In this paper, we report careful transport and magnetic measurements on several deuterated \( \kappa-(\text{ET})_2\text{Cu}[\text{N(CN)}_2] \)Br samples. By cooling the sample at different rates, it is found that cooling through 80 K has a dramatic effect on the normal state metal-insulator transition and the superconducting transition temperature. In-plane resistivity depends strongly on the cooling rate for temperatures below 80 K, above which all resistivity curves cooled at different rates converge. The cooling rate dependence is very analogous to that of the Bechgaard salt. We speculate that 80 K corresponds to a structural phase transition temperature in the anion chain. Cooling through 80 K at different rates will freeze the high temperature magnetic phase to low temperatures and the presence of local moments suppresses the superconducting transition temperature.

Single crystals of the deuterated \( \kappa-(\text{ET})_2\text{Cu}[\text{N(CN)}_2] \)Br superconductor were synthesized at the Argonne National Laboratory as described elsewhere.\(^12\) Several crystals were used in this study. The interlayer resistance was measured with use of the four-probe technique. Contact of the gold wires to the sample was made with a Dupont conducting paste. Typical contact resistance between the gold wire and the sample was about 1–10 \( \Omega \). A current of 1–10 \( \mu \text{A} \) was used to ensure linear \( I-V \) characteristics. The room temperature resistivity was (2 ± 0.25) \( \Omega \text{ cm} \). The sample was initially cooled slowly from room temperature to liquid helium temperature over 3 h. Subsequent coolings were done by warming up the sample slowly from below 10 K to about 140 K, and then cooled at different rates to below 10 K by pumping helium vapor in the sample space. The data were taken while the sample was slowly warmed up. Magnetic measurements were done with a Quantum Design SQUID magnetometer. Each measurement was done with the sample cooled in zero field to 5 K and magnetizations were done in an applied field of 1 Oe.

Figure 1 shows the resistivity as a function of temperature, \( \rho(T) \), for the sample cooled initially from a high temperature and subsequently raised to and cooled from several low temperatures of \( T_q = 35 \text{ K, 55 K, and 67 K} \). The data clearly overlap with one another in the same temperature range, independent of \( T_q \) and the cooling rate. Similar low \( T_q(< 80 \text{ K}) \) independence was observed when the sample was initially cooled at different rates from high temperatures.
For $T_q$ above 80 K, $\rho(T)$ is found to depend strongly on the cooling rate. Shown in Fig. 2 is a plot of $\rho(T)$ for the sample cooled down from 140 K at five different cooling rates. The five different curves marked 1 to 5 correspond to a cooling rate at 1 K/min, 10 K/min, 15 K/min, 30 K/min, and 60 K/min, respectively. The cooling rate is defined as the $dT/dt$ at around 80 K since the temperature does not decrease linearly with time. It is clear from the data that at $T > 80$ K, $\rho(T)$ curves branch out. The resistivity as well as the peak position changes according to the cooling rate. For $T > 80$ K, $\rho(T)$ curves overlap, regardless of the cooling rate. The inset is a plot of the peak resistivity, $\rho_{\text{peak}}$, versus the peak temperature, $T_{\text{peak}}$. A monotonic increase in $\rho_{\text{peak}}$ with decreasing $T_{\text{peak}}$ is observed.

The cooling rate has dramatic effect on the low temperature $\rho(T)$ and superconducting transition temperature $T_c$. Shown in Fig. 3 is an expanded view of the low temperature part of the data. Several features are clear: (a) The low $T$ resistivity increases with increasing $dT/dt$; (b) the superconducting transition temperature shifts lower with increasing $dT/dt$; (c) the $\rho(T)$ for the slowly cooled sample displays stronger semiconducting behaviors near $T_c$ and resistive jumps above $T_c$.

If we define the $T_c$ as the temperature where $\rho$ drops to 50%, 75%, and 90% of resistivity at 12 K, the $T_c$ is found to decrease quasilinearly with increasing $\rho(12 \text{ K})$, as shown in Fig. 4. The choice of resistivity at 12 K is somewhat arbitrary because of the temperature dependence above $T_c$, especially for the slowly cooled sample. Nevertheless, it gives a good qualitative description of the cooling rate dependence of $T_c$.

Similar cooling dependent magnetization measurements have been performed on another deuterated single crystal sample. Shown in Fig. 5 is an overlay of magnetization as a function of temperature for the sample cooled at different $T_q$’s. For $T_q \leq 78$ K, $M(T)$ basically overlaps. For 80 K $\leq T_q \leq 100$ K, $M(T)$ decreases in magnitude with increasing $T_q$. For $T_q \geq 100$ K, $M(T)$ curves of different $T_q$ are indistinguishable. It is clear that the $M(T)$ for the slowly cooled sample has the highest onset $T_c$ and the onset transition temperature gradually decreases once $T_q$ is greater than 80 K. Similar to the resistivity data, if the sample was initially cooled at different rates from high $T$, $M(T)$ for the low $T_q(< 80 \text{ K})$ will overlap with the $M(T)$ of the initial data.

The $T_q$ and cooling rate dependence of the resistivity and magnetization for the deuterated sample is very similar to the cooling rate dependence of resistivity in the (TMTSF)$_2$ClO$_4$.
Qualitatively similar cooling rate dependence has been observed for the Bechgaard salt; its superconducting transition temperature decreases with increasing cooling rate. Measurements of specific heat jump at the superconducting transition find that \( T_c \) as well as the volume fraction of superconducting phase decreases with increasing cooling rate.

The similarity suggests that 80 K is related to a possible structural phase transition. The nature of the transition is unclear. Several related anomalies have been reported in the nondeuterated compound.\(^9\) When cooled rapidly through 24 K, the resistivity of the Bechgaard salt is found to depend strongly on the cooling rate for \( T<24 \text{ K} \) and merges for \( T>24 \text{ K} \). The origin for the cooling rate dependence is associated with a structural phase transition of the anion chain at 24 K. Measurements of specific heat jump at the superconducting transition find that \( T_c \) as well as the volume fraction of superconducting phase decreases with increasing cooling rate.

The low temperature resistivity jumps may be signatures of antiferromagnetic transition. It is not clear how the resistivity near \( T_c \) is related to the cooling rate or volume fractions of the superconducting and magnetic phases. At first sight, it might be contradictory to the picture of an increasingly larger magnetic volumes since the upturn in \( \rho(T) \) is less pronounced with increasing cooling rate, somewhat similar to the reduced moment from the dc susceptibility measurement.\(^3\) However, it may be plausible that disordered magnetic state will contribute to the observed temperature dependence. Another possibility is that the measured resistivity in this temperature range is not intrinsic due to the nature of the mixed phases. The presence of various current paths might complicate the measured quantity.
Like its quasi-1D counterpart, rapid cooling through 80 K not only reduces the superconducting fraction, it suppresses the superconducting transition temperature as well. With increasing cooling rate or increased resistivity, the superconducting transition curves shift toward zero. The quasilinear $T_c$ dependence on $\rho(12 \text{ K})$ is qualitatively similar to the $T_c(\rho)$ in the nondeuterated compound.\textsuperscript{15} Although it is noted that the resistivity above $T_c$ is very flat for the nondeuterated compound, $\rho$ is rather temperature dependent for the deuterated system. Nevertheless, the similarity suggests that the reduction in $T_c$ may be of the same origin.

The linear dependence on $\rho$ implies that $\Delta T_c \sim 1/\tau$; here $\tau$ is the relaxation time of charge carriers. For nonmagnetic impurities at small concentrations, Anderson’s theorem that the $T_c$ is little affected by the amount of disorders works for most metallic superconductors. For dirty superconductors in the strong coupling limit, the $T_c$ is found to increase or decrease with an increasing residual resistivity $\rho$, dependent on the $T_{c0}$, the transition temperature in the clean limit.\textsuperscript{20} For various materials, $\delta T_c/\rho$, where $\tau=\left(T_c-\frac{T_{c0}}{2}\right)/T_{c0}$, was found to have a magnitude of $(1-100) \text{ m}\Omega \text{ cm}^{-1}$. For the organic superconductor studied here, a similar calculation would yield $\delta T_c/\rho \sim 2 \times 10^{-4} \text{ m}\Omega \text{ cm}^{-1}$. The very small $\delta T_c/\rho$ suggests against the dominant role of nonmagnetic disorders in the organic materials. In the presence of a secondary antiferromagnetic (AFM) phase, it is not clear how $T_c$ will be affected. One possibility is that the local moment due to canted spins in the AFM state will introduce spin scatterings. Another possibility is that the rapid cooling may induce localized moments such as the Cu$^{2+}$ ions in the superconducting phase. Both cases will give rise to a reduced $T_c$ (Ref. 21) and $\Delta T_c \sim \rho$. However, if we assume the cooling introduces a similar amount of the Cu$^{2+}$ ions, the fact that $\Delta T_c \sim 2 \text{ K}$ in the deuterated compound is much larger than a mere 0.5 K in the nondeuterated sample favors the former scenario. Another possibility, that the reduced $T_c$ may be related to an unconventional pairing mechanism, needs further exploration.

In summary, we have reported detailed transport and magnetic measurements and their cooling rate dependence in the deuterated $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br. Comparisons with the nondeuterated and the quasi-1D system demonstrate unequivocally a phase transition near 80 K, most likely in the anion chain. Rapid cooling through 80 K suppresses the superconducting phase and increases the magnetic phase. The reduction in $T_c$ may arise from the spin scattering of the canted moment in the antiferromagnetic phase. This calls for a careful structural determination in the $\kappa$-(ET)$_2X$ family and the role of anion chains in the interplay of superconductivity and magnetism.

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