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Structural disorder and its effect on the superconducting transition temperature in the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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In this paper, we report direct evidence of a structural transition in the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br near 80 K and the effect of disorder on the superconducting transition temperature. By cooling the sample from above 80 K, the interlayer magnetoresistance displays a bumplike feature, which increases sharply with increasing cooling rate. The rapidly cooled sample has a much larger resistivity and a lower transition temperature, which decreases linearly with increasing resistivity near the transition temperature. We propose that rapid cooling quenches the sample into a disordered state. Localized moments in the disordered state reduce the superconducting transition temperature. [S0163-1829(98)51522-6]

Charge transfer salts κ-(BEDT-TTF)$_2X$ [BEDT-TTF =bis(ethylenedithio)tetrathiafulvalene, abbreviated as ET], with X being $Cu(NCS)_2^-$, $Cu[N(CN)_2]Br^-$, and $Cu[N(CN)_2]Cl^-$, exhibit interesting magnetic and superconducting phase transitions.[1–5] They have a layered structure with alternating sheets of metallic (dimerized ET molecules) and insulating (anion, X) planes. κ-(ET)$_2$Cu(NCS)$_2$ and κ-(ET)$_2$Cu[N(CN)$_2$]Br are ambient pressure superconductors with the superconducting transition temperature T_c around 10 K and 11 K, respectively. The transition temperature is strongly dependent on the applied pressure with a typical $dT_c/dP \approx -3$ K/kbar.[6] Recent ^{13}C NMR and transport studies of κ-(ET)$_2$Cu[N(CN)$_2$]Br unveiled antiferromagnetic fluctuations in the normal state.[1,2] κ-(ET)$_2$Cu[N(CN)$_2$]Cl is an antiferromagnetic insulator at ambient pressure and becomes a superconductor with the highest T_c of 13 K under a slight pressure of 0.3 kbar.[6] The large pressure dependence demonstrates the critical role of lattice structure in the determination of magnetic and superconducting transitions, and calls for a careful investigation on the effects of structural defects.

In this paper we report studies of the effect of the cooling rate on the interlayer transport properties as well as its effect on T_c. By freezing the sample into different disordered states, we find that there is strong evidence for a structural transformation at around 80 K. Resistivity for the quenched sample increases with increasing cooling rate and T_c decreases linearly with increasing resistivity. The quenched state is also unstable against thermal fluctuations and decays gradually toward an equilibrium state.

Single crystals of the κ-(ET)$_2$Cu[N(CN)$_2$]Br superconductor were synthesized at the Argonne National Laboratory as described elsewhere.[7] Several crystals were used in this study. Data on one sample cooled at different rates are presented here. The interlayer resistance was measured with use of the four-probe technique. Contacts of the gold wires to the sample were made with a Dupont conducting paste. Typical contact resistance between the gold wire and the sample was about 1–10 Ω. A current of 1–10 μA was used to ensure linear I-V characteristics. The room temperature conductivity was $(1.5 \pm 0.1) \times 10^{-2}$ S cm^{-1}. 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.

Figure 1 is an overlay of interlayer resistivity as a function of temperature for a sample cooled at different rates. Clearly the resistivity curves separate out below about 80 K. The lowest curve, No. 1, corresponds to the slowest cooled sample (over 5 h from 140 K to below T_c). The curves, No. 2 to No. 5, shift upward in the sequence of increasing cooling rate at 1 K/min, 5 K/min, 20 K/min, and 60 K/min,

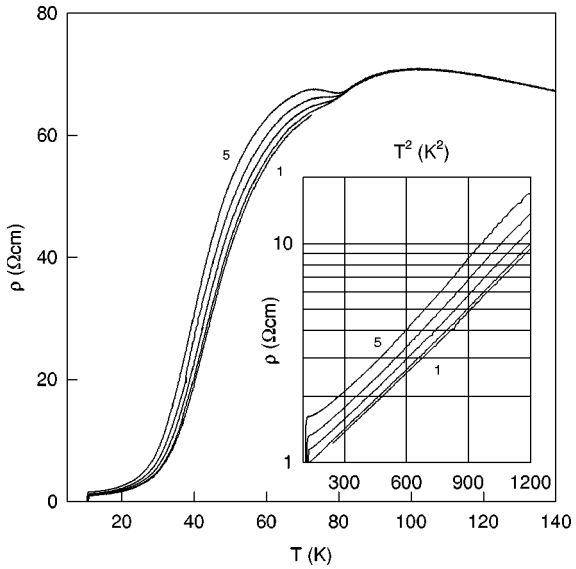

FIG. 1. An overlay of resistivity as a function of temperature for a sample cooled at different rates. The inset is a semilog plot of ρ versus T^2 at low temperatures.

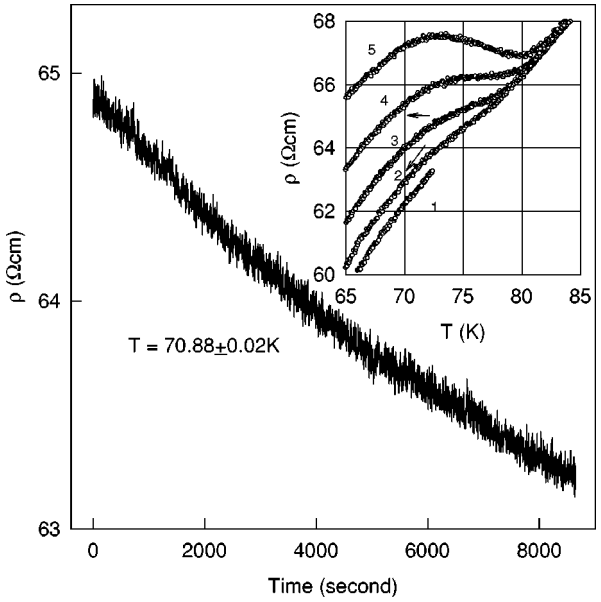

FIG. 2. Relaxation of resistivity at 70.88 K as a function of time. The inset is an expansion of temperature dependence of ρ near 80 K.

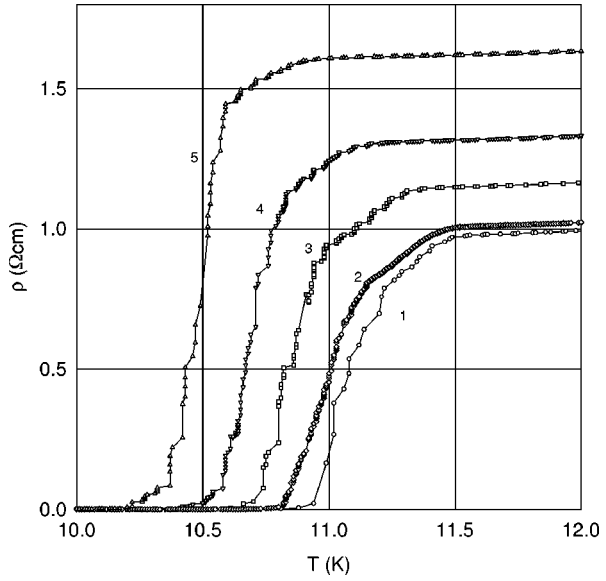

FIG. 3. Resistivity as a function of temperature near the superconducting transition for the sample cooled at different rates.

respectively. The No. 5 curve clearly shows a local maximum R near around 70 K. Above 80 K, all curves collapse into a single one, independent of the cooling rate, with a broad peak at 100 K. The inset shows an expanded view of the low temperature (10–34 K) resistivity as a function of T^2 in a semilog scale. The nearly parallel curves suggest that the resistivity can be fitted with $\rho(T)=\rho_0\exp(T/T_0)^2$ with $T_0=21$ K.

Figure 2 shows a typical time dependence of resistivity as a function of time. Here the measurement was done by cooling the sample from above 100 K to 70 K rapidly. The data were taken over a period of 2 h after the sample was stabilized at 70.88 ± 0.02 K in approximately 10 min. Because of the temperature fluctuations, the initial state was not well characterized. However, the data demonstrate clearly a relaxation of the system from a frozen state toward a thermal equilibrium state with resistivity decreasing monotonically. Shown in the inset is an expanded plot of Fig. 1 near 70 K. The relaxation from about 65 Ω cm to about 63 Ω cm corresponds approximately to a change from the fourth curve to the second curve, as shown by the arrows.

The cooling rate has a considerable effect on the superconducting properties as well. Shown in Fig. 3 is an overlay of the five resistive transitions curves with the same number assignment as in Fig. 1. The top curve corresponds to the most rapidly cooled sample, and the bottom curve the slowest cooled sample, with the top curve having about 60% higher resistivity than the bottom one. Clearly, the increasing cooling rate and consequently higher resistivity lead to a decreasing superconducting transition temperature.

If we choose the superconducting transition temperature as the temperature where resistivity has decreased to 50%, 75%, and 90% of resistivity at 12 K, we can plot thus defined T_c as a function of resistivity at 12 K, as shown in Fig. 4. Clearly, the T_c increases with decreasing ρ (12 K) monotonically. Except for the lowest resistivity point, four other points lie nicely in a straight line. The $T_c(\rho)$ lines defined with different criteria are parallel to each other.

The cooling rate dependence of the resistivity below 80 K and the independence above it suggest strongly a structural transition at this temperature. Above 80 K, the resistivity overlaps regardless the thermal history, with a peak at 100 K. While the 100 K resistivity maximum has been widely discussed as a Mott metal-insulator transition due to lattice contraction, the independence on cooling rate suggests that the π band is not affected by the process at 80 K.[8] In other words, the ET dimers are ordered at much higher temperature. Below 80 K, resistivity curves branch out depending on the cooling rate. It is worth pointing out that because the data were taken during the warming up of the sample slowly from below 10 K, the system has undergone considerable relaxation, especially near 80 K. The relaxation is dependent on the temperature and quenched state, as shown in the inset of

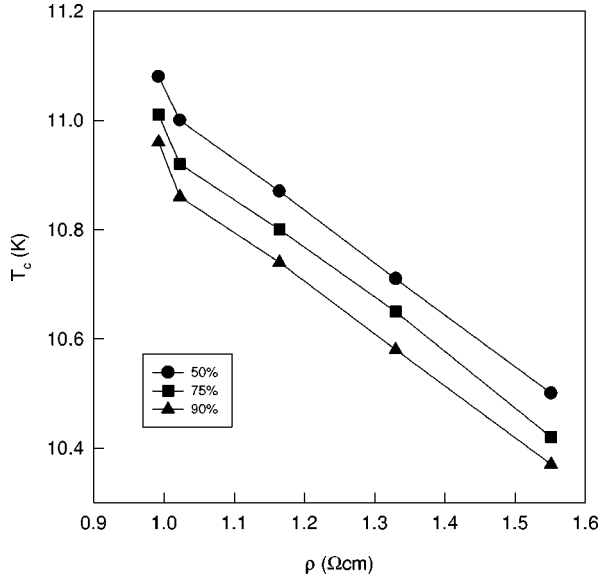

FIG. 4. The resistive transition temperature as a function of resistivity at 12 K.

Fig. 1 by the nearly parallel line of resistivity at low temperatures. Although the exponential T^2 dependence of resistivity is not understood at this point, it is possible that it is related to the antiferromagnetic fluctuations observed for this and similar compounds.[1,2]

Several closely related phenomena have been reported recently. Kund and co-workers have reported an anomalous jump in thermal expansion coefficient of lattice parameters, $\alpha=(1/l)(dl/dT)$, at 80 K.[9,10] In the direction along the polymer chain, a axis, the jump in α, $\Delta\alpha$, is found to be -8×10^{-5} K^{-1}. They attributed it to an order-disorder transition of the ethylene molecule due to its interaction with the polymeric anions. A dip in resistivity at this temperature has also been observed by several groups.[9–11] Very recently, effects of cooling rate have been studied in the deuterated κ-$(ET)_2Cu[N(CN)_2]Br$ compound.[4] From magnetic susceptibility and NMR measurements, Kawamoto *et al.* reported that rapid cooling through 80 K drives the superconducting phase into a magnetic phase. The disorder introduced by quenching disrupts the spin canting or the antiferromagnetic ordering.

Careful structural studies have been performed on the isostructural salts κ-$(BEDT\text{-}TTF)_2X$ with X being Cl, Br, and I.[12] Measurements show that there are two steric configurations for the ethylene groups. One configuration is the eclipsed arrangement of the end groups and the other is with a staggered arrangement. At room temperature, the ethylene groups are disordered. At 125 K, the x-ray diffractions show that ethylene groups for both $X=$Br and Cl compounds are ordered, while it remained disordered at 20 K for the $X=$I sample.[13] The data suggest that the 80 K anomaly is unlikely due to the order-disorder transition of the end groups. Recent relaxation measurements of resistivity at 77 K by quenching the sample from higher temperatures suggest that the order-disorder transition of the ethylene groups occurs at around 140 K, consistent with the x-ray results.[14] Other possible models of structural transition including a short range modulation and a superlattice structure have been proposed as well.[15,16]

While the origin of the 80 K anomaly is unclear, the presence of the jump in the a-axis thermal expansion coefficient at 80 K suggests strongly that quenching through 80 K will introduce some kind of lattice disorders. This can be pictured as an incomplete transition to the expanded lattice state when cooled rapidly through the transition. The disorders in turn lead to localizations of charge carriers and possibly localized magnetic moments. The effects of disorders on the superconducting transition temperature have been studied extensively.[17] For nonmagnetic disorders, Anderson's theorem that T_c is little affected by the amount of disorders works for most metallic superconductors. For dirty superconductors in strong coupling limit, the T_c is found to increase or decrease with an increasing residual resistivity ρ, dependent on the T_{c0}, the transition temperature in clean limit. The sign change in $dT_c/d\rho$ has been successfully explained as due to a competition between the attractive and repulsive effective electron-electron interaction.[18] For various materials, $\delta t/\rho$, where $t=(T_c-T_{c0})/T_{c0}$, was found to have a magnitude of $(1-100)(\mathrm{m}\Omega\,\mathrm{cm})^{-1}$. For the organic superconductor studied here, a similar calculation would yield $\delta t/\rho\sim-5\times10^{-4}(\mathrm{m}\Omega\,\mathrm{cm})^{-1}$. The extremely small $\delta t/\rho$ suggests the unlikelihood of decreasing T_c due to nonmagnetic disorders in the organic materials.

In the presence of magnetic impurities, the superconducting transition temperature has been shown to decrease linearly with the scattering rate[19] by $T_{c0}-T_c=(8\hbar/\pi k_B)(1/\tau)$, where $1/\tau$ is the scattering rate due to magnetic moments. If the disorders introduce localized moments, as suggested from the magnetic susceptibility measurements of Kawamoto *et al.*,[4] a reduction of T_c is expected due to spin scattering or pair breaking. Since the spin scattering rate is typically a small fraction of the potential scattering, $1/\tau$ can be assumed to be proportional to the total resistivity, i.e., $\rho=(m/ne^2)(1/\alpha\tau)$, with α being the fraction of spin to potential scattering. We can rewrite $T_{c0}-T_c=(8\hbar ne^2/m\pi k_B)\alpha\rho$. Using nominal numbers for the charge density and effective mass,[20] we find α in the order of 10^{-6}. It is also possible that a fraction of the disorders contains localized moments. In that case, the fractional contribution α of spin to lattice scattering will increase accordingly. Further measurements, such as H_{c2} as a function of T_c and comparative studies of other ET superconductors, are necessary to establish the picture.

In summary, we have reported a systematic study of the effect of cooling rate on the interlayer transport. The dependence of resistivity on cooling rate is consistent with a structural transition at 80 K. The structural disorders are likely to introduce localized moments, which suppress the superconducting transition temperature. Our results of T_c decreasing linearly with increasing resistivity are in agreement with the proposed picture.

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