Superconductor-insulator phase transformation of partially deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br by control of the cooling rate

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The electronic state of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is precisely controlled around the superconductor-insulator boundary by partial deuteration. As the salt approaches the boundary with progressive deuteration, the cooling rate influences the electronic state strongly; the low-temperature metallic phase is transformed into the insulating phase with collapse of the bulk superconductivity by the rapid cooling. This phenomenon is discussed in terms of the change in U/W and the possible effect of the disorder on the metallic (superconducting) phase near the Mott insulator, where U and W are the intradimer Coulomb repulsion and the bandwidth. [S0163-1829(99)01114-5]

A family of κ-(BEDT-TTF)$_2X$ show various electronic ground states depending on the anion (X). The salt of X = Cu[N(CN)$_2$]Cl is an antiferromagnetic insulator with a commensurate magnetic structure.[1] This is understood to be a Mott insulator driven by the strong electron-electron correlation. On the other hand, the salts with X = Cu[N(CN)$_2$]Br and Cu(NCS)$_2$ are superconductors with transition temperatures of 11.5 K (Ref. 2) and 9.5 K (Ref. 3), respectively. In the normal state of these salts, the presence of the antiferromagnetic spin fluctuations was indicated by the ^{13}C-NMR study.[4–7] The temperature dependence of the $(T_1T)^{-1}$ above 60 K is almost the same as that of the insulating Cu[N(CN)$_2$]Cl salt.[5] Thus these three salts have quite similar electronic states, at least, at high temperatures. The drastic difference in the ground state is caused by a slight change of the BEDT-TTF arrangement, which gives variation of the parameter U/W with U, the intradimer Coulomb repulsion, and W, the bandwidth.[8] This is based on the fact that the bandwidth is quite sensitive to the molecular arrangement in the conducting layer.

In this scenario it is considered that the Mott type critical boundary of the superconductor-insulator transition must exist in between the Cu[N(CN)$_2$]Br and Cu[N(CN)$_2$]Cl salts. One of the interesting subjects in this family is the critical phenomenon in the vicinity of the Mott transition. In our previous work,[9] deuteration of the BEDT-TTF molecules was found to be a promising way for this purpose. In reality, the fully deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br touches the Mott insulator region as evidenced by ^{13}C-NMR.[9] Recently we have succeeded in preparing the partially deuterated BEDT-TTF molecules and demonstrated that their Cu[N(CN)$_2$]Br salts interpolate between the nondeuterated and fully deuterated salts;[10] the progressive deuteration of the Cu[N(CN)$_2$]Br salt pushes the system toward the insulating side. This is because the contraction of the CD bond gives a slight modification to the molecular arrangement.[11] Now, we can control the Cu[N(CN)$_2$]Br system precisely in the vicinity of the Mott transition by the chemical method.

In the course of the study of the fully deuterated salts, the cooling rate through 80 K was found to affect the electronic phase.[9] The fast cooling further reduces the fraction of the minor superconducting phase, accompanied with decrease of the transition temperature.[9,12] The missing superconducting phase is transformed into a magnetic phase, that is, the Mott insulator. In the recent transport study,[13] the shift of the transition temperature was observed even in the nondeuterated Cu[N(CN)$_2$]Br salt. This is considered to be related to the two particular properties of the Cu[N(CN)$_2$]Br salt. One is that this salt is situated near the Mott transition. The other is the structural anomaly around 80 K which is characterized by the kink of the thermal expansion coefficient[14,15] and the kink with hysteresis in the resistive curve. So the cooling rate is another parameter which affects the electronic state of the Cu[N(CN)$_2$]Br salt.

In the present work, we have examined the cooling-rate effect in a series of progressively deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salts by the resistivity and ac susceptibility measurements at various cooling rates. The partially deuterated salts tuned to approach the Mott transition are found to get strong cooling rate dependence, where the metal-to-insulator transition is induced and the bulk superconductivity collapses. This phenomenon is discussed in terms of change in U/W and possible involvement of the disorder effect on the metallic phase near the Mott transition.

Single crystals of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (abbreviated κ-Br) were grown by the electrochemical oxidation of nondeuterated, partially, and fully deuterated BEDT-TTF molecules. The BEDT-TTF molecule has two ethylene

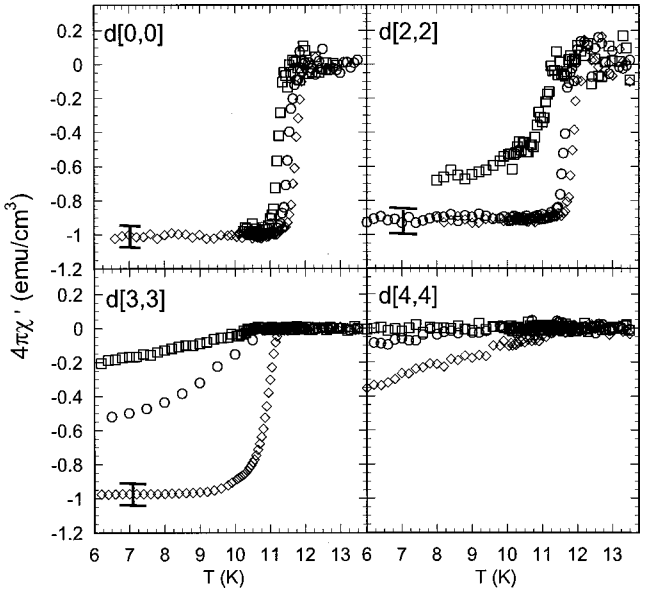

FIG. 1. ac susceptibility of $d[0,0]$-, $d[2,2]$-, $d[3,3]$-, and $d[4,4]$-κ-Br in the various cooling conditions. The data represented by open squares, circles, and diamonds are obtained in the conditions of rapid cooling (10 K/min), slow cooling (0.5 K/min), and annealing at 70 K for 12 h, respectively. The applied ac field is 5 mG in amplitude and 17 Hz in frequency in all the measurements.

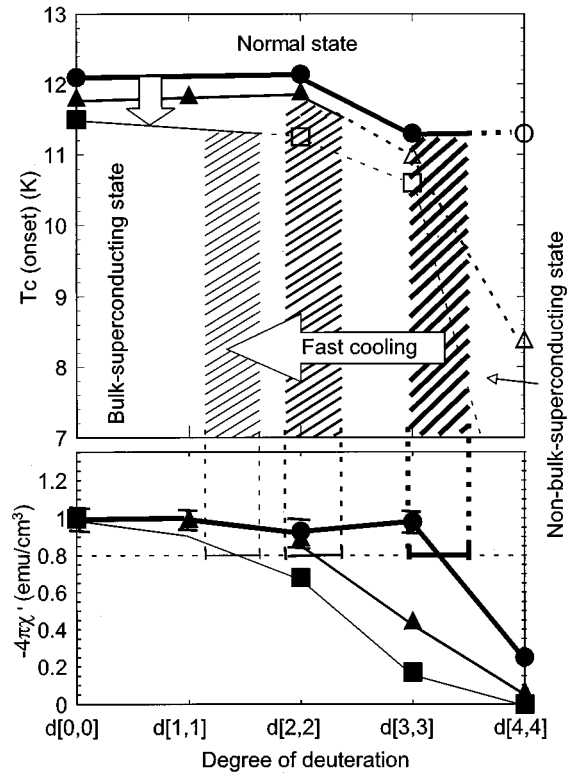

FIG. 2. Superconducting transition temperatures defined by the onset of the ac susceptibility (upper panel) and Meissner volume fraction at 8 K (lower panel) as a function of degree of deuteration. The circles (thickest line), triangles (intermediately thick line), and square (thin line) are in the annealed, slow cooled, and rapid cooled conditions, respectively. The open symbols in the upper panel are for the non-bulk-superconductivity. The bulk-nonbulk boundary is shown by the shaded region. For definition, see text. The arrows stand for the direction of the boundary shift by the increase of cooling rate.

groups, each of which contains four protons. In this paper, we use the notation of $d[n,n']$ to represent the number of the deuterium in each ethylene group. The details of the synthesis were given elsewhere.[10] The ac susceptibility and resistivity of these crystals were measured as functions of temperature and cooling rate from room temperature. The ac susceptibility $(\chi'-i\chi'')$ of a single crystal was measured with an ac field (5 mG in amplitude, 17 Hz in frequency) applied perpendicular to the conducting layer. The samples were mounted on the holder made by an insulating film with a small amount of grease. The resistivity was measured with the standard four-probe method, where the dc current (10 μA) was injected along the conducting plane. The gold wires of 15 μm in diameter were attached to the crystals with the gold paste. The samples were fixed on the holder with these lead wires. The measurements were performed at various cooling rates from room temperature.

Figure 1 shows the real part of the low-temperature ac susceptibility $(4\pi\chi')$ of the single crystals of $d[0,0]$-, $d[2,2]$-, $d[3,3]$-, and $d[4,4]$-κ-Br after cooled down at several speeds. The shapes of these crystals were approximated to ellipsoids with three different dimensions and then the ac susceptibility was corrected for the diamagnetizing factors according to the conventional formula.[16] In this procedure, ambiguity of about 10% of the full Meissner value is inevitable and is shown in the figure. The cooling conditions were rapid cooling (10 K/min), slow cooling (0.5 K /min), and annealing at 70 K for 12 h after the slow cooling. We also measured the ac susceptibility after an additional 12 h annealing at 70 K after the 12 h annealing, but the transition curves of the susceptibility did not change. So the 70 K annealing for 12 h is considered as the extremely slow cooling condition.

After the 12 h annealing, the $d[0,0]$, $d[2,2]$, and $d[3,3]$ samples show superconductivity with nearly full volume fraction, as seen in the figure, while $d[4,4]$-κ-Br is not a bulk superconductor although its onset is at 11.5 K. After the slow cooling, $d[0,0]$- and $d[2,2]$-κ-Br shows decrease of the transition temperature by ~ 0.2 K without deterioration of the sharpness and bulk nature of the transition. (The $d[1,1]$-κ-Br shows the similar profile of the transition, which is not shown in the figure.) For $d[3,3]$-κ-Br, however, one can see serious depression of the superconducting volume. For $d[4,4]$-κ-Br, the susceptibility reduces to as small as 10% of the perfect Meissner value. The fast cooling amplifies this effect. Although the effect on $d[0,0]$-κ-Br is still the decrease of the transition temperature alone, $d[2,2]$-κ-Br clearly loses the superconductiong volume. The loss of the superconducting phase is more drastic in $d[3,3]$-κ-Br. In $d[4,4]$-κ-Br we did not observe any appreciable diamagnetic signal. In this way, the control of the cooling rate and of isotope substitution leads to the transition from the full Meissner superconductor to the nonsuperconductor, which is very probably a magnetic insulator according to the previous NMR study.[8,9] This situation is depicted in Fig. 2, where the transition temperature defined by the onset of the transition curve and the value of $-4\pi\chi'(T=8\ \mathrm{K})$ characterizing the superconducting volume fraction are plotted in the upper and lower panels. The T_c line goes down as the cooling is faster.

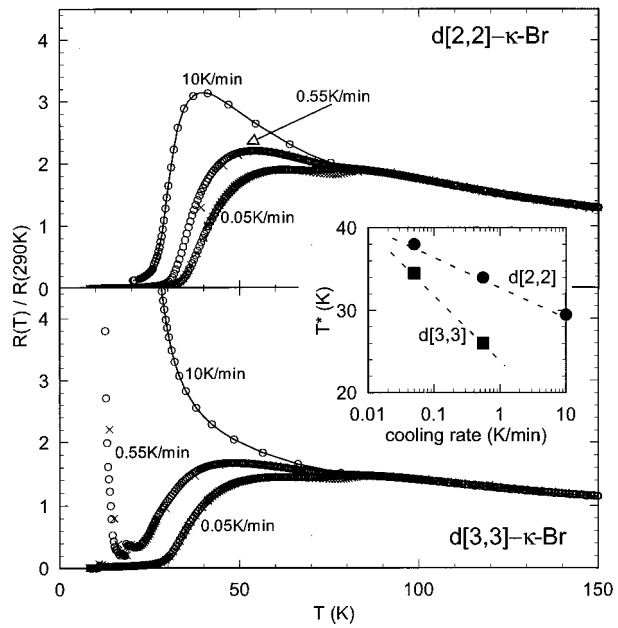

FIG. 3. Resistivity of $d[2,2]$- and $d[3,3]$-κ-Br as functions of temperature and cooling rate, which were obtained in cooling ($\bigcirc$) and warming ($\times$) processes. The inset shows the nonmetal-metal crossover temperatures as a function of cooling rate.

We defined the boundary between bulk and nonbulk superconductors at a value of $-4\pi\chi' = 0.8$, although this definition is arbitrary. It can be depicted in the shaded region, depending on the cooling rate. After the annealing, the boundary is located between $d[3,3]$- and $d[4,4]$-κ-Br. It shifts to around $d[2,2]$ in the slow cooling condition, and shifts further to the $d[1,1]$ direction in the fast cooling condition. As for the $d[n,n]$ dependence of T_c after the annealing, it is insensitive to the degree of deuteration up to $d[2,2]$ but shows a slight decrease in $d[3,3]$- and $d[4,4]$-κ-Br.

It is the $d[2,2]$ and $d[3,3]$ systems that are heavily influenced by the cooling speed. It is important to see the influence of the cooling process on the electronic state at high temperatures. Figure 3 shows the temperature dependence of resistivity which was measured simultaneously for $d[2,2]$ and $d[3,3]$ salts. The cooling rates are 0.05, 0.55, and 10 K/min which nearly correspond to the cooling conditions in the ac susceptibility measurements. For both salts the drastic cooling rate dependence appears below 80 K, where the resistive kink appears, while the resistivity at higher temperatures is unchanged. The increase of the cooling rate leads to enhancement of resistivity below 80 K. In other words, by the faster cooling, nonmetallic state is enhanced and encroaching upon the low-temperature metallic region. If the nonmetal-to-metal crossover temperature T^* is defined by that giving the peak in (dR/dT), T^* decreases with increase of the cooling rate as shown in the inset. It is obvious that the T^* shift becomes remarkable with the progressive deuteration (for the $d[0,0]$ salt, T^* does not show such a strong cooling rate dependence[13,17]). The $d[3,3]$ salt cooled at the rate of 0.55 K/min shows a reentrant metal-insulator transition around 15 K. Moreover, in the fastest cooling condition (10 K/min), $d[3,3]$ no longer falls into the metallic state but remains nonmetallic in the whole temperature range. After this measurement, we successfully reproduced the resistive curve initially observed at the 0.55 K/min cooling rate. This confirms that any damage such as microcrack was not introduced into the samples during these heat cycles. Thus, it is concluded that increase of the cooling rate gives metal-insulator transition and disappearance of the bulk superconductivity.

As seen above, the cooling rate effect is initiated at 80 K, where the resistivity has a kink. To the authors' knowledge, the only related phenomenon at this temperature is the anomaly in the thermal expansion and contraction of the lattice parameters.[14,15] With temperature decreased from 300 K, the in-plane a axis initially contracts but gradually turns to expansion, forming a broad minimum around 150 K. Then, it forms a sharp peak at 80 K, below which it turns to decrease. The in-plane c axis shows a kink at 80 K although it monotonously decreases from 300 K down to 4 K.[14] In other words, a sudden change of degree of the orthorhombicity occurs when the system passes through 80 K. While it is still unclear what is going on at 80 K, it is natural to consider that the present observation is triggered by this structural anomaly. In this context, the observed cooling rate dependence implies that the transformation into the stable structure below 80 K has a (temperature-dependent) long relaxation time of the order of hours or longer, as was encountered in β-$(BEDT\text{-}TTF)_2I_3$.[18] Then, the electronic structure is set by the metastable molecular arrangement depending on the cooling rate.

It is established that the present series of materials are situated just in the vicinity of the Mott insulator, because the fully deuterated salt and the Cl salt were found to have the magnetic properties typical of the Mott insulator. Therefore, the present metal-insulator transition controlled by the cooling rate is very likely to come from the variation of U/W due to the structural change below 80 K. As mentioned above, the structure below 80 K is represented by the anomalous decrease of degree of the orthorhombicity (c/a) and in-plane unit-cell volume with temperature lowered. If the thermal contraction is out of thermal equilibrium and distorted by fast cooling, the bandwidth might decreases and U/W can exceed the Mott critical value. This gives a reasonable explanation to the present results. The other aspect is possible introduction of disorder into the lattice as metastable nature because the order or disorder in the ethylene conformation degree of freedom is inferred to be involved in this structural anomaly. In the present case, the electrons are so strongly correlated as to be situated near the Mott insulator. The effect of disorder near the Mott transition is qualitatively different from the situation of the simple Anderson localization. In this respect, there is a theoretical suggestion that the disorder in the metallic state near the antiferromagnetic Mott insulator induces staggered moment.[19] The role of the disorder in the present case needs further investigation.

The present observation should be distinguished from the case of $(TMTSF)_2ClO_4$, where the fast cooling drives the superconducting state into the spin-density-wave (SDW) state.[20] This is believed to result from change of the Fermi-surface nesting condition due to the orientational disorder of ClO_4 between the TMTSF chain. What is relevant in the

present case is not the nesting but the electron correlation.

In summary, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br precisely controlled near the superconductor-insulator boundary by partial deuteration showed strong cooling rate dependence. The resistivity shows a change from metallic to insulating behaviors and the bulk superconductivity collapses by the rapid cooling. The insulating state appearing in the highly deuterated or rapidly cooled salts is considered to result from the slight increase in U/W and/or the disorder effect near the Mott insulator.

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