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Superconductor−Insulator Transition Controlled by Partial Deuteration in BEDT-TTF Salt

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The organic superconductor, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, has been attracting interest not only because of the highest T_c among the organic systems at ambient pressure[1] but also because the neighbor salt, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, is a magnetic insulator.[2,3] In our previous study, the Cu[N(CN)$_2$]Cl salt is found to have a commensurate magnetic structure with a staggered moment of greater than 0.4 μ_B per BEDT-TTF dimer.[4] Moreover, the ^{13}C NMR study indicated the presence of the antiferromagnetic spin fluctuations even for the superconducting Cu[N(CN)$_2$]Br and Cu(NCS)$_2$ salts.[5,6] Now, we are at the stage where the superconductor and the antiferromagnet should be understood on the same footing. This family is composed of members that are the key materials of condensed matter science because they can be model systems of the bandwidth (or U/W) controlled superconductor (S)−insulator (I) transition at fixed carrier density, in contrast to the case of the cuprates.

Since the formal charge on BEDT-TTF molecule is $^1/_2$, the dimer unit of BEDT-TTF molecules in κ-(BEDT-TTF)$_2$X turns out to have one hole, leading the band filling to $^1/_2$, where the S−I transition can be of the Mott type. We proposed a phase diagram for the κ-(BEDT-TTF)$_2$X family,[7,8] as shown in Figure 1, which is characterized by temperature vs U/W with U, the intradimer coulomb repulsion, and W, the width of the band constructed by the inter-dimer transfer integrals. The U/W is quite sensitive to the molecular arrangement in the conducting layer.

One will get further insight into the metal (superconductor)−nonmetal transition if the system is tuned around the boundary. To achieve it, two kinds of methods are conceivable. One is application of the "physical" pressure. Indeed, the pressure dependence of the transport properties of the Cu[N(CN)$_2$]Cl salt was investigated by many researchers. Another approach is the alloying of Cu[N(CN)$_2$]Br and Cu[N(CN)$_2$]Cl salts (ref 9). The advantage of the first method is the capability of adjusting the pressure continuously when He gas is used as the pressure medium. However, this method is not always applicable to every kind of physical measurement. As for the second method, possible inhomogeneity of the constituents often causes difficulties and the Br/Cl composition of the product is quite different from that in preparation.

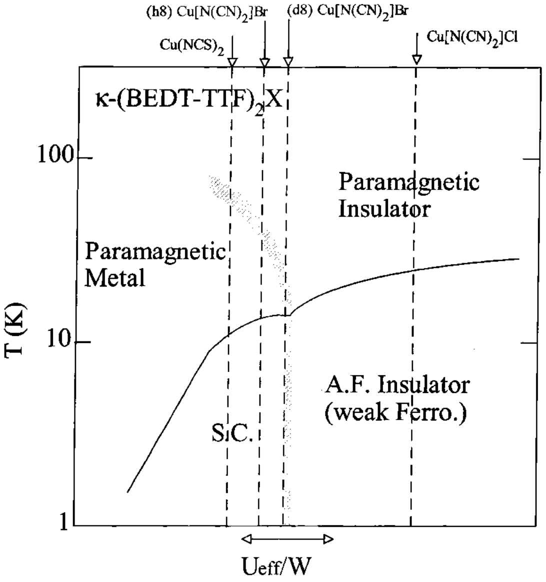

Figure 1. Conceptual phase diagram of κ-(BEDT-TTF)$_2$X systems.

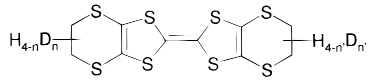

Figure 2. Partially deuterated d[n,n′]-BEDT-TTF molecules.

In our previous study of κ-(d8-BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, where the protons in the ethylene groups of BEDT-TTF are all substituted by deuterium, we found that this system is just in the critical region of the S−I transition; even a single crystal contains a major fraction of the insulating phase, which has the same antiferromagnetic ground state as in Cu[N(CN)$_2$]Cl salt and a minor fraction of the superconducting phase.[10] In this sense, this system can be viewed as a marginal insulator. This is not due to the mass change itself but because the contraction of the CD bond compared with the CH bond gives a slight modification to the molecular arrangement. In this paper, on the basis of this finding, we propose the third method, the partial deuteration of BEDT-TTF molecules, and demonstrate that this method provides a way to control the system with minimal inhomogeneity and to turn it finely around the M−I transition.

The molecules of d[0,0]-BEDT-TTF, d[1,1]-BEDT-TTF, d[2,2]-BEDT-TTF, d[3,3]-BEDT-TTF, and d[4,4]-BEDT-TTF (See Figure 2) were prepared with the conventional method from 1,2-dibromoethane enriched with the respective number of deterium. The isotope-labeled 1,2-dibromo,1-deutero-ethane and 1,2-dibromo,1,1,2-trideutero-ethane were synthesized using the gas-phase reaction of 1-deutero-ethylene and 1,1,2-trideutero-ethylene with bromine, respectively. The 1,2-dibromo,1,2-dideutero-ethane was synthesized from the gas-phase radical reaction of C_2D_2 and HBr under UV irradiation at room temperature.[11] The crystals of the radical salt were grown with the electrochmical oxidization in 1,1,2-trichroroethane with 10% EtOH.[1]

Our preliminary X-ray measurements at room temperature show the same value of the lattice parameter within 3σ for these partially deuterated compounds. These results are consistent with the

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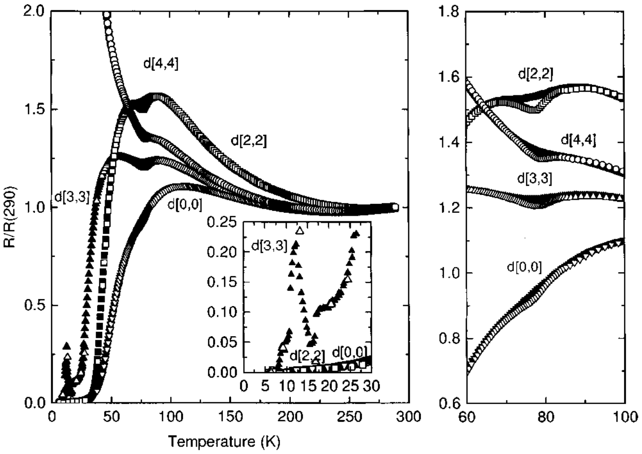

Figure 3. Resistivity of *d*[0,0]-(down triangle), *d*[2,2]-(square), *d*[3,3]-(up triangle) and *d*[4,4]-(circle)-κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br in the cooling (solid symbol) and warming (open symbol) processes. The low temperature region is expanded in the inset. The region shown by the dashed square in the left panel is expanded to the right panel.

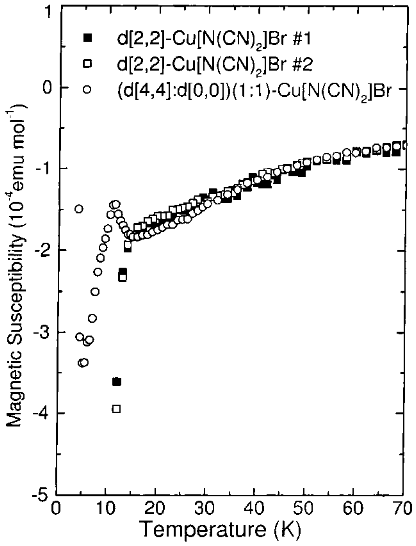

Figure 4. Magnetic susceptibility *d*[2,2]-κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (#1: solid square, #2: open square) and the alloys of *d*[0,0]- and *d*[4,4]-κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br with a ratio of *d*[0,0]:*d*[4,4] = 1:1 (open circle).

previous work for the *d*8 (*d*[4,4]) and h8 (*d*[0,0]) compounds.[12] A slight difference of structure is expected to affect the physical properties at low temperatures where the molecular motion of the ethylene group is frozen.

Figure 3 shows the temperature dependence of the electric resistivity of κ-(*d*[*n*,*n*]-BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salts ($n = 0$, 2, 3, 4) at a cooling rate of about 0.5 K/min. The measurements were performed simultaneously for the crystals in order to eliminate ambiguity of the cooling rate dependence.[10] It is noted that the kink anomaly at 80 K[13,14] is not affected by progressive deuteration, as seen in the figure. The temperature dependence of the resistivity shows systematic variation with the degree of deuteration. In the high-temperature range, all of the samples showed nonmetallic behaviors. However, the crossover to the metallic temperature dependence occurs at a lower temperature with the number of deuterium increased. If the nonmetal-to-metal crossover temperature, T^*, is defined by that giving the peak in (dρ/dT), T^* is 46 K, 41 K, and 29 K for *d*[0,0], *d*[2,2], and *d*[3,3] samples, respectively. (Because more than four crystals cannot be mounted in the present apparatus, the data of *d*[1,1] salt is missing in Figure 3. In a separate measurement of four samples including *d*[1,1] salt, we confirmed that the behavior of *d*[1,1] salt is between those of *d*[0,0] and *d*[2,2].) It is evident that the progressive deuteration of BEDT-TTF drives the system toward the metal−insulator boundary. It should be pointed out that the 80 K anomaly seems to trigger or amplify the low-temperature branching-off of the resistivity behavior because the *d*[*n*,*n*] dependence of dρ/dT is prominent below 78 K rather than above that, as seen in the right panel of Figure 3. At low temperatures, the *d*[0,0], *d*[1,1], and *d*[2,2] salts undergo superconducting transition, of which the bulk nature was confirmed by the magnetic susceptibility measurements with good reproducibility. The resistivity of the *d*[3,3] salt shows complicated temperature dependence at low temperature with sample dependence, because of the competition between the superconducting and the magnetic insulating phase. The dc and ac susceptibility characterization revealed that the *d*[3,3] crystal includes a superconducting phase as a major fraction and an insulating phase as a secondary fraction due to inevitable inhomogeneity quite near the S−I boundary. Thus, the *d*[3,3] salt is considered as a marginal superconductor. The S−I boundary is situated between the *d*[3,3] and *d*[4,4] salts.

As mentioned above, the system may be controlled by the alloying of different molecules; for example, *d*[0,0] and *d*[4,4] molecules. For comparison of the alloying and the partial deuteration, we prepared an alloy with *d*[0,0]:*d*[4,4] = 1:1, which should be equivalent to the partial deuteration of *d*[2,2], and characterized their magnetism. The dc susceptibility of the alloy and the *d*[2,2] crystals is shown in Figure 4. The *d*[2,2] samples show monotonic decrease in susceptibility down to 12 K, followed by a sudden decrease due to the superconducting diamagnetism. The agreement of the profiles between the two series of *d*[2,2] crystals is nearly perfect. On the other hand, susceptibility of the alloy shows an increase below 15 K as in like the case of the magnetic ordering in the *d*[4,4] salt, and then decreases below 11 K due to superconductivity. This indicates spatial inhomogeneity of superconducting and antiferromagnetic phases, which originates from inevitable density fluctuations of *d*[0,0] and *d*[4,4] BEDT-TTF molecules. Thus, the method of the partial deuteration, although it is a mixture of stereoisomers, is superior with respect to the application of the homogeneous effective pressure.

In the present study, we demonstrated that the partial deuteration of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br system made it possible to control the molecular arrangement in the two-dimensional BEDT-TTF sheet so finely that U/W of the system crosses the critical value of the Mott transition. Another analogous example is the deuteration of (DMe-DCNQI)$_2$Cu (ref 15), which is also situated near the M−I transition although the mechanism is quite different from the present case. These two studies suggest that the deuteration of the molecule can be a useful method applicable to the general cases where the system is to be tuned finely near the M−I transition.

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