Field switching of superconductor-insulator bistability in artificially tuned organics

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Layered organic superconductors situated in the vicinity of a superconductor-insulator (SI) phase boundary show switching between the SI bistable states by application of magnetic field. First, we show that an electronic phase of κ-(BEDT-TTF)$_2$[N(CN)$_2$]Br [BEDT-TTF denotes bis(ethylenedithio)tetrathiafulvalene] can be finely tuned so as to approach the SI boundary by combination of chemical modification of the BEDT-TTF molecules and regulation of cooling rate. Then, we demonstrate that the superconducting phase tuned in this way undergoes a field-induced first-order transition into the insulating phase.

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I. INTRODUCTION

A family of organic compounds, κ-(BEDT-TTF)$_2X$ [BEDT-TTF denotes bis(ethylenedithio)tetrathiafulvalene] have layered crystal structure with an alternating stack of the BEDT-TTF layers and the anion (X) layers. In the former layer responsible for electronic conduction and magnetism, dimers of the BEDT-TTF molecules are arranged like the checkerboard pattern.[1,2] Since the valency of the anion is -1, the BEDT-TTF dimer turns out to have one hole, which fills the dimer band by half. The salt with $X=$Cu[N(CN)$_2$]Cl is an insulator (I). The finding of the commensurate antiferromagnetic spin structure in this salt supports that it is a Mott insulator.[3–5] Indeed, theoretical investigations indicate the important role of the electron correlation in this family of compounds.[6] On the other hand, the salt with $X=$Cu[N(CN)$_2$]Br is a superconductor (S) with T_c of 11.5 K.[7] 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.[5] So this family can be a model system of the U/W-controlled SI transition with fixed band filling in contrast to the case of the high-T_c cuprates controlled by the band filling.

To make further approach to the SI boundary which should exist between the Cu[N(CN)$_2$]Br and Cu[N(CN)$_2$]Cl salts, we previously established two methods to control U/W. The first one is chemical modification of the BEDT-TTF molecule, which can modify the molecular arrangement. We prepared a series of progressively deuterated Cu[N(CN)$_2$]Br salts and found by transport and susceptibility measurements that the isotope substitution gives the fine tuning of the electronic phase across the SI boundary.[8–11] Secondly, the electronic states of the series of Cu[N(CN)$_2$]Br salts were found to be strongly influenced by cooling speed around 80 K,[9,10] where some structural anomaly occurs.[12] The fast cooling is known to give rise to conformational disorder of the BEDT-TTF molecules, which should change U/W and introduce electronic disorder. The magnetic characterization implied that the increase of cooling rate induces SI transition similar to the case of the U/W increase.[13] Indeed, a recent U/W evaluation based on the careful structural analysis of the Cu[N(CN)$_2$]Br salts shows that the deuteration and fast cooling both increase the U/W.[14] The control of the cooling rate serves to tune the phase around the SI boundary. The possible role of the disorder introduced by fast cooling will be discussed in Sec. IV.

In the present work, we first demonstrate the phase crossing through the SI boundary with nearly continuous variation of U/W by combination of the chemical modification of the BEDT-TTF molecules and the regulation of the cooling rate for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. Then, we show that the superconducting phase tuned so as to approach the boundary is switched into the magnetic insulating phase by magnetic field. This SI switching is the first-order transition.

II. EXPERIMENT

Single crystals of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br were grown by the electrochemical oxidation of nondeuterated, partially, and fully deuterated BEDT-TTF molecules. The BEDT-TTF molecule has two ethylene 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.[8] The electrical resistance and dc susceptibility of these crystals were measured as functions of temperature, cooling rate, and magnetic field normal to the conducting layer. The resistance 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 carbon paste. The samples were fixed on the holder with these lead wires. The dc susceptibility of a single crystal was measured using a quantum design superconducting quantum interference device magnetometer. The sample was mounted on the holder made by an insulating film with a small amount of grease. The measurements were performed at various cooling rates from room temperature.

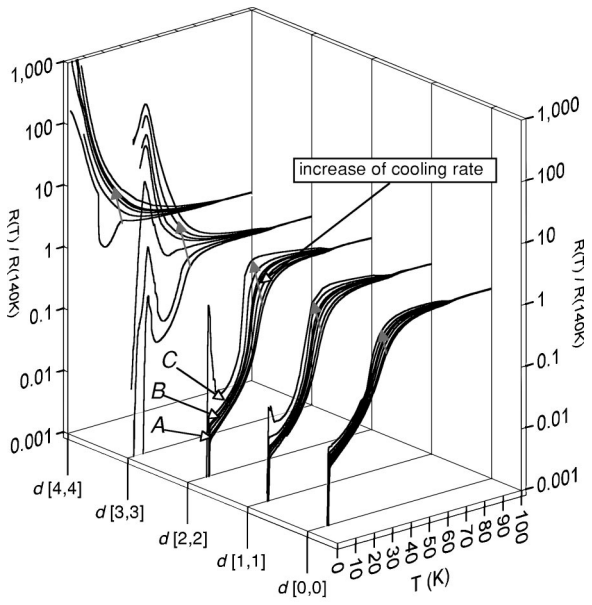

FIG. 1. Temperature dependence of resistance of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salts at a zero magnetic field as functions of $d[n,n]$, and cooling rate. The data are all normalized to the values at 140 K. The cooling rates are 0.018, 0.089, 0.61, 1.9, 3.3, 9.7, and 34 K/min for $d[0,0]$ salt; 0.018, 0.091, 0.56, 1.68, 3.3, 11, and 39 K/min for $d[1,1]$ salt; 0.018, 0.089, 0.65, 1.9, 3.3, 9.6, and 34 K/min for $d[2,2]$ salt; 0.018, 0.090, 0.52, 1.8, 3.0, 11, and 27 K/min for $d[3,3]$ salt; and 0.018, 0.091, 0.56, 1.7, 3.3, and 39 K/min for $d[4,4]$ salt. The alphabets $A-C$ correspond to the ones in Fig. 4.

III. RESULTS

A. Phase control

Figure 1 shows the temperature dependence of the electrical resistance of the Cu[N(CN)$_2$]Br single crystals with different degrees of deuteration and cooled at different speeds. All the samples were cooled down to 4.2 K at several speeds in a range of 0.018 K/min to 27–39 K/min, and then the resistance was measured with temperature elevated slowly. In a high-temperature range, all of the samples showed nonmetallic behavior. Depending on the cooling rate and the degree of deuteration, the data start to show systematic variations. As for the cooling rate dependence, the variation appears around 80 K. The less deuterated and/or slowly cooled salts show nonmetal-to-metal crossover and usual metal-to-superconductor transition at low temperatures. The crossover is shifted to the lower-temperature side with increase of deuterium and/or cooling rate. Further increase of them causes reentrant metal-insulator transition just before the superconducting transition. Finally, the insulating behavior is seen in the whole temperature range for the fully deuterated $d[4,4]$ salt. In this way, a systematic variation from the superconducting ground state to the insulating ground state was brought about by combination of the chemical and physical methods.

B. Field-induced metal-insulator transition

We performed the transport measurements under magnetic fields for all of the salts cooled down at various speeds

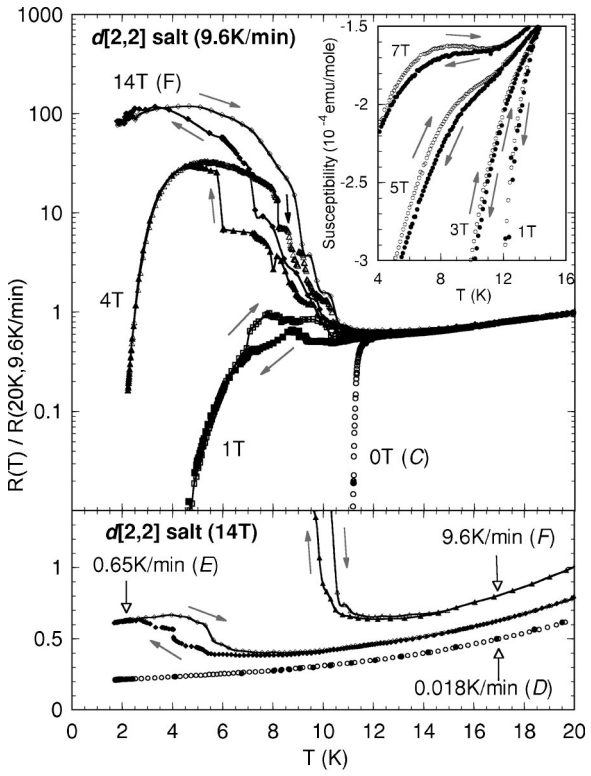

FIG. 2. Upper panel: The normalized resistance of $d[2,2]$ salt cooled at a rate of 9.6 K/min as functions of temperature and magnetic field. The data are plotted in logarithmic scale. The magnetic fields were applied normal to the conducting plane. Inset shows the static susceptibility of $d[2,2]$ salt cooled at a rate of 10 K/min as functions of temperature and magnetic field normal to the conducting plane. Lower panel: The cooling rate dependence of resistive curves of $d[2,2]$ salt under 14 T. The data are plotted in linear scale. The alphabets $C-F$ correspond to ones in Fig. 4. The closed and open symbols distinguish between the processes of ascending and descending temperature.

to pursue field-induced phases or phenomena in the vicinity of the SI boundary. A peculiar field-induced phenomenon was observed in the $d[1,1]$, $d[2,2]$, and $d[3,3]$ salts, depending on the cooling rate. The representative result (for $d[2,2]$ salt) among them is shown in Fig. 2. The resistance of $d[2,2]$ salt cooled down at a rate of 9.6 K/min is shown in the upper panel as functions of magnetic field and temperature. The magnetic field was applied normal to the conducting plane throughout the present experiments. Superconducting state is, in general, changed into the metallic state by application of magnetic fields in excess of upper critical field. Indeed this behavior was observed in the extremely slow cooling case (0.018 K/min), as seen in the lower panel. In the case of the 9.6 K/min cooling, however, application of an even low magnetic field of 1 T does not only suppress the superconducting transition to the lower-temperature side but generates a transition to a highly resistive state with large hysteresis between the processes of ascending and descending temperature. With further increase of magnetic field, the resistive state grows up with the hysteresis kept clear. Finally, under a high field of 14 T, the low-temperature resis-

tance amounts to two orders of magnitude larger than the normal-state resistance at 20 K.

The highly resistive state is considered as a nonmetallic state. However, the resistivity is saturated and even shows a slight decrease at low temperatures, which seems to contradict the view of the nonmetallic phase. We consider that it is attributable to the phase admixture of the minor metallic domains in the major insulating phase by the following reason. The range of the present bandwidth variation corresponds to equivalent pressures of as small as a few hundred bar or lower. In such a situation, an influence of the naturally existent disorder in the deuterium configuration or ethylene conformation might not be neglected; the slight fluctuations in the bandwidth could cause the phase mixture or separation in the critical region. Indeed such a phase separation between the antiferromagnetic phase and the minor metallic phases were clearly observed in a recent nuclear magnetic resonance (NMR) study on a $d[4,4]$ single crystal.[11] Through this fact, it is reasonable to consider that the low-temperature resistivity saturation comes from the slight inclusion of the neighboring metallic phase rather than to invoke an exotic but unknown metallic phase with an unusually large resistivity (100-1000 times of the normal-metallic resistivity). The low-temperature decrease of resistivity following the saturation at 14 T, which exceeds bulk H_{c2}, can be interpreted by survival of superconductivity with H_{c2} enhanced due to the size effect of tiny inclusions. Thus, as the primary consequence of the results, we conclude that the superconducting transition is replaced by the first-order metal-insulator transition with application of magnetic field. This is a unique field-induced SI switching phenomenon.

The inset shows magnetic susceptibility of a large $d[2,2]$-single crystal (3.6 mg). After the sample was cooled down at almost the same rate (10 K/min) as in the resistance measurement, the magnetic field was applied at 25 K, and then susceptibility was measured with temperature lowered and elevated. Under high magnetic fields, the superconducting diamagnetic susceptibility is depressed and the clear hysteresis between the processes of ascending and descending temperature is observable. This result again evidences the first-order character of this metal-insulator transition. Moreover, the data at the highest magnetic field of 7 T have a small hump as observed in the $Cu[N(CN)_2]Cl$ salt and, therefore, suggests the similar antiferromagnetic (AF) transition although the spin canting is much more suppressed.

The lower panel shows that this phenomenon appears depending on the cooling rate. Similarly, the field-induced SI switching appears with the progressive deuteration when the cooling rate is fixed. Both of the experimental results indicate that this field-induced first-order transition occurs in the superconducting phase near the superconducting-antiferromagnetic insulating (S-AFI) boundary. It should be noted that a similar SI switching phenomenon was reported for $Cu[N(CN)_2]Cl$ salt under pressure by Sushko *et al.*[15] This fact supports that the deuteration of the molecules and the increase of the cooling rate have an equivalent effect to application of (negative) pressure and therefore the variation of U/W. The present phase control is available at ambient pressure, which makes the detailed transport and magnetization measurements possible. In reality, the first-order character and the concomitance of the magnetic ordering were uncovered in the present ambient-pressure measurements. At present, we can expect further researches by other methods not available under pressure, such as specific-heat measurement. In addition, such an ambient-pressure phase control of the molecule-based conductor opens a way to the possible application to the molecular device.

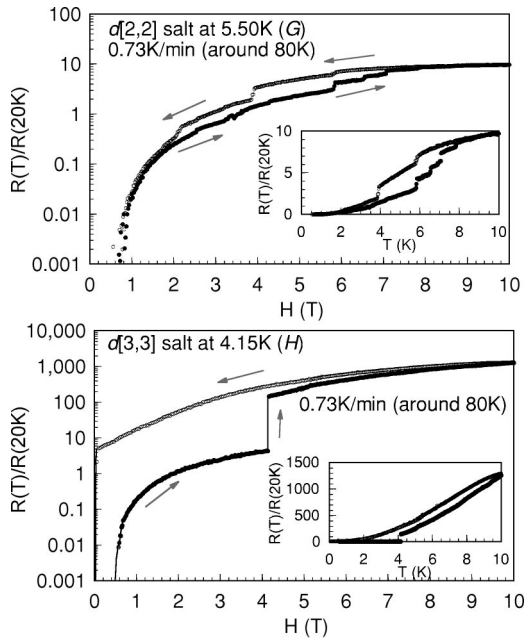

FIG. 3. Magnetic-field dependence of the normalized resistance of $d[2,2]$ and $d[3,3]$ salts at fixed temperatures. The data are plotted in logarithmic and linear (inset) scales. These measurements correspond to the alphabets *G* and *H* in Fig. 4.

C. Field-induced SI transition

Moreover, we made resistance measurements under field sweep for the salts in the superconducting phase near the S-AFI boundary. The $d[2,2]$ and the $d[3,3]$ salts were cooled at a rate of 0.73 K/min down to 5.50 K and 4.15 K, respectively, at a zero field. After that, the resistance was measured under the sweeping magnetic field at respective temperatures. Figure 3 shows the results in linear (inset) and logarithmic scales. With ascending field from 0 T, the superconducting state becomes resistive at low fields less than 1 T and then is changed into the highly resistive states through small (for $d[2,2]$ salt) or big (for $d[3,3]$) salt) resistive jumps. The different resistance values at the highest magnetic field may reflect the degree of the metallic phase admixture because the $d[3,3]$ salt is near the S-AFI boundary compared with the $d[2,2]$ salt; As the system goes apart from the boundary, the admixture of the metallic phase to the insulating host will be possibly stepped up if there is some imperfection in the present U/W control. When the magnetic field turns to the descending process from 10 T, the clear hysteresis shows up for both salts. This evidences the occurrence of the field-induced first-order superconductor-insulator transition near the S-AFI boundary.

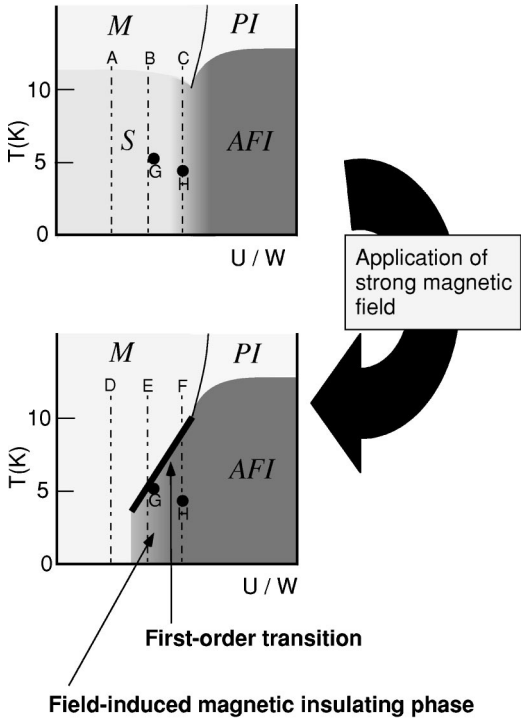

FIG. 4. The conceptual phase diagrams. *M*, PI, S, and AFI stand for metallic, paramagnetic insulating, superconducting, and antiferromagnetic insulating phases, respectively. The alphabets *A*–*H* correspond to the measurements in Figs. 1, 2 and 3. In a strong magnetic field, the superconducting phase well off the S-AFI boundary at a zero field is transformed into the metallic phase. In the vicinity of the boundary, however, the superconducting phase is changed into the field-induced magnetic insulating phase. At the same time, the first-order transition line appears as indicated by the thick line.

IV. DISCUSSION

The conceptual phase diagram around the S-AFI boundary at zero or low magnetic fields is depicted at the upper panel in Fig. 4 according to the previous works.[5,16] With the present findings, one can draw a phase diagram under strong magnetic fields (the lower panel). The dash-dotted lines and closed circles with alphabets of A–H in Fig. 4 stand for the positions of the present measurements, which are marked with the respective alphabets in Figs. 1, 2, and 3. In the phase diagram at a zero field, the superconducting (S) phase and antiferromagnetic insulating (AFI) phase abut on each other. In the region far from the boundary, the superconducting phase is transformed into the normal-metallic phase (*M*) by application of high fields, as was observed in the experiment *D*. In the vicinity of the boundary, however, the experiments *E* and *F* indicate that the line of the first-order transition from the *M* phase to the AFI phase should exist as shown in the figure.

The appearance of this field-induced AFI phase can be explained if this phase is thermodynamically stable compared with the normal-metallic phase, which usually takes the place of the superconducting phase under magnetic field. The magnetization measurements indicate the existence of the weak ferromagnetism due to the spin canting in the AFI phase of the $Cu[N(CN)_2]Cl$ salt.[3,17] However, the spin canting-induced magnetization is not so prominent in the present salts as seen in the inset of Fig. 2.

The present observation is compared with relevant phenomena in other systems. The field-induced SI transitions were observed in thin films[18] and under-doped high-T_c cuprates[19] with the nature of the quantum phase transition or crossover in sharp contrast with the first-order nature in the present case. The important factor for them is considered to be the disorder, of which characteristic constant is the critical sheet resistance $h/4e^2 = 6.5\ \mathrm{k}\Omega$. As for the case of the present material, the normal-state layer sheet resistance of the $d[2,2]$ salt cooled down at 0.6 K/min to 13 K, where the field-induced SI switching is clearly observed as seen in the experiment *E* in Fig. 2, is about 1 kΩ with ambiguity of a factor of 2. This is well below the critical value. These contrasting characters indicate that the present SI transition is qualitatively different from the previous ones in origin.

On the other hand, the disorder effect on the superconductivity of BEDT-TTF-based organics has been extensively discussed in the β-$(BEDT\text{-}TTF)_2I_3$ salt. This salt shows the superconductivity with a maximum T_c of 8.0 K,[20–22] where the superconducting state is strongly affected by the anion alloying[23] and by the incommensurate superlattice, which can be removed by annealing or pressure treatment.[21,22,24,25] As for the alloy case, the T_c reduction with alloying seems continuous and does not involve a first-order transition into a highly resistive state in contrast to the present case. For the effect of the incommensurate superlattice, although T_c is reduced from 8.0 K to 1.5 K or less, there is no signature of the first-order transition. In this case, the NMR spectra, which probes the local spin susceptibility, gives additional information; it shows broadening in presence of the incommensurate superlattice, while it is sharpened in the absence of the superlattice,[26] which suggests the existence of the disorder for the conduction system. The present $Cu[N(CN)_2]Br$ system, however, does not show appreciable broadening in the NMR spectra even if the sample is cooled rapidly.[27] In this sense, the disorder effect in the present series of the salts is much less prominent than in β-$(BEDT\text{-}TTF)_2I_3$ salt. Moreover, it should be in mind that the nonmetallic phase comes out when the superconductivity is suppressed by magnetic field in the present case.

In this way, there is no evidence that the disorder plays a crucial role for the present phenomena. When one tries to analyze the present field-induced phenomenon, the most important point is that this phenomenon occurs in the vicinity of the S-AFI boundary in the phase diagram. The disorder, if any, in the strongly correlated electrons in such a situation possibly affects the electronic state in a different manner. There are theoretical suggestions that the disorder in the metallic state near the antiferromagnetic Mott insulator induces staggered moment.[28,29] Its role in the present case needs further investigation.

In the sense that the present phenomenon appears around the Mott transition, the situation is similar to the very light-doping region of the cuprates. A unified theoretical scheme based on the SO(5) symmetry of superconductivity and antiferromagnetism was originally proposed by Zhang[30] for the phase diagram of high-T_c cuprates. The Monte Carlo simu-

lation based on this scheme provides a result of particular interest for the present high-field phase diagram. Namely, Hu *et al*. predicted the appearance of the field-induced first-order normal-to-antiferromagnetic transition.[31] That is, just the present observation. It is well known that there are so many similarities between the organics and cuprates, such as quasi-two-dimensionality, strong correlation of the conducting electron, appearance of (very probably) *d*-wave superconductivity, and interplay between superconductivity and antiferromagnetism. The essential ingredients for the SO(5) scheme are shared by the two systems. Indeed, Murakami and Nagaosa successfully applied the SO(5) scheme to explain the NMR relaxation rates of the present organics.[32] While we expect future theoretical works that stand on a microscopic viewpoint to explain the phenomena reported here, the SO(5) scheme, which was originally proposed for the high-T_c cuprates, might be giving an explainable way for the SI switching phenomenon in organics.

V. CONCLUSION

We observed a field-induced superconductor-insulator transition (FI-SIT) in quasi-two-dimensional organic superconductors, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, neighboring the Mott insulators and proposed a phase diagram at high magnetic fields. The transition is of the first order against temperature and field, that contrasts with the continuous nature of the FI-SIT in conventional thin films and cuprates. The present results show a class of FI-SIT.

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