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Field-induced metal-insulator transition in partially deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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A ^{13}C-NMR study on nondeuterated and partially deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br is reported, where BEDT-TTF is bis(ethylenedithio)tetra-thiafulvalene. By using a BEDT-TTF molecule with ^{13}C as one of its central carbons, we could estimate the density of states from the Knight shift and the spin-lattice relaxation rate. Although the reduced mass effect predicted from the specific-heat measurement was not observed in the ^{13}C-NMR spectrum, a metal-to-antiferromagnetic phase transition was observed with a phase separation at around 18 K on the half-deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br under a high magnetic field. No such transition occurred in the half-deuterated salt under a zero or low field. These results point to a first-order field-induced metal-insulator transition. These findings can explain the complex phenomena observed near the phase boundary under a high magnetic field.

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A family of organic conductors, κ-(BEDT-TTF)$_2$X salts, have a crystal structure consisting of layers of conducting BEDT-TTF and insulating anion. Owing to this structure, these salts have a quasi-two-dimensional electron system. κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br shows ambient-pressure superconductivity (SC) with the highest T_c among all organic conductors.[1] Although κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl shows an antiferromagnetic (AF) ordered state at ambient pressure,[2] it shows SC under low pressure.[3] These results suggest that SC in the κ phase is closely related to the AF ordered state and that these salts belong to the class of strongly correlated electron systems, along with high-T_c cuprates. Many theoretical models have been developed for strongly correlated electron systems.[4–6]

As mentioned above, the superconducting phase occurs in the vicinity of the AF insulating phase. To investigate electronic states near the SC-AF boundary, it is important to examine the phase across this boundary. One approach is to apply pressure; alternative approaches are to control the process of selective deuteration of ethylene groups in the BEDT-TTF,[7] or to control the instantaneous cooling rate at 80 K.[8] The phase diagram of κ-phase salts was investigated under hydrostatic helium gas pressure for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl.[9,10] The first-order phase boundary between the SC and AF phases was described via ^{1}H-NMR and ac susceptibility. A phase separation in the SC-AF phase was observed near the phase boundary.[9,11] Nakazawa *et al.*[12] predicted a reduced mass effect near the phase boundary in partially deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salts based on specific-heat measurements under a high magnetic field. Electric conductivity measurements on κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl under pressure,[13] and more recently on half-deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salts within the metallic phase near the phase boundary,[14] point to a field-induced metal-resistive state transition. The mechanism of this field-induced transition and the nature of the resistive state are still unknown. Thus, a detailed microscopic investigation of what occurs at the phase boundary under high magnetic field is essential.

^{13}C-NMR is one of the most powerful tools to investigate electronic properties microscopically. To study the properties near the phase boundary, we prepared ^{13}C-enriched, partially deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br salt and performed ^{13}C-NMR. Typically, ^{13}C-NMR studies on κ-(BEDT-TTF)$_2$X salts have been conducted using BEDT-TTF molecules with double-^{13}C-enriched central ^{13}C$=$^{13}C carbon.[15–18] Due to the strong dipole coupling between the ^{13}C$=$^{13}C nuclei, the spectrum of the two central ^{13}C sites are split into four lines,[16,19] and the spin-lattice relaxation rates T_1^{-1} on each ^{13}C site are mixed. This splitting prevents quantitative analysis of each ^{13}C site of the BEDT-TTF molecule. To overcome these difficulties, we used BEDT-TTF molecules with ^{13}C as one of the central carbons, as shown in Fig. 1(a). This enabled us to quantitatively compare our NMR results with results from other experiments, e.g., the spin susceptibility, γ, obtained from specific-heat experiments.[12]

There are four magnetically inequivalent molecular orientations in the unit cell, and each BEDT-TTF molecule has two central carbons as shown in Fig. 1(b). Thus, eight lines are observed for an arbitrary field orientation, while only two lines are observed when a magnetic field is oriented perpen-

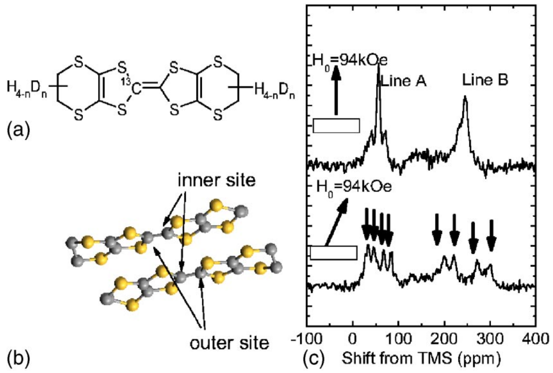

FIG. 1. (Color Online) (a) Molecular structure of single-side ^{13}C-enriched BEDT-TTF. (b) Dimer structure of BEDT-TTF molecule. (c) NMR spectrum under some field directions $T=300$ K.

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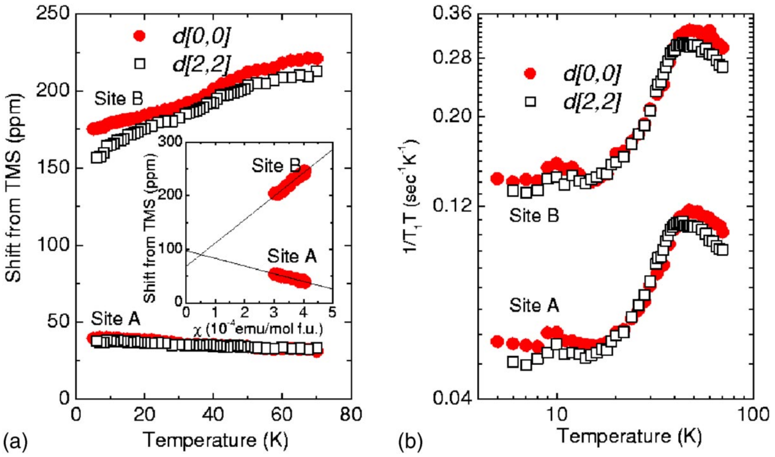

FIG. 2. (Color Online) (a) Temperature dependence of ^{13}C-NMR shift from TMS for $d[0,0]$ (solid circles) and $d[2,2]$ salts (open squares). Inset: K-χ plot of the $d[0,0]$ salt. (b) Temperature dependence of $(T_1\mathrm{T})^{-1}$ of $d[0,0]$ (solid circles) and $d[2,2]$ (open squares) salts.

dicular to the conducting layer because the four molecule orientations in the unit cell are equivalent. Indeed, as shown in Fig. 1(c), we observed eight lines under an arbitrary magnetic direction, and only two lines (labeled A and B) corresponded to the outer and inner sites, respectively, under a magnetic field applied perpendicular to the conducting layer at room temperature.

To observe the metallic state at low temperatures, we applied an external field of 94 kOe perpendicular to the conducting layer, in similar fashion to specific-heat experiments.[12] The sample was then slowly cooled at a rate of 0.3 K/min, during which time it showed an almost full superconducting volume under a zero or low magnetic field.[8]

Figure 2(a) shows the temperature dependence of the shifts of the spectrum on each site (all shifts are given in ppm) relative to tetramethylsilane (TMS). In this paper, we use the notation $d[n,n]$ to represent the number of deuterium atoms on either side of the ethylene group. The shifts on both sides show the same temperature dependence as the spin susceptibilities of this salt. From the K-χ plot [inset of Fig. 2(a)], we estimated the chemical shifts and hyperfine coupling constants for lines A and B to be 67.9 ppm and 2.44 kOe/μ_B, and 97.4 ppm and −0.801 kOe/μ_B, respectively.

The temperature dependence of $(T_1T)^{-1}$ is shown in Fig. 2(b). $(T_1T)^{-1}$ on both sites show the same temperature profile as the shift. The nuclear relaxation profiles of each site follow a single exponential function. These results confirm that we have succeeded in observing the relaxation on each site independently. The $(T_1T)^{-1}$ of the $d[0,0]$ salt has a peak around 45 K and decreases with the depression of the magnetic fluctuation below 45 K. In the low-temperature region $(T_1T)^{-1}$ shows almost temperature-independent behavior, indicating that, at low temperatures, the function reflects the density of state of the metallic state. These results are consistent with previous ^{13}C-NMR studies.[15–19]

Specific-heat measurements revealed the γ value of a $d[2,2]$ salt to be less than half of that of a $d[0,0]$ salt. Because the density of states is proportional to the effective mass, the Knight shift (K) and $(T_1T)^{-1/2}$ of deuterated salts were also expected to be reduced compared to those of nondeuterated salt. However, the shift did not show such a large decrease. Moreover, at low temperatures, the $(T_1T)^{-1}$ of the $d(2,2)$ salt, which should be a quarter of that of the $d(0,0)$ salt, had almost the same value. In contrast to the specific-heat measurement results, no reduced Knight shift and $(T_1T)^{-1}$ measurement results show that the density of states in a $d[2,2]$ salt is not reduced, but rather virtually identical to that in a $d[0,0]$ salt.

What are the differences between $d[2,2]$ and $d[0,0]$ salts? As shown in Fig. 3(a), in the $d[2,2]$ salt, we found the new broad NMR lines C and D below 16 K, with a large shift of 0.3 and 0.9 MHz, respectively. We plotted the temperature dependence of the intensity $\times T$ of the sum of lines A and B and the sum of lines C and D in Fig. 3(b). The intensity of lines A and B began to decrease at around 18 K, decreasing to about 50% by 5 K. Concurrently, the intensity of C and D increased, compensating for the decrease in the intensity of A and B. These results pointed to the appearance of a new phase and the phase-separation behavior of the metallic (A and B) and new (C and D) phase. The volume of the new phase increased with decreasing temperature. To elucidate the large shift in the new phase, we also measured the NMR spectrum at 58 kOe. If the large shift stemmed from strong paramagnetism, the shift frequency would be expected to be proportional to the external field. However, as shown in Fig. 3(c), the shift frequency of neither line is proportional to the external field; they show the same value under 94 kOe. That shift frequency was independent of external field suggested the emergence of an internal field originating from a magnetic ordering phase. Thus, these lines suggest the commensurate AF structure, as in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl Refs. 2 and 20 and κ-(BEDT-TTF-d[4,4])$_2$Cu[N(CN)$_2$]Br.[21] Under the high magnetic field, the ordered moments flopped perpendicular to external field, and made the internal field parallel to external field through the anisotropic hyperfine coupling tensor. Assuming the AF structure predicted by Miyagawa *et al.*,[20] the line C is assigned to the outer site, the line D is assigned to the inner site in the AF phase, and the amplitude of the moment is estimated to be 0.2 μ_B per BEDT-TTF dimer.

This phase-separation behavior can explain the contradiction between the results of NMR and specific-heat measurements. In the latter, the volume of metallic phase was reduced through phase separation under a high magnetic field. Macroscopic measurements underestimated the density of

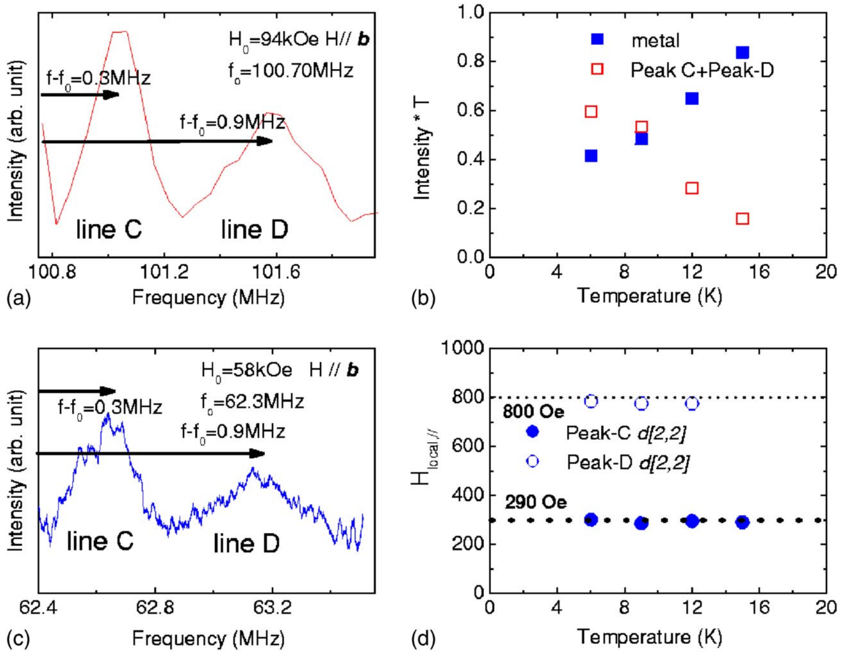

FIG. 3. (Color online) (a) The new NMR lines observed at 6 K under 94 kOe. (b) The temperature dependence of the NMR intensity $\times T$ of the $d[2,2]$ salt. (c) The new NMR lines observed at 6 K under 58 kOe. (d) The temperature dependence of the local field of new lines under 94 kOe.

states. NMR, on the other hand, can detect the AF and metallic phase separately, and the Knight shift and the $(T_1T)^{-1}$ reflect the density of states in the metallic phase.

In the case of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl salts and rapidly cooled $d[4,4]$-salts, $(T_1T)^{-1}$ shows a divergent peak at T_N and the staggered moments in the ordered state gradually increase from T_N with decreasing temperature.[2,11,16] These results predict a second-order transition. However, as shown in Fig. 3(d), the moment amplitudes are independent of temperature. Moreover $(T_1T)^{-1}$ did not show a divergent peak around 18 K. These results suggest that the metal-to-antiferromagnetic transition is first order. Indeed, both of the temperature and field dependences of the electric conductivity showed the hysteresis behavior.[14]

Our NMR sample was shown to have a superconducting volume fraction of 100% using the SQUID magnetometer as in a previous study.[8,12] To determine the magnetic fraction under a low magnetic field, we also measured the temperature dependence of the ^{1}H-NMR under a low magnetic field (10 kOe) applied normal to the conducting plane. If the commensurate AF transition occurs, we should be able to observe 80$\sim$100 kHz spectrum splitting as in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$Cl] (Refs. 2 and 9) with line broadening. However, as shown in Fig. 4(a), the ^{1}H-NMR spectrum showed no splitting and broadening of the spectrum, and the value of the intensity $\times T$ did not change from 5 to 50 K. Up to 30 kOe, we could not observed any splitting or broadening of the spectrum. We thus confirmed that the AF transition does not occur under a low magnetic field of less than 30 kOe. Figure 4(b) shows the temperature dependence of the NMR spectrum under 40 kOe. In contrast to the results under 10 kOe, we observed line splitting at 60 kHz under 15 K as in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. These results predicted the field-induced metal-insulator transition in a slowly cooled $d[2,2]$ salt.

To confirm the field-induced metal-insulator transition by ^{13}C-NMR, we also measured the field dependence of the spectral weight in the metallic phase (A and B). As shown in Fig. 5, above 50 kOe, the spectral weight in the metallic phase decreased to low temperatures as it did at 94 kOe. However, the decrease of spectral weight is less than 20% and we cannot observe the lines from the AF phase at 30 kOe.

Based on the results of ^{1}H and ^{13}C-NMR, the threshold of the field-induced metal-insulator transition is between 30 and 40 kOe. Indeed, the resistivity jump behavior was observed around 40 kOe with hysteresis in the field dependence of the resistivity measurement performed by Taniguchi *et al.*[14]

Recently, the phase diagram of κ-(BEDT-TTF)$_2$X was investigated by ^{1}H-NMR and resistivity measurement[9,10] as shown in Fig. 6(a). Near the boundary, the phase separation

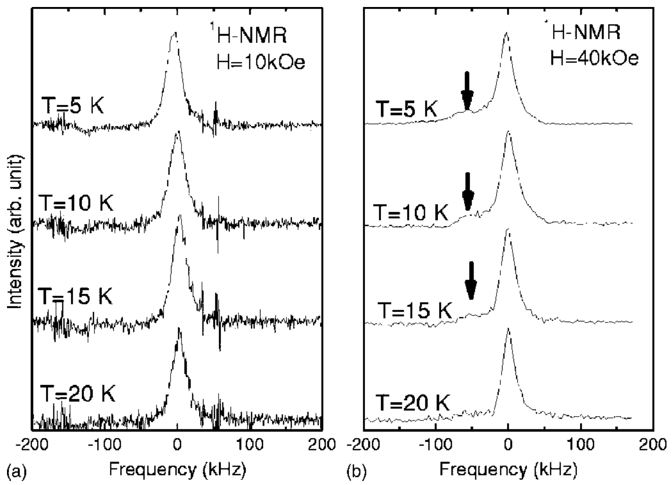

FIG. 4. The temperature dependence of the ^{1}H-NMR spectra of $d[2,2]$ salt at (a) 10 and (b) 40 kOe.

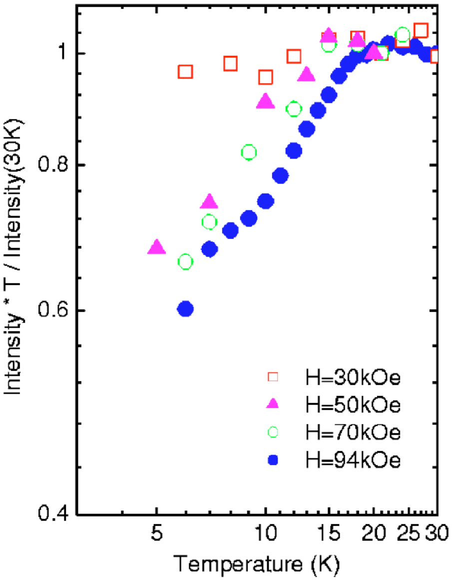

FIG. 5. (Color Online) The field dependence of the spectrum weight in the metallic phase (*A* and *B*).

of the SC and AF phases was confirmed. The results also indicated a phase separation of the Paramagnetic insulator (PI) and Paramagnetic metal (PM) phases. In our ^{13}C-NMR studies, however, no phase separation of PI and PM was observed. The application of a magnetic field generates a high resistive state with large hysteresis. Thus, the results were attributed to the field-induced transition from PM to the resistive state shown in Fig. 6(b). Our results also reveal that, microscopically, this resistive state corresponds to the AF magnetic ordering state, which is the same as in the insulating state in the phase diagram. One possible explanation of this field-induced metal-insulator transition is that because of the weak ferromagnetism associated with spin canting,[2] the AF state is more stable than the normal metallic state under a high magnetic field.

Moreover, it should be noted that the field-induced metal-insulator transition temperature is above the temperature of the SC-AF boundary. As shown in Fig. 6(b), these results suggest that there is not only a second-order insulator-antiferromagnetic boundary, but also a first-order metal-antiferromagnetic boundary with the phase separation under a high field. Indeed, the ac-susceptibility measurement for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl suggests a first-order metal-to-nonmetal transition, and this transition line merges with the AF transition line at low temperatures.[9] These results are attributable to the first-order normal-to-antiferromagnetic transition.

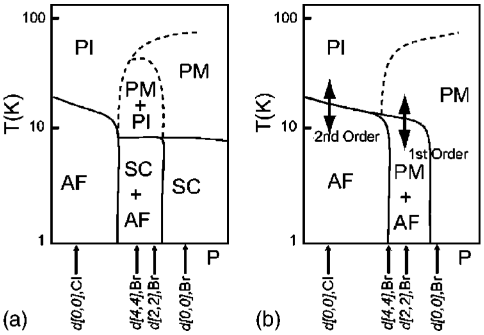

FIG. 6. The conceptual phase diagram under (a) zero field and (b) high magnetic field.

One possible basis for the theoretical prediction of the field-induced first-order AF insulator phase is the SO(5) scenario for the unification of magnetism and superconductivity.[6,22] The field-induced first-order normal-to-antiferromagnetic transition is predicted by the Monte Carlo simulation by Hu *et al.*[23] Presently, there are no theoretical models which explain the overall features of the κ-(BEDT-TTF)$_2$X system. However, our findings near the phase boundary should contribute to the theoretical development of this system.

In conclusion, we have performed ^{13}C-NMR on partially deuterized κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, and found evidence of a field-induced metal-insulator transition for the $d[2,2]$ salt at the microscopic scale. Our results suggest that this transition is a first-order metal-to-AF insulator transition.

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