Antiferromagnetic Organic Metal Exhibiting Superconducting Transition, κ-(BETS)₂FeBr₄ [BETS = Bis(ethylenedithio)tetraselenafulvalene]

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The recent development of organic conductors and the studies on their Fermiologies have changed completely the old image of the organic conductors. Nowadays, organic metals are regarded as "clean systems" with well-defined Fermi surfaces. The designability of organic systems has encouraged many chemists to produce completely new types of conducting systems. It seems that a considerable interest is presently focused on the systems consisted of π donor molecules and inorganic magnetic anions such as the paramagnetic organic superconductor, (BEDT-TTF)₄-(H₂O)Fe(C₂O₄)₃·(C₆H₅CN) [BEDT-TTF = bis(ethylenedithio)-tetrathiafulvalene].[1] The largest target among these systems may be the magnetic organic superconductor. We have recently found an exotic organic conductor, λ-BETS₂FeₓGa₁₋ₓBrᵧCl₄₋ᵧ (0 < x < 1, 0 < y < 0.5) exhibiting a superconductor-to-insulator or superconductor-to-metal transition [BETS = bis(ethylenedithio)-tetraselenafulvalene; λ represents the structure type of crystal].[2−4] The interaction between π metal electrons of BETS molecules and localized Fe³⁺ magnetic moments of the anions is essential in breaking the superconducting state of these systems. Here, we report an unprecedented antiferromagnetic organic metal exhibiting a superconducting transition at ambient pressure.

Unlike λ-BETS₂MCl₄ (M = Ga, Fe) with superconducting (M = Ga) or insulating (M = Fe) ground state, κ-BETS₂MX₄ (M = Ga, In, Fe; X = Br, Cl) retains the metallic state down to 2 K.[5−7] The crystal structure and the extended Hückel tight-binding band calculation suggest κ-BETS₂MCl₄ to be a two-dimensional metal,

Figure 1. The magnetic susceptibility of the plate crystals of κ-BETS₂-FeBr₄ oriented with the crystal planes parallel to each other. χ∥ (■) and χ⊥ (□) represent the magnetic susceptibilities for the fields applied to the directions approximately parallel (H∥) and perpendicular (H⊥) to the crystal plane, respectively.

which is consistent with the recent low-temperature magnetoresistance experiments.[8−10] In this work, we have examined the magnetic and electric properties of κ-BETS₂FeBr₄ down to 2 and 0.5 K, respectively, to check the possibility of the antiferromagnetic ordering of Fe³⁺ spins and/or the possibility of superconductivity of π electron system.

The crystals were prepared electrochemically from the 10% ethanol chlorobenzene solution containing BETS and [(C₂H₅)₄N]-[FeBr₄]. We have previously reported the structures of the crystals of λ- and κ-BETS₂MX₄ (M = Ga, Fe, In; X = Cl, Br).[5] There is no essential difference between the molecular arrangements in κ-BETS₂FeBr₄ and κ-BETS₂FeCl₄.[5,6] In the orthorhombic lattice, the conduction layers composed of BETS dimers and the layers of tetrahedral anions with localized magnetic Fe³⁺ moments are arranged alternately along the *b* direction.

The susceptibilities were measured on the sample of plate crystals of κ-BETS₂FeBr₄ (0.96 mg) oriented with the crystal planes parallel to each other. The magnetic field (500 Oe) were applied along the directions approximately parallel (∥) and perpendicular (⊥) to the average crystal plane. Figure 1 shows the temperature dependence of susceptibilities (χ∥, χ⊥) at 2−300 K. Both χ∥ and χ⊥ could be well fitted by Curie−Weiss plot at 100−300 K, where χ∥T and χ⊥T were almost constant: χ∥, χ⊥ = $C/(T - \theta)$; C = 4.70 K·emu·mol⁻¹, θ = −5.5 K. The constant C (= 4.70 K·emu·mol⁻¹) was approximately equal to 4.38 K·emu·mol⁻¹ [= $N_A g^2 \mu_B S(S + 1)$] expected for the $S = {}^5/_2$ localized spin system with g = 2.0. Therefore the FeBr₄⁻ anion is considered to be in high-spin state.[11] As seen from the inset of Figure 1, the susceptibility takes a maximum around 3 K and shows a slight but fairly sharp decrease around 2.5 K. Below 2.5 K, χ⊥ tends to be constant while χ∥ decreases with lowering temperature. These results indicate the onset of antiferromagnetic ordering of Fe³⁺ spins around 2.5 K (~T_N; Néel temperature).

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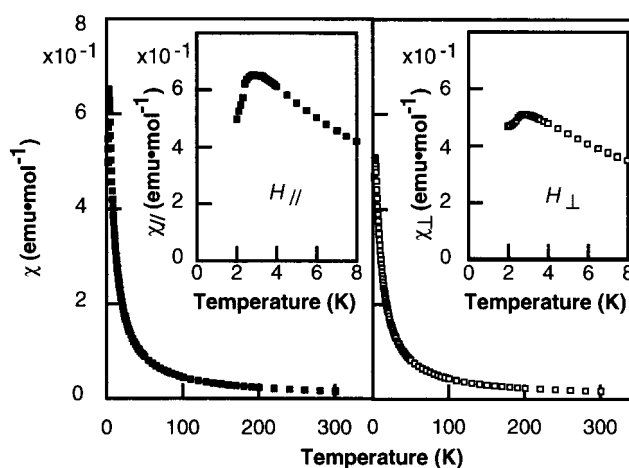
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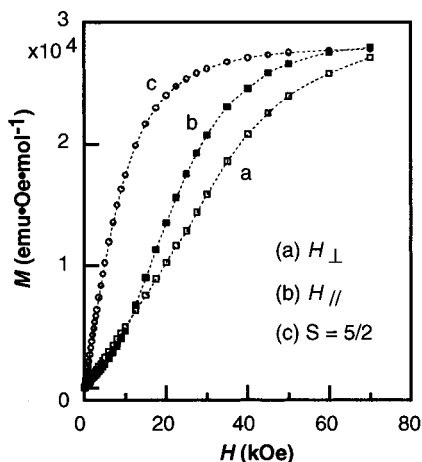
Figure 2. The field (H) dependence of the magnetization (M) of κ-BETS$_2$-FeBr$_4$ at 2 K. The curves a and b represent the magnetizations under the magnetic field $H_\perp$ and $H_\parallel$, respectively. Brillouin function with $S = {}^5/_2$ is also shown for comparison (curve c).

That is, κ-BETS$_2$FeBr$_4$ is the first organic conductor with the antiferromagnetic metal phase at ambient pressure. As shown in Figure 2, the field (H) dependence of magnetization (M) indicates the antiferromagnetic spin structure is not so simple. Since the M–H curve was measured at 2 K which is only 0.5 K lower than T_N, the field dependence of magnetization was not so sharp. But the M–H curve is reminiscent of a characteristic helical spin structure similar to that of MnP or Cr$_{1/3}$NbS$_2$ (Figure 2).[12–14] The helical plane is considered to be parallel to the *ac* plane (∥ crystal plane). When the field is applied in the *ac* plane (or helical plane), the metamagnetic behavior appears around 20 kOe. The magnetization increases rapidly to approach the saturation value of $S = {}^5/_2$ spin system. When magnetic field is perpendicular to the *ac* plane, the magnetization increases linearly with increasing external field and tends to be saturated around 70 kOe. It should be noted that a helical spin structure has been proposed for the other modification λ-BETS$_2$FeCl$_4$ based on the theoretical analysis of the generalized Kondo Lattice model, where the RKKY (Ruderman–Kittel–Kasuya–Yoshida) type indirect exchange interaction is essential.[15] The magnetic susceptibility of κ-BETS$_2$FeBr$_x$Cl$_{4-x}$ ($x \approx 1.0, 2.0, 2.5, 3.0$), whose examination is now in progress, indicates a similar magnetic behavior but the direction of the easy spin axis seems to be changed by small Br–Cl exchange. Similar rotation of easy axis of spin structure by the Br–Cl exchange has been observed in the antiferromagnetic insulating state of λ-BETS$_2$FeBr$_x$Cl$_{4-x}$.[16]

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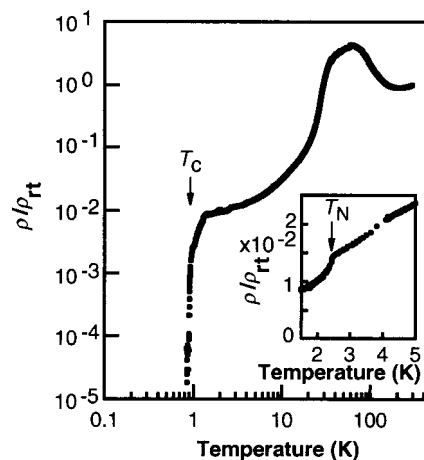

Figure 3. The resistivity of κ-BETS$_2$FeBr$_4$ at 0.5–300 K measured along the *ac* plane.

Contrary to the normal metal behavior of κ-BETS$_2$FeCl$_4$, κ-BETS$_2$FeBr$_4$ with large metal tetrabromide anions shows anomalous resistivity peak at low temperature.[5] In addition, unlike κ-BETS$_2$FeCl$_4$ with almost constant resistivity at low temperature,[5] κ-BETS$_2$FeBr$_4$ shows the resistivity decrease with lowering temperature even below 4 K. Therefore, we measured resistivity down to 0.5 K. As shown in Figure 3, the resistivity decreases very slowly down to about 200 K. Then it increases fairly sharply to take a characteristic peak around 60 K, below which resistivity decreases very rapidly.[17] As seen from the inset of Figure 3, the resistivity shows a small drop around 2.5 K ($\sim T_N$). This clearly shows that the resistivity is depressed by the onset of the ordering of Fe^{3+} spins and can be regarded as a direct evidence for the important role of interaction between π metal electrons and localized magnetic moments. The superconducting transition was observed at about 1.0 K. By applying weak magnetic field ($\sim$70 Oe) perpendicular to the conduction plane at 0.6 K, the superconducting state was broken. Thus, the present study has revealed the existence of a new organic conductor exhibiting the transition from antiferromagnetic metal phase to superconducting phase. We have recently found that the superconducting state of λ-BETS$_2$Fe$_x$Ga$_{1-x}$Br$_y$Cl$_{4-y}$ ($0.35 < x < 1, y < 0.5$)) is broken by the development of antiferromagnetic ordering of Fe^{3+} spins to result in the superconductor-to-insulator or superconductor-to-metal transition.[3,4] However, unlike λ-BETS$_2$Fe$_x$Ga$_{1-x}$Br$_y$Cl$_{4-y}$, κ-BETS$_2$FeBr$_4$ undergoes the transition from antiferromagnetic metal phase to superconducting phase. It will be an important future problem to study whether the antiferromagnetic spin ordering and superconductivity coexist below Néel temperature.

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