

Superconductor-to-Insulator Transition in an Organic Metal Incorporating Magnetic Anions: λ -(BETS)₂(Fe_xGa_{1-x})Cl₄ [BETS = bis(ethylenedithio)tetraselenafulvalene; $x \approx 0.55$ and 0.43]

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Since the first observation, more than 15 years ago, of superconductivity in an organic-molecule-based compound, (TMTSF)₂PF₆ (TMTSF = tetramethyltetraselenafulvalene),¹ an increasing large number of organic superconductors have been discovered.² As of today, κ -(BEDT-TTF)₂Cu[N(CN)₂]Br and κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene) show the highest T_c values (11.6 K at ambient pressure and 12.8 K at 0.3 kbar, respectively).^{3,4} More recently, the interplay between magnetism and superconductivity found in inorganic conducting systems such as ternary compounds, heavy Fermion systems, high- T_c oxides, etc., has become one of the most attractive subjects also in organic conductors. For example, an organic superconductor containing a magnetic anion, (BEDT-TTF)₄(H₂O)Fe(C₂O₄)₃·C₆H₅CN with $T_c = 7$ K, has been recently reported.^{5,6} In this compound however, no significant interaction between the conduction electrons and the localized spins of the magnetic anions was observed.

The BEDT-TSF molecule (bis(ethylenedithio)tetraselenafulvalene, designated hereafter BETS) is the modification of BEDT-TTF obtained by substituting selenium for sulfur in the central TTF fragment.⁷ Most of the cation radical salts derived from BETS exhibit metallic properties.^{8,9} Among these salts, the λ -(BETS)₂GaY_xZ_{4-x} (Y, Z = F, Cl, or Br) compounds

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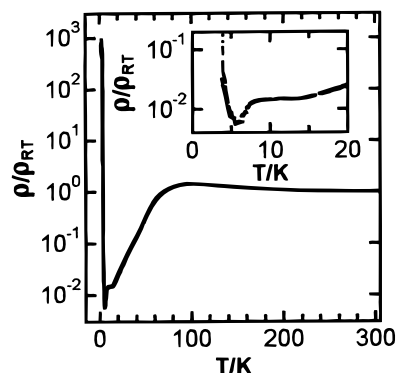


Figure 1. Temperature dependence of the resistivity of λ -(BETS)₂-(Fe_{0.55}Ga_{0.45})Cl₄ at ambient pressure. The inset shows the partial superconducting behavior just above the MI transition temperature.

undergo a superconducting transition.¹⁰ By contrast, its isostructural analogue λ -(BETS)₂FeCl₄ exhibits a coupled metal-to-insulator and antiferromagnetic transition at 8.5 K, suggesting the important role of the interaction between the π electrons of BETS and the d electrons of the high-spin Fe³⁺ ion.^{11,12}

We have previously examined the resistivity of the λ -(BETS)₂-(Fe_{0.48}Ga_{0.52})Cl₄ phase down to 4.2 K and observed a superconducting transition at 4.6 K.¹¹ Recently, we have successfully prepared the crystals of λ -(BETS)₂(Fe_xGa_{1-x})Cl₄ of sufficient quality and found a superconducting (SC) transition and a subsequent superconductor-to-insulator (SC-I) transition.

Needle-shaped crystals of λ -(BETS)₂(Fe_xGa_{1-x})Cl₄ were grown electrochemically.¹³ The stoichiometry of the crystals was determined to be $x = 0.55$ by electron probe microanalysis (EPMA). The distribution of the x -values within one crystal and between crystals was fairly sharp ($\Delta x = \pm 3\%$). Electrical resistivity was measured by the conventional four-probe method in the temperature range of 300–2 K. High-pressure measurements were carried out using a clamp-type cell. The static magnetic susceptibility was measured down to 2 K by using a SQUID magnetometer.

Figure 1 shows the temperature dependence of the resistivity of λ -(BETS)₂(Fe_{0.55}Ga_{0.45})Cl₄ at ambient pressure. As in the case of the pure λ -(BETS)₂GaCl₄ and λ -(BETS)₂FeCl₄ phases,^{10,11} the resistivity increases gradually when decreasing the temperature and shows a maximum around 100 K. Below this temperature, the resistivity sharply decreases down to ~ 15 K. Below 6 K, a resistivity increase indicating the metal-to-insulator transition (MI) is observed. Similar temperature-dependent resistivity variations were observed for more than 10 other

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(13) BETS was synthesized according to the previously reported method (Kato, R.; Kobayashi, H.; Kobayashi, A. *Synth. Met.* **1991**, 42, 2093). The preparation conditions of the crystals of λ -(BETS)₂(Fe_xGa_{1-x})Cl₄ were as follows: (I) For $x \approx 0.55$, 7.8 mg of BETS, 24.2 mg of [(C₂H₅)₄N]FeCl₄ and 31.4 mg of [(C₂H₅)₄N]GaCl₄ were dissolved in 20 mL of chlorobenzene containing 10% ethanol. Platinum wires were used as electrodes, and a constant voltage of 3.2 V was applied. The temperature was maintained at 21(±1) °C. (II) For $x \approx 0.43$, 5.0 mg of BETS, 20.9 mg of [(C₂H₅)₄N]FeCl₄ and 20.9 mg of [(C₂H₅)₄N]GaCl₄ were dissolved in 20 mL of chlorobenzene containing 10% ethanol. A constant voltage of 3.1 V was applied. The temperature was maintained at 20(±1) °C.

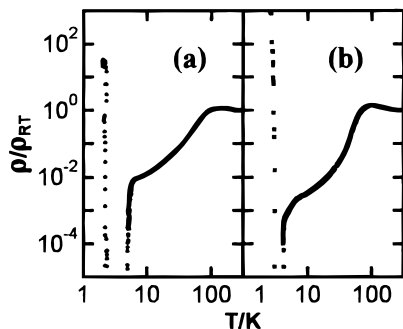


Figure 2. (a) Temperature dependence of the resistivity of λ -(BETS) $_2$ -(Fe $_x$ Ga $_{1-x}$)Cl $_4$ ($x \approx 0.55$) at 1 kbar (samples *a*; the resistivity of sample *a* at ambient-pressure is shown in Figure 1). (b) Temperature dependence of the resistivity of λ -(BETS) $_2$ -(Fe $_x$ Ga $_{1-x}$)Cl $_4$ ($x \approx 0.43$) at ambient pressure.

crystals ($T_{MI} = 4.5 \pm 0.5$ K). Some crystals show small drops of resistivity just above T_{MI} , which may be indicative of a *partial* superconducting transition (see inset of Figure 1). The temperature dependence of the resistivity of four crystals of λ -(BETS) $_2$ (Fe $_{0.55}$ Ga $_{0.45}$)Cl $_4$ (samples *a*–*d*) was determined at 1 kbar. A typical example is shown in Figure 2a (sample *a*). Below 100 K, the resistivity rapidly decreases when decreasing the temperature and drops to zero at 4.1–5.4 K. The samples *a*–*c* maintained the zero resistivity state throughout a certain temperature range, and a resistive state is suddenly restored at lower temperatures, resulting in a SC-I transition. Superconducting transition temperature (T_c) and SC-I transition temperature (T_{SC-I}) are 5.4 and 2.3 K for sample *a*, 4.6 and 3.6 K for sample *b*, and 4.1 and 2.5 K for sample *c*, respectively. The superconducting state of sample *d* is maintained from 4.5 down to 2 K. However, the large sample dependence of T_{SC-I} observed for samples *a*–*c* suggests that sample *d* might also undergo a SC-I transition below 2 K. Above 1.5 kbar, the SC-I transition is not observed for all the samples and the superconducting state is maintained down to 2 K.

These results obtained for crystals with $x \approx 0.55$ suggest that crystals with a slightly higher Ga content should exhibit a similar SC-I transition at ambient pressure. Therefore, crystals of λ -(BETS) $_2$ (Fe $_x$ Ga $_{1-x}$)Cl $_4$ with $x \approx 0.43$ were prepared and the resistivity measurements were made on six crystals. As shown in Figure 2b, the crystal showed a SC transition at 4.0–4.5 K and a SC-I transition at 3.0–3.6 K. Thus, the SC-I transition of λ -(BETS) $_2$ (Fe $_x$ Ga $_{1-x}$)Cl $_4$ observed at 1 kbar for $x \approx 0.55$ is confirmed at ambient pressure for $x \approx 0.43$.¹⁴

The magnetic susceptibility of the λ -(BETS) $_2$ (Fe $_x$ Ga $_{1-x}$)Cl $_4$ ($x \approx 0.43$) phase was measured down to 2 K on a sample made of a collection of identically oriented crystals. As shown in Figure 3, a susceptibility drop indicative of the SC transition is observed around 4.2 K for magnetic fields parallel ($H_{||}$) and perpendicular (H_{\perp}) to the long axis of the needle-shaped crystals. The susceptibility becomes strongly anisotropic below 3.4 K, where the SC-I transition occurs. When the magnetic field is parallel to the conduction plane (*ac* plane), H_{c2} (upper critical field) will be larger than that for the field perpendicular to it. Therefore the recovery of the susceptibility below 3.4 K for

(14) We have previously observed only SC transition in λ -(BETS) $_2$ (Fe $_{0.48}$ Ga $_{0.52}$)Cl $_4$. If the resistivity measurements were made down to 2 K, the SC-I transition would be also observed.

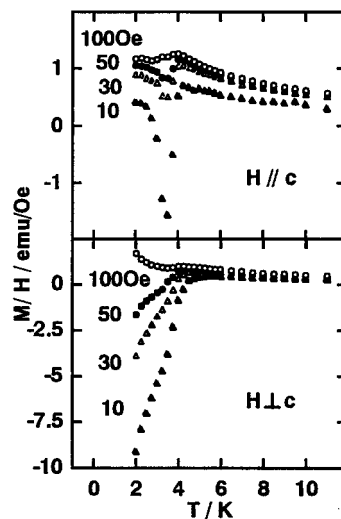


Figure 3. Temperature and field dependence of the magnetic susceptibility (M/H) of sample made of a collection of identically oriented crystals of λ -(BETS) $_2$ (Fe $_x$ Ga $_{1-x}$)Cl $_4$ ($x \approx 0.43$). The measurements for $H \parallel c$ (needle axis of the crystal) and $H \perp c$ were made for the same sample.

the small field (e.g., 10 Oe) parallel to *c* will be irrelevant to the superconductivity. The anisotropy and the field dependence of the susceptibility indicate the insulating state to be antiferromagnetic (AF) one with the spin flop field of about 50 G. It should be recalled that λ -(BETS) $_2$ FeCl $_4$ takes an antiferromagnetic insulating state below 8.5 K.^{11,15} Since λ -(BETS) $_2$ -GaY $_4$ Z $_{4-x}$ (Y, Z = F, Cl, or Br) ($0 < x < 1$) without magnetic ions shows only a superconducting transition,¹⁰ it is clear that the Fe $^{3+}$ ions play a crucial role in the destabilization of the superconducting state.

It is well-known that antiferromagnetic order and superconducting state coexist in inorganic systems such as ErRh $_4$ B $_4$ and HoMo $_6$ S $_8$ ¹⁶ and the dense Kondo heavy Fermion compounds.¹⁷ In the present λ -(BETS) $_2$ (Fe $_x$ Ga $_{1-x}$)Cl $_4$ systems, by contrast, antiferromagnetism and superconductivity compete with each other. A similar SC-I transition was also observed in κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl within the small pressure range of 0.3–0.5 kbar, where an antiferromagnetic order could be associated with an insulating state.¹⁸ However, the unique SC-I transition observed in the λ -(BETS) $_2$ (Fe $_x$ Ga $_{1-x}$)Cl $_4$ phases, in which the magnetic ions Fe $^{3+}$ play an essential role, is to our knowledge unprecedented. This result should open new avenues for the quest of novel magnetic organic superconductors.

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