

Pressure-Induced Superconducting Transition of λ -(BETS)₂FeCl₄ with π -d Coupled Antiferromagnetic Insulating Ground State at Ambient Pressure [BETS = Bis(ethylenedithio)tetraselenafulvalene]

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In the recent studies on organic conductors containing magnetic ions such as Fe³⁺ and Cu²⁺, the role of the interaction between π conduction electrons of organic molecules and localized magnetic moments of anions is of central interest. The system with weak π -d interaction such as the paramagnetic organic superconductor (BEDT-TTF)₄(H₂O)[Fe(C₂O₄)₃](C₆H₅CN) [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene] will exhibit normal metallic or superconducting properties.¹ On the other hand, the system like the title compound λ -(BETS)₂FeCl₄ with strong π -d coupling is expected to exhibit various novel electric and magnetic properties owing to the interplay between π and d electrons [BETS = bis(ethylenedithio)tetraselenafulvalene].^{2,3} In fact, λ -(BETS)₂FeCl₄ undergoes a very unique antiferromagnetic transition, where the interaction between localized magnetic moments and strongly correlated π conduction electrons plays an essential role. The large magnetic moments of Fe³⁺ ions will induce the π spins on donor molecules to develop a π -d coupled antiferromagnetic spin structure. Thus, the antiferromagnetic transition and the metal-to-insulator transition take place cooperatively in λ -(BETS)₂FeCl₄ at 8.5 K.² The tendency of the localization of π electrons related to the electron correlation effect will be diminished with increasing pressure because the π electron system will take a normal metallic state under high pressure. Then the π and d electron systems tend to be decoupled to each other and the antiferromagnetic order of Fe³⁺ spins and π conduction electrons will coexist in λ -(BETS)₂FeCl₄ at high pressure.⁴ Furthermore, λ -type BETS conductors show very interesting new transporting phenomena such as a superconductor-to-insulator transition and a superconductor-to-metal transition when the magnetic Fe³⁺ ions are diluted by nonmagnetic Ga³⁺ ions.⁵ In the present paper, the discovery of the superconductivity in this unique π -d electron system λ -(BETS)₂FeCl₄ is reported.

Thin needle crystals of λ -(BETS)₂FeCl₄ were prepared by the electrochemical oxidation according to the reported conditions.⁶ The λ -type BETS crystal has a triclinic lattice. The needle axis

of the crystal is almost parallel to the *c* axis, which corresponds to the magnetic easy axis of the antiferromagnetic spin structure.^{3,7,8} The conduction layer composed of BETS molecules is parallel to the *ac* plane. The electrical resistivities were measured using the clump-type high-pressure cell from room temperature to about 0.55 K. The electrical resistivities were also measured under the magnetic field applied almost parallel and perpendicular to the conduction layer.

Figure 1 shows the temperature dependence of resistivity under high pressure. As reported before, the resistivity increases gradually down to ca. 90 K at ambient pressure, indicating the strong correlation of π conduction electrons.² Then it decreases down to about 8.5 K, below which the π -d coupled antiferromagnetic insulating state develops. The broad resistivity maximum around 90 K disappeared at high pressure and the metal-to-insulator transition temperature (*T*_{MI}) was depressed. These results are in good agreement with the previously reported ones: *T*_{MI} = 4.0 K at 2.0 kbar and 2.6 K at 2.5 kbar.² Around 3.0 kbar, the superconducting transition was observed (*T*_C ≈ 1.8 K). *T*_C was decreased with increasing pressure.

Owing to the π -d coupling, λ -(BETS)₂FeCl₄ exhibits a characteristic field dependence of the conducting properties. Several years ago, Goze et al. first discovered the field-restored highly conducting state (FRHCS) of λ -(BETS)₂FeCl₄.^{9,10} The antiferromagnetic insulating ground state is destabilized under magnetic field and the metallic state is restored above 110 kOe. At high magnetic field, the Fe³⁺ spins (*S* = 5/2) are oriented ferromagnetically. Consequently, the π and d electron systems tend to be decoupled and the metallic state with ferromagnetically oriented Fe³⁺ spins is realized. To see FRHCS at high pressure, the magnetic field was applied to the crystal at 2.5 kbar and 0.55 K, where the system takes the π -d coupled antiferromagnetic insulating state at zero field (see Figure 1). The resistivity showed a sharp decrease around 55 kOe, showing the recovery of metallic state (FRHCS). The critical field at 2.5 kbar was half of that at ambient pressure.

Figure 2a shows the field dependence of resistivities at 3.5 kbar and 0.55 K, where the system has a superconducting ground state. When the magnetic field was applied perpendicular to the conduction layer, the nonzero resistivity began to appear at 4.5 kOe, and the increase of resistivity was saturated at 8.0 kOe. The suppression of the superconducting transition by magnetic field is also presented in Figure 2b. On the other hand, in the case of parallel magnetic field, the superconducting state began to be broken at 0.5 kOe, where the resistivity increased sharply. Then it increased gradually up to 13 kOe (Figure 2a). These results suggest an anisotropic electronic structure of the system.

λ -(BETS)₂FeCl₄ showed a metal-to-insulator transition at 2.5 kbar and a superconducting transition at 3.5 kbar (Figures 1 and

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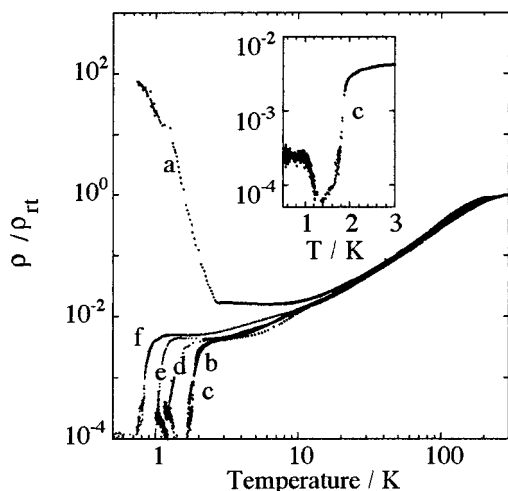


Figure 1. The resistivity of λ -(BETS) $_2$ FeCl $_4$ at 2.5 (a), 3.0 (b), 3.2 (c), 4.0 (d), 4.5 (e), and 5.0 (f) kbar. The inset shows the anomalous resistivity behavior observed at 3.2 kbar.

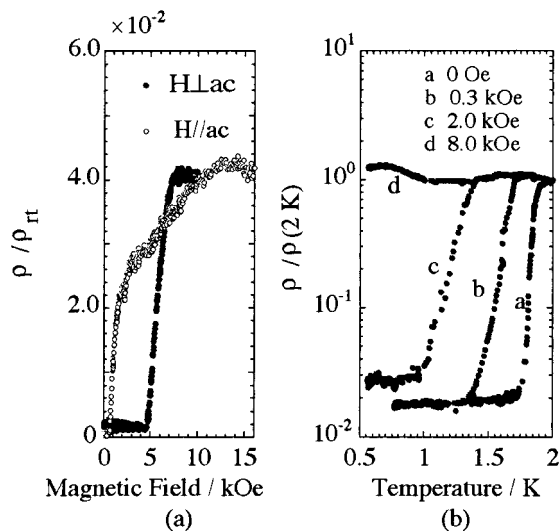


Figure 2. (a) The magnetic field dependence of the resistivities of λ -(BETS) $_2$ FeCl $_4$ at 3.5 kbar and 0.55 K. The magnetic field is approximately parallel or perpendicular to the conduction (ac) plane. (b) The suppression of the superconducting transition under magnetic field applied perpendicular to the ac plane.

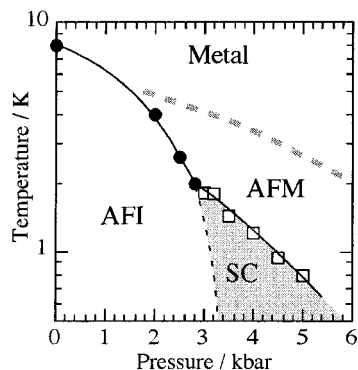


Figure 3. The phase diagram of λ -(BETS) $_2$ FeCl $_4$. The bold broken line shows the pressure dependence of the peak temperature of the susceptibility (ref 4). AFI = antiferromagnetic insulating phase, SC = superconducting phase, and AFM = antiferromagnetic metal phase.

3). However, the phase boundary between the antiferromagnetic insulating phase and the superconducting phase is not clear. An anomalous resistivity increase observed around 1.3 K at 3.0–3.2 kbar seems to be a trace of a superconductor-to-insulator transition

(see inset of Figure 1). By applying very weak magnetic field (0.3 kOe), this anomalous resistivity increase was suppressed and the superconducting state was stabilized. The pressure dependence of T_C was almost equal to that of the λ -type BETS superconductor without Fe^{3+} ions: $dT_C/dP \approx -0.5$ deg/kbar for λ -(BETS) $_2$ FeCl $_4$ and -0.5 to -0.7 deg/kbar for λ -(BETS) $_2$ GaBr $_x$ Cl $_{4-x}$ ($x = 0.0$ – 1.5).^{11,12} Since the lattice constants of λ -(BETS) $_2$ FeCl $_4$ are almost equal to those of λ -(BETS) $_2$ GaCl $_4$,¹³ the π electron states of these two salts will closely resemble each other if the π - d interaction is not included. The T_C value of λ -(BETS) $_2$ GaCl $_4$ at 3 kbar is reported to be about 3 K,¹² which is about 1 K higher than T_C of λ -(BETS) $_2$ FeCl $_4$ at 3 kbar.

As mentioned above, recent studies on magnetic susceptibility of the high-pressure metallic phase of λ -(BETS) $_2$ FeCl $_4$ showed the susceptibility peak suggesting antiferromagnetic ordering of Fe^{3+} spins.⁴ For example, at 3.5 kbar, above which the insulating phase is absent, the susceptibility peak observed at 4 K and the spin-flop behavior indicate the coexistence of π conduction electrons and antiferromagnetically ordered Fe^{3+} spins at low temperature. On the other hand, the present study shows that λ -(BETS) $_2$ FeCl $_4$ undergoes a superconducting transition at 1.5 K. Combining these data, it may be said that this superconducting transition around 3.5 kbar is a transition from an antiferromagnetic metal phase to a superconducting phase. The transition from an antiferromagnetic metal phase to a superconductor phase has been recently observed also in another modification of BETS conductors, κ -(BETS) $_2$ FeBr $_4$. That is, κ -(BETS) $_2$ FeBr $_4$ undergoes successive phase transitions with lowering temperature from a paramagnetic metal state to an antiferromagnetic metal state at 2.5 K (T_N) and from an antiferromagnetic metal state to a superconducting state at 1.0 K (T_C).¹⁴ Concerning magnetic superconductors, intensive studies have been made on (RE)Mo $_6$ S $_8$, (RE)Mo $_6$ Se $_8$, and (RE)Rh $_4$ B $_4$ for the last two decades.¹⁵ For these compounds, magnetic transitions occur below T_C . The transition from an antiferromagnetic metal phase to a superconducting phase is a rather rare case even in inorganic compounds, and reported about several compounds: the typical example is a heavy-fermion system, URu $_2$ Si $_2$.¹⁶ In organic systems, the antiferromagnetic metal-to-superconductor transition has been first observed in κ - and λ -type BETS conductors with magnetic Fe^{3+} ions.

The mechanism of magnetic interaction between Fe^{3+} moments in these organic molecular salts is the most important problem.¹⁰ Since the $\text{Fe}\cdots\text{Fe}$ separation is large in the λ -type structure (>6 Å), the antiferromagnetic interaction between Fe^{3+} ions is thought to be mediated by π electrons of BETS molecules at the antiferromagnetic phase.² Brossard et al. have proposed the possibility of development of helical spin structure mediated by RKKY type exchange interaction in λ -(BETS) $_2$ FeCl $_4$.¹⁰ From the thermodynamical viewpoint, it seems to be difficult for the high-temperature order (magnetic order) to be broken by the onset of another order (superconductivity) developed at lower temperature. The experimental evidence for the coexistence of the antiferromagnetic order and superconductivity is highly desired.

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