

Highly Correlated Organic Conductor with Magnetic Anions Exhibiting a π -d Coupled Metal-Insulator Transition, λ -(BETS)₂FeBr_xCl_{4-x} (BETS = Bis(ethylenedithio)tetraselenafulvalene)

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Molecular organic ferromagnetic metals have recently become attractive targets in the development of new organic conducting systems. To find a clue for the design of such novel systems, organic conductors with interaction between metal electrons and magnetic moments must be prepared in a first step. However, in the systems so far studied, the conduction electrons and magnetic moments are separated and the interaction between them is weak. The recent discovery of the paramagnetic organic superconductor (ET)₄[(H₂O)Fe(C₂O₄)₃]·C₆H₅CN (ET = bis(ethylenedithio)tetrathiafulvalene) was very encouraging.¹ More recently, a superconducting transition and a subsequent superconductor-to-insulator transition have been observed in a series of λ -type BETS-based (BETS = bis(ethylenedithio)tetraselenafulvalene) conducting salts with mixed magnetic counteranions, λ -(BETS)₂(Fe_xGa_{1-x})Cl₄.² It has been also reported that the metal-insulator transition (MI) observed at 8.5 K for the pure λ -(BETS)₂FeCl₄ phase is coupled with a concomitantly occurring antiferromagnetic transition.³ In this paper, we report an unexpectedly large increase of MI transition temperature (T_{MI}) and the contrastive strong decrease of the Fe^{••}Fe antiferromagnetic interaction in λ -(BETS)₂FeCl₄ by the partial exchange of Cl to Br, which suggests a novel "spin structure model" characteristic of highly correlated organic conducting systems with magnetic anions.

Thin needle crystals of λ -(BETS)₂FeBr_xCl_{4-x} ($x = 0.5, 0.6,$ and 1.1) were prepared by electrocrystallization according to a procedure similar to that used in the preparation of λ -(BETS)₂GaY_xZ_{4-x} (Y, Z = F, Cl, or Br).^{4,5} The Br content (x) was determined by electron probe microanalysis (EPMA). The cell dimensions obtained by a Rigaku AFC-5R four-circle diffractometer are approximately equal to that of the λ -(BETS)₂-GaBr_xCl_{4-x} phase^{4,5} and are almost linearly dependent on x : $V(\text{\AA}^3) = 1783.7 + 8.5x$. Resistivities were measured along the needle axes of the crystals (llc). The dc magnetization measurements were made on the oriented thin needle crystals ($Hllc$) with a SQUID magnetometer (Quantum Design MPMS-7).

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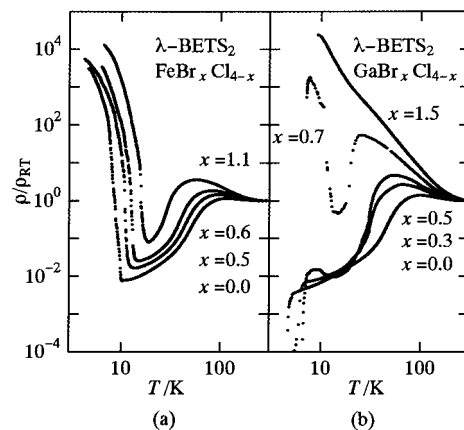


Figure 1. Temperature dependence of the electrical resistivity of λ -(BETS)₂FeBr_xCl_{4-x} salts (this work) and λ -(BETS)₂GaBr_xCl_{4-x} salts.^{4,5}

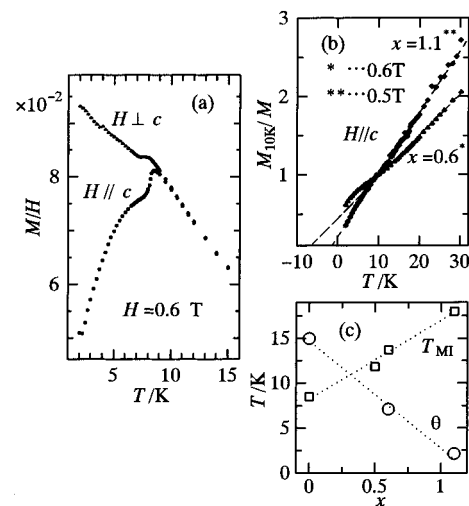


Figure 2. (a) Magnetization curves of λ -(BETS)₂FeCl₄. (b) Curie-Weiss plots of λ -(BETS)₂FeBr_xCl_{4-x}. The plots of λ -(BETS)₂FeCl₄ was omitted because the Weiss temperature has been already reported.^{3,8b} (c) The Br content (x) dependence of metal-insulator transition temperature, T_{MI} (\square), and Weiss temperature, θ (\circ), of λ -(BETS)₂FeBr_xCl_{4-x}.

Figure 1 shows the temperature-dependent electrical resistivity of λ -(BETS)₂FeBr_xCl_{4-x} phase compared to that of λ -(BETS)₂-GaBr_xCl_{4-x}.^{4,5} Except for the low-temperature region, the resistivity behaviors of the Fe and Ga systems resemble to each other, indicating that their π electron states are essentially the same. With increasing x , the broad resistivity maximum observed for λ -(BETS)₂FeBr_xCl_{4-x} becomes prominent, and T_{MI} increases almost linearly as a function of x (Figure 2c). Quite surprisingly, the exchange of only one Cl to one Br doubles T_{MI} . It has been reported that for the pure λ -(BETS)₂FeCl₄ salt this resistivity maximum disappears and that T_{MI} decreases at high pressure.³ The increase in x makes the unit cell volume larger and gives rise to a negative "chemical pressure" effect on the resistivity behavior.^{4,5}

The gradual resistivity increase in the high-temperature region can hardly be ascribed to a small bandgap, but is probably due to the strong correlation of π electrons because the simple extended-Hückel tight-binding band calculations afford two-dimensional Fermi surfaces.³ Quite similar Fermi surfaces have been also calculated for κ -(ET)₂Cu[N(CN)₂]Cl, which exhibits a gradual resistivity increase at ambient pressure and a superconducting transition at 12.8 K and 0.3 kbar.⁶ It is believed that, owing to the strong correlation of π electrons, κ -(ET)₂Cu[N(CN)₂]Cl possesses an antiferromagnetic spin structure at low temperature and ambient pressure, with π electrons localized

on each ET dimer.⁷ The magnitude of the broad resistivity maximum below 100 K can be regarded as a rough measure of the magnitude of the electron correlation. Thus, it may be said that a strong electron correlation favors the MI transition of λ -(BETS)₂FeBr_xCl_{4-x}.

Figure 2a shows the magnetization (M) of the pure λ -(BETS)₂-FeCl₄ salt measured by adopting the zero-field cooling process to confirm the previously reported discontinuous drop of M at T_{MI} .^{8,9} At about 1.2 T, the magnetization drop at T_{MI} became very small even for the field parallel to the c axis (|| easy axis), which is ascribed to the spin-flop transition.^{8,9} The magnitude of M of λ -(BETS)₂FeBr_xCl_{4-x} is indicative of a high-spin state of the Fe³⁺ ion, and the anisotropy of M suggests the antiferromagnetic state below T_{MI} . The Weiss temperature (θ) determined by Curie-Weiss plots between T_{MI} and 30 K is given in Figure 2b,c. Considering that the magnetization is dominated by the high-spin Fe³⁺ ions, the decrease of the antiferromagnetic Fe³⁺-Fe interaction with increasing x is in striking contrast to the large enhancement of T_{MI} , indicating that the Fe³⁺-Fe interaction cannot be the driving force of the MI transition.

It is well-known that a highly correlated electron system tends to adopt an antiferromagnetic insulating state.¹⁰ A recent theoretical approach by Seo and Fukuyama of the ground state of the π electron system of λ -(BETS)₂GaBr_xCl_{4-x} led to the conclusion that this system is located near the boundary between an antiferromagnetic phase and a spin gap phase.¹¹ According to this analysis, if the onsite Coulombic interaction exceeds some critical value, antiferromagnetic spin ordering emerges and eventually leads to an insulating state which can be considered as two-dimensional localized spin system. Since the resistivity behavior indicates that the conduction electron state of the Fe and Ga systems are essentially the same, a similar situation should occur in the π electron system of λ -(BETS)₂FeBr_xCl_{4-x}. Needless to say, there is another spin system in λ -(BETS)₂FeBr_xCl_{4-x}, that is the d spin system of the Fe³⁺ ions. Therefore, the MI transition of λ -(BETS)₂FeCl₄ might be a cooperative AF transition of π and d spin systems. As mentioned before, the magnetization shows a discontinuous drop at T_{MI} for the field parallel to the c axis ($H_{||c}$) ($\Delta M/M = 0.07-0.08$) (Figure 2a),⁹ while the anomaly becomes inconspicuous for H_{\perp} . As the ratio of the paramagnetic susceptibilities of localized π and d spin systems is roughly equal to μ_{π}^2/μ_d^2 (≈ 0.085), the role of the π electron spin seems to be crucial for the large drop of M ($\Delta M = 1.2 \times 10^{-2}$ emu/mol, which is more than 20 times larger than the paramagnetic susceptibility of λ -(BETS)₂GaBr_xCl_{4-x}⁵). On the basis of these facts, a possible spin structure model may be proposed (Figure 3a). As in κ -(ET)₂Cu[N(CN)₂]-Cl with almost one 1/2 spin on each ET dimer,⁷ in λ -(BETS)₂-FeCl₄ where the intradimer interaction is more than 3 times

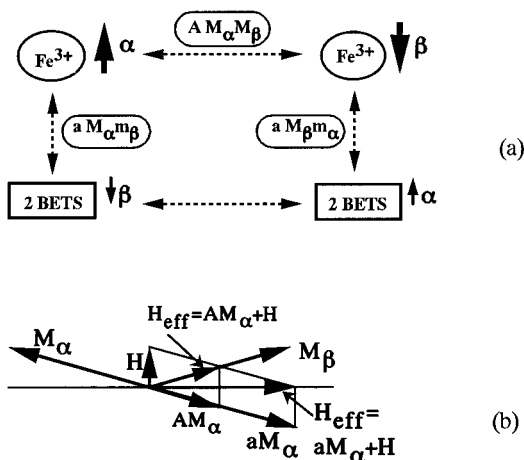


Figure 3. (a) Schematic representation of spin structure model of λ -(BETS)₂FeCl₄. (b) The effective magnetic field of π spin system with applying field normal to the c axis.

larger than the other intermolecular interactions,³ one π electron tends to localize on each BETS dimer. Thus, an antiferromagnetic coupling can be expected between π and d spin systems.

Owing to the large magnetic moment of Fe³⁺, the magnetization of the d spin system will be determined almost independently of π spin system, while that of the π spin system may be assumed to be governed by the external field and the effective field originating from antiferromagnetic interaction between d and π systems. The origin of ΔM at T_{MI} was considered for the two typical following cases: (i) $H_{||c}$ (easy axis^{8,9}) and (ii) H_{\perp} . For case i, according to the simple antiferromagnetic model, the magnetic susceptibility of the d spin system (χ_d) will be about $1/A$ at T_{MI} , where $AM_{\alpha}M_{\beta}$ is the exchange interaction of α and β sublattices of the d spin system ($M_{\alpha}(M_{\beta})$ is the magnetization of $\alpha(\beta)$ site). Therefore, $\delta M_{\alpha}(=\chi_d H) \approx H/A$ and the effective field then induced on the β site of the π spin system by the external field H will be $\delta H_{\text{eff}} = H - (a/A)H$, where $aM_{\alpha}m_{\beta}$ is the exchange interaction between the π and d systems. If $a \approx 2A$, δH_{eff} becomes $-H$. The π spin system will then be magnetized along the $-H$ direction as if the susceptibility would become negative, resulting in the 8% drop of M . For case ii, when $a \approx 2A$, the effective field on the β site of the π spin system will be approximately zero along the direction of the external field H (see Figure 3a). Consequently, the magnetization drop will become very small for H_{\perp} , which is consistent with the experimental results. According to this model, the small ΔM above 1.2 T (\approx spin-flop field^{8,9}) described before is easily understandable.

More detailed studies are needed to establish the spin structure model of λ -(BETS)₂FeCl₄. However, the enhanced electron correlation suggested by the resistivity measurement of λ -(BETS)₂FeBr_xCl_{4-x} and the simple consideration on the origin of the anomalous drop of M in λ -(BETS)₂FeCl₄ at T_{MI} indicate the important role of π -d coupling. The highly correlated organic conductor with magnetic anion will certainly be a fertile field to produce various new aspects of organic conducting systems.

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