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A novel superconductor with insulating magnetic ground state

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Contents

Abstract

The BETS conductor with mixed anions, λ-$BETS_2Fe_xGa_{1-x}Cl_4$ (BETS = bis(ethylenedithio)tetraselenafulvalene) exhibited an unprecedented superconductor-to-insulator (SC–I) transition around $x = 0.43$ at ambient pressure. The large drop in magnetic susceptibility at T_c ($\approx$4.2 K) and its recovery at T_{SC-I} ($\approx$3.2 K) clearly showed that this SC–I transition reflects an intrinsic nature of the crystal. The magnitude of *ac* susceptibility (≈ -40 emu mol^{-1}) at 4 K, where the system is in the superconducting state, gave the

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Meissner volume fraction of about 75%. The anisotropy and field dependence of magnetization below T_{SC-I} indicate the insulating ground state to be antiferromagnetic with easy axis parallel to *c*. The systematic examination of the resistivities of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ showed that the system undergoes a MI transition at $x > x_{c1}$ (≈ 0.5), SC transition at $x < x_{c2}$ (≈ 0.35) and SC–I transition at $x_{c2} < x < x_{c1}$. The SC–I transition was also observed in λ-$BETS_2Fe_xGa_{1-x}Cl_4$ ($x \approx 0.55$) at 1 kbar, which exhibited a metal–insulator (M–I) transition at ambient pressure. The high-pressure resistivity measurements revealed a superconducting transition in λ-$BETS_2Fe_{0.7}Ga_{0.3}Cl_4$. Based on these resistivity measurements, the preliminary P-T-*x* phase diagram of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ was obtained. The anisotropy and field dependence of the susceptibilities of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ ($x = 1.0$, 0.7, 0.55 and 0.43) suggested the characteristic π-d coupled antiferromagnetic structure of the insulating ground state. The Br-containing system, λ-$BETS_2Fe_xGa_{1-x}BrCl_3$ was semiconducting at ambient pressure. But λ-$BETS_2Fe_xGa_{1-x}BrCl$ ($x = 0.5$) exhibited a SC–I transition ($T_c = 7$ K and $T_{SC-I} = 3$ K) at 2 kbar. While λ-$BETS_2Fe_xGa_{1-x}BrCl$ ($x \approx 0.1$–0.2) showed a SC–M (metal) transition around 1.5 kbar. It was quite surprising that the susceptibility of λ-$BETS_2Fe_xGa_{1-x}BrCl$ ($x \approx 0.1$) showed the antiferromagnetic ordering of the diluted Fe^{3+} spins around 4 K at ambient pressure. The recovery of the metallic state below T_{SC-M} in this system seems to be connected with the magnetic ordering of Fe spins.

Keywords: Organic superconductors; Superconducting phase transition; Superconductor-insulator transition; Superconductor-metal transition; Antiferromagnetism

1. Introduction

Since the first discovery of an organic superconductor, $TMTSF_2PF_6$ (TMTSF = tetramethyltetraselenafulvalene) in 1980 [1], great progress has been achieved in the development of new molecular conductors. In 1986, the first molecular superconductor based on coordination compounds, $TTF[Ni(dmit)_2]_2$ (TTF = tetrathiafulvalene; dmit = 1,3-dithiol-2-thione-4,5-dithiolate) was also discovered [2,3]. Considering that all the organic superconductors ever reported are based on donor molecules having TTF-like skeletons, $M(dmit)_2$ (M = Ni, Pd) systems occupy an important position because the superconductivity of $M(dmit)_2$ systems has also been found in the conductors without TTF-like donor molecules, where only $M(dmit)_2$ molecules are responsible for the formation of the conduction bands [3–5]. Thanks to large progress in the concept of the molecular design of two-dimensional metals achieved in the middle 1980s, where the analyses based on the simple tight-binding band picture played an essential role, the development of molecular metals and superconductors becomes fairly easy. Consequently, the number of molecular superconductors has rapidly increased and molecular superconductors are no longer rare materials. However, the variety of molecular superconductors is rather limited. Most of the molecular superconductors developed can be classified into a very small number of types of conductor, namely, α- (or θ-), β-, κ-type organic conductors and $M(dmit)_2$ superconductors with and without TTF-donors. Recent interest concerning the development of new molecular conducting systems has focused on the enhancement of the superconducting transition temperature T_c. However, in spite of the increasing number of organic superconductors, enhancement of the highest T_c record of an organic superconductor has not changed since 1990, when an organic superconductor κ-BEDT-$TTF_2Cu[N(CN)_2]Cl$ ($T_c = 12.8$ K at 0.3 kbar) [6,7] was discovered. It is well-known that this T_c-value is more than one-order of magnitude lower than that of a Cu-oxide superconductor. Nevertheless the molecular conductor has continuously attracted great interest from physicists and chemists because the designability and the large variety inherent in molecular systems are believed to generate a completely new class of conducting system.

Recently, considerable attention has been paid to molecular conducting systems incorporating magnetic ions such as Fe^{3+} and Cu^{2+}. The π-d interactions in these systems are expected to produce a new type of conductor where not only π conduction electrons but also localized d spins play an essential role. Although the preparation of usual Bechgaard type organic conductors with magnetic anions seems to be the easiest way to get 'magnetic conductors', the interaction between π conduction electrons and 3d localized magnetic moments of the transition metal ions is considered to be weak because the overlap between π and d orbitals will be very small in these systems. Therefore the stabilization of the metallic state will be essential to study of the π-d interactions in these organic conducting systems. However, only several examples are known so far and the π-d interactions are revealed to be very weak in almost all these systems. A good example may be the first paramagnetic organic superconductor, β''-$(BEDT\text{-}TTF)_4(H_2O)Fe(C_2O_4)_3]\cdot(C_6H_5CN)$ ($T_c = 7$ K) discovered in 1995 [8].

By use of the strong tendency of the BETS molecule to give stable metallic states, we have tried to prepare the BETS metals incorporating magnetic ions such as Fe^{3+}, Cu^{2+}, Co^{2+} and Mn^{2+} where BETS (bis(ethylenedithio)tetraselenafulvalene) is a π donor molecule analogous to BEDT-TTF [9,10]. Crystals of BETS conductors with tetrahalide anions MX_4 (M = Ga, Fe; X = Cl, Br) are polymorphic. The plate crystals have orthorhombic lattices with 'κ-type arrangements' of BETS molecules. Similar to other κ-type organic conductors, the crystals possess metallic ground states. The thin needle crystals have triclinic lattices with 4-fold quasi-stacking structures of BETS molecules whose structure type was named as 'λ-type one'. Hereafter we will concentrate our attention only upon λ-type BETS conductors.

We have previously reported that λ-$BETS_2FeCl_4$ undergoes a characteristic insulating transition around 8.5 K [10–12]. At 8.5 K, π conduction electrons are localized and π and d spin systems are considered to produce a π-d coupled antiferromagnetic spin structure. The isostructural system without magnetic anions, λ-$BETS_2GaCl_4$ exhibits a superconducting transition, even though the resistivity behavior above 20 K closely resembles that of λ-$BETS_2FeCl_4$ [9,13]. Thus it is clear that the λ-type BETS conductor is an exceptional conductor where the π-d coupling can play a crucial role. The electrical properties of λ-type BETS conductors with tetrahalide anions MX_4 can be controlled by mixing metal atoms (Fe, Ga) and/or halogen atoms (Cl, Br). We have recently reported an unprecedented superconductor-to-insulator (SC–I) transition in λ-$BETS_2Fe_xGa_{1-x}Cl_4$ [14,15]. We present here the electric and magnetic properties of λ-$BETS_2Fe_xGa_{1-x}Cl_4$. The SC–I and SC–M (metal) transitions of λ-$BETS_2Fe_xGa_{1-x}BrCl_3$ will be also briefly reported.

2. Experimental

BETS was prepared as previously reported [16]. The crystals of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ were grown electrochemically from ethanol (10%)-chlorobenzene mixed solution containing BETS, $[(C_2H_5)_4N]FeCl_4$ and $[(C_2H_5)_4N]GaCl_4$. The x-value was determined by electron probe microanalyses (EPMA). Resistivities were measured by the conventional four probe method along the needle axes of the crystals ($//c$) usually down to about 2 K. The high-pressure experiments were made by using a clamp-type cell. Magnetic susceptibilities were measured with a SQUID magnetometer (QUANTUM DESIGN MPMS-7 and MPMS-2).

3. Results and discussion

3.1. Resistivities of λ-$BETS_2Fe_xGa_{1-x}Cl_4$

Fig. 1 shows the relation between the x-value of the crystal of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ determined by EPMA (x_{cryst}) and the mixing ratio of $[(C_2H_5)_4N]FeCl_4$ and $[(C_2H_5)_4N]GaCl_4$ in the solution (x_{sol}) from which the crystal was grown. The value of x_{cryst} was roughly equal to x_{sol}. The small sample dependence of the resistivity behavior of the crystal in the same batch suggests a fairly homogeneous distribution of Ga and Fe in the crystals of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ and seems to be consistent with the fact that the size of $FeCl_4^-$ is almost equal to that of $GaCl_4^-$. Fig. 2 shows the x-dependence of the resistivity. As mentioned before, λ-$BETS_2FeCl_4$ ($x = 1.0$) undergoes a metal–insulator (M–I) transition around 8.5 K below which an unique π-d coupled antiferromagnetic spin structure develops [11,17] and λ-$BETS_2GaCl_4$ ($x = 0.0$) exhibits a superconducting transition around 6 K [13,18]. The broad

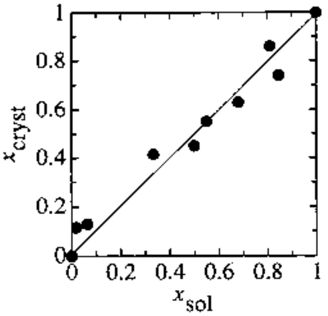


Fig. 1. The relation between x of the crystal (x_{cryst}) determined by EPMA and the mixing ratio of $[(C_2H_5)_4N]FeCl_4$ and $[(C_2H_5)_4N]GaCl_4$ in the solution (x_{sol}), from which the crystals were grown.

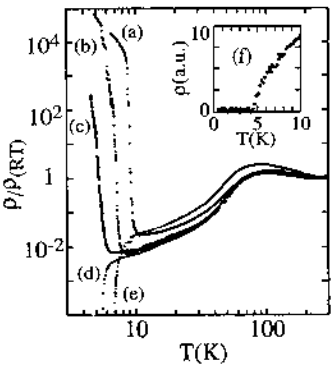


Fig. 2. The resistivities of λ-$BETS_2Fe_xGa_{1-x}Cl_4$: (a) $x = 1.0$, (b) $x = 0.84$, (c) $x = 0.63$, (d) $x = 0.13$, (e) $x = 0.0$, (f) $x = 0.35$ (inset).

resistivity maximum around 90 K suggests a strong correlation of π conduction electrons. Besides the low temperature region (< 20 K), the resistivity behavior was essentially x-independent, indicating that the π conduction electron state of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ is almost unchanged by varying the mixing ratio of Fe and Ga. This is in striking contrast to the strong y-dependence of the resistivity behavior of λ-$BETS_2MBr_yCl_{4-y}$ (M = Ga, Fe), which is explained in terms of 'negative chemical pressure' produced by the exchange of smaller Cl atoms to larger Br atoms [13,17,18]. In Br-containing system, the temperature corresponding to the broad resistivity maximum decreases with increasing Br-content (y). At $y > 0.8$, the system becomes semiconducting down to low temperature. As seen from Fig. 2, the M–I transition temperature (T_{MI}) of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ decreases from 8.5 K ($x = 1.0$) to 4.5 K ($x = 0.5$) with decreasing x. At $x < 0.5$, a superconducting transition was observed. T_c decreases slowly with increasing x: $T_c = 6$ K ($x = 0.0$) and 4.2 K ($x = 1.0$). Around $x = 0.45$, an unprecedented SC–I transition was observed (see Fig. 3): $T_c \approx 4.2$ K and $T_{SC-I} \approx 3$ K). The system with $x = 0.35$ exhibits a simple superconducting state down to 0.5 K (see inset of Fig. 2). Based

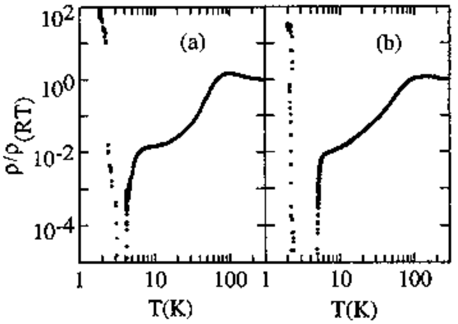


Fig. 3. (a) The resistivity of λ-$BETS_2Fe_xGa_{1-x}$ Cl_4 ($x = 0.43$) at ambient pressure. (b) The resistivity of λ-$BETS_2Fe_xGa_{1-x}$ Cl_4 ($x = 0.55$) at 1 kbar.

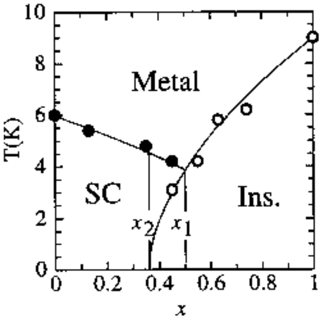


Fig. 4. The T-x phase diagram of λ-$BETS_2Fe_xGa_{1-x}Cl_4$. The superconductor-to-insulator (SC–I) transition is observable at $x_2 < x < x_1$.

on these data, the T–x phase diagram of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ was obtained (Fig. 4). The SC–I transition can be observed at $x_2 < x < x_1$: $x_1 \approx 0.5$ and $x_2 \approx 0.35$. To our knowledge, the SC–I transition has not been observed in any inorganic and organic conducting systems at least at ambient pressure. The SC–I transition was also observed at high pressure. The system with $x = 0.55$ exhibited a M–I transition at ambient pressure but exhibited a SC–I transition at 1 kbar ($T_c \approx 4.5$ K and $T_{SC-I} \approx 2.5$ K) (see Fig. 3). At 2–6 kbar, the system showed only superconducting transitions. Above 6 kbar the metallic state was stabilized down to low temperature.

Recently we have examined the resistivity of the Br-containing system λ-$BETS_2Fe_xGa_{1-x}BrCl_3$ ($x \approx 0.5$). As mentioned above, due to the large Br-content ($y > 0.8$) the system becomes a semiconductor at ambient pressure. However it exhibited a SC–I transition at 2 kbar ($T_c \approx 7$ K and $T_{SC-I} \approx 3.2$ K) (Fig. 5). Compared with the SC–I transition of the system without Br atoms, T_c was fairly enhanced and the temperature range where the system retained the superconducting state became much wider. At 2.8 kbar, the system showed a simple superconducting

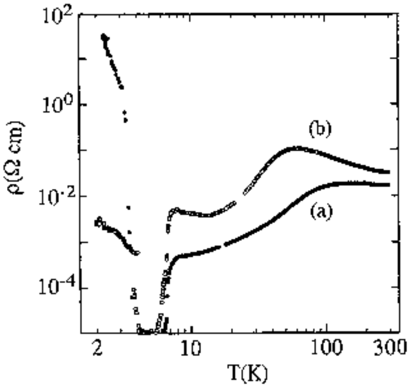


Fig. 5. The resistivities of λ-$BETS_2Fe_xGa_{1-x}BrCl_3$. (a) SC–I transition of λ-$BETS_2Fe_{0.5}Ga_{0.5}BrCl_3$ at 2 kbar and (b) SC–M transition of λ-$BETS_2Fe_{0.2}Ga_{0.8}BrCl_3$ at 1.5 kbar.

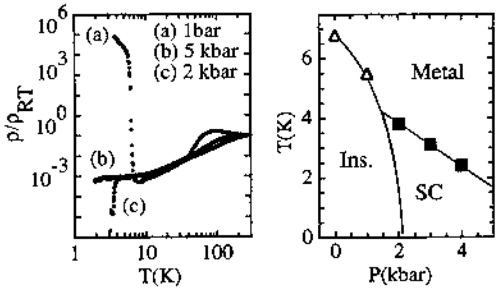


Fig. 6. Pressure dependence of the resistivity and T-P phase diagram of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ ($x \approx 0.7$).

transition ($T_c = 7.2$ K). In addition, we have recently observed a superconductor-to-metal (SC–M) transition around 1.5 kbar in λ-$BETS_2Fe_xGa_{1-x}BrCl_3$ ($x \approx 0.1$–0.2): $T_c \approx 7$ K and $T_{SC-I} \approx 3.5$ K. Similar to λ-$BETS_2Fe_{0.5}Ga_{0.5}BrCl_3$, this system is a semiconductor at ambient pressure. The electron correlation enhanced by incorporating Br atoms will be responsible for the semiconducting properties of this Br-rich system [17]. At high pressure, the electron correlation effect is diminished and the difference in the π-d coupling between the systems with different Fe-contents ($x = 0.5$ and 0.1–0.2) becomes crucial. Then the Fe-rich system shows the SC–I transition and the small-Fe system undergoes the SC–M transition. It is well known that the SC–M transition has been observed in $HoMo_6S_8$ and $ErRh_4B_4$, where the superconducting states are broken by the onset of ferromagnetic order of the magnetic moments of rare earth atoms [19,20]. Since the superconducting states of all the λ-$BETS_2GaBr_yCl_{4-y}$ systems without Fe^{3+} ions are stable down to low temperature [13,18], it is clear that the π-d interaction is essential in breaking the superconducting state of λ-$BETS_2Fe_xGa_{1-x}BrCl_3$.

Since the superconducting transition was observed at high pressure in λ-$BETS_2Fe_xGa_{1-x}Cl_4$ ($x = 0.55$), the resistivity behavior of Fe-rich system was examined at high pressure. Fig. 6 shows the pressure dependence of the resistivity and the P-T phase diagram of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ ($x \approx 0.7$). At ambient pressure the system undergoes a M–I transition around 7 K but becomes a superconductor above 2 kbar. Similar examinations were made on the crystals with various x-values and the preliminary P-T-x phase diagram of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ was obtained (Fig. 7).

Since the insulating phase of λ-$BETS_2FeCl_4$ is antiferromagnetic, the insulating phase neighboring on superconducting phase of λ-$BETS_2Fe_{0.7}Ga_{0.3}Cl_4$ is considered to be antiferromagnetic (see Fig. 6). In fact, as mentioned below, the anisotropy and field dependence of the magnetic susceptibility of λ-$BETS_2Fe_{0.7}Ga_{0.3}Cl_4$ indicated the antiferromagnetic nature of the insulating phase. The superconducting phase and the neighboring antiferromagnetic insulating phase are common features of the phase diagrams of representative organic superconductors such as Bechgaard salts and κ-type BEDT-TTF superconductors. In these systems, the antiferromagnetic spin excitation is expected to be related to the superconducting mechanism. However, it is quite doubtful that the antiferromagnetism of λ-$BETS_2Fe_xGa_{1-x}Cl_4$

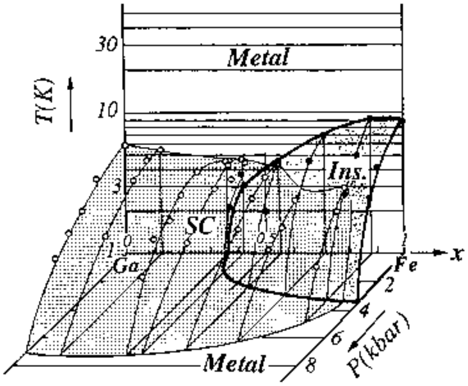


Fig. 7. P-T-x phase diagram of λ-$BETS_2Fe_xGa_{1-x}Cl_4$.

contributes to the superconducting transition. The SC–I transition suggests the competition between the antiferromagnetism and superconductivity in λ-$BETS_2Fe_xGa_{1-x}Cl_4$.

3.2. Magnetic properties of λ-$BETS_2Fe_xGa_{1-x}Cl_4$

Considering an almost full Meissner state in the superconducting phase of λ-$BETS_2GaCl_4$ [18], the large Meissner volume fraction might be expected in the superconducting state of λ-$BETS_2Fe_xGa_{1-x}Cl_4$. On the other hand, owing to the small superconducting temperature range between T_c and T_{SC-I} (1–1.5K) of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ ($x \approx 0.43$), the Meissner volume fraction of this system will become very small if the homogeneity in the distribution of Fe and Ga atoms is insufficient. We have previously reported the magnetic susceptibility of oriented thin needle crystals of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ ($x \approx 0.43$) [14]. However, we have recently found that the susceptibility reported in Ref. [14] was incorrect for the field perpendicular to c because of the effective pressure produced by the freezing of grease used to keep the crystals in the glass capillary. Therefore we re-examined the

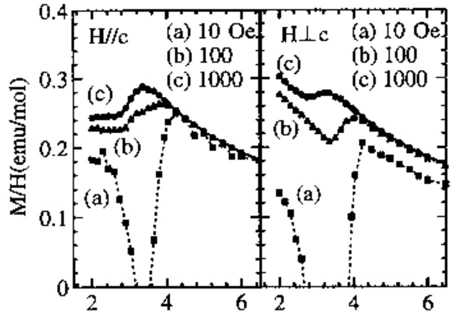


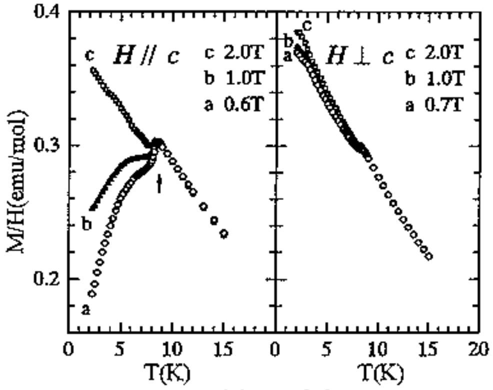
Fig. 8. The susceptibilities of the thin needle crystals of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ ($x = 0.43$).

susceptibilities carefully on the two samples. Both samples gave essentially the same result. Fig. 8 shows the temperature dependence of the susceptibility. The large susceptibility drops around 4 K and recovery around 3 K clearly showed that the system once transformed to a superconducting state then reverted to a non-superconducting state at lower temperature. The susceptibility was increased with increasing magnetic field up to about 500 Oe, which is considered to be related to the gradual vanishing of the superconductivity. Small and field-independent susceptibility for the field parallel to *c* axis at 500–100 Oe indicates the antiferromagnetic insulating state with easy axis parallel to *c*, where the *c* axis is parallel to the needle axis of the crystal and the conduction plane is parallel to the *ac* plane. From the *ac* susceptibility at 4 K, the Meissner volume fraction was estimated to be 75% for the $x \approx 0.47$ system, which undoubtedly showed that the SC–I transition is a bulk transition.

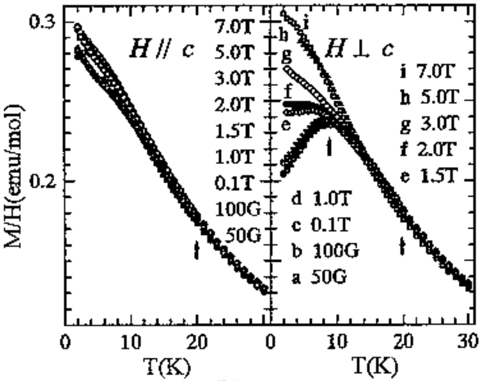
In order to clarify the magnetic properties of the insulating state, the susceptibilities of λ-BETS$_2$Fe$_x$Ga$_{1-x}$Br$_y$Cl$_{4-y}$ were measured. In the case of pure Fe system, the magnetic properties of λ-BETS$_2$FeBr$_y$Cl$_{4-y}$ changed systematically with changing Br-content (y) [17]: (1) At y ca. 0.0, the system takes π-d coupled antiferromagnetic insulating state below $T_{\mathrm{M-I}}$. The easy axis is approximately parallel to *c* and the spin flop field is 1.2 T (Fig. 9a). (2) Around y ca. 0.4, the π-d coupling becomes loose and the M–I transition temperature and temperature of the antiferromagnetic ordering of Fe^{3+} spins tend to be separated. (3) At $y > 0.65$, the M–I transition and antiferromagnetic Fe spin ordering is decoupled and the easy axis of the d spin system becomes approximately perpendicular to *c* with spin flop field of about 2 T (Fig. 9b). Thus it is clear that the magnetic properties are strongly dependent on the Br-content.

The typical susceptibility behavior of λ-BETS$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ is presented in Fig. 10. Similar to a pure FeCl$_4$ system, the susceptibility drop at $T_{\mathrm{M-I}}$ and spin flop behavior were observed for the field parallel to *c* in the $x \approx 0.7$ system. Therefore, λ-BETS$_2$Fe$_{0.7}$Ga$_{0.3}$Cl$_4$ is considered to take the π-d coupled antiferromagnetic insulating state with easy axis parallel to *c* below $T_{\mathrm{M-I}}$. Combining the results shown in Figs. 8, 9a and 10, it may be said that the insulating state of λ-BETS$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ ($x > 0.35$) takes the π-d coupled antiferromagnetic spin structure with easy axis parallel to *c*.

As mentioned before, λ-BETS$_2$Fe$_{0.1}$Ga$_{0.9}$BrCl$_3$ is semiconducting at ambient pressure and exhibits a SC–M transition around 1.5 kbar. The magnetic susceptibility at ambient pressure suggested that the Fe^{3+} spins are ordered antiferromagnetically at low temperature with easy axis perpendicular to *c*. Considering small density of Fe^{3+} ions in λ-BETS$_2$Fe$_{0.1}$Ga$_{0.9}$BrCl$_3$, the observation of magnetic order was quite an unexpected result. The direction of the easy axis ($\perp c$) and the relatively large spin flop field (1.5 T) is reminiscent of those of λ-BETS$_2$FeBr$_{0.8}$Cl$_{3.2}$ (Fig. 9b). This direction of the easy axis ($\perp c$) is almost perpendicular to that of the antiferromagnetic insulating phase in λ-BETS$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ ($//c$). As mentioned before, λ-BETS$_2$Fe$_{0.1}$Ga$_{0.9}$BrCl$_3$ exhibits a SC–M transition. At first sight, the metallic state restored below $T_{\mathrm{SC-M}}$ seems to be identical to the metallic state above



(a) $y = 0.0$



(b) $y = 0.8$

Fig. 9. Magnetic susceptibilities of λ-BETS$_2$FeBr$_y$Cl$_{4-y}$.

T_c. However, since the superconducting state becomes more stable than the metallic phase at T_c, the restored metallic state must be more stable than the high-temperature metallic phase. One possible mechanism for reducing the free energy in the low-temperature metallic phase may be related to the antiferromagnetic ordering of Fe spins. It has been found that in the pure FeCl$_4$ system, the antiferromagnetism and metallic state can coexist [21] but there may be the possibility that the antiferromagnetism of Fe spins and superconductivity compete with each other. When the Fe content is large, the antiferromagnetic order will destroy the superconducting state and induces the π-d coupled insulating antiferromagnetic structure to result in the SC–I transition. However when the Fe density is too small to develop the π-d coupled spin structure, antiferromagnetic Fe spin order cannot localize the π electrons and the π electron system retains the metallic property even when the superconducting state is broken. Then the system will become a metal with antiferromagnetically ordered diluted Fe spins.

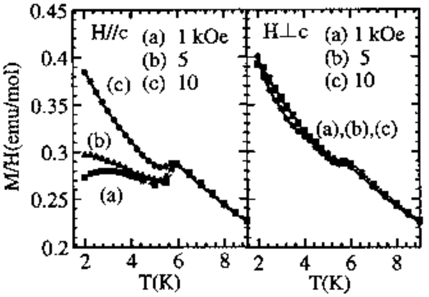


Fig. 10. Magnetic susceptibilities of λ-BETS$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ ($x \approx 0.7$).

In conclusion, λ-BETS$_2$Fe$_x$Ga$_{1-x}$Br$_y$Cl$_{4-y}$ exhibited the SC–I and SC–M transition. The SC–M transition has been observed in inorganic superconductors such as HoMo$_6$S$_8$ and ErRh$_4$B$_4$, where the ferromagnetism of rare earth atoms destroys the superconducting states. On the other hand, the SC–I transition is an unprecedented transition. The π-d coupled antiferromagnetic state will be responsible for this novel transport phenomena.

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