Magnetic properties of λ-$BETS_2$ $(Fe_xGa_{1-x})Cl_4$ exhibiting a superconductor-to-insulator transition $(0.35<x<0.5)$

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The crystal of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ with $x\approx 0.45$ undergoes successive superconducting and superconductor-to-insulator transitions around liquid helium temperature. The large diamagnetic susceptibility (≈ -35 emu/mol at 4 K) observed in the superconducting phase of the system with $x\approx 0.47$, which exhibits a superconducting transition at 4.3 K and superconductor-to-insulator transition at 3.7 K, can be regarded as evidence for the bulk nature of the superconductor-to-insulator transition. The anisotropy of the susceptibility and spin-flop behavior indicate that the system takes a *π-d* coupled antiferromagnetic insulating ground state, which is essentially the same as that of λ-$(BETS)_2FeCl_4$ exhibiting a coupled metal-insulator and antiferromagnetic transition at 8.5 K. The easy axis is parallel to the *c* direction. Unlike the Ga-rich system ($x<0.35$) with superconducting ground state, the Fe-rich system such as λ-$(BETS)_2(Fe_{0.7}Ga_{0.3})Cl_4$ shows a metal-insulator transition at ambient pressure. At high pressure, however, the *π* and *d* electrons tend to be independent of each other and the system takes a superconducting ground state.

Since the discovery of the first organic superconductor in 1980,[1] an enormous progress has been achieved in the field of molecular conductors. Contrary to the old image of the organic conductors, the organic conducting systems are now regarded as essentially clean systems with well-defined Fermi surfaces consistent with the simple tight-binding band picture. In addition, the low-dimensionality and strong electron correlation due to the small and anisotropic transfer integrals between *π* molecules characterize the electronic properties of these systems. Most of the organic conductors currently studied are so-called Bechgaard-type conductors, D_2X, composed of planar *π* donor molecules (*D*) and inorganic anions (*X*). Until recently, the role of the anions has been considered to be less important because the conduction bands of D_2X systems are formed only from the highest occupied molecular orbitals of donor molecules. But this situation is now being changed by the development of new organic conductors with the magnetic anions where the interaction between *π* metal electrons of donor molecules and localized magnetic moments of the anions is expected to produce new transport phenomena. In 1995, the first paramagnetic organic superconductor, $\beta''\sim$(BEDT-TTF)$_4(H_2O)Fe(C_2O_4)_3]\cdot(C_6H_5CN)$ was reported.[2] But in this conductor, the *π-d* interaction was found to be almost negligible. We have examined a series of organic conductors based on the BETS molecules and tetrahedral anions MX_4^- ($M=$Ga, Fe; $X=$Cl, Br)), where BETS [=bis(ethylenedithio)tetraselenafulvalene] is a selenium-substituted BEDT-TTF analog. The crystals of $(BETS)_2MX_4$ prepared electrochemically are polymorphic.[3–6] The *κ*- and λ-type salts are two main modifications. The plate crystals with *κ*-type structure [*κ*-$(BETS)_2MX_4$)] possess metallic states around liquid-helium temperature. We have recently found the first ambient-pressure antiferromagnetic organic metal *κ*-$(BETS)_2FeBr_4$ ($T_N\approx 2.5$ K), which exhibits a superconducting (SC) transition around 1 K.[7] The small but sharp drop of the resistivity at Néel temperature clearly shows the existence of *π-d* interaction. A helical spin structure was suggested from the magnetization curve at 2 K. A superconductivity has been also found in the isostructural system without magnetic ions, *κ*-$(BETS)_2GaBr_4$.[8] On the other hand, the thin needle-shaped crystal of λ-$(BETS)_2MX_4$ has a fourfold quasistacking molecular arrangement along the *a* axis and exhibits a variety of electronic properties depending on the mixing ratio of *M* and *X* atoms [λ-$(BETS)_2Fe_xGa_{1-x}Br_yCl_{4-y}$]. BETS molecules form conduction layers parallel to the ac planes (the needle axis of the crystal is parallel to *c*). The MX_4^- anions are located between BETS layers. The extended Hückel tight-binding band calculation gave two-dimensional Fermi surface similar to that of well-known *κ*-type BEDT-TTF superconductors.[4] The crystal of λ-$(BETS)_2GaCl_4$ exhibits a superconducting transition,[9,10] whose anisotropy of H_{c2} indicates the system to be a highly anisotropic three-dimensional system.[11] On the other hand, λ-$(BETS)_2FeCl_4$ undergoes a sharp metal-insulator (M-I) transition at $T_{\rm MI}$ ($=8.5$ K) and ambient pressure, where an antiferromagnetic (AF) transition simultaneously takes place.[4,12–14] This behavior has been interpreted in terms of a *π-d* coupled AF spin structure below $T_{\rm MI}$.[12,14] With increasing magnetic field, the M-I transition is suppressed.[13] We have found an unprecedented superconductor-to-insulator (SC-I) transition at ambient pressure in λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ ($x\approx 0.45$).[15–17]

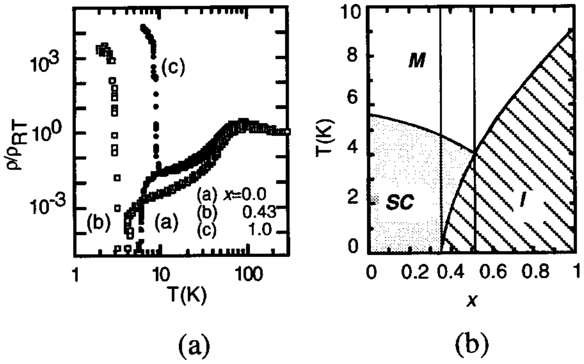

FIG. 1. (a) Typical examples of the temperature dependencies of the resistivities of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ ($x=0$, 0.43, 1.0). (b) Temperature-composition phase diagram of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ drawn on the basis of the data mainly reported in Ref. 16. M = metal, SC = superconductor, and I = insulator.

In this paper, we report the magnetic properties of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ ($x=0.43$, 0.47, 0.55, 0.70).

The typical resistivity behavior of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ and the schematic drawing of the phase diagram of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ are shown in Fig. 1.[16] Roughly speaking, the resistivity behavior above 10 K is independent of the x value. The resistivity increases gradually with decreasing temperature and takes a round maximum around 90 K. Then, it decreases fairly rapidly. This behavior suggests the strong correlation of π conduction electrons. When the content of nonmagnetic Ga^{3+} ions is large, the system shows a SC transition. While in the system where Fe^{3+} ions are dominant, the d spins of Fe^{3+} ions tend to couple with the π electrons to produce the AF insulating state.[12] A SC-I transition was observed at $0.35<x<0.5$ [see Fig. 1(b)].[16] We had previously measured the magnetic susceptibility of λ-$(BETS)_2(Fe_{0.43}Ga_{0.57})Cl_4$ exhibiting a SC-I transition.[15] However, the obtained susceptibility was found to be affected by the ''effective pressure'' produced by the freezing of the grease used to keep the thin needle-shaped crystals in the glass capillary. Therefore, we have reexamined the susceptibilities on two samples of oriented thin needle crystals of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ ($x=0.43$, 0.47) exhibiting SC-I transition by using a SQUID magnetometer: the first one was the former λ-$(BETS)_2(Fe_{0.43}Ga_{0.57})Cl_4$ sample used in the previous susceptibility measurements[15] and the other one consisted of freshly prepared crystals with $x=0.47$ (this value of $x=0.47$ was determined by EPMA [(electron probe microanalysis) and was in good agreement with that estimated from the magnitude of the susceptibility of the metallic phase, where Fe^{3+} ($S=\frac{5}{2}$) is in the paramagnetic state]. Figure 2 shows the susceptibilities of the first sample with $x=0.43$. When the old crystals ($x=0.43$) were washed by organic solvents to remove the grease, the long thin needle crystals were shortened, which made the alignment of the crystals difficult. The measurements were made with increasing temperature from 2 K, where the crystals are in a nonsuperconducting state (field heating process). The sharp susceptibility (M/H) drop around 2.5 K and its recovery around 4 K observed at 10 Oe correspond to SC-I and SC transitions, respectively. The ac susceptibility of λ-$(BETS)_2(Fe_{0.47}Ga_{0.53})Cl_4$ (fresh sample) measured at low frequency (0.5 Hz) and low amplitude (0.1 Oe) showed that the system is in a SC state at 3.8–4.3 K [Fig. 3(a)]. The small temperature range of the SC state in the $x=0.47$ system is of course consistent with the phase diagram shown in Fig. 1(b). The value of the magnetization at 4 K (≈−35 emu/mol) was about 75% of the full Meissner value of this system (≈−50 emu/mol), where the diamagnetic correction was not made. Considering the possible inhomogeneity of the polycrystalline samples and the fact that this value was obtained just below the superconducting transition temperature because of the very narrow temperature range of the SC state, this diamagnetic susceptibility was unexpectedly large and can be regarded as a clear evidence for the bulk nature of the SC-I transition. To our knowledge, λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ ($x\approx 0.45$) may be the first conductor exhibiting a bulk SC-I transition. The M-H curve at 4 K of λ-$(BETS)_2(Fe_{0.47}Ga_{0.53})Cl_4$ measured for the field perpendicular to the needle axis ($H_\perp$) gave a minimum around 3 Oe ($\approx H_{ci}$) which are much smaller than the field corresponding to the minimum susceptibiulity of λ-$(BETS)_2GaCl_4$ ($H_\perp \approx 20$ Oe).[10] From the M-H curve, the dc susceptibility

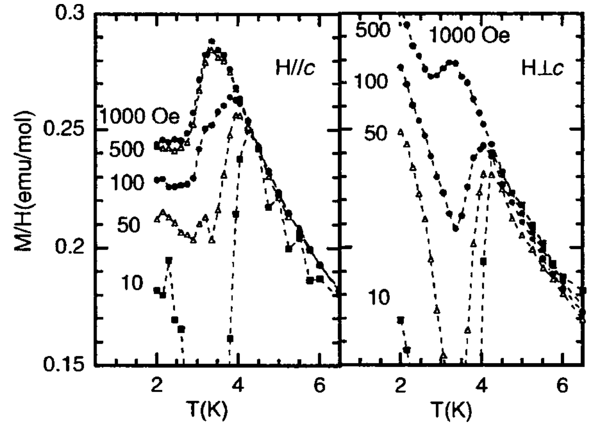

FIG. 2. Field dependence of susceptibility of oriented thin needle-shaped crystals of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ ($x=0.43$) for the field parallel and perpendicular to the needle axis ($\parallel c$).

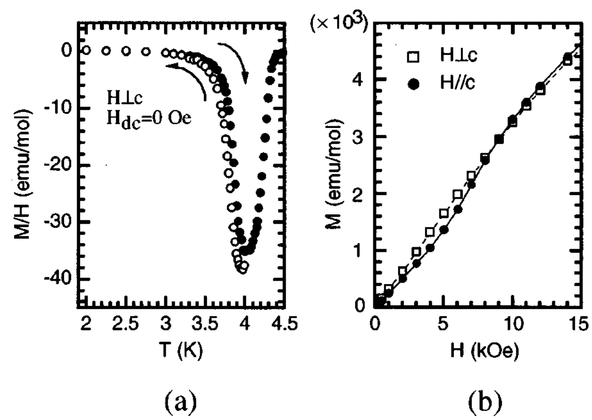

FIG. 3. (a) The ac susceptibility of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ ($x=0.47$) (the amplitude of 0.1 Oe, 0.5 Hz). The open and closed circles indicate the cooling and heating process, respectively. The diamagnetic susceptibility corresponding to the full Meissner state is −50 emu/mol. (b) The M-H curve of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ ($x=0.47$) at 2 K. The spin-flop behavior can be seen around 6 kOe for the field parallel to c.

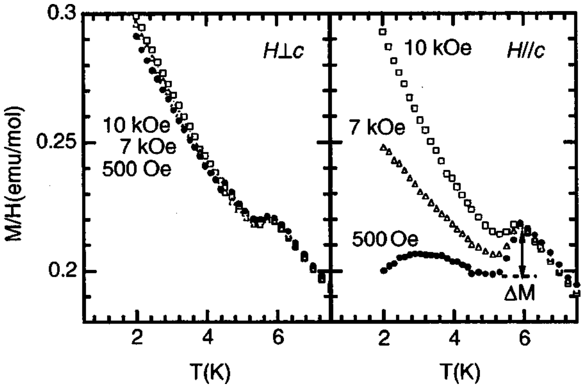

FIG. 4. Field dependence of susceptibility of oriented thin needle-shaped crystals of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ ($x=0.70$) for the field parallel and perpendicular to the needle axis ($\parallel c$).

(M/H) was estimated to be about -25 emu/mol below 2 Oe, which was about 70% of the ac susceptibility value at 4 K (-35 emu/mol).

In order to see the nature of the insulating state of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ system, the susceptibility of the phase with $x\approx 0.7$ was measured. This phase exhibits a M-I transition around 6.8 K [see Fig. 1(b)]. The susceptibility at ambient pressure showed a sharp drop at T_{MI} (see Fig. 4) and spin-flop behavior around 7.5×10^3 Oe for the field parallel to the needle axis ($H_\parallel$). On the other hand, the susceptibility for $H_\perp$ was almost field independent. This susceptibility behavior is essentially the same as that of λ-$(BETS)_2FeCl_4$,[12,14] indicating a π-d coupled AF insulating phase below T_{MI} where the easy axis is parallel to c. As reported before,[12] the susceptibility drop at T_{MI} [ΔM (see Fig. 3)] can be considered to be a sign of development of a π-d coupled AF spin structure. In λ-$(BETS)_2FeCl_4$, $\Delta M/H$ can be estimated as 0.021 emu/mol from the susceptibility data reported in Ref. 14, which corresponds to 7.1% of the total susceptibility ($\Delta M/M=0.071$), while $\Delta M/H$ of λ-$(BETS)_2(Fe_{0.7}Ga_{0.3})Cl_4$ was estimated to be 0.020 emu/mol and $\Delta M/M$ was about 0.093. Since the susceptibility of λ-$(BETS)_2(Fe_{0.7}Ga_{0.3})Cl_4$ is about 70% of λ-$(BETS)_2FeCl_4$, the magnitude of ΔM corresponds to the 6.5% ($=0.093\times 0.70$) of the susceptibility of λ-$(BETS)_2FeCl_4$, which is roughly equal to 7.1%. Similar susceptibility behavior was also found in λ-$(BETS)_2(Fe_{0.43}Ga_{0.57})Cl_4$. As seen from Fig. 2, the susceptibility of this system is almost field independent around 500–1000 Oe, where the SC state is suppressed. A fairly sharp susceptibility drop characteristic of the development of the π-d coupled AF insulating phase can be seen at $T_{SC\text{-}I}$ for $H_\parallel$. The $\Delta M/M$ was estimated at about 0.15. The magnitude of ΔM corresponds to the 6.4% ($=0.15\times 0.43$) of the susceptibility of λ-$(BETS)_2FeCl_4$, which is again roughly equal to 7.1%. Thus, it is concluded that π-d coupled AF spin structure is realized when λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ is in an insulating ground state. The M-H curve of λ-$(BETS)_2(Fe_{0.47}Ga_{0.53})Cl_4$ showed a spin-flop behavior around 6 kOe for the field parallel to c [Fig. 3(b)]. That is, similar to the easy axis of λ-$(BETS)_2FeCl_4$, the easy axis of the AF spin structure of this system is parallel to c. The spin-flop field (H_f) of 6 kOe is about 60% of that of λ-$(BETS)_2FeCl_4$ ($H_f\approx 10$ kOe).[13,14,18] Similar susceptibility behavior was also observed in λ-$(BETS)_2(Fe_{0.55}Ga_{0.45})Cl_4$ ($H_f\approx 7$ kOe). The anomaly observed in the field dependence of the magnetization of λ-$(BETS)_2(Fe_{0.55}Ga_{0.45})Cl_4$ around 4.5 K at 2 kOe corresponds to the M-I transition [Fig. 5(a)]. The arrows suggest that the M-I transition temperature is suppressed with increasing magnetic field. Similar phenomena have been discovered by Goze *et al.* in λ-$(BETS)_2FeCl_4$, where ‘‘the field restored highly conducting state’’ appears above the critical field (H_0) of 110 kOe.[19] As mentioned before, π electrons tend to be localized at low temperature owing to the strong electron correlation and the interaction with neighboring d spins of Fe^{3+} to form the π-d coupled antiferromagnetic spin structure.[12] With increasing magnetic field, the Fe^{3+} spins will tend to be oriented ferromagnetically. Then the system cannot retain the π-d coupled antiferromagnetic spin structure and π metal electrons will be restored. This may be a simple interpretation of the origin of the field restored highly conducting state. The H_0 of λ-$(BETS)_2(Fe_{0.55}Ga_{0.45})Cl_4$ was 75–80 kOe. Therefore, both H_f and H_0 of λ-$(BETS)_2(Fe_{0.55}Ga_{0.45})Cl_4$ are about 70% of those of λ-$(BETS)_2FeCl_4$. The ratio of H_f/H_0 was about 0.1. Thus, the nature of the insulating ground state of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ at $x>0.35$ is considered to be essentially the same as that of pure $FeCl_4$ salt (see Fig. 1). It may be of interest that the AF structure is realized in the fairly diluted Fe^{3+} systems such as the $x\approx 0.35$ system, where the two-thirds of the anion sites are occupied by nonmagnetic Ga^{3+} ions. Since the shortest Fe...Fe distance in λ-type crystals is longer than 6 Å, the AF interaction between Fe^{3+} ions must be mediated by π electrons of BETS molecules.[4] Recent magnetic susceptibility experiments by SQUID magnetometer indicates that the Weiss temperature ($|\theta|$) of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ changes almost linearly with decreasing x at $x>0.35$ and is constant at $x<0.35$: $\theta\approx -8$ K at $x=1.0$, -1.7 K at $x<0.35$.[20] The x independence of θ at $x<0.35$ indicates the ‘‘decoupling’’ of π-d electron systems by the dilution of magnetic ions, where λ-

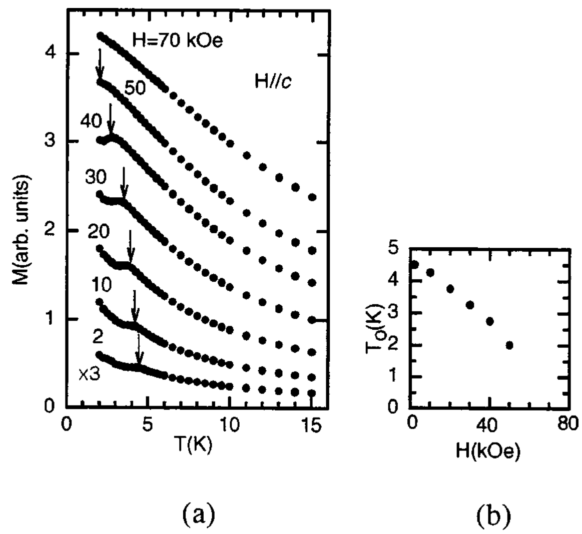

FIG. 5. (a) Field dependence of the magnetization of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ ($x=0.55$). The characteristic temperature indicated by arrow [T_0(K)] corresponds to the M-I transition temperature (at least for weak magnetic field). (b) Field dependence of T_0(K) suggesting the suppression of the M-I transition temperature with increasing magnetic field.

$(BETS)_2(Fe_xGa_{1-x})Cl_4$ takes a SC ground state.

Since the destruction of the SC state at low temperature has never been observed in the system without Fe^{3+} ions λ-$(BETS)_2GaBr_xCl_{4-x}$ ($x<2.0$),[9,10] it is clear that the *π-d* interaction plays a crucial role in breaking the SC state. As suggested before, when the Fe^{3+} density is high, the *π* electrons are fixed through *π-d* coupling to result in the coupled M-I and AF transition. We have recently found that the *π* and *d* electron systems of λ-$(BETS)_2FeCl_4$ tend to be separated from each other at high pressure. Then it is impossible for Fe^{3+} spins to induce the AF spin ordering in *π* electron system and λ-$(BETS)_2FeCl_4$ becomes a *π* metal with antiferromagnetically ordered Fe^{3+} spins at high pressure.[21] If the *π* and *d* electron systems of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ having *π-d* coupled AF insulating ground state at ambient pressure also tend to be independent of each other with increasing pressure, it is expected that the system will exhibit a SC transition at high pressure. In fact, λ-$(BETS)_2(Fe_{0.7}Ga_{0.3})Cl_4$ with a M-I transition at ambient pressure shows a SC transition above 2 kbar.[17] At high pressure the characteristic broad resistivity maximum around 90 K indicating the strong correlation of *π* electrons is suppressed, which seems to be related to the reduction of *π-d* coupling and appearance of the SC state.

In summary, we have examined the magnetic properties of crystals of λ-$(BETS)_2(Fe_xGa_{1-x})Cl_4$ exhibiting a SC-I transition ($x\approx0.43$, 0.47) or M-I transition ($x\approx0.55$, 0.70) and found that the characteristic SC-I transition is a bulk transition. These systems commonly take the *π-d* coupled AF ground state. With increasing magnetic field, the system shows a spin-flop transition at H_f (<10 kOe) and the ''field restored metallic state'' above H_0 (<110 kOe). The ratio of these two critical fields (H_f/H_0) is about 0.1. The strength of *π-d* coupling is a key factor in determining the nature of the ground state. When the *π-d* coupling is weakened by reducing Fe content and/or by applying pressure, the SC ground state is realized.

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