Successive Antiferromagnetic and Superconducting Transitions in an Organic Metal, κ-$(BETS)_2FeCl_4$

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The ac magnetic measurements on an organic metal, κ-$(BETS)_2FeCl_4$ down to 60 mK revealed successive antiferromagnetic and superconducting phase transitions at about 0.65 K ($\approx T_N$) and 0.1 K ($\approx T_C$), respectively. These transitions correspond to the similar transitions in the Br-analogue, κ-$(BETS)_2FeBr_4$ but the transition temperatures of $FeCl_4$ system are significantly lower than those of $FeBr_4$ system (T_N = 2.5 K; T_C = 1.1 K).

In the recent studies on organic conductors, a considerable interest is focused on the systems consisted of π donor molecules and inorganic magnetic anions. More than several years ago, we have examined a series of BETS [= bis(ethylenedithio)tetraselenafulvalene] conductors with tetrahalogeno-metallate anions, MX_4 (M=Ga, In, Fe; X=Cl, Br). There are two main modifications in these compounds, λ- and κ-$(BETS)_2\ MX_4$.[1] λ-$(BETS)_2GaCl_4$ is the first BETS superconductor.[2] The superconducting transition has been recently discovered also in λ-$(BETS)_2FeCl_4$ at high pressure.[3] Furthermore, an unprecedented superconductor-to-insulator transition has been observed in λ-type BETS conductors with mixed magnetic and non-magnetic anions, λ-$(BETS)_2Fe_{1-x}Ga_xCl_4$, where the interaction between localized magnetic moments of Fe^{3+} ions and π conduction electrons play an essential role.[4] The κ-type compounds have characteristic two-dimensional arrangements of BETS molecules (see Figure 1) and possess metallic states at low temperatures. Recently, we have discovered the first organic metal antiferromagnet exhibiting a superconducting transition, κ-$(BETS)_2\ FeBr_4$.[5] Although the magnetic susceptibility measurements down to 2K and the resistivity measurements down to 0.5 K in κ-$(BETS)_2FeBr_4$ have revealed the succsessive antiferromagnetic and superconducting transitions,[5] neither magnetic phase transition down to 2 K nor a superconducting phase transition down to 0.5 K has been found in its Cl analogue κ-$(BETS)_2FeCl_4$ so far.[6,7] For the purpose of surveying whether the difference of these two materials is essential or not, we carried out the magnetic measurements on κ-$(BETS)_2FeCl_4$ in ultralow temperature region using *ac*-SQUID magnetometer.

The crystals of title compound κ-$(BETS)_2FeCl_4$ were obtained electrochemically from monochlorobenzene solution containing BETS and $(Et_4N)FeCl_4$, according to the method described previously.[1] The *ac* magnetic susceptibilities χ_{ac} were measured in the range 60 mK–7 K. Polycrystalline sample was used. It was cooled by a home-made dilution refrigerator and measured by a home-made cas system based on the *dc*-SQUID magnetometer (Conductus Inc.). The system uses the oscillating field of a few milli-Oe and the frequency 175 Hz. The geomagnetic field of about 300 mOe is reduced by 1/100 using a μ metal shield. Then, the measurement was done at the field less than 10 mOe. Absolute value of χ_{ac} was calibrated so that the temperature dependences at $2 < T < 7K$ agrees with the χ_p value obtained by the high temperature measurement using another machine.[8,9] The χ_p value of this compound suggests the high spin states (S=5/2) of Fe^{3+}.[8]

The temperature dependence of χ_{ac} of κ-$(BETS)_2FeCl_4$ is shown in Figure 2. The χ_{ac} value monotonously increased from 7 K with decreasing temperature. It takes a peak at 0.65K, below which χ_{ac} showed a sharp decrease. Then χ_{ac}

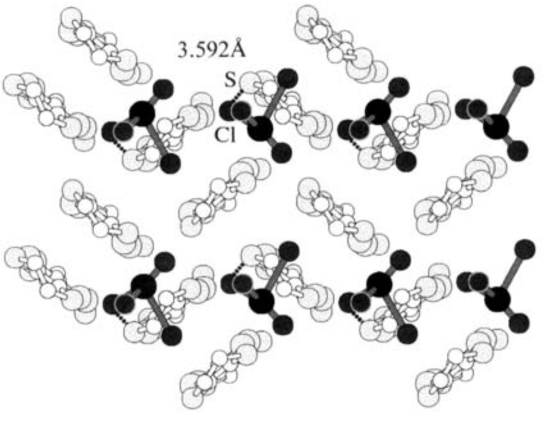

Figure 1. Crystal packing of κ-$(BETS)_2FeCl_4$. κ-$(BETS)_2FeBr_4$ is isostructural. Hydrogen atoms are omitted for clarity. $FeCl_4$ anions are darkend for distinction.

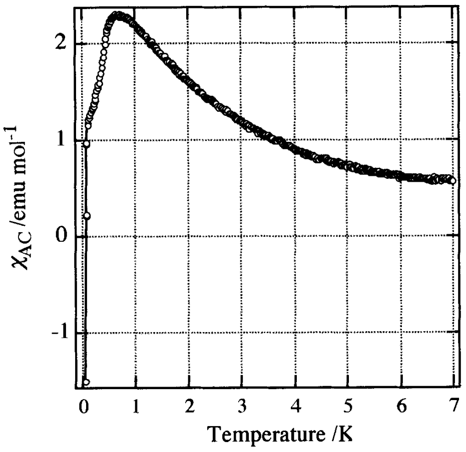

Figure 2. The temperature dependence of *ac*-magnetic susceptibility for κ-$(BETS)_2FeCl_4$ (polycrystalline sample).

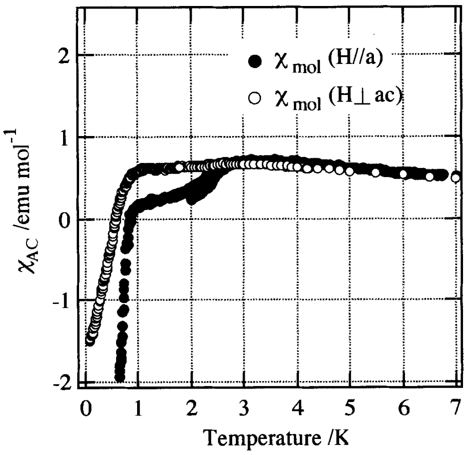

Figure 3. The temperature dependencies of ac-magnetic susceptibility for κ-(BETS)$_2$FeBr$_4$. (*ac*-field *H* perpendicular (●) and parallel (○) to the *ac*-plane (crystal plane), respectively.)

continued to decrease with decreasing temperature, and exhibited a drop around 0.1 K. This drop is so sharp that the χ_{ac} value falls down far across the zero value. Therefore it is considered to be a Meissner signal, i.e., this point is the superconducting phase transition T_C (= 0.1 K, onset).

In order to compare the susceptibility behavior of FeCl$_4$ salt with that of FeBr$_4$ salt,[5,10] the susceptibility of κ-(BETS)$_2$FeBr$_4$ was also measured down to 60 mK by using oriented plate crystals. As shown in Figure 3, the susceptibility behavior of FeBr$_4$ salt quite resembles that of FeCl$_4$ salt besides the magnitude of the critical temperatures. The anomaly around 2.5 K due to the antiferromagnetic transition ($T_N \approx 2.5$ K) is consistent with the result of previous susceptibility measurements down to 2 K.[5,10] Almost constant χ_{ac} between 2.5 K and 1 K for the field perpendicular to the conduction plane suggests the antiferromagnetic structure with easy axis parallel to the *ac*-plane (//conduction plane).[10] The susceptibility drop below ca. 1 K corresponds to the superconducting transition at 1.1 K.[5,10] The similarity between the susceptibility behavior of κ-(BETS)$_2$FeBr$_4$ and that of κ-(BETS)$_2$FeCl$_4$ indicates that the magnetic transition of κ-(BETS)$_2$FeCl$_4$ at 0.65 K is an antiferromagnetic transition. One can notice that the antiferromagnetic phase transition temperature of κ-(BETS)$_2$FeCl$_4$ is exceedingly lower than that of the Br-analogue ($T_N \approx 0.65$ K (Cl), 2.5 K (Br)). It seems that the magnetic interactions among the Fe^{3+} spins in κ-(BETS)$_2$FeCl$_4$ are significantly weaker than in κ-(BETS)$_2$FeBr$_4$. This lowering of T_N apparently makes a contradiction from a crystallographic viewpoint; the unit cell of κ-(BETS)$_2$FeCl$_4$ is crystallographically more contracted compared to that of κ-(BETS)$_2$FeBr$_4$. For example, the distance between the nearest neighbor anions in κ-(BETS)$_2$FeCl$_4$ is shorter ($d_{\mathrm{Fe}^{3+}\cdots\mathrm{Fe}^{3+}} = 5.88$ Å) than in the Br-analogue ($d_{\mathrm{Fe}^{3+}\cdots\mathrm{Fe}^{3+}} = 5.92$ Å). Regarding the pathway of the magnetic interaction among the Fe^{3+} spins, the distance between the Fe$^{3+}\cdots$Fe^{3+} or Br$\cdots$Br (4.14 Å) is so long that the magnetic interactions through this pathway will not reflect the Néel temperature T_N = 2.5 K for κ-(BETS)$_2$FeBr$_4$. It is thought that the magnetic interaction is mediated by the π-electron states of BETS, where the S$\cdots$X (X=Cl or Br) contact between BETS and FeX$_4$ plays a crucial role. However, there is no essential difference in the S$\cdots$X distances; $d_{\mathrm{S}\cdots\mathrm{X}} = 3.592$ Å for X = Cl; 3.693 Å for X = Br, both distances are 0.06 Å shorter than the sum of the van der Waals radii, evenly. Therefore the change of T_N should be explained in terms of the difference of the halogen atom itself. The energy levels of the π-orbital of BETS and *d* orbital of Fe are higher than the *p*-orbital of the halogen atom, and the energy level of the *p*-orbital of Br atom is higher than that of Cl atom. Accordingly the π–*d* interaction between BETS and FeX$_4$ through X atom will be larger in Br salt than in Cl salt. This will lead to the difference in the magnitude of magnetic interaction in κ-(BETS)$_2$FeX$_4$. Detailed theoretical analysis is needed in this point to elucidate the universality of the relationship between the π–*d* interaction and T_N.

The superconducting phase transition temperature of κ-(BETS)$_2$FeBr$_4$ is much higher than that of κ-(BETS)$_2$FeCl$_4$. To our experience, T_C of organic superconductor tends to be suppressed with increasing the metallic nature of the system. It should be noted that κ-(BETS)$_2$FeBr$_4$ with T_C of 1.1 K exhibits a characteristic resistivity hump around 60 K. While κ-(BETS)$_2$FeCl$_4$ with T_C of about 0.1 K shows a normal metal behavior down to 0.5 K, indicating the relatively large stability of the metal state.

In conclusion, we found successive antiferromagnetic and superconducting transitions in κ-(BETS)$_2$FeCl$_4$. The κ-(BETS)$_2$ FeX$_4$ (X=Cl, Br) salts were hereby proved to be a metallic antiferromagnet system, and both of them were found to be a superconductor. But both transition temperatures T_N and T_C of κ-(BETS)$_2$FeCl$_4$ are considerably lower than those of κ-(BETS)$_2$FeBr$_4$. The lowering of T_N will be rationalized in terms of the energy level of the *p*-orbital of the halogen atom. The lowering of T_C will be related to the stable metal state of κ-(BETS)$_2$FeCl$_4$. More detailed study is needed to clarify the relation between magnetic interaction and superconductivity in these systems.

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