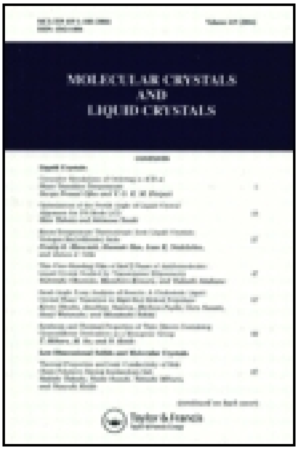

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Antiferromagnetic organic superconductors, bets 2 FeX 4 (X=Br, Cl)

Hayao Kobayashi [a] , Emiko Fujiwara [a] , Hideki Fujiwara [a] , Hisashi Tanaka [a] , Takeo Otsuka [b] , Akiko Kobayashi [b] , Madoka Tokumoto [c] & Patrick Cassoux [d]

[a] Institute for Molecular Science, Okazaki, 444-8585, Japan

[b] Research Centre for Spectrochemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113-0033

[c] Electrotechnical Laboratory, Tsukuba, 305-8568, Japan

[d] Précurseurs Moléculaires et Matériaux, ICC/CNRS, 205 Route de Narbonne, Toulouse Cedex, 31077, France

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ANTIFERROMAGNETIC ORGANIC SUPERCONDUCTORS, BETS$_2$FeX$_4$ (X=Br, Cl)

Hayao Kobayashi, Emiko Fujiwara, Hideki Fujiwara*
and Hisashi Tanaka
Institute for Molecular Science, Okazaki 444-8585, Japan

Takeo Otsuka and Akiko Kobayashi
Research Centre for Spectrochemistry, Graduate School of
Science, The University of Tokyo, Hongo, Bunkyo-ku,
Tokyo 113-0033

Madoka Tokumoto
Electrotechnical Laboratory, Tsukuba 305-8568, Japan

Patrick Cassoux
Précurseurs Moléculaires et Matériaux, ICC/CNRS,
205 Route de Narbonne, 31077 Toulouse Cedex, France

Crystals of BETS conductors containing FeX_4^- ($X = Cl$, Br) anions are polymorphic. λ-BETS$_2$FeCl$_4$ undergoes a π-d coupled antiferromagnetic insulating transition at about 8.5K. But it exhibits a paramagnetic metal – antiferromagnetic metal transition and superconducting transition at high pressure. κ-BETS$_2$FeX$_4$ ($X = Cl$, Br) are antiferromagnetic organic superconductors with the transition temperatures of $T_N = 2.4\,K$ (Br), 0.45 K (Cl) and $T_c = 1.1\,K$ (Br) and 0.1 K (Cl). Resistivity step observed at T_N is the first direct evidence for π-d interaction in organic metals. No distinct anomaly in the specific heat at T_c and the anisotropy of the recovery of resistivity under magnetic field at $T < T_c$ suggest the coexistence of superconductivity and magnetic order in λ-BETS$_2$FeBr$_4$. In contrast to the case of κ-BETS$_2$FeBr$_4$ exhibiting three-dimensional magnetic transition, small entropy of the transition of κ-BETS$_2$FeCl$_4$ indicates the low-dimensionality of the spin system.

Keywords: antiferromagnetic organic superconductor; BETS; magnetic organic superconductor; organic superconductor

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*Corresponding author. E-mail: hayao@ims.anl.gov

INTRODUCTION

Since the discovery of the first organic superconductor [1], an extraordinarily large progress has been achieved in the field of molecular conductors. In 1980s, a number of molecular superconductors including the system composed of transition metal complex molecules were developed [2,3]. Very recently, superconductivity of hole-doped C_{60} system was observed at 52 K by using field effect transistor technique [4]. We have recently succeeded to develop a three-dimensional metal composed of single component planar molecules [5]. But most of representative molecular conductors extensively studied in the last two decades are the conductors composed of TTF-like π donor molecules (D) and inorganic anions (X), D_2X. Since the development of new molecular superconductors was the main motif of the chemists in this field in 1980s, there was no special reason to use magnetic anions, which had been considered to unsuitable for the development of molecular superconductors. However, an increasing interest has been recently focused on so-called π-d systems constructed of π donor molecules and magnetic anions. In early 1990s, we have prepared a series of organic metals based on BETS (= bis(ethylenedithio)tetrathiafulvalene) molecules and FeX_4^- (X = Cl, Br) anions and analogous non-magnetic anions MX_4^- (M = Ga, In) with the aim of developing multi-functional magnetic organic conductors [6]. There had been no example of magnetic organic metal at that time. But the first paramagnetic superconductor discovered in 1995 [7]. Very recently, ferromagnetic organic metal has been also developed [8].

BETS SUPERCONDUCTORS WITH MAGNETIC Fe^{3+} IONS

There are mainly two modifications in $BETS_2MX_4$ salts (λ and κ). Considering that almost no organic metal had been known to exhibit an evidence for π-d interaction, BETS conductors are very unique [9]. In contrast to λ-$BETS_2GaCl_4$ exhibiting a superconducting transition [10], λ-$BETS_2FeCl_4$ shows a π-d coupled antiferromagnetic insulating transition [9,11–13]. But it undergoes antiferromagnetic and superconducting transitions at high pressure [9,14]. Furthermore, the Ga/Fe mixed system, λ-$BETS_2Fe_xGa_{1-x}Cl_4$ shows unprecedented superconductor-to-insulator transition [15]. The pressure-temperature-composition phase diagram of λ-$BETS_2Fe_xGa_{1-x}Cl_4$ is shown in Figure 1. Recently, we have discovered antiferromagnetic organic superconductors, κ-$BETS_2FeX_4$ at ambient pressure [16–18].

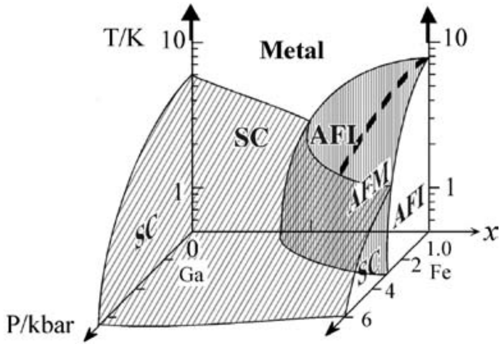


FIGURE 1 Pressure-temperature-composition phase diagram of λ-BETS$_2$Fe$_x$ Ga$_{1-x}$Cl$_4$. AFI: antiferromagnetic insulating phase; AFM: antiferromagnetic metal phase; SC: superconducting phase.

RESISTIVITY, SUSCEPTIBILITY AND SPECIFIC HEAT, OF κ-BETS$_2$FeX$_4$ (X = Cl, Br)

As reported before, κ-BETS$_2$FeBr$_4$ shows a characteristic round resistivity maximum around 60 K [6]. While κ-BETS$_2$FeCl$_4$ exhibits a normal metallic

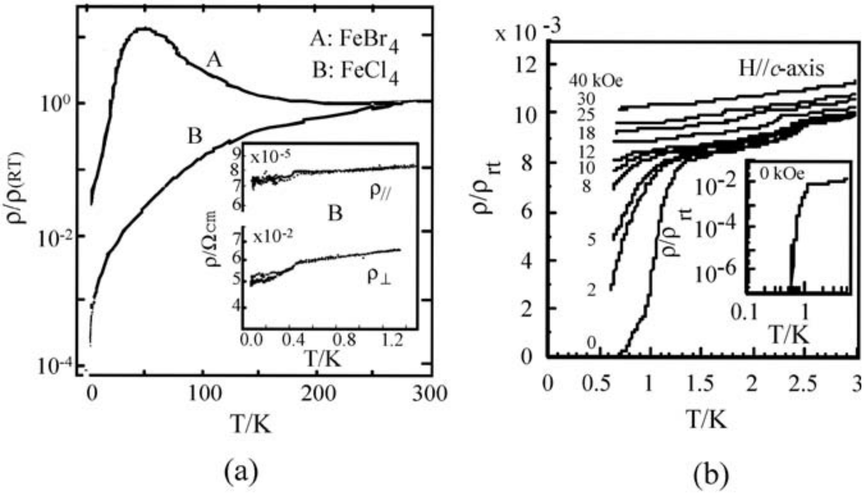
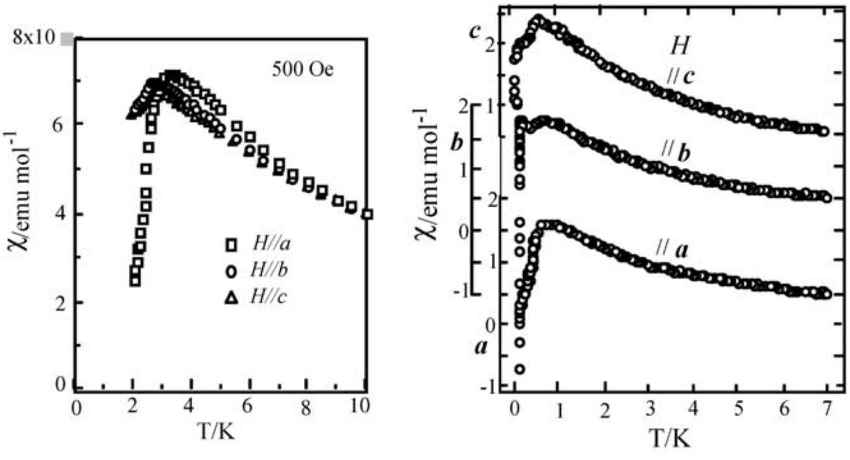


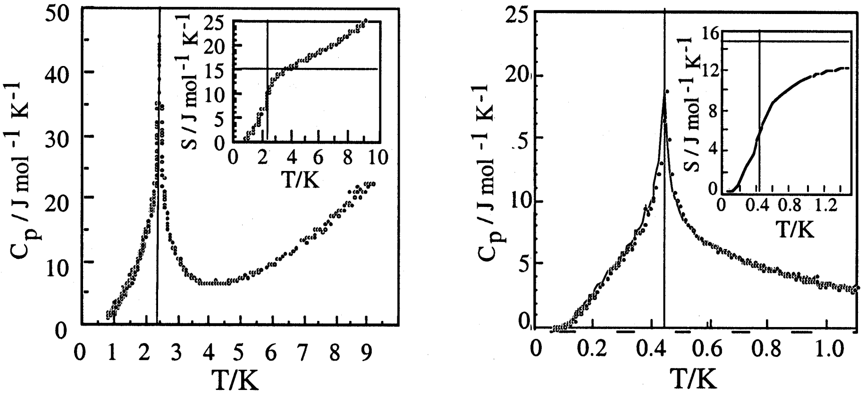
FIGURE 2 (a) Resistivities of κ-BETS$_2$FeX$_4$ (X = Cl, Br). The inset is low-temperature resistivity of κ-BETS$_2$FeCl$_4$. (b) Magnetic field effect on the superconducting transition of κ-BETS$_2$FeBr$_4$. The inset shows the resistivity drop at 0 kOe.



(a) (b)

FIGURE 3 Magnetic susceptibilities of (a) κ-BETS$_2$FeCl$_4$ and (b) κ-BETS$_2$FeCl$_4$.

behavior down to 2 K (Figure 2a). At low temperature, small step indicating the ordering of Fe^{3+} spins was observed in both systems (see Figure 2b and the inset of Figure 2a). In fact, the anisotropy of magnetic susceptibilities clearly showed antiferromagnetic transition: $T_N = 2.4$ K (FeBr$_4$) and 0.45 K (FeCl$_4$) (Figure 3). Thus the resistivity step is regarded to be the first direct



(a) (b)

FIGURE 4 Specific heat and entropy (inset) of (a) κ-BETS$_2$FeCl$_4$ and (b) κ-BETS$_2$FeCl$_4$.

evidence for the existence of π-d interaction between localized magnetic moments and π metal electrons in organic conductors. Furthermore, κ-BETS$_2$FeX$_4$ underwent a superconducting transition ($T_c = 1.1\,\mathrm{K}$ (Br), 0.1 K (Cl)). The specific heat (C_p) of κ-BETS$_2$FeBr$_4$ gave a λ-type peak at 2.4 K (Figure 4a) and the calculated entropy of $14.9\,\mathrm{J\,mol^{-1}K^{-1}}$ ($= \mathrm{R}\,ln\,6$) (see the inset of Figure 4a), indicating three-dimensional magnetic order at T_N. While small entropy of the magnetic transition of κ-BETS$_2$FeCl$_4$ showed the low-dimensionality of the spin system (Figure 4b). No distinct anomaly of C_p at T_c and the magnetic field effect on the recovery of resistivity at $T < T_c$ in κ-BETS$_2$FeBr$_4$ suggest that κ-BETS$_2$FeBr$_4$ is antiferromagnetic organic superconductor where superconductivity and magnetic order coexist. Since the energy level of 4p orbital of Br atom with larger electron cloud is higher than that of 3p orbital of Cl atom, the stronger d-p mixing can be expected in "d-like orbital" of FeBr$_4^-$ anion. Consequently, stronger interactions between d-like orbitals of adjacent FeX$_4^-$ anions and d-like orbitals of FeX$_4^-$ and π orbitals of BETS are expected in FeBr$_4^-$ salt.

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