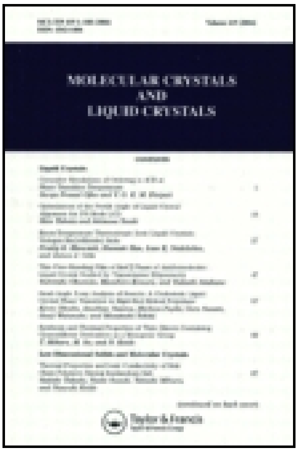

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Magnetic Organic Superconductors Based on BETS Molecules--Interplay of Conductivity and Magnetism

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Version of record first published: 18 Oct 2010

To cite this article: Hayao Kobayashi, Emiko Fujiwara, Hideki Fujiwara, Hisashi Tanaka, Itaru Tamura, Zhang Bin, Victor Gritsenko, Takeo Otsuka, Akiko Kobayashi, Madoka Tokumoto & Patrick Cassoux (2003): Magnetic Organic Superconductors Based on BETS Molecules--Interplay of Conductivity and Magnetism, Molecular Crystals and Liquid Crystals, 379:1, 9-18

To link to this article: http://dx.doi.org/10.1080/713738603

Mol. Cryst. Liq. Cryst., Vol. 379, pp. 9-18
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1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290090192

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Among six BETS (=bis(ethylenedithio)tetraselenafulvalene) superconductors, the systems with FeX_4^- (X=Cl, Br) anions exhibit salient electronic properties due to the coupling between π and d electron systems. λ-$BETS_2FeCl_4$ undergoes successive transitions as, antiferromagnetic insulating phase → metallic phase with ferromagnetically oriented Fe^{3+} spins → superconducting phase (*H*//conduction plane) → metallic phase, with increasing magnetic field. κ-$BETS_2FeX_4$ exhibits successive antiferromagnetic and superconducting transitions with decreasing temperature. Resistivity anomaly observed at antiferromagnetic transition temperature indicates an evidence for the coupling between π and d electron systems

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

INTRODUCTION

The discovery of the first organic superconductor (Bechgaard salt) in 1980 has opened new era of the chemistry and physics of molecular conductors[1]. Its crystal structure gave an important hint to develop the molecular metals with two-dimensional electronic band structures[2]. In fact, various types of molecular metals with two-dimensional cylindrical Fermi surfaces were prepared in the later half of 1980s. The typical example is κ-type organic superconductors[3]. However, the investigation on the development of new organic superconductors seemed to be rather faded out recently because the elevation of T_c has been long stopped since the discovery of κ-(BEDT-TTF)$_2$ Cu[N(CN)$_2$]Cl [4]. On the other hand another stream started to grow around the middle of 1990s. That is, the development of new molecular conductors such as paramagnetic organic superconductor and ferromagnetic metal based on BEDT-TTF molecules and magnetic anions has attracted an increasing interest[5,6]. Although the interaction between π metal electrons in the two-dimensional donor layers and the localized 3d magnetic moments of the anion sites is expected to produce bi-functional properties, it seems to be not so easy to develop the organic conductors with considerable π-d coupling.

About a decade ago, we have tried to prepare organic conductors incorporating magnetic moments with the aim of examining the possibility of developing an organic conductors such as “organic Kondo system”, where π metal electrons interact with localized magnetic moments of the anions at low temperatures[7]. We have prepared BETS conductors with magnetic anions such as $FeCl_4^-$ and $FeBr_4^-$ and also analogous nonmagnetic anions such as $GaCl_4^-$, $GaBr_4^-$, $InCl_4^-$ and $InBr_4^-$ (BETS = bis(ethylenedithio)tetraselena-fulvalene). Here, we report the results of the recent investigation on the electric and magnetic properties of BETS conductors with tetrahalide metal anions.

ELECTRICAL PROPERTIES OF BETS CONDUCTORS WITH TETRAHALIDE ANIONS

Crystals of BETS conductors with tetrahalide anions MX_4^- (M=Fe, Ga, In, Tl; X=Cl, Br) were prepared electrochemically. There are mainly two modifications. Needle crystals with triclinic unit cells named λ-type crystals were obtained when $[(C_2H_5)_4N]MCl_4$ (M=Ga, Fe) were used as electrolyte. Crystals of the other modification with orthorhombic κ-type structures were obtained as plate crystals for all these MX_4^- anions. At first sight, the variety of λ-type salt seems to be very limited. However, due to the close similarity of the lattice constants of the $GaCl_4$ and $FeCl_4$ systems, Ga and Fe atoms can be easily exchanged to produce the alloy system, λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ ($0<x<1$) exhibiting various novel electronic properties. As reported before, the resistivity behavior of λ-$(BETS)_2GaCl_4$ closely resembles that of λ-$(BETS)_2FeCl_4$ except for low temperature region. Both salts show gradual resistivity increase with decreasing temperature and take round resistivity maxima around 100 K (see Figure 1). Then the resistivities decrease very rapidly[8,9]. Around 6 K, λ-$(BETS)_2GaCl_4$ undergoes a superconducting transition. While λ-$(BETS)_2FeCl_4$ exhibits a coupled antiferromagnetic and metal-insulator transition around 8.5 K, which clearly shows an importance role of the π-d coupling in $FeCl_4$ salt. The Cl atoms of the MCl_4^- can be partially exchanged by Br atom. The unit cell volume is increased with increasing Br-content. Then the π electron system feels effectively "negative pressure" and the system tends to become a semiconductor. In fact, λ-$(BETS)_2GaBr_{1.5}Cl_{2.5}$ shows a semiconducting behavior. But by applying "real pressure" to this Br-rich semiconducting system, the system becomes a superconductor. Around 3 kbar, the resistivity of λ-$(BETS)_2GaBr_{1.5}Cl_{2.5}$ is almost constant down to 100 K and then decreases rapidly. The system shows a superconducting transition at about 10 K[9] (see the inset of Figure 1).

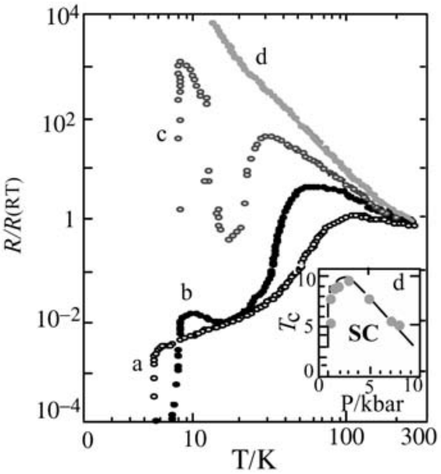

FIGURE 1 The temperature dependence of the resistivity of λ-$BETS_2GaBr_xCl_{4-x}$: x= 0 (a), 0.5 (b), 0.7 (c), 1.5 (d). The inset is the pressure dependence of superconducting transition temperature (T_c) of λ-$BETS_2GaBr_{1.5}Cl_{2.5}$.

Contrary to λ-type salts, every κ-type salt is metallic at low temperatures. The systems with small size anions such as $GaCl_4^-$ and $FeCl_4^-$ exhibit smooth resistivity decrease with lowering the temperature but the systems with relatively large size anions such as $GaBr_4^-$ and $FeBr_4^-$ exhibit round resistivity maxima around 60-70 K (T_P), which is related to the “negative chemical pressure effect of Br atoms”.

Recently, the electrical resistivity experiments were made on κ-$(BETS)_2TlCl_4$ to see the anion size effect. But all the crystals examined were destructed around 220 K. However we noticed that the resistivity measurements can be performed by coating the crystal with epoxy resin because the “effective pressure” produced by the contraction of the epoxy resin at low temperature suppresses the destruction of the crystal to some extent. The crystal coated by epoxy resin showed a superconducting transition below 2.5 K (Figure 2)[10].

The low-temperature X-ray diffraction experiments made by using the crystal coated by epoxy resin showed the doubling of the lattice constant *c* around 210 K (*a, b, c* → *a, b,* 2*c*). In Table 1, six BETS superconductors with MX_4^- anions ever discovered are listed.

We have also examined BETS conductors with magnetic dianions such as $CoCl_4^{2-}$, $CoBr_4^{2-}$ and $MnBr_4^{2-}$. The 2:1 complex $(BETS)_2CoCl_4$ was insulator but the 4:1 salts with κ- and θ-type molecular arrangements were metallic down to ca. 50 K ($CoBr_4{2^-}$ and $MnBr_4^{2-}$) or 0.7 K ($CoCl_4^{2-}$). The antiferromagnetic interaction between localized magnetic moments (Co^{2+} (S=3/2), Mn^{2+} (S=5/2)) is very weak because the anion layers of these salts are composed of anions and crystal solvents.

TABLE 1 The temperatures characterizing the electric and magnetic properties of BETS superconductors.

salt[a]	λ-$GaCl_4$	λ-$FeCl_4$	κ-$FeCl_4$	κ-$FeBr_4$	κ-$GaBr_4$	κ-$TlCl_4$
T_p[b]	90 K	90 K	normal metal	60 K	70 K	——[c]
T_N		8.5 K[d]	0.45 K[e]	2.4 K[e]		
T_c	6 K	2 K (at 3 kbar)	0.17 K	1.1 K	1 K	2 K[f]

[a] λ- and κ-$(BETS)_2MX_4$ are abbreviated to λ- and κ-MX_4, respectively.

[b] The temperature corresponding to the round resistivity peak.

[c] Resistivity measurements of κ-$(BETS)_2TlCl_4$ could not be made due to the destruction of crystal around 220 K.

[d] Antiferromadnetic and metal-insulator transitions take place cooperatively at 8.5 K.

[e] κ-$(BETS)_2FeX_4$ (X=Cl, Br) undergoes a paramagnetic metal-to-antiferromagnetic metal transition.

[f] Resistivity measurements were made on the crystal coated by epoxy resin.

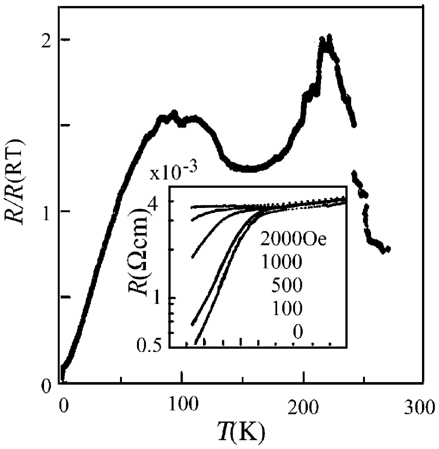

FIGURE 2 Temperature dependence of the resistivity of κ-(BETS)$_2$TlCl$_4$. The crystal coated by epoxy resin was used. The inset is the field dependence of the superconducting transition.

COUPLING OF π AND d ELECTRON SYSTEMS IN BETS CONDUCTORS WITH Fe^{3+} IONS

As mentioned before, λ-(BETS)$_2$FeCl$_4$ undergoes π-d coupled antiferromagnetic insulating transition at 8.5 K. That is, at ambient pressure, the magnetic transition and electronic transition take place cooperatively at the same temperature. However, these two transitions will tend to be separated by applying pressure, because the interaction between Fe^{3+} spins will be enhanced at high pressure while the metal-insulator (MI) transition will be suppressed by pressure. In fact, the MI transition temperature is rapidly decreased and superconducting transition appears above 3 kbar (see Table 1), suggesting that π electron system of λ-type salt tends to take a superconducting ground state when π-d coupling is weakened[11].

Similar to the case of λ-(BETS)$_2$GaBr$_x$Cl$_{4-x}$ (see Figure 1), the π electron system of λ-(BETS)$_2$FeBr$_x$Cl$_{4-x}$ tends to be semiconducting with increasing Br-content. Therefore, the metal-insulator transition temperature (T_{MI}) is enhanced in Br-rich system. For example, T_{MI} of λ-$(BETS)_2FeBr_{0.7}Cl_{3.3}$ is about twice of λ-$(BETS)_2FeCl_4$ (see Figure 3). While the magnetic susceptibility indicates that Fe^{3+} spin system of λ-$(BETS)_2FeBr_{0.7}Cl_{3.3}$ undergoes an antiferromagnetic transition around 8 K (magnetic transition temperature (T_N) to be approximately independent of Br-content system)[12]. It is well known that T_{MI} of λ-$(BETS)_2FeCl_4$ is completely suppressed above 11T, where π metal electrons and ferromagnetically oriented Fe^{3+} moments coexist. However, T_{MI} of λ-$(BETS)_2FeBr_{0.7}Cl_{3.3}$ is unchanged at least up to 12 T (Figure 3). That is, contrary to the case of superconducting transition, the considerable π-d coupling is essential to realize the field-restored metallic state. Of course, T_{MI} is decreased at high pressure, where field-restored metallic state can be observed.

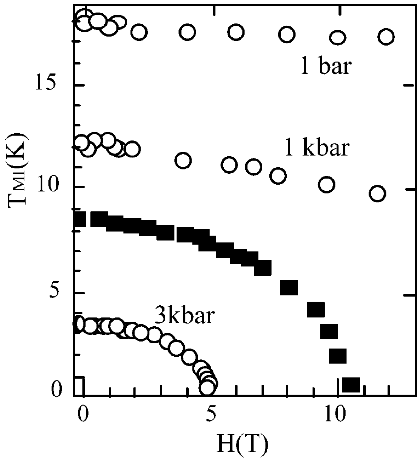

FIGURE 3 The magnetic field dependence of the metal-insulator transition temperature (T_{MI}) of λ-$(BETS)_2FeBr_{0.7}Cl_{3.3}$ at 1bar, 1 kbar and 3 kbar. (open circle). The closed squares are those of λ-$(BETS)_2FeCl_4$ at 1bar.

Recently the field-induced superconducting state (FISC) was discovered in λ-(BETS)$_2$FeCl$_4$ above 17 T[13]. Similar phenomena were also found in λ-(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$. We have examined the resistivity of λ-(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ (x≈ 0.4) which exhibits a successive metal→superconductor→insulator transitions with decreasing temperature. By applying magnetic field (*H*), the insulating ground state tended to change to a superconducting state (*H*⊥*b** or a metallic state (*H*//*b**). When *H* is perpendicular to *b**, the superconducting phase around zero-magnetic field is continuously changed to the "field-induced superconducting state".

In contrast to λ-(BETS)$_2$FeCl$_4$, κ-(BETS)$_2$FeCl$_4$ exhibits a smooth resistivity decrease down to very low temperatures (see Figure 4). The temperature dependence of the resistivity shows a step at 0.45 K, which agrees well with the antiferromagnetic transition temperature

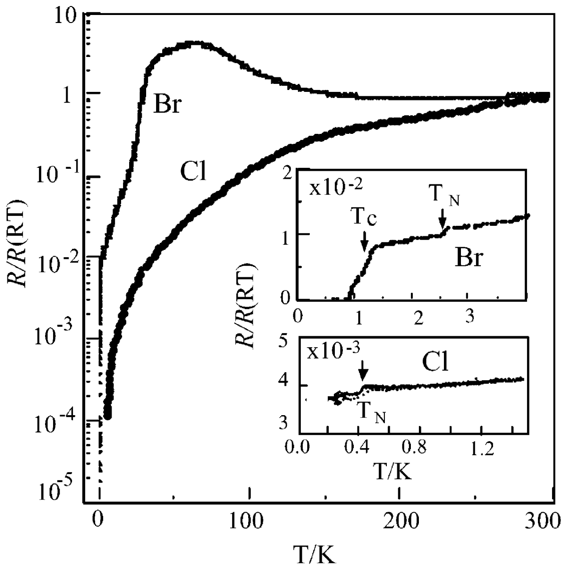

FIGURE 4 Temperature dependencies of the resistivities of κ-(BETS)$_2$FeCl$_4$ (Cl) and κ-(BETS)$_2$FeBr$_4$ (Br).

(T_N) (see inset of Figure 4)[14]. Magnetic susceptibility and μSR experiments revealed the superconducting transition to be 0.17 K [14,15]. κ-$(BETS)_2FeBr_4$ also shows a resistivity step at the antiferromagnetic transition temperature (2.4 K) and superconducting transition at 1.1 K [16]. Recent specific heat measurements suggested the 2.4 K transition of κ-$(BETS)_2FeBr_4$ and the 0.45 K transition of κ-$(BETS)_2FeCl_4$ to be pure magnetic transitions. In addition, the transition entropy of κ-$(BETS)_2FeCl_4$ showed the low-dimensionality of the Fe^{3+} spin system. A characteristic resistivity peak of κ-$(BETS)_2FeBr_4$ around 60 K was suppressed by applying pressure and the superconducting transition was decreased (e.g., 0.8 K at 2.5 kbar). These features are consistent with the concept of "negative chemical pressure effect of Br atom."

Acknowledgments
This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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