Temperature-Composition Phase Diagram of the Organic Alloys, λ-$BETS_2(Fe_xGa_{1-x})Cl_4$, with Mixed Magnetic and Non-Magnetic Anions

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(Received April 10, 1998; CL-980271)

The electrical properties of a series of λ-type BETS conductors, λ-$BETS_2(Fe_xGa_{1-x})Cl_4$ can be controlled continuously by varying the x-value. The system shows a metal-insulator transition for $x>x_1$ ($x_1 \approx 0.5$) and a superconducting transition for $x<x_1$. The T-x phase diagram indicates that the system shows the superconductor-insulator transition for $x_2<x<x_1$ ($x_2 \approx 0.35$).

Recently much attention has been focused on the role of the magnetic ions such as Fe^{3+} and Cu^{2+} incorporated in the organic metals because even a weak interaction between π conduction electrons in organic molecules and localized d-spins in the anion sites is expected to produce novel π-d coupled electrical properties at low temperatures.[1-3] In order to examine this possibility, the development of organic conductors with magnetic anions and stable metallic states at low temperatures is required. However only several examples have been known so far and the π-d interactions have been revealed to be very weak in almost all these systems. We have previously described a characteristic organic metal with magnetic anions, λ-$BETS_2FeCl_4$ where the antiferromagnetic and metal-insulator (MI) transitions take place cooperatively at 8.5 K.[3,4] In the insulating ground state, a coupled antiferromagnetic spin structure of d (Fe^{3+}) and π electron systems was proposed.[5] By contrast, the analogous system without magnetic anions, λ-$BETS_2GaCl_4$ exhibits a superconducting ground state.[6] We have recently reported a superconductor-to-antiferromagnetic insulator transition in λ-$BETS_2(Fe_xGa_{1-x})Cl_4$ ($x \approx 0.5$).[7] In this paper, the general feature of the T-x phase diagram of λ-$BETS_2(Fe_xGa_{1-x})Cl_4$ is presented.

The black thin needle crystals of λ-$BETS_2(Fe_xGa_{1-x})Cl_4$ were prepared electrochemically from 10% ethanol-containing chlorobenzene solutions of BETS, $[(C_2H_5)_4N]FeCl_4$ and $[(C_2H_5)_4N]GaCl_4$. The x-values were determined by EPMA (electron probe microanalyses). The resistivities were measured along the needle axes of the crystals by the conventional four-probe method down to 4 K. The resistivity of the crystal with x=0.36 was also measured down to 0.5 K to determine the phase boundary between superconducting and insulating phases.

Both λ-$BETS_2GaCl_4$ and λ-$BETS_2FeCl_4$ crystallize into the triclinic systems.[3,8] Considering the close similarity of their lattice constants, it might be expected that the $GaCl_4^-$ and $FeCl_4^-$ ions can be easily replaced with each other. As shown in Figure 1, the mixing ratio of $[(C_2H_5)_4N]FeCl_4$ and $[(C_2H_5)_4N]GaCl_4$ in the solution is approximately equal to the x-value of the crystal. This indicates that λ-$BETS_2(Fe_xGa_{1-x})Cl_4$ is an organic alloy with randomly mixed anions. The values of the resistivities of

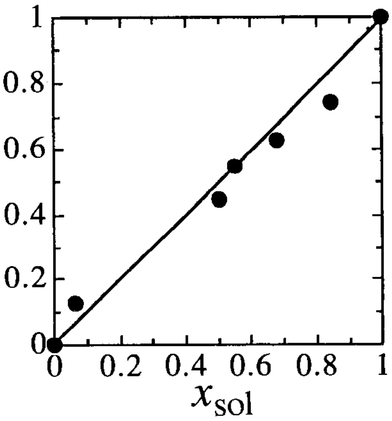

Figure 1. The relation between x of the crystal (x_{cryst}) determined by EPMA and the mixing ratio of $[(C_2H_5)_4N]FeCl_4$ and $[(C_2H_5)_4N]GaCl_4$ in the solution (x_{sol}), from which the crystals were grown.

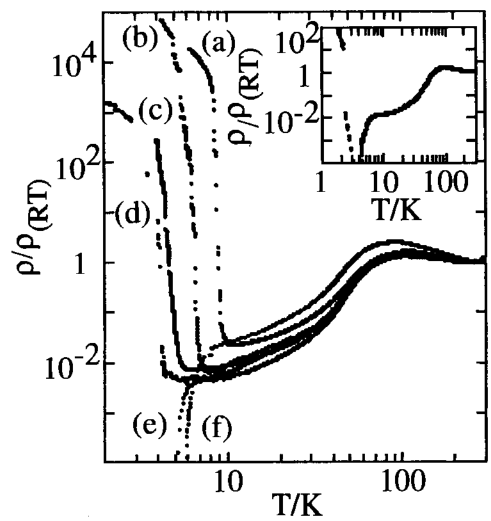

Figure 2. Temperature dependence of the resistivities of λ-$BETS_2(Fe_xGa_{1-x})Cl_4$: (a) x= 1, (b) x= 0.84, (c) x= 0.63, (d) x= 0.55, (e) x= 0.13, (f) x= 0. The inset shows the SC-I transition of λ-$BETS_2(Fe_{0.43}Ga_{0.57})Cl_4$.

the resulting λ-$BETS_2(Fe_xGa_{1-x})Cl_4$ crystals are approximately independent of x ($\rho(RT) \approx 30\ S\ cm^{-1}$). The resistivity increases gradually with decreasing temperature down to about 90 K (Figure 2). Below this temperature, the resistivity decreases fairly rapidly. The temperature dependence of the resistivity above 10

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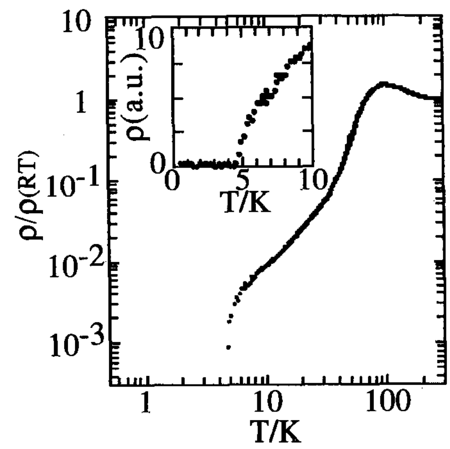

Figure 3. Temperature dependence of the resistivity of λ-$BETS_2(Fe_{0.36}Ga_{0.64})Cl_4$.

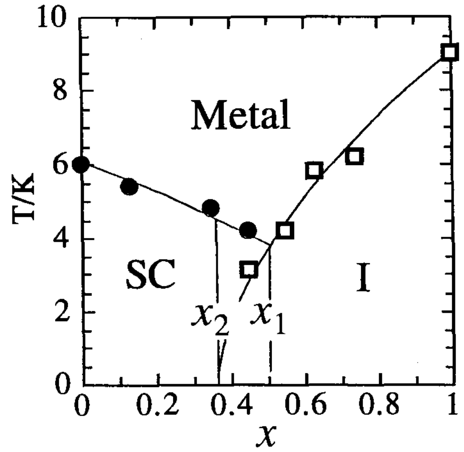

Figure 4. The *T*-*x* phase diagram of λ-$BETS_2(Fe_xGa_{1-x})Cl_4$. The superconductor (SC)-to-insulator (I) transition can be seen at $x_2<x<x_1$.

K was essentially the same for all the crystals. Below 10 K, the resistivity behavior changes systematically with *x*. The MI transition temperature ($=T_{MI}$) was reduced from 8.5 K (x=1) to about 4.5 K ($x\approx0.55$) with decreasing *x*. At $x<0.5$, a superconducting transition appears. T_c gradually increases with decreasing *x*.[9] We showed that the superconductor-to-insulator (SC-I) transition was observed at x=0.43.[7] A small resistivity dip indicating the "partial SC-I transition" has been also observed at x=0.55.[7] The resistivity of the crystal with $x\approx0.36$ showed a superconducting transition at 4.7 K but no indication of SC-I transition was obtained down to 0.5 K (Figure 3). Therefore the crystal with $x<0.35$ may be considered as possessing a superconducting ground state. Combining these results and the reported data on the SC-I transition at $x\approx0.5$, the *T*-*x* phase diagram shown in Figure 4 is proposed.

In conclusion, the general feature of the *T*-*x* phase diagram was determined by the resistivity measurements on λ-$BETS_2(Fe_xGa_{1-x})Cl_4$. The crystal exhibits a MI transition at $x>x_1$ and a superconducting transition at $x<x_1$, where x_1 is about 0.5. At $x_2(\approx0.35)<x<x_1$, the system exhibits the SC-I transition. λ-$BETS_2(Fe_xGa_{1-x})Cl_4$ may be the first organic alloy whose ground state can be controlled continuously from a superconducting state to an antiferromagnetic insulating state by changing the mixing ratio of the non-magnetic ($GaCl_4^-$) and magnetic ($FeCl_4^-$) anions.

References and Notes

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9 The onset temperature of the resistivity drop associated with the superconducting transition was sample-dependent but the offset temperature exhibited a systematic *x*-dependence. Therefore, the offset temperature was taken as T_c in this work.