Electrical and Magnetic Properties of BETS Conductor with Modified λ-type Structure, λ'-$(BETS)_2GaBr_4$

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(Received October 14, 1998; CL-980784)

The resistivity and the magnetic susceptibility of BETS conductor with modified λ-type structure, λ'-$(BETS)_2GaBr_4$ are 0.06 Ω cm and 4×10^{-4} emu mol^{-1} at room temperature. In contrast to the semimetal-to-insulator transition at ambient pressure, the system showed an unusual high-pressure resistivity behavior below 50 K. Very sensitive pressure dependence of the resistivities will be consistent with the semimetallic Fermi surface obtained by extended Hückel tight-binding band calculation.

In the field of molecular conductors, λ-$(BETS)_2GaBr_xCl_{4-x}$ salts, which consist of organic π-donor molecules BETS [=bis(ethylenedithio)tetraselenafulvalene] and mixed tetrahalogeno gallate anions,[1-3] seem to gain an increasing interest because they exhibit not only superconductivity but also anomalous insulating behavior around 10 K ($0.5 < x < 0.75$), which will contribute to make clear an essential role of π-π electron correlation in the organic superconductors.[3] Furthermore, the unprecedented superconductor-to-insulator transition was also found in the similar system containing Fe^{3+} ions, λ-$(BETS)_2Fe_yGa_{1-y}Cl_4$ ($0.35 < y < 0.5$).[4] By changing the bromine content of mixed tetrahalogeno gallate anions, the physical properties of λ-$(BETS)_2GaBr_xCl_{4-x}$ salts can be continuously controlled. However, λ-$(BETS)_2GaBr_xCl_{4-x}$ can be obtained only in the range of bromine contents of $0 \le x < 2$. In the range of $2 < x \le 4$, a modified λ-type (or λ'-type) BETS salt is obtained.[3,5] In this letter, we report the crystal structure, electrical resistivity, magnetic susceptibility of λ'-$(BETS)_2GaBr_4$.

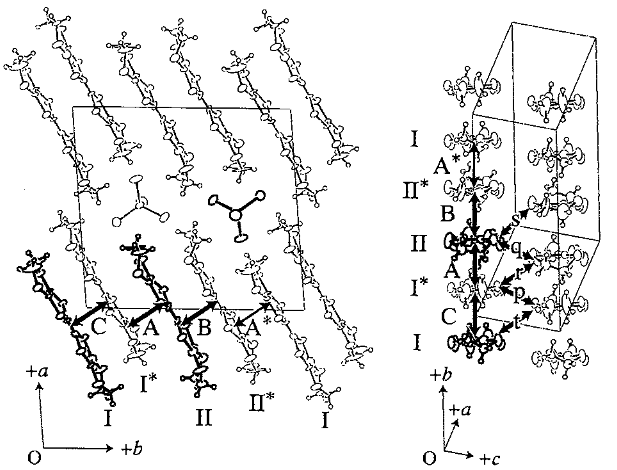

Figure 1. Crystal structure of λ'-$(BETS)_2GaBr_4$ viewed along the *c* axis (a) and along the long molecular axis (b). There are two crystallographically independent BETS molecules I and II. The molecule with symbol * indicates the molecule derived from the inversion symmetry.

Needle crystals of λ'-$(BETS)_2GaBr_4$ were grown electrochemically from the 90% chlorobenzene and 10% ethanol solution or absolute tetrahydrofuran solution containing BETS and $(Et_4N)GaBr_4$. The constant current of 0.5 μA was applied. The lattice constants and X-ray reflection data were obtained by using four-circle diffractometer (Rigaku RASA-7R). The 8498 unique reflections were observed. The electrical resistivities were measured by the conventional four-probe method from room temperature to about 4 K. The anisotropy of magnetic susceptibility was measured on the SQUID magnetometer (Quantum Design, MPMS-5S), by using the oriented needle crystals in a quartz capillary.

The crystal data are: triclinic $P\overline{1}$, a = 16.360(4), b = 17.329(3), c = 6.6379(8) Å, α = 91.80(1), β = 98.90(2), γ = 94.53(2) °, V = 1851.5(6) Å^3, F_w =1533.84 (calculated as $C_{20}H_{16}Br_4GaS_8Se_8$), $Z = 2$, D_{calc} = 2.751 g cm^{-3}, R = 0.047, R_w = 0.031. The crystal structure of λ'-$(BETS)_2GaBr_4$ is shown in Figure 1. The general feature of the crystal structure closely resembles that of λ-type salt. There are two crystallographically independent BETS molecules (I, II shown in Figure 1), which form a fourfold column along the *b*-axis direction periodically (I-I*-II-II*). Similar to the anions in the λ-type crystals, the anions occupy the open sites surrounded by terminal ethylene groups of BETS. Owing to the close halogen···BETS contacts in the λ-type structure, the large $GaBr_4^-$ anions cannot be accommodated in the open sites of the λ-type structure. Therefore the slanting angle of the long axis of BETS molecule against the molecular stacking direction increases discontinuously to accommodate the large size anions, $GaBr_xCl_{4-x}$ ($x > 2.0$) and λ-type structure is deformed into λ'-type one. The nearest sulfur···halogen atom distance is 3.623 Å, which is longer than that of λ-$(BETS)_2GaCl_4$, 3.433 Å.[5]

The intermolecular overlap integrals of the highest occupied molecular orbitals (HOMO's) of BETS molecules were calculated. The overlap integrals are large along the *b* direction (A = 8.885, B = 30.636, C = 21.926 ($\times10^{-3}$)) and small along the *c* direction (p = -1.218, q = -2.095, r = 0.525, s = 1.546, t = 3.990 ($\times10^{-3}$)). Along the *b* -axis (molecular stacking direction), the strong interactions, **B** and **C** and the weak interaction A are arranged as, A, **B**, A, **C**, A, **B**, A, **C**,....(see Figure 1). On the other hand, in λ-$BETS_2GaCl_4$,[6] the strong interaction **A** (= 24×10^{-3}) and the weak interactions B (= 9.8×10^{-3}) and C (= 5.8×10^{-3}) are arranged as, **A**, B, **A**, C, **A**, B, **A**, C,..... It has been pointed out that the conduction electrons of λ-salts are strongly correlated but the electronic state tends to approach the normal metallic one with increasing the small interaction C.[5] Since the weak interaction A of λ'-structure is much larger than C of λ-structure, the λ'-salt will show the stronger metallic nature than λ-salt. In fact, unlike the semiconducting nature of λ-salt at

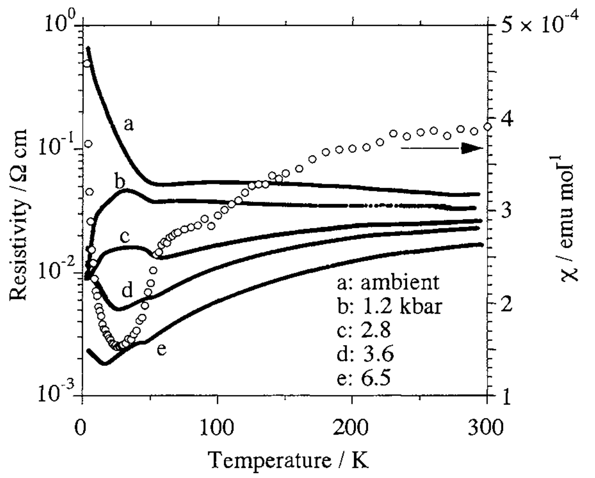

Figure 2. The temperature dependencies of high pressure resistivities (dots) and magnetic susceptibility (empty circles) of λ'-(BETS)$_2$GaBr$_4$. The susceptibility was measured for the magnetic field parallel to the needle axis of the crystals.

least at higher temperature region, the resistivity of λ'-salt shows the "semimetallic temperature dependence" above *ca.* 50 K (Figure 2), which suggests less important role of electron correlation in λ'-salt.

Resistivities of λ'-type salt were measured by conventional four probe method (see Figure 2). From room temperature to about 50 K, there was little temperature dependence of resistivity and the room temperature resistivity ρ_{rt} was about 0.06 Ω cm. Below 50 K, the resistivity increased rapidly. The resistivity at 4 K was 2×10^1-1×10^3 times larger than the room-temperature value, which also depended on the crystal quality. The 50 K-transition was also observed by the magnetic susceptibility measurements (see Figure 2). The magnetic susceptibilities were measured for the field perpendicular and parallel to the needle axes of the crystals but no anisotropy was observed. The susceptibility corrected for diamagnetic contribution was about 4×10^{-4} emu mol^{-1} around 300 K and gradually decreased as lowering temperature. After exhibiting a fairy sharp drop around 50 K, the susceptibility increased below 25 K, which will be ascribed to the paramagnetic impurities. By assuming 1/2 spins, the density of paramagnetic impurities was estimated to be 0.037 spins mol^{-1}. This susceptibility behavior is consistent with the semimetal-to-insulator transition suggested from the resistivities.

The pressure dependence of resistivity was measured on two crystals obtained from different batches. Both showed essentially the same results. At 1.2 kbar, the semimetal-to-insulator transition was suppressed and a characteristic broad resistivity maximum and subsequent fairly sharp resistivity decrease were observed around 30 K and below 10 K, respectively (see Figure 2). However, around 3.6 kbar, the metallic state was stabilized down to 30 K, below which the resistivitiy increased very gradually.

As shown in Figure 3, the band structure calculated on the basis of extended Hückel tight binding approximation gave hole and electron Fermi surfaces, which also suggests the semimetallic nature of the system. The decrease of susceptibility and almost constant resistivity at T > 50 K indicate the gradual diminishing of the Fermi surfaces with lowering temperature. This suggests that the energy separation between the highest energy branch (band 1) and the second highest branch (band 2) increases with decreasing temperature. When the minimum energy of the band 1 becomes higher than the maximum energy of the band 2 around, the system will transform to non-magnetic insulating state (see Figure 3). This may be the origin of the semimetal-to-insulator transition of λ'-(BETS)$_2$GaBr$_4$ around 50 K. Since the crystal has fourfold quasi-stacking structure, no change of the lattice periodicity is required for such phase transition. In fact, the X-ray oscillation photograph taken at 8 K gave no indication of the change of the lattice periodicity. Very sensitive pressure dependence of the resistivity behavior is consistent with the semimetallic Fermi surfaces, which will be sensitive to the small structural change.

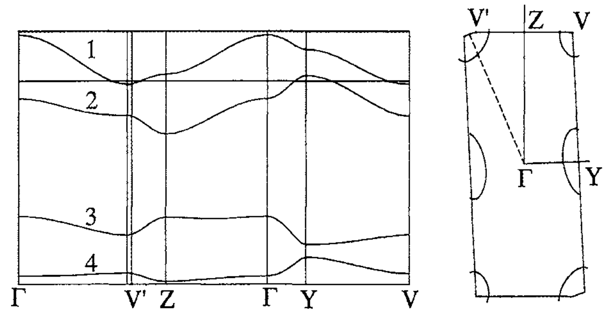

Figure 3. The energy dispersions of band structures (a) and a Fermi surface (b) of λ'-(BETS)$_2$GaBr$_4$.

Thus, despite of the apparent similarity of the λ- and λ'-systems, the electronic state of these two BETS conductors are completely different. Unlike λ-salt with strongly correlated two-dimensional electronic state, λ'-salt has a semimetallic state, where the electron correlation does not play an important role.

References

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6 In λ-(BETS)$_2$GaCl$_4$, the intermolecular overlap integrals are: A = 23.834, B = 9.843, C = 5.762, p = -1.273, q = -3.066, r = 3.693, s = 4.830, t = 0.408 ($\times 10^{-3}$).