A New Organic Superconductor, λ-BETS$_2$GaBrCl$_3$ [BETS = bis(ethylenedithio)tetraselenafulvalene]

Hayao Kobayashi,*[a] Hideto Tomita,[a] Toshio Naito,[a] Hisashi Tanaka,[b] Akiko Kobayashi[b] and Taro Saito[b]

[a] *Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274, Japan*
[b] *Department of Chemistry, School of Science, The Unviersity of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan*

A new organic superconductor, λ-BETS$_2$GaBrCl$_3$, exhibits an onset of the superconducting transition at 7.5–10 K with a broad resistivity maximum at 55–60 K and a second resistivity increase below *ca.* 15 K, probably related to the electron localization effect owing to disorder of the tetrahedral anions; the superconducting state persists up to 14 kbar.

Since the first discovery of the organic superconductor TMTSF$_2$PF$_6$, about 55 organic superconductors have been discovered including seven M(dmit)$_2$ (M = Ni, Pd; dmit = 1,3-dithiole-2-thione-4,5-dithiolate) compounds.[1] All of them consist of planar π molecules with peripheral chalcogen atoms. Among the various constituent molecules investigated, BEDT–TTF [bis(ethylenedithio)tetrathiafulvalene] has produced the most organic superconductors, with various molecular arrangements called β-, γ-, θ- and κ-types. In particular, the κ-type superconductors are famous for their characteristic two-dimensional crystal and electronic structures[2] and high transition temperatures (T_c) up to 13 K.[1,3]

Recently, we have reported the first organic superconductor based on the BETS [bis(ethylenedithio)tetraselenafulvalene] molecule, λ-BETS$_2$GaCl$_4$ with a T_c of 8 K.[4] Similar to κ-type BEDT–TTF superconductors with T_cs of 10–13 K, λ-BETS$_2$GaCl$_4$ exhibits anomalous non-metallic behaviour down to 100 K. This characteristic, highly conducting state followed by a superconducting transition with a fairly high T_c suggests that the λ-type BETS superconductor and the 'high T_c' κ-type BEDT–TTF superconductors share a common electronic band nature. In contrast to the similarity in the electrical behaviour, the molecular arrangement of the λ-type salt is quite different from those of the κ-type salts. It is of importance to study the λ-type organic superconductor more closely, and to compare it with 'high T_c' κ-type BEDT–TTF superconductors to clarify the key factor which determines superconducting transition temperatures in organic systems.

It is well known that T_c decreases with the unit cell volume. This indicates that T_c will be enhanced if the unit cell is expanded without significant change of the molecular arrangement. As the first attempt to enlarge the cell volume of λ-BETS$_2$GaCl$_4$, we have examined a BETS complex with an analogous but larger, tetrahedral anion, GaBrCl$_3$.

[Et$_4$N][GaBrCl$_3$] was prepared by mixing [Et$_4$N]Br and GaCl$_3$ in ethanol. Crystalline [Et$_4$N][GaBrCl$_3$] was precipitated immediately. The crystals of λ-BETS$_2$GaBrCl$_3$ were obtained electrochemically.† Two types of BETS$_2$GaBrCl$_3$ crystals were obtained. Similarly to the BETS conductors with tetrahedral anions MX$_4$ (M = Ga, Fe, In; X = Cl, Br),[5] X-ray diffraction experiments have revealed that the thin needle-shaped crystal has the λ-type structure and the plate crystal has the κ-type structure.

The electrical resistivity was measured by the usual four-probe method. Four gold wires were bonded to the needle-shaped crystals with conducting gold paint. The high-pressure resistivity measurements were made using a clamp-type high-pressure cell and silicone oil as the pressure medium. All the crystals examined showed almost identical resistivity behaviour. The temperature dependence of the resistivities of the needle-shaped crystals is given in Fig. 1.‡ A small resistivity maximum was observed at 55–60 K, which corresponds to the resistivity maximum of λ-BETS$_2$GaCl$_4$ at around 100 K. Then the resistivity decreased rapidly, reaching a minimum at around 12–15 K. After a characteristic resistivity increase, the superconducting transition occurs at 7 K. Except for the increase at around 10 K, the general feature of the temperature dependence of the resistivity of λ-BETS$_2$GaBrCl$_3$ resembles that of λ-BETS$_2$GaCl$_4$. The resistivity increase around 10 K seems to be related to the possible electron localization effect (Anderson localization) owing to orientational disorder of the GaBrCl$_3$ anions. The GaBrCl$_3$ anion is located in a general position, but the room temperature crystal structure analysis suggested a positional disorder of the halogen atoms (Cl, Br).§ The refinement of the occupancy probabilities of the four halogen positions showed the positional disorder and the existence of two preferred positions for the Br atom. The occupancy probabilities of the Br atom are 35% for positions *A* and *B* and 15% for *C* and *D* (Fig. 2). It seems natural that the Ga–X bond lengths for *A* and *B* are a little longer than those for *C* and *D*, since the crystal structure analyses of κ-BETS$_2$GaX$_4$ (X = Cl, Br) showed that the Ga–Br distance is 0.145 Å longer than that of Ga–Cl;[6] the difference in bond lengths between Ga–(*A*,*B*) and Ga–(*C*,*D*) (0.031 Å) is almost equal to 0.145 Å × (35 − 15%) (= 0.029 Å).

The resistivities were re-examined with extremely slow cooling rates in order to avoid the freezing of the orientational disorder as much as possible. It took 80 h to decrease from room temperature to liquid He temperature (slow process). This cooling rate was about 20 times slower than that of the normal process. The small resistivity maximum appeared at 55 K, a little lower than the corresponding temperature in the normal process (60 K). The resistivity increase in the lower temperature region (< 15 K) still persisted, but the magnitude of the increase became smaller and the onset of the superconducting transition was enhanced to *ca.* 10 K (Fig. 1). The mid-point was about 8 K, almost equal to that of λ-BETS$_2$GaCl$_4$.[4] Except for some κ-type BEDT–TTF superconductors,[1,3] the transition tempera-

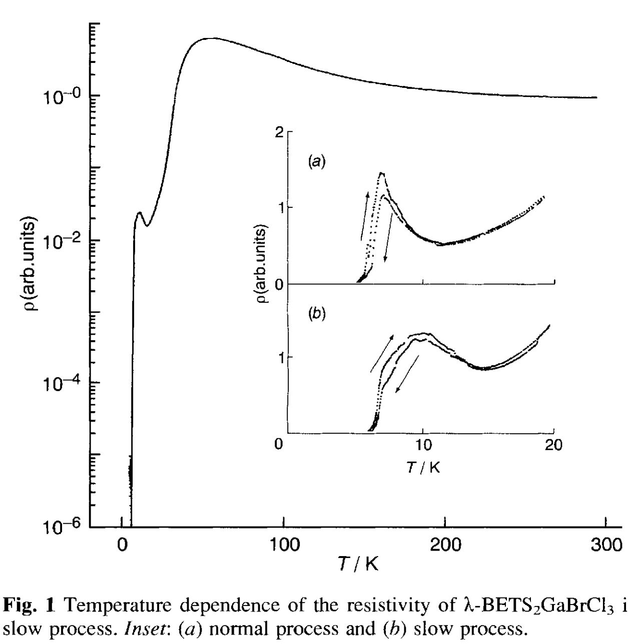

Fig. 1 Temperature dependence of the resistivity of λ-BETS$_2$GaBrCl$_3$ in slow process. *Inset*: (*a*) normal process and (*b*) slow process.

tures of these two λ-type BETS superconductors are higher than those of other ambient-pressure organic superconductors.

High-pressure resistivity measurements showed that the T_c decreases almost linearly with increasing pressure (Fig. 3). But the pressure (p) dependence of T_c ($dT_c/dp = -0.49$ K kbar^{-1}) is very small compared with those of the other typical organic superconductors. The superconducting state of λ-BETS$_2$GaBrCl$_3$ seems to remain up to 14 kbar. In the case of κ-(BEDT–TTF)$_2$Cu[N(CN)$_2$]Cl with the highest T_c, the T_c is extremely pressure sensitive (−3.4 K kbar^{-1}),[7] while dT_c/dp of the first κ-type organic superconductor, κ(BEDT–TTF)$_2$I$_3$ is −0.8 K kbar^{-1} and that of λ-BETS$_2$GaCl$_4$ is −0.9 K kbar^{-1}.[8] These pressure dependences of the T_cs are normal in view of the expected decreases in the state densities [$D(\varepsilon_F)$] owing to the increase in band widths with increasing pressure. However, the pressure effect in λ-BETS$_2$GaBrCl$_3$ is exceptionally small. In organic superconductors such as β-(BEDT–TTF)$_2$I$_3$, the electron localization effect (Anderson localization) owing to lattice disorder has been known to suppress the T_c.[9,10] In the case of λ-BETS$_2$GaBrCl$_3$, the disorder of the tetrahedral anion would freeze at low temperatures and tend to localize conduction electrons, which seems to be consistent with the resistivity increase in the low temperature region. Pressure enhances the metallic nature of the system, which would reduce the suppressing effect on T_c owing to electron localization. Thus, λ-BETS$_2$GaBrCl$_3$ has two opposite pressure effects, whose combination seems to produce a weak pressure dependence of T_c. The increase of the resistivity below 15 K indicates that the disorder still remains even in the slow process, which may be why the T_c of λ-BETS$_2$GaBrCl$_3$ was not enhanced despite the enlargement of the unit cell. However, if the disorder of the tetrahedral anion could be completely removed, the T_c would be enhanced.

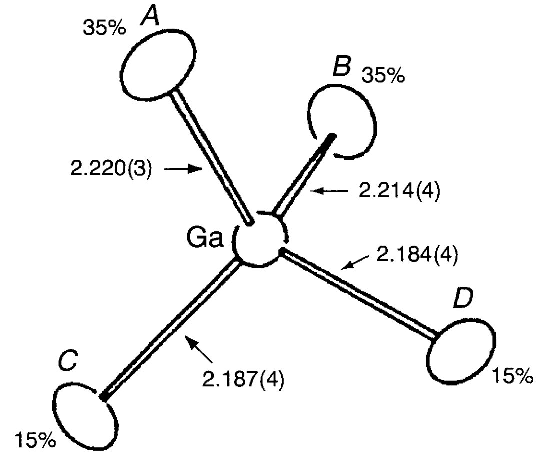

Fig. 2 Bond lengths (Å) and occupancy probabilities (*A–D*) of Br of GaBrCl$_3$

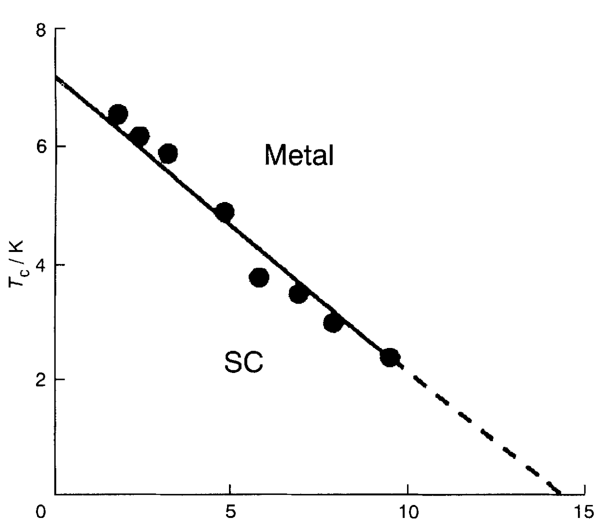

Fig. 3 Pressure dependence of the superconducting transition [T_c (mind-point)] of λ-BETS$_2$GaBrCl$_3$; measurements taken from normal process

The examination of BETS conductors with analogous anions is now in progress, and will be reported elsewhere.

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Footnotes

† Satisfactory elemental analysis (C, H, Cl) was obtained.

‡ The resistivity of the plate crystal with the κ-type structure decreases monotonously with decreasing temperature down to 4 K. The resistance ratio of ρ(300 K)/ρ(4 K) was *ca.* 10^3. It should be noted that the crystal of BETS$_2$GaBrCl$_3$ seems to deteriorate in air. The resistivity measurements of the old crystals of λ-BETS$_2$GaBrCl$_3$, which were kept in a normal glass sample tube for two months, exhibited large resistivity increases at low temperature and a marked depression of the superconducting transition temperatures (or no superconducting transitions down to 4.2 K).

§ The lattice constants of λ-BETS$_2$GaBrCl$_3$ are: a = 16.231(4), b = 18.628(4), c = 6.6108(8) Å, α = 98.34(1), β = 96.70(2), γ = 112.48(2)°, V = 1794.6(7) Å^3. The cell volume is 20 Å^3 larger than that of λ-BETS$_2$GaCl$_4$. The structure was refined by using 8134 unique reflections. The final R value was 0.040.

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