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Electric and magnetic properties and phase diagram of a series of organic superconductors λ-BETS$_2$GaX_zY_{4-z} [BETS=bis(ethylenedithiotetraselenafulvalene; X,Y=F, Cl, Br; $0<z<2$)]

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The physical properties of a series of organic superconductors with fourfold quasistacking structures, λ-BETS$_2$GaX_zY_{4-z} [BETS=bis(ethylenedithiotetraselenafulvalene; X,Y=F, Cl, Br; $0<z<2$)] are changed continuously by tuning the value of z. The compound λ-BETS$_2$GaBr$_z$Cl$_{4-z}$, has a superconducting ground state for $0<z<z_c$ (≈ 0.8) and a semiconducting state for $z_c<z<2.0$. The maximum T_c is about 10 K, showing the existence of a 10-K class of non-ET organic superconductors [ET=bis(ethylenedithio)tetrathiafulvalene]. The temperature dependence of the resistivity closely resembles that for κ-type ET superconductors but the susceptibility behavior is different. The susceptibility of λ-BETS$_2$GaBr$_{1.5}$Cl$_{2.5}$ is isotropic and decreases fairly sharply below 30 K. No indication of a spin-flop transition was observed at 10 K, suggesting that the insulating phase that neighbors the superconducting phase is not antiferromagnetic at least down to 10 K. [S0163-1829(97)50738-7]

Since the discovery of the organic superconductor TMTSF$_2$PF$_6$,[1] a number of molecular superconductors have been developed by using planar π molecules such as TMTSF, BEDT-ITF,[2] $M(dmit)_2$,[3] etc. Bechgaard salts TMTSF$_2X$ (X=PF$_6$,ClO$_4$,...) and κ-type BEDT-TTF (or ET) conductors are representative organic superconductors whose low-temperature properties have been intensively investigated. In spite of the large difference in the dimensionality of π-metal bands, the phase diagrams of these two organic superconductors seem to share a common nature, that is, the superconducting phase neighbors in the antiferromagnetic insulating phase. In Bechgaard salts, the magnetic insulating ground state originates from the one dimensionality of the metallic band, whereas the strong electron correlation in two-dimensional metal is considered to be responsible for the appearance of the magnetic phase of κ-type ET superconductors. At high pressure, the magnetic insulating states of TMTSF and ET systems are changed to superconducting states. A typical example of the phase diagram of organic conductors can be seen in the series of the isomorphous Bechgaard salts of TMTCF$_2X$, [C(chalcogen atom)=S or Se]. With increasing pressure, the ground state of TMTCF$_2X$ system tends to change in the following manner: spin-Peierls state→spin-density wave (SDW) state→superconducting state→metallic state.[4]

The antiferromagnetic insulating phase was also found in the $dmit$ superconductor, β-[(CH$_3$)$_4$N][Pd($dmit$)$_2$]$_2$.[5,6] Contrary to a Bechgaard salt, this system is composed of the closed-shell cations and π-acceptor molecules [Pd($dmit$)$_2$]. β-[(CH$_3$)$_4$N][Pd($dmit$)$_2$]$_2$ exhibits a superconducting transition above 5 kbar ($T_c \approx 6$ K),[5] while NMR and ESR studies gave an evidence of the antiferromagnetic ground state at ambient pressure.[7] The dimeric molecular arrangement of β-[(CH$_3$)$_4$N][Pd($dmit$)$_2$]$_2$ resembles that of TMTCF$_2X$ and is quite different from the dimeric arrangement of the so-called κ-type ET superconductor. But the weakly semiconducting behavior of β-[(CH$_3$)$_4$N] [Pd($dmit$)$_2$]$_2$ at ambient pressure and fairly large amplitude of the antiferromagnetic magnetization of $0.22\mu_B$ per Pd($dmit$)$_2$ dimer at low temperature reminds us of the high-pressure superconductor κ-ET$_2$Cu[N(CN)$_2$]Cl having the commensurate antiferromagnetic ordering with moment of $(0.4-1.0)\mu_\mathrm{B}$/ET dimer.[8] Thus despite the large difference in the component molecules and molecular arrangements, there seem to be many molecular superconductors where the antiferromagnetic insulating states are located near the superconducting phase.

In this paper, the phase diagram of a series of organic superconductors based on BETS molecules having mixed-halide gallium anions is reported. BETS(=bis(ethylene dithio)tetraselenafulvalene) is a π-donor molecule analogous to ET, where four S atoms in the central TTF skeleton are changed to Se atoms.

We have recently found the organic superconductors with mixed-halide gallium anions, λ-BETS$_2$Ga(X_zY_{4-z}) (X,Y =F, Cl, Br; $0<z<1.7$).[9,10] The crystals of λ-type BETS salts have triclinic unit cells and fourfold quasistacking arrangements of BETS's along the a axes. The lattice constants of λ-BETS$_2$GaCl$_4$ are $a=16.172$ Å, $b=18.616$, $c=6.607$, α=98.38°, β=96.75, γ=112.56, and $V=1784$ Å^3.[10] There are crystallographically independent two BETS's and one GaCl$_4^-$. The differences between the first and second oxidation potentials of ET and BETS are 0.28 and 0.22 eV, respectively, indicating relatively small U of BETS.[11] The intermolecular overlap integrals (S) of the highest occupied molecular orbitals of BETS molecules, which were calculated on the basis of an extended Hückel approximation, were larger than those of typical ET conductors such as β-ET$_2$I$_3$ with a similar stacking structure.[12] Large S and small U are consistent with the strong metallic nature of the BETS conductor.[13] One strong ($s \approx 0.3$ eV) and two weak ($w \approx w' \approx s/3$) intermolecular interactions are repeated along the fourfold molecular stacks ($swsw'swsw'$...). Owing to the fairly large intermolecular transverse interaction ($t \approx w/2$), the extended Hückel tight-binding band calculation gave two-dimensional energy bands. Four energy branches are separated into two upper and two lower branches by a midgap of about 0.3 eV. The two upper bands are effectively half filled. One- and two-dimensional Fermi surfaces similar to those of κ-type ET superconductors were obtained.

The chlorine atom in $GaCl_4^-$ can be exchanged by bromine and fluorine atoms. The unit cell volume of λ-$BETS_2GaF_zCl_{4-z}$ ($z \approx 1.0$) was 1782 Å^3 and that of λ-$BETS_2GaBr_zCl_{4-z}$ was almost linearly dependent on the z value: 1792 Å^3 ($z \approx 0.5$), 1808 Å^3 ($z \approx 1.5$). X-ray diffraction experiments showed that λ-$BETS_2GaBr_zCl_{4-z}$ takes λ-type structure at $0 < z < 1.8$ and modified λ-type structure (or λ'-type structure) at $2.0 < z < 4.0$. the electrical properties of the λ'-type crystal are different from those of the λ-type one. The superconducting transition of the λ'-type crystal has not been observed so far. The z value was estimated by the electron probe microanalysis and/or x-ray determination of the unit cell volume. It may be easily imagined that the decrease of the unit cell volume by adopting small size anions will produce the ''effective pressure.'' It should be noted here that there are two types of positional disorders in λ-$BETS_2GaBr_zCl_{4-z}$. One is orientational disorder of tetrahedral $GaX_zY_{4-z}^-$ anion. The other originates from the halogen exchange reaction of $GaX_zY_{4-z}^-$ in the solution during the preparation of the crystals. NMR spectra of $GaBr_nCl_{4-n}^-$ dissolved in the organic solvent revealed the existence of the five chemical species of $GaBr_nCl_{4-n}^-$ ($n = 0$, 1, 2, 3, 4, and 5) even when pure $GaBr_nCl_{4-n}$ was used. Therefore the chemical formula of $BETS_2GaBr_zCl_{4-z}$ must be regarded as the stoichiometry averaged over the anion sites. X-ray refinements of four independent halogen positions in λ-$BETS_2GaCl_zF_{4-z}$ and λ-$BETS_2GaBr_zCl_{4-z}$ have revealed that two of four positions are preferred by large size atoms (Br atom in $GaBr_zCl_{4-z}$ and Cl atoms in $GaCl_zF_{4-z}$). The remaining two positions tend to be occupied by the smaller halogen atoms.[10] Usually the electrical properties of organic conductors are strongly influenced by the lattice disorder. But fortunately the resistivity behavior of λ-$BETS_2GaX_zY_{4-z}$ showed the disorder effect to be not serious.

Resistivities were measured along the thin needle axes of the crystals ($\parallel c$). As shown in Fig. 1, the resistivity of λ-$BETS_2GaCl_4$ showed a broad maximum around 90 K, indicating the strong correlation of a π-electron system. Then the resistivity decreased rapidly and exhibited a superconducting transition. The onset temperature of the resistivity drop was sample dependent (9–6 K) but the distribution of the offset temperature was rather sharp (5–6 K). At high pressure, the resistivity maximum disappeared, indicating the normal metallic state. At the same time T_c decreased ($dT_c/dP = -0.7°$ kbar).

The resistivity of λ-$BETS_2GaCl_zF_{4-z}$ ($z \approx 3.0$) decreased with lowering temperature and exhibited the superconducting transition at 3.5 K (Fig. 1). This behavior resembles the resistivity behavior of λ-$BETS_2GaCl_4$ at high pressure, consistent with the idea of the ''effective pressure'' in the system with smaller anions.

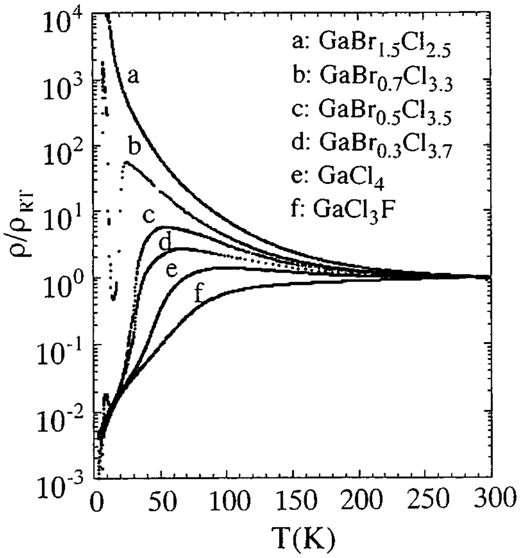

FIG. 1. Resistivities of λ-$BETS_2GaX_zY_{4-z}$.

Contrary, in λ-$BETS_2GaBr_zCl_{4-z}$ ($z \approx 0.3$–0.5), the broad resistivity maximum became prominent, which appeared at 40–60 K. Then the resistivity decreased very rapidly and transformed to the superconducting state at 6.5–8 K. Around $z = 0.5$, a sample-dependent resistivity peak indicating the existence of an insulating phase bordering on the superconducting phase appeared around 9 K. At high pressure, the resistivity behavior became that of normal metal and T_c decreased almost linearly with increasing pressure. The pressure dependence of T_c of λ-$BETS_2GaBr_zCl_{4-z}$ ($z = 0.3$–0.6) was $dT_c/dP = -0.5°$/kbar.

λ-$BETS_2GaBr_zCl_{4-z}$ ($z \approx 0.7$) exhibited a semiconducting behavior down to 25 K (Fig. 1), where the resistivity was about 50 times larger than the room-temperature value. Then the resistivity decreased down to 15 K by about two orders of magnitude and increased sharply down to 8 K, where the onset of the superconducting transition was observed. This extremely strong change of the resistivity indicates that the system passed successively through the nonmetallic, metallic, insulating, and superconducting phases with lowering temperature.

When the z value becomes large ($z > 1.0$), the system showed a semiconducting behavior at ambient pressure. In the case of λ-$BETS_2GaBr_zCl_{4-z}$ ($z \approx 1.5$), the resistivity increased gradually with lowering temperature. But this insulating state was easily changed into the superconducting state by applying pressure (Fig. 2). The anomalous resistivity behavior below 7.5 K at 1.25 kbar may be ascribed to the inhomogeneous distribution of ''effective pressure.'' The superconducting transition temperature reached its maximum at about 3 kbar. The onset temperature of the transition was 10.7 K and the midpoint temperature was 9.7 K, which is almost equal to that of the first κ-type 10-K class of ET superconductor, κ-$ET_2Cu(NCS)_2$[$T_c(^{12}C) = 9.6$ K (Ref. 14)].

The above-mentioned resistivity behavior of λ-type BETS superconductor resembles closely that of the κ-type ET su-

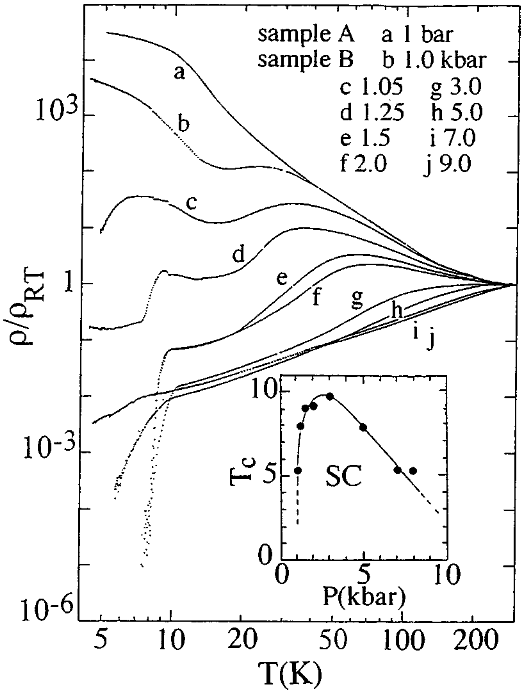

FIG. 2. Pressure dependencies of resistivities and superconducting transition temperature (inset) of λ-BETS$_2$GaBr$_{1.5}$Cl$_{2.5}$.

perconductor. However, susceptibility behavior obtained by a SQUID magnetometer was different from that of the κ-type ET superconductor. Unlike κ-type BETS$_2$GaCl$_4$ with Pauli-like constant susceptibility and stable metallic state, the susceptibility of polycrystalline samples of λ-BETS$_2$GaCl$_4$ increased gradually with decreasing temperature down to T_c.

The susceptibility of λ-BETS$_2$GaBr$_z$Cl$_{4-z}$ ($z \approx 0.3$) was also increased gradually down to 20 K and then decreased very slightly down to T_c. The susceptibility (χ) of λ-BETS$_2$GaBr$_z$Cl$_{4-z}$ ($z \approx 0.7$) exhibited a clear maximum around 45 K, where the resistivity showed no anomaly (Figs. 1 and 3). Two small anomalies corresponding to the nonmetal-to-metal (NM-M) and metal-to-insulator (M-I) transitions were observed around 27 K (small jump of χ) and 15 K (small drop of χ), respectively.

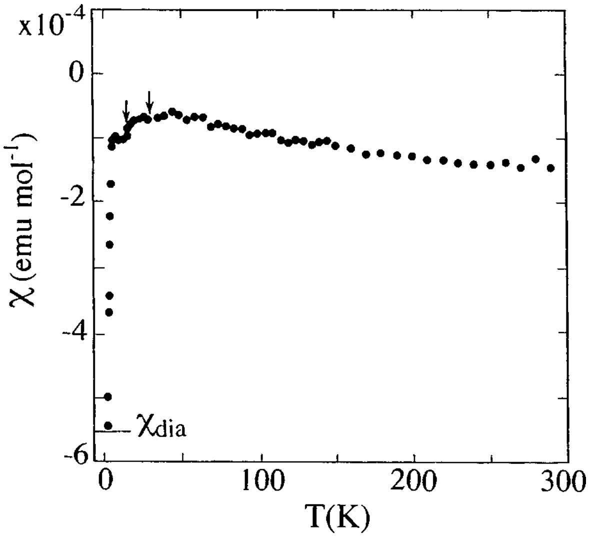

FIG. 3. Susceptibility of polycrystalline sample of λ-BETS$_2$GaBr$_{0.7}$Cl$_{3.3}$. The arrows indicate the temperatures of nonmetal-to-metal and metal-to-insulator transitions.

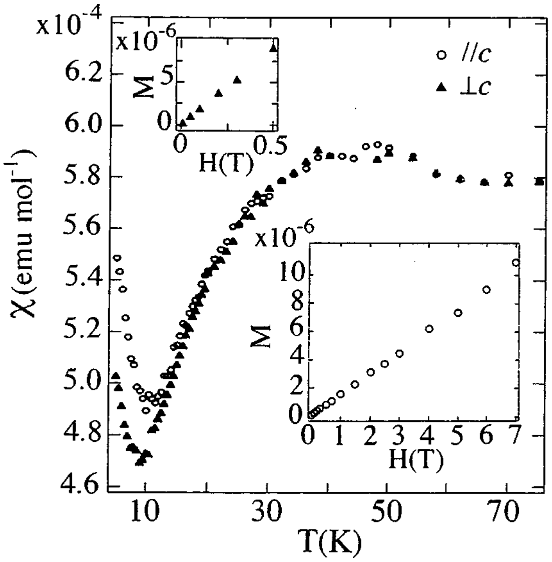

FIG. 4. Susceptibility and magnetization (insets) of oriented thin needle crystals of λ-BETS$_2$GaBr$_{1.5}$Cl$_{2.5}$.

Similar decrease of the susceptibility at low temperature was also observed in the insulating λ-BETS$_2$GaBr$_z$Cl$_{4-z}$ ($z \approx 1.5$), whose anisotropy of the magnetic susceptibilities was measured by using the oriented thin needle crystals. The magnetic susceptibility was increased slowly with lowering temperature down to about 45 K. Then the susceptibility decreased (Fig. 4). Considering the weaker stability of Br-containing crystals, the increases of the susceptibility below 10 K may be ascribed to the paramagnetic lattice defects. The fairly sharp decrease of the susceptibility below 30 K indicates the magnetic phase transition. The susceptibilities parallel and perpendicular to the needle axis showed no anisotropy above 10 K, which indicates the nonantiferromagnetic nature of the transition. It has been reported that the spin-flop transitions were observed at about 0.3 T in κ-ET$_2$Cu[N(CN)$_2$]Cl with canted antiferromagnetic spin structure[8] and at about 0.5 T in TMTSF$_2M$F$_6$ (M

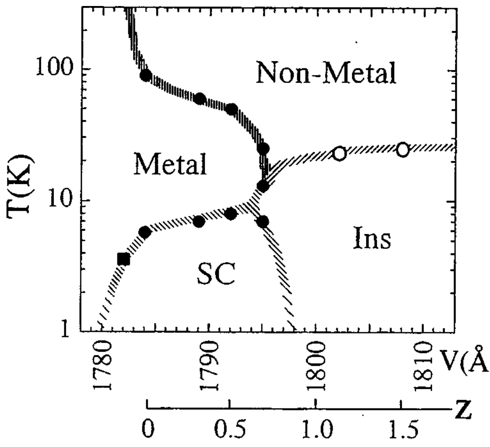

FIG. 5. Phase diagram of λ-BETS$_2$GaBr$_z$Cl$_{4-z}$. Solid circles [a square indicates T_c of λ-BETS$_2$GaCl$_z$F$_{4-z}$ ($z \approx 1.0$)] were obtained from the resistivity data and open circles were obtained from susceptibility data.

=P, As) with the SDW ground state.[15] However, in λ-$BETS_2GaBr_{1.5}Cl_{2.5}$ no indication of the spin-flop transition was obtained for $M_\parallel$ and $M_\perp$ at 10 K ($M_\parallel$ and $M_\perp$ are the magnetization for the field parallel and perpendicular to the needle axes of the crystals). This is consistent with the isotropic susceptibility behavior. Consequently, the low-temperature state seems not to be a simple antiferromagnetic state but probably has a nonmagnetic nature down to at least 10 K.

In contrast to the close resemblance in the electrical properties, the magnetic properties of λ-type BETS conductors differ from those of κ-type ET conductors. The most conspicuous difference be tween λ- and κ-type conductors can be seen in the crystal structures. κ-$ET_2Cu[N(CN)_2]X$ (X =Cl, Br) has the characteristic two-dimensional arrangement of ET dimers, where every ET molecule is crystallographically equivalent. In contrast, λ-type BETS salt has fourfold quasistacking structure, where two BETS molecules are independent. As mentioned before, one strong (s) and two weak (w,w') intermolecular interactions are repeated along the stacking direction ($swsw'swsw'\dots$). According to Miyagawa *et al.*, almost one localized spin is distributed on every ET dimer in κ-$ET_2Cu[N(CN)_2]Cl$.[8] Considering the close resemblance in the high-temperature semiconducting behaviors of λ- and κ-type conductors, it might be permissible to imagine similar electron localization in a λ-type salt. Then, the system will tend to take the nonmagnetic spin-Peierls-like state because of the fourfold quasistacking structure. Although the fairly large transverse intermolecular interaction will limit the validity of the simple one-dimensional picture, the nonmagnetic behavior down to 10 K will be related to these structural characteristics of the λ-type salt.

In conclusion, we have found a series of organic superconductors with fourfold quasistacking structure, λ-$BETS_2GaBr_zCl_{4-z}$, whose physical properties can be controlled continuously by the chemical modification of the anion size. The highest T_c of about 10 K shows the existence of 10-K class non-ET organic superconductors. The magnetic susceptibility of the insulating state located near the superconducting phase is isotropic down to 10 K.

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[1] D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. (France) Lett. **41**, L-95 (1980).

[2] J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M.-H. Whangbo, *Organic Superconductors* (Prentice-Hall, Englewood Cliffs, NJ, 1992).

[3] P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark, and A. E. Underhill, Coord. Chem. Rev. **110**, 115 (1991).

[4] D. Jerome, Science **252**, 1509 (1991).

[5] A. Kobayashi, R. Kato, A. Miyamoto, T. Naito, H. Kobayashi, A. C. Clark, and A. E. Underhill, Chem. Lett. **1991**, 2163.

[6] A. Kobayashi, R. Kato, R. A. Clark, A. E. Underhill, A. Miyamoto, K. Bun, T. Naito, and H. Kobayashi, Synth. Met. **56**, 2927 (1993).

[7] K. Seya, Y. Kobayashi, T. Nakamura, T. Takahashi, Y. Osako, H. Kobayashi, R. Kato, and A. Kobayashi, Synth. Met. **70**, 1043 (1995).

[8] K. Miyagawa, A. Kawamoto, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **75**, 1174 (1995).

[9] H. Kobayashi, T. Udagawa, H. Tomita, K. Bun, T. Naito, and A. Kobayashi, Chem. Lett. **1993**, 1559; L. K. Montgomery, T. Burgin, J. C. Huffman, J. Ren, and M.-H. Whangbo, Physica C **219**, 490 (1994).

[10] H. Tanaka, A. Kobayashi, T. Saito, K. Kawano, T. Naito, and H. Kobayashi, Adv. Mater. **8**, 812 (1996).

[11] G. C. Papavassiliou, A. Terzis, and P. Delhaes, in *Organic Conductive Molecules and Polymers*, edited by H. S. Nalwa (Wiley, Chichester, NY, 1997).

[12] H. Kobayashi, R. Kato, and A. Kobayashi, Synth. Met. **19**, 623 (1987).

[13] R. Kato, H. Kobayashi, and A. Kobayashi, Synth. Met. **42**, 2093 (1991).

[14] U. Geiser, J. M. Williams, K. D. Carlson, A. M. Kini, H. H. Wang, R. A. Klemm, J. R. Ferraro, S. K. Kumar, K. R. Lykke, P. Wurz, D. H. Parker, S. Fleshler, J. D. Dudek, N. L. Eastman, P. B. Mobley, J. M. Seaman, J. D. B. Sutin, G. A. Yaconi, and P. Stout, Synth. Met. **56**, 2314 (1993).

[15] K. Mortensen, Y. Tomkiewicz, T. D. Schultz, and E. M. Engler, Phys. Rev. Lett. **46**, 1234 (1981); K. Mortensen, Y. Tomkiewicz, and K. Bechgaard, Phys. Rev. B **25**, 3319 (1982).