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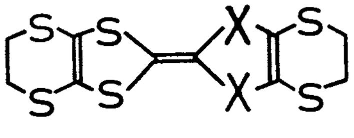
Superconducting Transition Temperature of the Organic Alloy System. κ-[(BEDT-TTF)$_{1-x}$(BEDT-STF)$_x$]$_2$Cu[N(CN)$_2$]Br

Toshio NAITO,* Akihito MIYAMOTO, Hayao KOBAYASHI,
Reizo KATO,† and Akiko KOBAYASHI††
Department of Chemistry, Faculty of Science, Toho University,
Miyama 2-2-1, Funabashi, Chiba 274
† Institute for Solid State Physics, The University of Tokyo,
Roppongi, Minatoku, Tokyo 106
†† Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

The superconducting transition temperature (T_C) was investigated by alloying (BEDT-TTF)$_2$Cu[N(CN)$_2$]Br with (BEDT-STF)$_2$Cu[N(CN)$_2$]Br. The T_C of the former rapidly decreased with doping the latter. The relation between stoichiometry and structure is also discussed.

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (where BEDT-TTF is the acronym of bis(ethylene)dithiotetrathiafulvalene and often further abbreviated to ET) is one of the most interesting organic superconductor due to its second highest T_C reported to date.[1] We report the dependence of T_C on the ratio (x) in the κ-[(BEDT-TTF)$_{1-x}$(BEDT-STF)$_x$]$_2$Cu[N(CN)$_2$]Br (where BEDT-STF implies bis(ethylene)dithiodiselenadithiafulvalene and is abbreviated to STF below) in order to contribute to the better understanding of the superconductivity of the κ-type organic superconductors.



X=S; bis(ethylenedithio)tetrathiafulvalene (ET)
X=Se; bis(ethylenedithio)diselenadithiafulvalene (STF)

Various single crystals of different stoichiometries (x) were prepared by electrochemical method. The two donors of ET and STF were well mixed in the mortar and dissolved in the mixed solvent of chlorobenzene and 1,1,2-trichloroethane containing 10% ethanol. Constant current of 0.8 μA was applied for a few days at 19 °C, after which black shiny blocks harvested on the platinum electrode. The average size of the crystal used in the resistivity measurement was approximately 0.5×0.5×0.2 mm^3. The electrical conductivity of each single crystal was measured by usual dc four-probe method. After conductivity measurements, five (#1-#5) crystals were submitted to X-ray crystal structure analyses.

The x-value was determined by the refinement of the occupancy probability of Se (or S) in the TTF-skeleton. As is well-known, a κ-type superconductor has its unique two-dimensional array of paired π-donors.[2] The crystal of κ-$ET_2Cu[N(CN)_2]Br$ belongs to orthorhombic system with space group Pnma(a=12.942, b=30.016, c=8.539 Å, Z=4).[1] One of the ET molecules is crystallographically independent. In the alloy system, κ-$[(ET)_{1-x}(STF)_x]_2Cu[N(CN)_2]Br$, with almost identical lattice constants, (e.g. #4 : a=12.934, b=30.070, c=8.536 Å) ET and STF molecules are arranged at random. Thus, the large x-value involves serious randomness in the two-dimentional conduction layer. The obtained x-values, R-factors and the numbers (N) of the independent reflections ($2\theta \leq 55$ (MoKα)) used for the structure refinements of the crystals (#1-#5) are : #1, x=0.0, R=0.051, N=1208 ; #2, x=0.10, R=0.050, N=1947 ; #3, x=0.18, R=0.074, N=2373 ; #4, x=0.20, R=0.061, N=2036 ; #5, x=0.63, R=0.051, N=1953.

Figure 1 shows the temperature dependence of the electrical resistivities of the crystals of different stoichiometries. One of their characteristics is the common feature that some of them (#3,#4) do not have maxima below 100 K, which are often observed in κ-type organic superconductors.[3,4] The resistivity maximum becomes inconspicuous with decreasing T_C and disappears in the crystal with T_C lower than 8 K. The resistivity of the crystal without superconductivity decreases monotonously down to low temperature. Thus underlying mechanism of the resistivity maximum mentioned above has remained to be clarified yet, still our data demonstrate that its magnitude is related to the stability of the superconducting phase, in other words the height of T_C.

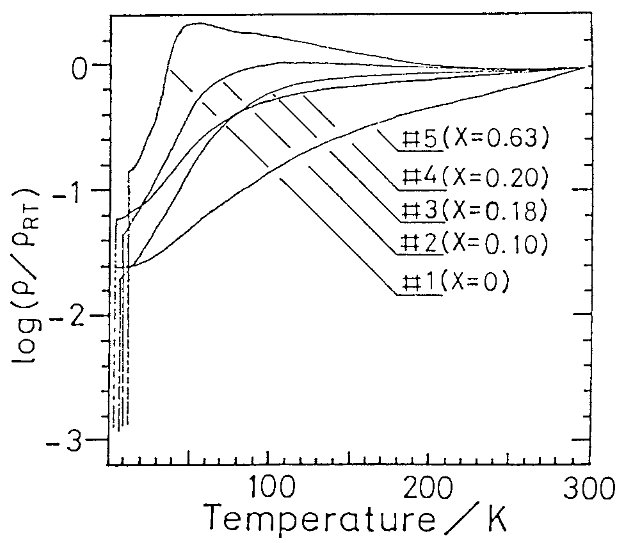


Fig. 1. The temperature dependence of the electrical resistivity of the title compounds of various x's.

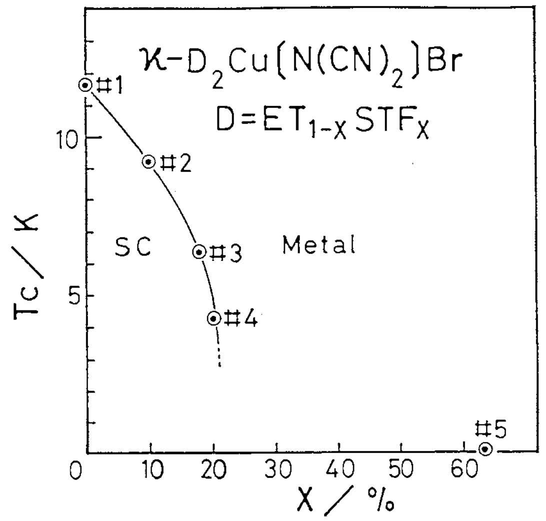


Fig. 2. The relation between T_c and x.

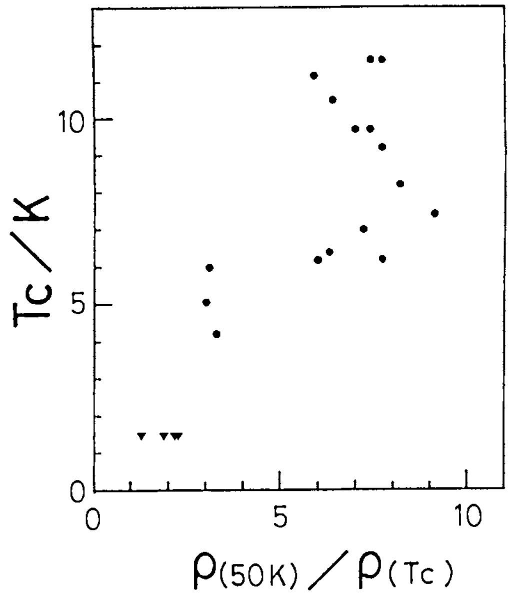


Fig. 3. The relation between resistance ratio (RR) and T_c. The RR (●) was taken tentatively as $\rho(50\ K)/\rho(T_c)$ if superconductivity was observed at the higher temperature than 1.5 K, otherwise (▼) it means $\rho(50\ K)/\rho(1.5\ K)$.

Figure 2 shows the relation between T_c and x. It can be seen that increasing x lowers the T_c markedly and the superconductivity is completely suppressed within 25% doping of STF. It is well known that the T_c of an organic superconductor is strongly depressed by the introduction of the randomness.[5-7] In the case of β-type ET superconductors with mixed trihalide anions such as I_3, IBr_2, and I_2Br, the systematic studies on the relation between T_c and composition (mixing ratio) have been reported.[6] In the present system the randomness is introduced in the conduction layer. As mentioned before the temperature dependence of the resistivity (ρ) was not simple. The system of single phase (x=0) exhibited a resistance maximum at 50 K, which shifted little by little to the higher temperature with increasing x and the system with large x showed a monotonous decrease of ρ. In order to clarify the effect of the randomness, the relation between resistance ratio (RR) and T_c was examined (Fig. 3). The RR was taken tentatively as $\rho(50\ K)/\rho(T_c)$ (or $\rho(50\ K)/\rho(1.5\ K)$ in the case superconductivity was not exhibited) since all the samples examined exhibited metallic behavior below 50 K. The small RR implies frequent scatterings of the conduction electrons by the defects. Though its value is considered to depend on the direction along which resistivity measurement is made, clear-cut grouping can be seen in Fig. 3. The RR value of the system with T_C higher than 6 K falls in the range of 6-9, while that with T_C lower than 6 K has the value of around 3 and non-superconducting (down to 1.5 K) salt does lower than 2.5.

In summary the relation between T_C and composition (x) in the organic alloy system κ-[(ET)$_{1-x}$(STF)$_x$]$_2$Cu[N(CN)$_2$]Br was investigated. The T_C is rapidly decreased with x and the superconductivity is completely destroyed within x≃25%. Larger x diminishes both the resistance hump and the resistance ratio (RR). It is also observed that the T_C enhances according to the RR.

References

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