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Organic superconductor with an incommensurate anion structure: $(\text{MDT-TSF})(\text{AuI}_2)_{0.44}$

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The degree of charge transfer and the upper critical field of the organic superconductor $(\text{MDT-TSF})(\text{AuI}_2)_x$ have been investigated (MDT-TSF: methylenedithio-tetraselenafulvalene). The x-ray oscillation photograph indicates that the anion lattice is incommensurate with the donor lattice, and the chemical composition is $(\text{MDT-TSF})(\text{AuI}_2)_{0.44}$. The charge-transfer degree of this salt is 0.44. The electrical resistivity and the Seebeck coefficient indicate that this salt is a good Fermi liquid above the superconducting transition temperature. The upper critical fields show anisotropic three-dimensional character in spite of the complicated incommensurate structure, and are within the Clogston-Chandrasekhar paramagnetic limit in all directions.

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From the discovery of the organic superconductor $(\text{TMTSF})_2\text{PF}_6$ (TMTSF: tetramethyl-tetraselenafulvalene), most organic conductors showing superconductivity have had stoichiometric compositions; the ratios of the donor molecules to anions are represented by an integer.[1] The band fillings of these compounds are usually 3/4 filling, and this corresponds to effective half-filling by the dimerization gap. Although $\kappa\text{-(BEDT-TTF)}_4\text{Hg}_{3-\delta}X_8$ [BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene, $X=$ Cl, Br] has an incommensurate anion structure, the transport properties show strong sample dependence and the superconducting state appears only under high pressure.[2,3] High-T_c superconductors have a carrier doped energy band and the physical properties are controlled by the doping level. On the contrary, in organic conductors the ratio of the on-site Coulomb repulsion (U) to energy band width (W) are controlled by physical and chemical pressures. For example, in $\kappa\text{-(BEDT-TTF)}_2\text{Cu}[\text{N(CN)}_2]X$ ($X=\text{Br}$, Cl) the Mott insulating state changes to superconducting phase by controlling U/W under applied pressure.[4] By contrast there is no example that the ground state changes from the Mott insulator to a superconductor by the carrier doping effect (band filling control).

Recently, Takimiya *et al.* have synthesized MDT-TSF (depicted in Fig. 1), which is a selenium analog of MDT-TTF (MDT-TTF: methylenedithio-tetrathiafulvalene), and have discovered superconductivity in the AuI_2 salt of MDT-TSF.[5] Although the only superconductor based on MDT-TTF $[\kappa\text{-(MDT-TTF)}_2\text{AuI}_2]$ has the κ structure with strong dimerization,[6] the AuI_2 salt of MDT-TSF has a uniform donor stacking along the a axis. However, the exact composition and the anion position of this salt have not been determined from the ordinary structure analysis. Therefore, the charge-transfer degree has not been known exactly. In the present work, we have decided the charge-transfer degree from an x-ray investigation. From this we can discuss the energy band and the Fermi surface. We have also measured the thermoelectric power, and the magnetoresistance, from which the anisotropy of the coherence length are investigated.

Single crystals were prepared by the electrocrystallization reported in Ref. 5. The x-ray oscillation photographs were taken by a Rigaku Raxis II area detector with graphite monochromated Mo-$K\alpha$ radiation ($\lambda=0.71070$ Å) at room temperature. The band structure was calculated on the basis of the extended Hückel method.[7] Electrical resistivity was measured by the four-probe method along the a axis with an ac current (usually 100 μA) down to 1.5 K. Thermoelectric power measurement was carried out by the two terminal method along the a axis down to 1.5 K. For the magnetoresistance measurements, the sample was mounted on a cryostat in a 9 T superconducting magnet (Oxford Inst.), with two degrees of rotational freedom with respect to the magnetic field, and was cooled to 1.65 K.

Figure 1 is an x-ray oscillation photograph in which the vertical direction is parallel to the donor stacking axis (a^* axis). This photograph displays clear incommensurate layer lines at $a/d=0.436$, 1.321, and 1.762 reciprocal lattice units based on the donor subcell. All these layer lines are composed of well-defined spots even at room temperature, and are not diffusive. This observation indicates the three-dimensional order of the anion molecules. The layer lines at

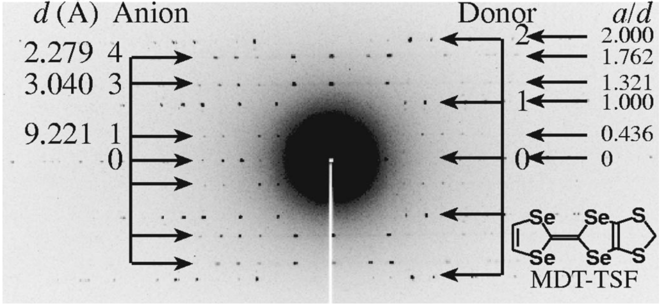

FIG. 1. X-ray oscillation photograph along the a axis taken at room temperature. On the right side is shown a/d: the inverse of d(Å) multiplied by the lattice constant $a=4.016$ Å.

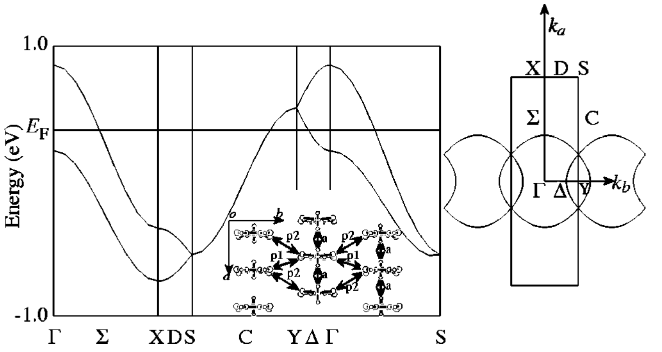

FIG. 2. Energy band structure, the Fermi surface, and donor arrangement projected along the molecular long axis of (MDT-TSF) $(AuI_2)_{0.44}$.

$a/d = 0.436$, 1.321, and 1.762, respectively, correspond to $n = 1$, 3, and 4 lines of the subcell constant $a' = 9.221$ Å. This lattice constant is in agreement with the length of the AuI_2 anion. The $n = 2$ line is not found clearly in spite of the clear $n = 3$ line, because the latter ($d = 3.04$ Å) comes from the average bond length of Au-I. The clear spots at $n = 1$ indicate that the anion structure is not a random infinite chain composed of Au and I, but has a discrete unit of I-Au-I.

The ratio of a to a' unambiguously determines the AuI_2 content to be $x = a/a' = 0.436$, namely (MDT-TSF) $(AuI_2)_{0.436}$. This composition is consistent with the results of both the energy dispersion spectroscopy (1:0.434) and the elemental analysis (1:0.44). Although the closest integer ratio of donor to anion is 9:4 (1:0.444), this seems to exceed the error of the x-ray investigation. Therefore, we have to conclude an incommensurate composition, (MDT-TSF) $(AuI_2)_{0.44}$ based on these three experiments.

All ambient-pressure organic superconductors so far known have commensurate structures and 3/4-filled conduction bands. It is noteworthy that (MDT-TSF)$(AuI_2)_{0.44}$ corresponds to small electron doping to the 3/4 filling. Although the charge-transfer degree is not 0.5 per donor molecule in κ-(BEDT-TTF)$_4$Hg$_{3-\delta}X_8$, this salt has no donor stacking structure. Therefore, (MDT-TSF)$(AuI_2)_{0.44}$ is the first organic superconductor with an incommensurate chain structure.

Since the definite charge-transfer degree is known, it is possible to calculate the energy band structure from the donor arrangement. Intermolecular overlap integrals of the highest occupied molecular orbital (HOMO) calculated by the extended Hückel method are $S_a = -27.3$, $S_{p1} = 3.06$, and $S_{p2} = 12.8 (\times 10^{-3})$ (inset of Fig. 2).[8] Figure 2 shows the energy band structure and the Fermi surface calculated on the basis of the tight binding approximation. The band dispersion along the a axis ($W_{\|a}$) is 1.21 eV and $W_{\|b}$ is 0.32 eV. The energy bands are degenerated on the C line owing to the lattice symmetry (*Pnma*).[11] Therefore, the Fermi surface consists of overlapping cylinders, whose cross section is 44% of the first Brillouin zone. Although the calculation in Ref. 5 has predicted open Fermi surface, the Shubnikov–de Haas oscillation has been observed very recently, in agreement with the present calculation.[12] Therefore, (MDT-TSF) $(AuI_2)_{0.44}$ is not a one-dimensional but a two-dimensional system. However, the potential of the incommensurate anion lattice is not included in the above calculation. It is a future problem to clarify the effect of the incommensurate anion.

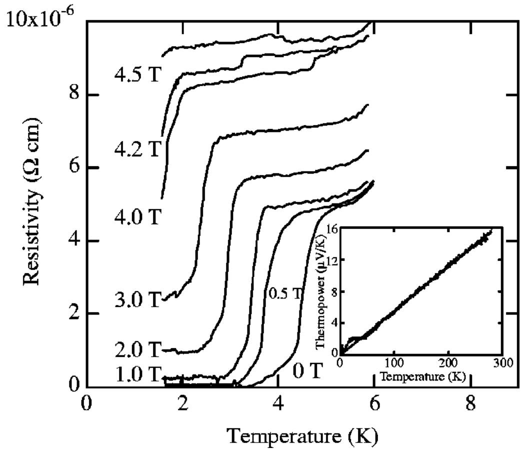

FIG. 3. Low-temperature electrical resistivities under various magnetic fields ($B \| a$). The inset figure is the temperature dependence of thermoelectric power. The solid line is a linear fitting.

The temperature dependence of the electrical resistivity shows a power-law behavior ($\rho \propto T^{1.6}$) suggesting a good Fermi-liquid character,[5] and the resistivity drops to zero below 5.1 K (onset T_c) as shown in Fig. 3. The midpoint superconducting transition temperature is 4.5 K. This midpoint T_c is in agreement with the critical temperature determined by the temperature dependence of the magnetization in the previous report.[5] The critical temperature smoothly decreases

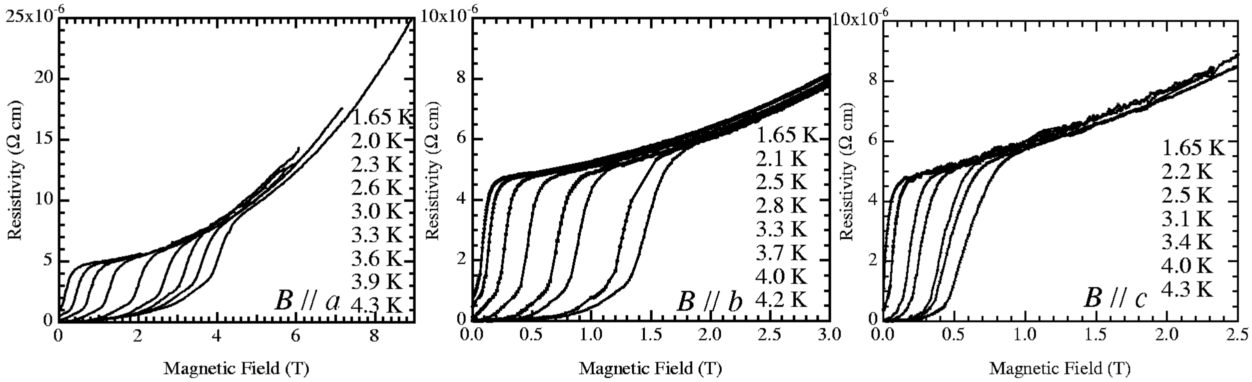

FIG. 4. Magnetic field dependence of resistivities [(a) $B \| a$, (b) $B \| b$, and (c) $B \| c$] under various temperatures.

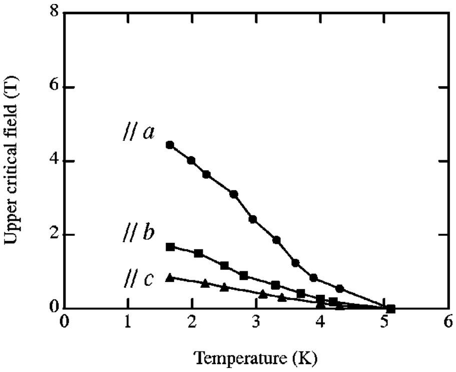

FIG. 5. Temperature dependence of the upper critical fields.

as the applied magnetic field increases, and the resistive broadening does not appear. This suggests that the present compound is a three-dimensional superconductor. The thermoelectric power (Seebeck coefficient) linearly decreases as the temperature decreases (inset of Fig. 3). From this slope, the transfer integral along the donor stacking direction is evaluated to be 425 meV, if we assume the one-dimensional tight-binding approximation.[13] The estimated band width ($W=4t_{\parallel}=1.7$ eV) is anomalously large among organic conductors. This also means that the one-dimensional approximation is not good as expected from the calculated band structure (Fig. 2). The thermopower has a hump below 50 K, probably originating from phonon drag. Phonon drag in clean metals is expressed by[14]

$$Q=Q_{\mathrm{cell}}+Q_{\mathrm{elec}}=\frac{k_{\mathrm{B}}}{e}\frac{4\pi^4}{5}\left(\frac{T}{\Theta}\right)^3+\alpha T, \tag{1}$$

where Θ is the Debye temperature and α is the coefficient depending on the band structure. If we naively use the above equation, we can estimate the Debye temperature of (MDT-TSF)$(\mathrm{AuI}_2)_{0.44}$ to be about 300 K. This looks reasonable, because the Debye temperature of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ has been estimated as 213 K from the specific heat.[15]

Figure 4 shows the magnetic field dependence of the electrical resistivities under various temperatures. The magnetoresistance exhibits power law ($\rho\propto B^n, 1.5\leqslant n\leqslant 2.6$) in the normal conducting phase. Figure 5 shows the temperature dependence of the upper critical fields of (MDT-TSF)$(\mathrm{AuI}_2)_{0.44}$, determined from 95% recovery of the expected magnetoresistance. The value of $B_{c2\parallel a}(T)$ is almost the same as $B_{c2\parallel}(T)$ of κ-(MDT-TTF)$_2$AuI$_2$, and moreover the $B_{c2\parallel c}(T)$ exhibits also the same value as $B_{c2\perp}(T)$ of the MDT-TTF salts.[16] The upper critical fields are anisotropic in the conducting plane $[B_{c2\parallel a}(T)$ and $B_{c2\parallel b}(T)]$ in contrast with nearly isotropic β-(BEDT-TTF)$_2$I$_3$.[17] We can estimate the Ginzburg-Landau (GL) coherence lengths $\xi_{\parallel a}$, $\xi_{\parallel b}$, and $\xi_{\parallel c}$ from the following relation[18]

$$\xi_{\parallel i}(T)=\sqrt{\frac{\Phi_0}{2\pi}\frac{B_{c2\parallel i}(T)}{B_{c2\parallel j}(T)B_{c2\parallel k}(T)}}, \tag{2}$$

where Φ_0 is the flux quantum. The coherence lengths are estimated as $\xi_{\parallel a}\approx 319$ Å, $\xi_{\parallel b}\approx 121$ Å, and $\xi_{\parallel c}\approx 61$ Å at $T=1.65$ K. The zero temperature coherence lengths calculated by the relation of $\xi_{\parallel i}(T)=\xi_{\parallel i}(0)\sqrt{T_c/(T_c-T)}$ are $\xi_{\parallel a}(0)\approx 262$ Å, $\xi_{\parallel b}(0)\approx 100$ Å, and $\xi_{\parallel c}(0)\approx 50$ Å. The transverse coherence length ($\xi_{\parallel c}$) is much longer than the thickness of the conducting sheet $c/2=12.712$ Å, indicating that the superconductivity is not two-dimensional but considerably three-dimensional. This reminds us that the coherence length perpendicular to the conducting plane in κ-(MDT-TTF)$_2$AuI$_2$, in which the Hebel-Slichter coherence peak has been found in ^{1}H NMR,[19] is also longer than the inter layer distance.[16] Anisotropic three-dimensional superconductivity is characteristic of the MDT-T*CF* ($C=$ S, Se) donors. This contrasts with the usual organic superconductors represented by BEDT-TTF salts, which show strong two-dimensionality.

Superconductivity is suppressed by the Pauli pair breaking mechanism; the external field destroys the spin-singlet state of the Cooper pair, imposing the so-called Clogston-Chandrasekhar paramagnetic limit. For (MDT-TSF)$(\mathrm{AuI}_2)_{0.44}$ this is given by $B_{\mathrm{P}}=1.85T_c\approx 9.5$ T from the onset $T_c=5.1$ K.[18] All upper critical fields lie below this paramagnetic limit in our measured temperature range (Fig. 5). In κ-(MDT-TTF)$_2$AuI$_2$, the upper critical field in the conducting sheet is also below the paramagnetic limit.[16]

Therefore, the anisotropy of the upper critical fields is due to an orbital pair breaking mechanism coupled with band structure anisotropy. Since the coherence length at zero temperature in a given direction is proportional to the corresponding component of the Fermi velocity, v_{F}, the coherence length anisotropy in the ab plane is related to the anisotropy of the band dispersion, *W*, as

$$\xi_{\parallel a}(0)/\xi_{\parallel b}(0)=v_{\mathrm{F}\parallel a}/v_{\mathrm{F}\parallel b}=\frac{aW_{\parallel a}}{(b/2)W_{\parallel b}}. \tag{3}$$

From the obtained coherence lengths and the lattice constants ($a=4.016$ Å and $b=12.513$ Å), the anisotropy of the band dispersion is estimated as $W_{\parallel a}/W_{\parallel b}=4.1$. This is in good agreement with the result of our band calculation ($W_{\parallel a}/W_{\parallel b}=3.8$).

In summary, the x-ray oscillation photograph provides unambiguous evidence of nonstoichiometric composition, (MDT-TSF)$(\mathrm{AuI}_2)_{0.44}$ and the incommensurate anion structure. The upper critical fields are within the paramagnetic limit in all directions. The coherence lengths indicate that (MDT-TSF)$(\mathrm{AuI}_2)_{0.44}$ is an anisotropic three-dimensional superconductor. These findings prove the unique position of the present compound among the organic superconductors.

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