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| Authors | Tadashi Kawamoto,Takehiko Mori,Kengo Enomoto,Takako Konoike,Taichi Terashima,Shinya Uji,Hiroshi Kitagawa,Kazuo Takimiya,Tetsuo Otsubo |
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Disordered polyhalide anion effect on the Fermi surface of the incommensurate organic superconductor (MDT-TSF) $\text{I}_{0.77}\text{Br}_{0.52}$

Tadashi Kawamoto* and Takehiko Mori

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Kengo Enomoto, Takako Konoike,[†] Taichi Terashima, and Shinya Uji

National Institute for Materials Science, Tsukuba, Ibaraki 305-0003, Japan

Hiroshi Kitagawa

Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan

Kazuo Takimiya and Tetsuo Otsubo

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

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The effect of disorder in polyhalide anions is investigated in terms of the degree of charge transfer and the Fermi surface in the incommensurate organic superconductor (MDT-TSF) $\text{I}_{0.77}\text{Br}_{0.52}$, where MDT-TSF is methylenedithio-tetraselenafulvalene. The Raman spectra suggest that the infinite polyhalide chains include the asymmetric trihalide anion I_2Br^- and that the degree of charge transfer from the donor molecule to the anion is 0.429, estimated from the lattice constants. The Shubnikov–de Haas (SdH) oscillation is in good agreement with this charge transfer degree. The beating behavior of the SdH oscillation gives a large interlayer transfer integral, which is consistent with a corrugated conducting sheet structure. The randomness of the disordered anions reduces the periodicity of the incommensurate anion potential; this destroys the Fermi surface reconstruction by the incommensurate anion potential. The factor dominating the superconducting transition temperature is not the randomness of the polyhalide anions but the effective cyclotron mass enhancement, i.e., the many-body effect.

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I. INTRODUCTION

In many organic superconductors, the ratio of donor molecules to anions is represented by an integer; it is typically 2:1.^{1,2} The energy band filling of these compounds is 3/4, and this corresponds to effective half filling in the presence of a dimerization gap. The donor-anion ratio takes a definite number for a given combination of donors and anions, and the ratio is not variable as in many inorganic compounds such as high- T_c cuprate superconductors, in which the ground state is controlled by carrier number. The ground states of organic compounds are regulated by the bandwidth by means of, for example, pressure.

In contrast to stoichiometric compounds with 1/2 or 3/4 band filling, nonstoichiometric compounds have provided us opportunities to study the effects of unusual band fillings on electronic states.^{3,4} (MDT-TSF)(AuI_2)_{0.436} (MDT-TSF is methylenedithio-tetraselenafulvalene) is an organic superconductor categorized in this group [Fig. 1(a)].⁵ In this superconductor, we have found an incommensurate anion structure and a unique Fermi surface reconstruction caused by the incommensurate anion potential.^{6–8} Consequently, the band filling deviates from conventional 3/4 filling; it is 0.782. (MDT-TSF)(I_3)_{0.422} also shows superconductivity at ambient pressure, and the degree of charge transfer differs from that of the AuI_2 salt.^{4,9,10} To the best of our knowledge, the MDT-TSF series salts are the only organic incommensurate crystals showing superconductivity based on an asymmetric donor molecule, although ambient pressure superconductivity

has been reported in another nonstoichiometric compound, $\kappa\text{-(ET)}_4\text{Hg}_{2.89}\text{Br}_8$ [ET is bis(ethylenedithio)tetrathiafulvalene], based on a symmetric donor molecule.¹¹

MDT-TSF superconductors have a uniform donor stacking along the a axis and the donors form a corrugated conducting sheet on the ab plane [Figs. 1(b) and 1(c)]. The crystallographic c axis is perpendicular to the ab plane, because the crystal system is orthorhombic. Linear anion chains exist along the a axis. We have carried out detailed investigations of a mixed halide salt of MDT-TSF with $T_c = 4.0$ K at ambient pressure. X-ray oscillation photographs and the results of elemental analysis have given us the composition of the salts as (MDT-TSF) $\text{I}_{0.77}\text{Br}_{0.52}$ despite the use of tetrabutylammonium- IBr_2 in the crystal growth.⁹ We cannot determine the degree of charge transfer, because the polyhalide exists in many forms (e.g., monoanion, trihalide anion, and pentahalide anion) in solids.¹² A mixed polyhalide anion may form a random potential for conducting molecules. Mixed anions markedly reduce the superconducting transition temperature, as observed in $\beta\text{-(ET)}_2X$ with $X = (\text{I}_3)_{1-x}(\text{IBr}_2)_x$,¹³ where the effect of randomness dominates the appearance of superconductivity. By contrast, the incommensurate organic conductor with mixed polyhalide anions, (MDT-TS) $\text{I}_{0.85}\text{Br}_{0.41}$, where MDT-TS is 5*H*-2-(1,3-diselenole-2-ylidene)-1,3,4,6-tetrathiapentalene, has a lower metal-insulator transition temperature than (MDT-TS)(AuI_2)_{0.441} and a higher superconducting transition temperature than the AuI_2 salt under high pressure.^{14,15} This suggests that the effect of the randomness of

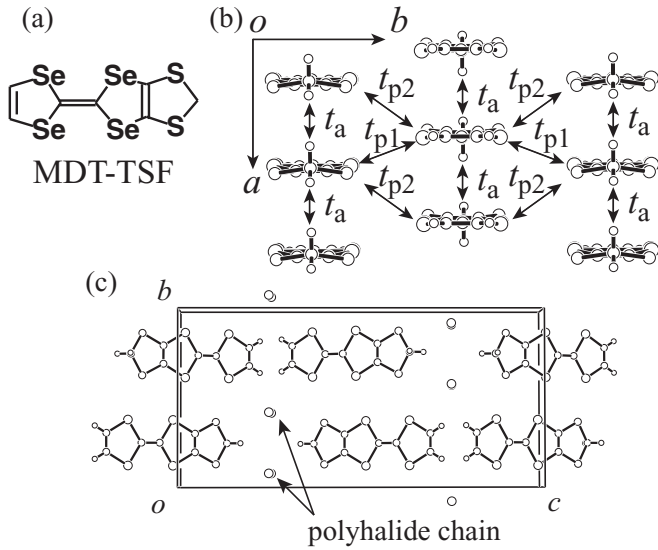


FIG. 1. (a) MDT-TSF molecule. Crystal structure projected along the molecular long axis (b) and projection onto the bc plane (c) of (MDT-TSF) $I_{0.77}Br_{0.52}$.

anions differs between the commensurate and incommensurate crystal structures. Therefore, (MDT-TSF) $I_{0.77}Br_{0.52}$ is an important material for investigating the effect of a disordered anion structure on the electronic state.

In the present paper, we report disordered polyhalide anions based on trihalide anion units determined by the Raman spectra and Fermi surface topology by the Shubnikov-de Haas (SdH) oscillations. The charge transfer degree is also determined from the Raman spectra and SdH oscillations. The randomness of the disordered anions does not dominate the superconducting transition for incommensurate organic superconductors based on MDT-TSF.

II. EXPERIMENT

Single crystals were prepared by electrocrystallization.⁹ Raman spectra were measured by He-Ne laser excitation ($\lambda = 632.8$ nm) using a single monochromator with a supernotch filter and a microscope. Scattered radiation was detected using a Princeton charge-coupled device camera system operated at 153 K. Laser power beamed at the crystal was held at <20 μ W to avoid laser damage. Wave-number calibration was performed by referring to the emission spectrum of a Ne lamp. The band structure was calculated by the extended Hückel method and tight-binding approximation.¹⁶ The transfer integrals t_i are estimated from the intermolecular overlap integrals S_i as $t_i = E \times S_i$, in which the energy level of the highest occupied molecular orbital E is taken to be -10 eV, and the interaction modes (a , $p1$, and $p2$) are defined in Fig. 1(b). The same atomic-orbital parameters as those of (MDT-TSF)(AuI₂)_{0.436} were used.^{4,8} For the SdH measurements, the samples were mounted on a one-axis rotator in a dilution refrigerator in a 20 T superconducting magnet at the National Institute for Materials Science, and the measurements were carried out by the four-probe method along the a axis with ac current (0.6 mA) down to 60 mK. Lock-in amplifiers and preamplifiers were used for high-sensitivity detection.

III. RESULTS AND DISCUSSION

Figure 2 shows the a -parallel Raman spectra of (MDT-TSF) $I_{0.77}Br_{0.52}$ at various temperatures. The Raman lines mainly consist of the 108 cm^{-1} peak and its overtones. Although a small peak at 129 cm^{-1} is also clearly observed at 4 K, the n th Raman peak of this line is observed at $\nu_n = (108n + 21)$ cm^{-1} . The absence of a peak at approximately 168 cm^{-1} eliminates both IBr_2^- and Br_3^- .^{17,18} Free Br_2 (~ 306 cm^{-1}) and free I_2 (~ 210 cm^{-1}) are not observed in the Raman spectra.¹⁸ The pentahalide anions (I_5^- and Br_5^-) are also eliminated because of the absence of the ~ 160 cm^{-1} peak.^{12,18} The present Raman spectrum at 4 K is similar to that of I_2Br^- salts, because the Raman lines are observed at 113, 132, and 217 cm^{-1} for tetrabutylammonium- I_2Br .¹⁷ However, the small peak at 129 cm^{-1} is also observed in (MDT-ST)(I₃)_{0.417} at low temperatures [MDT-ST is 5*H*-2-(1,3-dithiol-2-ylidene)-1,3-diselena-4,6-dithiapentalene].¹⁹ The strong Raman peak at 108 cm^{-1} and its overtones are usually observed in the I_3^- salts.^{10,12,17-19} Therefore, we cannot eliminate the possibility of production of I_3^- anions. The elemental analysis demonstrates that the ratio of iodine to bromine is about 3:2; we cannot find an optimal structure from the Raman spectra. The complete anion structure is unknown, but the Raman spectra indicate that the polyhalide chain is composed of trihalide anion units. This is important for determining the degree of charge transfer.

The positions of some vibrational modes of organic conductors are sensitive to the charge of the organic donor or acceptor molecules. Infrared spectroscopy is not a good tool for investigating these vibrational modes owing to the strong

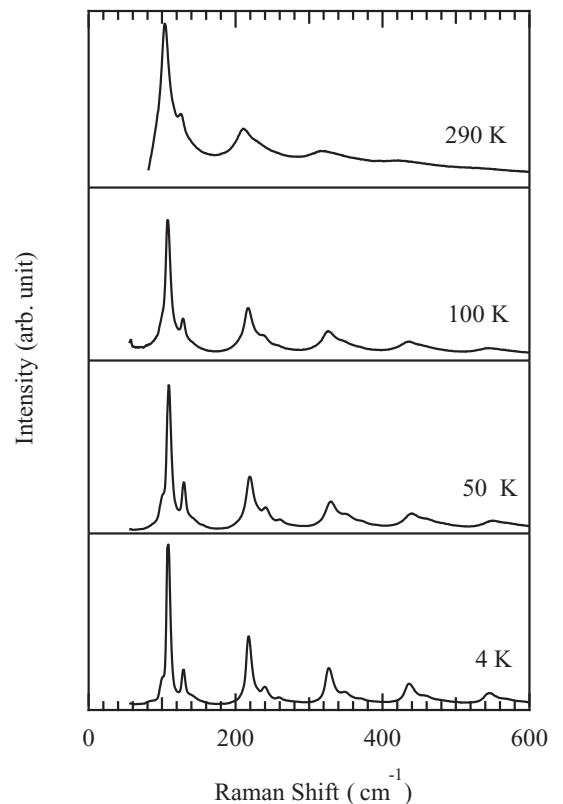


FIG. 2. Raman spectra of (MDT-TSF) $I_{0.77}Br_{0.52}$ measured for polarization $\parallel a$ axis at various temperatures.

dispersion of the charge transfer (CT) band in the infrared region. On the other hand, the CT band does not appear in the Raman spectrum, and the electron-phonon coupling does not have a marked effect on the position of the a_g mode. Although the central C=C bond stretching between the two five-member rings is very charge sensitive in a TTF molecule (TTF is tetrathiafulvalene), this mode is not Raman active because of the asymmetric shape of the MDT-TSF molecule. Therefore, we have investigated the C=C stretching mode along the molecular short axis, i.e., the ring C=C stretching mode.

Figure 3 shows the Raman spectra of neutral MDT-TSF, (MDT-TSF)(I₃)_{0.422}, (MDT-TSF)(AuI₂)_{0.436}, and (MDT-TSF)I_{0.77}Br_{0.52}. There are two Raman lines. Although the Raman line at 1499 cm⁻¹, ν_1 , in neutral MDT-TSF linearly decreases as the charge transfer degree ρ increases, the Raman line at 1520 cm⁻¹, ν_2 , increases with increasing ρ .¹⁰ The neutral MDT-TTF molecule, where MDT-TTF is methylenedithio-tetrathiafulvalene, exhibits two strong Raman lines at 1510 and 1551 cm⁻¹; the first line is assigned to the ring C=C bond.²⁰ This Raman line shifts to 1470 cm⁻¹ for κ -(MDT-TTF)₂AuI₂. This indicates that the Raman shift decreases by about 40 cm⁻¹ for a 0.5 charge transfer degree. In the BO [BO is bis(ethylenedioxy)tetrathiafulvalene] and ET salts, the Raman shift from the ring C=C bond decreases with increasing ρ .^{21,22} For the MDT-TSF compounds, the first Raman line ν_1 comes from the ring C=C bond and is related to the degree of charge transfer as $\nu_1 = 1499 - 67.63\rho$.^{4,10} The charge transfer degree of the present compound is estimated as $\rho = 0.42(2)$,

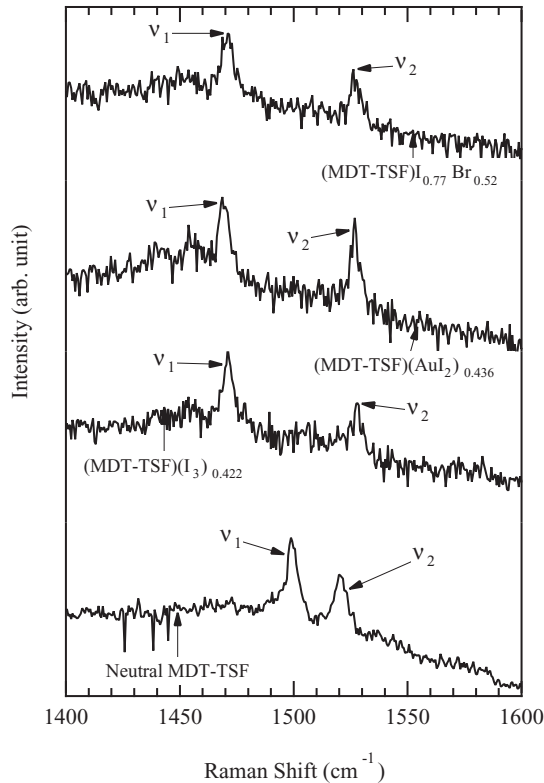


FIG. 3. Raman spectra of MDT-TSF salts and neutral MDT-TSF at room temperature. The spectra without the I_{0.77}Br_{0.52} salt are cited from our previous work.¹⁰

which is in agreement with that estimated from the x-ray oscillation photographs, assuming that the infinite anion chain is composed of trihalide anion units. The anion lattice should be expressed as $a' = 3 \times 3.125(8) = 9.375(24)$ Å; thus, $\rho = a/a' = 0.429(1)$ is the charge transfer degree.⁹ We will use this value for the present compound because of the small error.

The obtained charge transfer degree $\rho = 0.429(1)$ is between those of (MDT-TSF)(I₃)_{0.422} and (MDT-TSF)(AuI₂)_{0.436}. This is explained by the crystal structure and anion length. The length of the a axis of the donor lattice of the I_{0.77}Br_{0.52} salt, 4.026(8) Å, is almost the same as those of the I₃ salt, 4.013(4) Å, and the AuI₂ salt, 4.016(6) Å. On the other hand, the length of the trihalide anion [$a' = 9.38(2)$ Å] is smaller than that of I₃⁻ [$a' = 9.51(1)$ Å],⁹ but is larger than that of AuI₂⁻ [$a' = 9.221(6)$ Å];⁶ this is in agreement with the general relationship of the anion lengths, AuI₂⁻ < I₂Br⁻ < I₃⁻.² The lattice constant suggests that the present compound includes I₂Br⁻, expected from the Raman spectra.

As the actual degree of charge transfer is known, it is possible to calculate the energy band structure without using the incommensurate anion potential. The calculated transfer integrals are $t_a = 90.3$, $t_{p1} = -11.0$, and $t_{p2} = -34.6$ meV. Figure 4 shows the energy band structure and Fermi surface calculated by the tight-binding approximation. The Fermi surface consists of overlapping cylinders. The cross-sectional area of the γ orbit, $S_{F,\gamma}$, is 6.8% and that of the δ orbit, $S_{F,\delta}$, is 42.9% of the first Brillouin zone, S_{BZ} . It is important that the area of the δ orbit, $S_{F,\delta}/S_{BZ}$, is equal to the degree of charge transfer.

To estimate the δ -orbit area experimentally, SdH oscillation measurements were carried out. Figure 5(a) shows the magnetic field dependence of the electrical resistance at 60 mK ($B \parallel c$). Above 14 T, the magnetoresistance shows an oscillating behavior. The oscillatory part (SdH signal) of the resistance represented by $[R(B) - R_0(B)]/R_0(B)$, rescaled by the nonoscillatory background $R_0(B)$, is shown in the inset of Fig. 5(a). Nodes are clearly found in the SdH signal; this beating behavior of the SdH oscillation originates from the warping cylindrical Fermi surface. The fast Fourier transformation (FFT) spectrum shows three peaks: γ , δ_1 , and δ_2 [Fig. 5(b)]. We consider that the peak at approximately 250 T is a ghost peak, because the position of this peak strongly depends on temperature. The frequencies obtained are summarized in Table I along with the ratios of the cross-sectional area to the first Brillouin zone based on the donor lattice. The

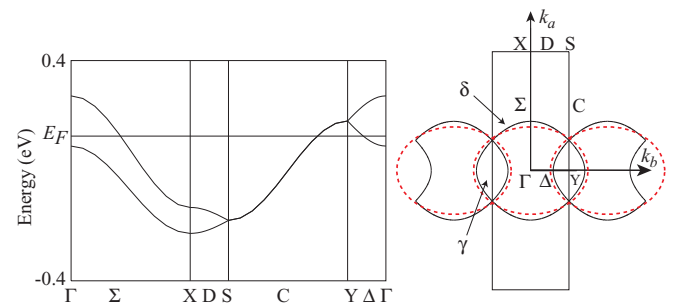


FIG. 4. (Color online) Energy band structure and Fermi surface. The dotted lines are the results obtained on the basis of the SdH oscillations.

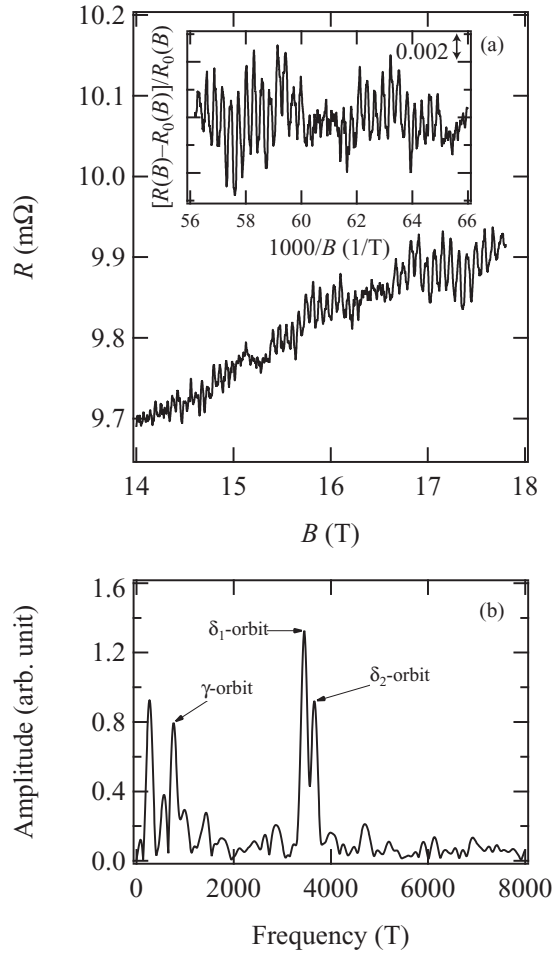


FIG. 5. (a) Magnetoresistance of (MDT-TSF) $I_{0.77}Br_{0.52}$ at 60 mK ($B \parallel c$). The inset shows the SdH signal. (b) FFT spectrum of the SdH oscillation.

uncertainty of the SdH frequencies in Table I is given by the full width at half maximum of the peak in the FFT spectrum. The cross-sectional area of the observed γ orbit is slightly larger than that obtained in the band calculation. If we assume an elliptical Fermi surface, we can draw the Fermi surface with $k_{F,b}/k_{F,a} = 1.3$ from the SdH oscillation (Fig. 4). Although the calculated energy bands degenerate on the C line owing to the donor lattice symmetry ($Pnma$),²³ the observation of the γ orbit indicates that the symmetry is broken at low temperatures. The reason for this is not yet clear, but a possible scenario is a slight structural change of the donor arrangement, as observed in κ -(ET) $_2I_3$.^{24,25} This broken symmetry makes the δ orbit a magnetic breakdown orbit. The observation of the magnetic breakdown orbit in the low-field region indicates a small energy gap at the zone boundary. It is difficult to uniquely determine the energy gap (the magnetic breakdown field B_0) in our present data, because the oscillation amplitude of the magnetic breakdown δ_1 and δ_2 orbits is larger than that of the γ orbit even in the low-field region [Fig. 5(a)]. However, this means that the breakdown field is smaller than that of κ -(ET) $_2Cu(NCS)_2$, because only a small pocket is observed in the low-field region and the breakdown orbit is observed above ~ 20 T in the SdH oscillation for κ -(ET) $_2Cu(NCS)_2$.²⁶ We should mention that the values of B_0 estimated by some groups

TABLE I. Shubnikov-de Haas frequencies, cross-sectional Fermi surface areas, effective cyclotron masses, and Dingle temperatures.

| Orbit | F (T) | S/S_{BZ} (%) | m^*/m_0 | T_D (K) |
|------------|-----------------------|----------------|-----------|-----------|
| γ | $0.76(8) \times 10^3$ | 9.3(10) | 3(1) | 4(1) |
| δ_1 | $3.46(8) \times 10^3$ | 42.2(10) | 3.0(3) | 1.5(2) |
| δ_2 | $3.66(8) \times 10^3$ | 44.6(10) | 3.2(2) | 1.8(1) |

are scattered between 15 and 41 T for κ -(ET) $_2Cu(NCS)_2$.^{26–30} This indicates the difficulty of the estimation of B_0 .

As shown in Fig. 6(a), the SdH frequency roughly exhibits a $1/\cos\theta$ dependence as expected for quasi-two-dimensional electronic systems, where θ is the angle between the magnetic field and the c axis on the bc plane. The FFT spectrum at $\theta = 15^\circ$ does not show clear peaks because of the Zeeman-spin-splitting zero state.^{31,32} Moreover, the FFT spectrum at $\theta = 20^\circ$ gives only one δ orbit; this indicates that the Fermi surface is a warped cylinder and that the extremal minimum (maximum) cross-sectional orbit is the δ_1 (δ_2) orbit.

SdH signals are analyzed conventionally using the Lifshitz-Kosevich (LK) formula for the FFT amplitude.^{31,32} The temperature dependences of the oscillation amplitudes divided by temperature, so-called mass plots, are presented in Fig. 6(b).

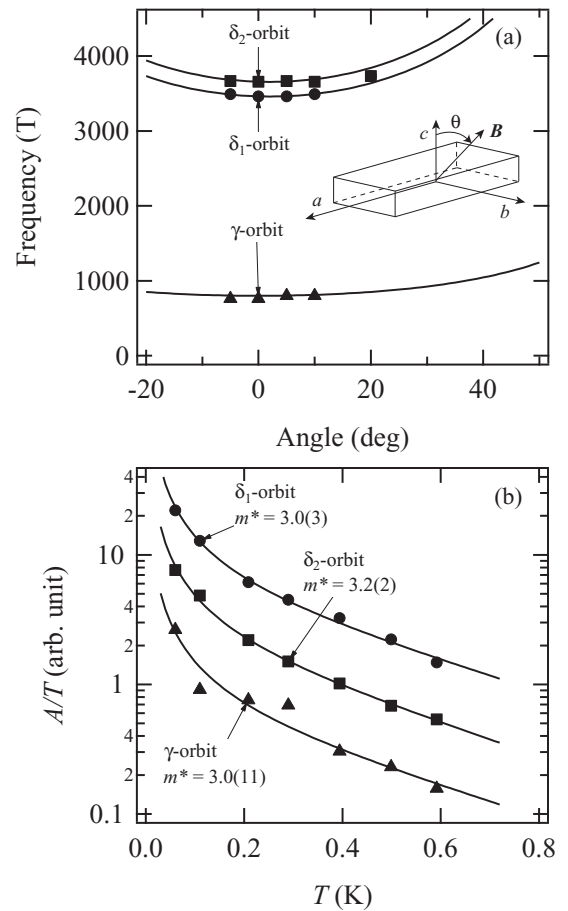


FIG. 6. (a) Angular dependence of SdH frequency. Solid lines show the $1/\cos\theta$ dependences. (b) Temperature dependences of the SdH oscillation amplitudes divided by temperature (mass plots). Solid lines are the fits to the data.

The solid lines are the results calculated using the LK formula. The determined effective cyclotron mass ratios m^*/m_0 (m_0 is the free-electron mass) are listed in Table I. The Dingle temperatures T_D , simply determined from the field dependence of the oscillation, are also shown in Table I. The Dingle temperatures in Table I for γ and δ approximately give the lower and upper limits, respectively, because the γ and δ orbits are expected to include some Bragg reflection and magnetic breakdown points.

In the case of the warped cylindrical Fermi surface, the energy dispersion can be expressed by

$$E(\mathbf{k}) = E(k_a, k_b) - 2t_{\perp} \cos(k_c d), \quad (1)$$

where t_{\perp} is the interlayer transfer integral and d is the interlayer spacing along the c direction. The maximum frequency difference of the SdH oscillation with a beat structure is related to the interlayer transfer integral by

$$\Delta F = \frac{4\overline{m^*}t_{\perp}}{e\hbar}, \quad (2)$$

where $\overline{m^*}$ is the average effective cyclotron mass, e is the elementary electronic charge, and \hbar is the Plank constant.³² We obtain $t_{\perp} = 2(1)$ meV from the set of δ_1 and δ_2 orbits; this is the same as that of (MDT-TSF)(AuI₂)_{0.436}.^{7,8} However, this is much larger than those of κ -(ET)₂X, where the X = Cu(NCS)₂ salt shows 0.04 meV and the X = I₃ salt shows 0.06 meV.^{33,34} The large interlayer interaction is characteristic of MDT-TSF superconductors, because the conducting layer is not flat but corrugated, as shown in Fig. 1(c).

We discuss the polyhalide anion effect on the electronic state. The reconstruction of the Fermi surface by the third harmonic incommensurate anion potential $3\mathbf{q} = 3\rho\mathbf{a}^*$ has been observed in (MDT-TSF)(AuI₂)_{0.436},⁷ where ρ is equal to the degree of charge transfer: 0.436. This characteristic reconstruction is related to the intensity of the anion sublattice reflections observed in the x-ray oscillation photographs. The x-ray $3\mathbf{q}$ intensities are even stronger than the intensities of the other $n\mathbf{q}$ spots, where n is an integer. The same Fermi surface reconstruction has also been observed in the incommensurate organic superconductor (MDT-ST)(I₃)_{0.417}.³⁵ The incommensurate potential is significantly smaller than that caused by the donor molecules, and the conduction electrons perturbatively experience the incommensurate potential. Judging from the x-ray experiments, the dominant sublattice potential is given by the $3\mathbf{q} = 3 \times 0.429\mathbf{a}^*$ vector in the present compound.⁹ The vector $3\mathbf{q}$ is associated with the average distance between halogen atoms [3.125(8) Å at room temperature] in real space. Our previous results require that the Fermi surface is reconstructed using $3\mathbf{q}$, and a new closed orbit, the β orbit in the AuI₂ salt, with $F \sim 420$ T should be observed.

However, our experimental result does not show such an extra orbit with reasonable magnitude. In (MDT-TSF)I_{0.77}Br_{0.52}, no Bragg reflection due to the trihalide anion periodicity, $a' = 9.38(2)$ Å, has been observed. Therefore, no periodic potential due to the anions is formed on the electronic state; the Fermi surface is not reconstructed. The anions form some random potential, but the observation of the SdH oscillations shows that this random potential is small.

Although the present compound has the lowest superconducting transition temperature ($T_c = 4.0$ K) among the MDT-TSF superconductors, the difference between the highest and lowest T_c 's is only ~ 1.5 K.⁹ It seems that the randomness of the polyhalide anion does not predominantly affect T_c in MDT-TSF superconductors. This differs from β -(ET)₂(I₃)_{1-x}(IBr₂)_x, where superconductivity has been observed in a limited range: $x \leq 0.25$ and $x \geq 0.75$.¹³ On the other hand, the effective cyclotron masses of the present compound are smaller than those of other MDT-TSF superconductors.^{7,10} The MDT-TSF superconductors show a trend: the higher the T_c of the material, the larger the effective cyclotron mass. In κ -(ET)₂Cu(NCS)₂ and α -(ET)₂NH₄Hg(SCN)₄, the SdH oscillations under high pressure show that, the higher the T_c , the larger the effective cyclotron mass.^{30,36} These results indicate that mass enhancement, i.e., the many-body effect, is a major factor that increases T_c for many organic superconductors.³⁷

IV. CONCLUSION

The Raman spectra and SdH oscillations are in agreement with the degree of charge transfer of (MDT-TSF)I_{0.77}Br_{0.52}, 0.429, obtained from the lattice constants. The observation of the SdH oscillation indicates that the present compound has a clean electronic system despite its disordered anion structures. The interlayer transfer integral is much larger than that of conventional organic superconductors. Among MDT-TSF superconductors, the superconducting transition temperature of the present compound is the lowest and the effective cyclotron mass is also the smallest. These results show that the many-body interaction is important for increasing the superconducting transition temperature. The randomness of the polyhalide anions changes the features of the Fermi surface reconstruction, but does not alter the superconductivity.

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*kawamoto@o.cc.titech.ac.jp

[†]Present address: Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan.

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