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# Structural and transport properties of the incommensurate organic superconductor $(\mathrm{MDT\text{-}ST})(\mathrm{I}_3)_{0.417}$

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The incommensurate anion sublattice and transport properties of the organic superconductor $(\mathrm{MDT\text{-}ST})\mathrm{I}_{1+\delta}$ [MDT-ST: 5*H*-2-(1,3-dithiol-2-ylidene)-1,3-diselena-4,6-dithiapentalene] are investigated. The Raman spectra as well as the incommensurate spots observed in the x-ray-oscillation photograph provide clear evidence that the polyiodide chain is composed of $\mathrm{I}_3^-$ units. From these, the composition is determined to be $(\mathrm{MDT\text{-}ST})(\mathrm{I}_3)_{0.417}$, and the degree of charge transfer is 0.417. The thermoelectric power shows large negative phonon drag at low temperatures in spite of the clean metallic resistive behavior. That the fundamental Raman line of the $\mathrm{I}_3^-$ chains is split into two lines below 150 K without any extra satellite reflections in the x-ray photographs suggests the possibility of a small structural change in the anion lattice.

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Most organic superconductors have stoichiometric compositions; the ratios of donor molecules to anions are represented by an integer (typically 2:1).[1] The band fillings of such compounds are usually three-quarters filled, and this corresponds to an effective half-filled band in the presence of the dimerization gap. Therefore, it is generally considered that a commensurate lattice with an effective half-filled band is a requirement of superconductivity.

$(\mathrm{MDT\text{-}TSF})(\mathrm{AuI}_2)_{0.436}$ is an organic superconductor with no effective half-filled band, where MDT-TSF is methylenedithio-tetraselenafulvalene.[2] We have determined the incommensurate anion structure and the unique Fermi-surface reconstruction by the incommensurate anion potential in this superconductor.[3–5] Consequently, the band filling deviates from the usual three-quarters or half filled and is 0.782. When we replace half of the selenium atoms in MDT-TSF with sulfur, the resulting donor, called MDT-ST, forms similar incommensurate organic superconductors with linear anions (Fig. 1),[6] which exhibit uniform donor stacking with the head-to-head mode along the *a* axis, and no disorder. The donors form a conducting sheet on the *ab* plane. However, the degree of charge transfer is unknown. We have carried out detailed investigations of $(\mathrm{MDT\text{-}ST})\mathrm{I}_{1+\delta}$, whose difference from the previous MDT-TSF salt lies in that the anion is iodide instead of $\mathrm{AuI}_2^-$. It is well known that iodide exists in the form of $\mathrm{I}^-$, $\mathrm{I}_2$, $\mathrm{I}_3^-$, and $\mathrm{I}_5^-$ in solids.[7] Thus, we have to clarify the components of the polyiodide chains in order to determine the degree of charge transfer. We report herein the basic physical properties of this superconductor. The composition and the degree of charge transfer are precisely determined from the results of Raman and x-ray investigations. The transport properties are also presented.

Single crystals were prepared by electrocrystallization.[6] Raman spectra were measured by He-Ne laser (632.8 nm) excitation using a single monochromator with a supernoch-filter and a microscope. Laser power beamed at the crystal was held at $<20$ $\mu$W to avoid laser damage. Wave-number calibration was effected by referring to the emission spectrum of a Ne lamp. The x-ray-oscillation photographs were taken by an imaging plate with graphite monochromated Mo-$K\alpha$ radiation. The band structure was calculated on the basis of the extended Hückel method and the tight-binding approximation.[8] The same atomic-orbital parameters as those of MDT-TSF were used.[5] Electrical resistivity was measured by the four-probe method with ac current (usually 100 $\mu$A). Thermoelectric power was measured with the two-terminal method.

Figure 2 shows the Raman spectra of $(\mathrm{MDT\text{-}ST})\mathrm{I}_{1+\delta}$ at room temperature. The spectrum along the *a*-axis demonstrates that the polyiodide chain is composed of $\mathrm{I}_3^-$ units because the Raman lines consist of the 104 $\mathrm{cm}^{-1}$ peak and its overtones and because the spectrum shows neither a peak at 160 $\mathrm{cm}^{-1}$ originating in the linear $\mathrm{I}_5^-$, nor a shoulder around 145 $\mathrm{cm}^{-1}$ because of the asymmetric stretching mode of discrete $\mathrm{I}_3^-$.[7] The observed Raman shift at around 100 $\mathrm{cm}^{-1}$ is known as the symmetric stretching mode of $\mathrm{I}_3^-$ in an infinite linear chain. On the other hand, the *b*-parallel spectrum shows no Raman line originating in the iodide anion. These observations indicate the existence of the iodide chain running along the *a* axis.

Figure 3 shows an x-ray-oscillation photograph in which the vertical direction is parallel to the donor stacking axis ($a^*$ axis). This photograph clearly displays incommensurate layer lines. The present compound is classified under the *column composite structure* type defined in Ref. 9. We distinguish the donor lattice and the anion lattice by indices *h*

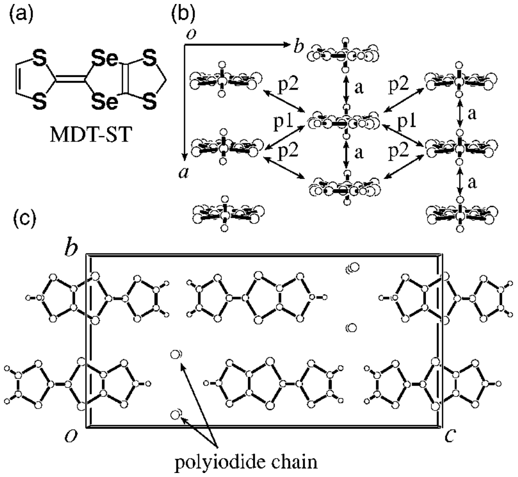

FIG. 1. (a) MDT-ST molecule. (b) and (c) Crystal structures of $(\text{MDT-ST})(I_3)_{0.417}$.

and $h'$, respectively. The anion layer line is strongest at $h'=3$, because this corresponds to the average I-I spacing (3.163 Å). Although other layer lines are clearly observed, the $h'=1$ line is quite obscure. This indicates longitudinal modulation where the I atoms are displaced along the chain ($\|a$) with modulating I-I distances.[10] In the longitudinal modulation, the intensity of the incommensurate scattering reaches a maximum at a moderately large angle along $a^*$. We can explain all the incommensurate spots by assuming the periodicity of the $I_3^-$ sublattice ($h'=1$). The donor lattice constants are $a=3.961(1)$, $b=12.361(2)$, $c=25.392(5)$ Å, and $\alpha=\beta=\gamma=90°$. By contrast, the least-squares fit to the anion lattice gives $a'=9.489(8)$, $b'=12.175(5)$, $c'=25.33(1)$ Å, and $\alpha'=\beta'=\gamma'=90°$. We consider that the $b$ and $c$ axes are common to both the donor and the anion lattices. The ratio $a/a'=0.4174(4)$ gives the chemical formula, $(\text{MDT-ST})(I_3)_{0.417}$. The obtained degree of charge transfer, $\rho=0.417$, is slightly smaller than that of $(\text{MDT-TSF})(\text{AuI}_2)_{0.436}$. The $a$ axis of the donor lattice of the present compound is shorter than that of the MDT-TSF salt, in agreement with the replacement of two selenium atoms with sulfur atoms. By contrast, the length of $I_3^-$ ($a'$) is larger than that of $\text{AuI}_2^-$. Consequently, the anion content determined by $a/a'=0.417$ is smaller than that of $(\text{MDT-TSF})(\text{AuI}_2)_{0.436}$.

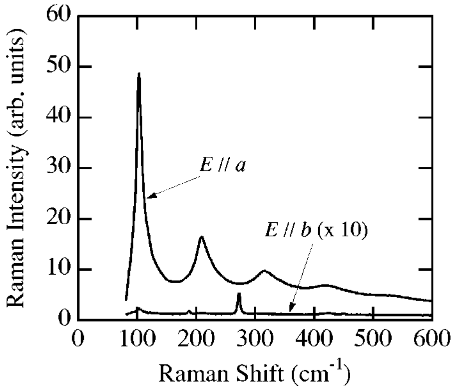

FIG. 2. The Raman spectra of $(\text{MDT-ST})(I_3)_{0.417}$ measured for polarization $\|a$ and $\|b$ axes at room temperature.

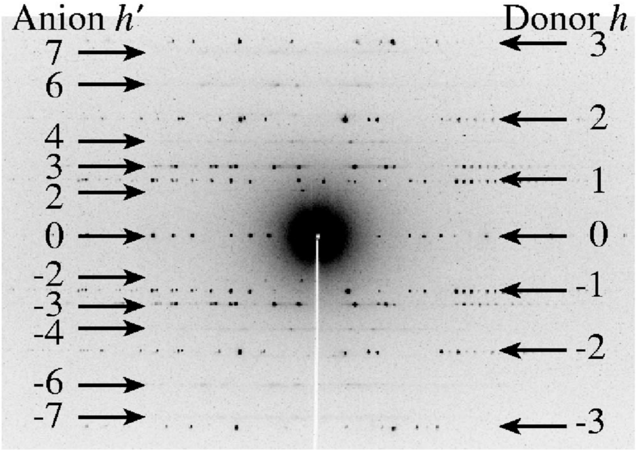

FIG. 3. X-ray-oscillation photograph along the $a^*$ axis taken at room temperature.

As the definite degree of charge transfer is known, it is possible to calculate the energy band structure from the donor arrangement. The calculated transfer integrals are $t_a=104$, $t_{p1}=-8.8$, and $t_{p2}=-34.1$ meV. Figure 4 shows the energy band structure and the Fermi surface calculated on the basis of the tight-binding approximation. The band filling is 0.792, which deviates from the usual filling of 0.75 or 0.5. The energy bands are degenerated on the C-line owing to the donor lattice symmetry (*Pnma*). Therefore, the Fermi surface consists of overlapping cylinders whose cross-sectional area is 41.7% of the first Brillouin zone.

The room-temperature electrical resistivity anisotropy, $\rho_{\|c}/\rho_{\|a}$, is estimated to be 20 from $\rho_{\|a}\sim 0.001\ \Omega$ cm and $\rho_{\|c}\sim 0.02\ \Omega$ cm. However, this value may be underestimated because of the ambiguity of $\rho_{\|c}$ on the thin crystal. Figure 5 shows the temperature dependence of the normalized electrical resistances $R_{\|a}$ and $R_{\|c}$. Although $R_{\|a}(T)$ shows power-law behavior ($R\propto T^{1.5}$), $R_{\|c}(T)$ has an upward curvature. The superconducting transition temperature $T_c$ is determined to be 4.3 K from the midpoint of the resistive transition (Fig. 5). This $T_c$ is slightly higher than the previous one (3.8 K), which is probably because of batch dependence. In this paper, we report data of crystals from the same batch.

Figure 6 shows the temperature dependence of the thermoelectric power (Seebeck coefficient) $Q(T)$, along the $a$ axis. In the high-temperature region, the thermoelectric

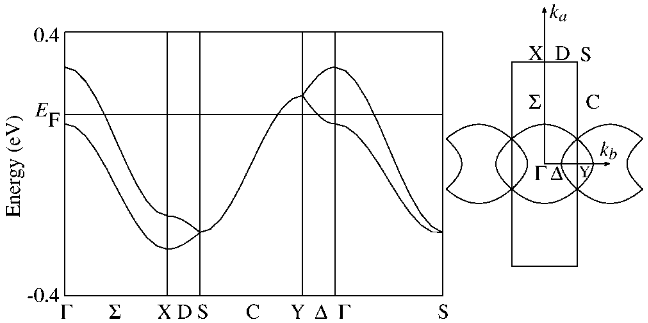

FIG. 4. Energy band structure and the Fermi surface.

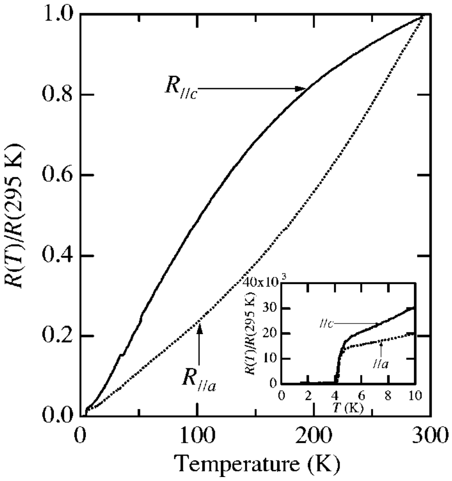

FIG. 5. Temperature dependence of relative resistance. The inset is the low temperature region.

power is decreased with decreasing temperature. $Q(T)$ becomes negative below 67 K and reaches a minimum at 28 K. Below this temperature, $Q(T)$ approaches zero and abruptly drops to zero at $T_c$. The change of the sign is due to the negative phonon-drag thermoelectric power associated with an Umklapp process electron-phonon scattering.[11]

The low-temperature Raman spectra associated with the iodide chains along the $a$ axis are shown in Fig. 7. The fundamental Raman line is split into two below 150 K. Both the original and the new Raman shifts are nearly independent of the temperature. Although the anion is not the discrete $I_3^-$ but the polyiodide chain composed of $I_3^-$ units, the new Raman line around 130 cm$^{-1}$ may be due to the asymmetric stretching mode of the discrete $I_3^-$.[12] The Raman line splitting indicates that the environment of the polyiodide chain is different between the low- and the high-temperature regions, i.e., some structural modulation occurs in the anion lattice at 150 K.

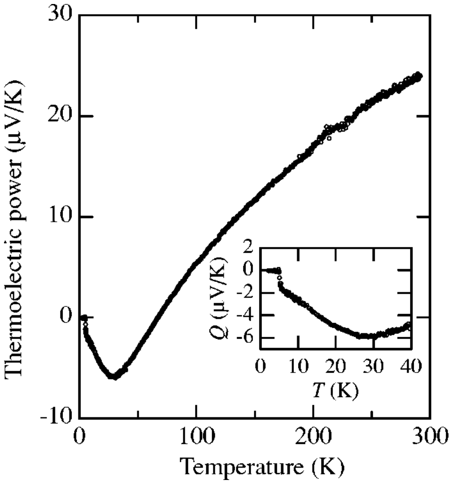

FIG. 6. Temperature dependence of thermoelectric power. The inset shows the low-temperature region.

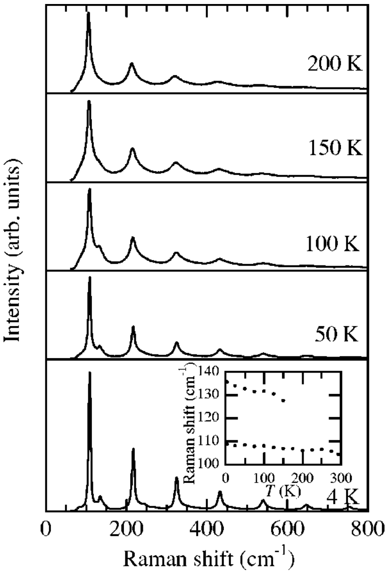

FIG. 7. The $a$-parallel Raman spectra under various temperatures. The inset is the temperature dependence of the fundamental Raman lines.

We carried out low-temperature x-ray experiments at 18.5 K to study the anion modulation. However, we could not observe any extra satellite reflections whose intensities are higher than the noise level, 1/500 of the Bragg reflections. This result indicates that the structural change is very small or the anion modulation is not of long-range order. Both explanations are reasonable because the electrical resistivity is not affected by the anion modulation. Figure 8 shows the temperature dependence of the lattice parameters and the cell volumes, where the $a'$ axis of the anion cell is one-third of the $I_3^-$ lattice. All lattice parameters are smoothly decreased as the temperature is decreased. The donor lattice constants at 18.5 K are $a=3.8950(5)$, $b=12.283(2)$, $c=25.286(4)$ Å, and $\alpha=\beta=\gamma=90°$. The calculated transfer integrals based on the 18.5 K crystal structure are $t_a=123$, $t_{p1}=-8.5$, and $t_{p2}=-39.8$ meV. Although $t_a$ and $t_{p2}$ are increased, $t_{p1}$ is slightly decreased as the temperature is decreased. The calculated Fermi surface shows no appre-

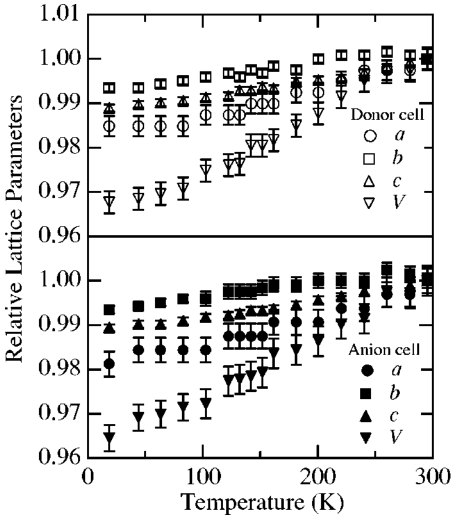

FIG. 8. Temperature dependence of the lattice parameters.

ciable difference from that based on the room-temperature structure.

(MDT-ST)(I$_3$)$_{0.417}$ has a composite structure of polyiodide chains. Several organic conductors, such as (TTT)$_2$I$_3$ (TTT: tetrathiotetracene),[13] (TTM-TTF)(I$_3$)$_{0.823}$ (TTM-TTF: tetrakis(methylthio)tetrathiafulvalene),[14] and (TTM-TTP)(I$_3$)$_{5/3}$ (TTM-TTP: 2,5-bis[4,5-bis(methylthio)-1, 3-dithiol-2-ylidene]-1,3,4,6-tetrathiapentalene),[15] are known to have poly-triiodide chains. All of them are one-dimensional conductors and show charge localization in the low-temperature region. The present compound is an organic superconductor that includes polyiodide chains of $\mathrm{I}_3^-$ units. The color of the present compound is metallic golden olive, similar to that of the above TTT and TTP salts.[15] This is attributed to the charge-transfer transition in the polytriiodide chain.[15]

Thermoelectric power is a transport property that is sensitive to small changes of the electronic structure.[11] Although (MDT-ST)(I$_3$)$_{0.417}$ shows a negative phonon-drag peak, another *incommensurate* organic superconductor (MDT-TSF)(AuI$_2$)$_{0.436}$ shows the usual positive phonon-drag peak.[3] In organic superconductors, $\beta$-(ET)$_2$I$_3$ [ET: bis(ethylenedithio)tetrathiafulvalene] shows a similar $Q(T)$ behavior to that of (MDT-ST)(I$_3$)$_{0.417}$.[16] $\beta$-(ET)$_2$I$_3$ exhibits structural phase transition at 200 K, which gives rise to the formation of a superstructure that is *incommensurate* with the underlying lattice.[17] The fundamental Raman line probing the triiodide anion of $\beta$-(ET)$_2$I$_3$ is split into three below this temperature.[12] In resistivity measurements, $d\rho/dT$ shows a peak at this temperature.[18] The phase transition is not clear in the electrical resistivity, but is obvious in the thermoelectric power. The first derivatives of the resistance of (MDT-ST)(I$_3$)$_{0.417}$, $dR_{\parallel a}(T)/dT$ and $dR_{\parallel c}(T)/dT$, have no clear peak. Judging from the low-temperature Raman results, (MDT-ST)(I$_3$)$_{0.417}$ has two kinds of iodide chains in the low-temperature region,[12] thereby lowering the symmetry of the anion lattice. The low-temperature x-ray photograph, however, does not detect the modulation. These results indicate that the iodide modulation is quite weak in contrast with that of $\beta$-(ET)$_2$I$_3$, or is not of long-range order. However, these two cases agree in terms of the absence of $dR(T)/dT$ anomaly. The anion lattice symmetry was not analyzed because we could not observe the long anion cell, $a' \sim 9.5$ Å, even at low temperature.

In summary, (MDT-ST)(I$_3$)$_{0.417}$ is an incommensurate organic superconductor with a polyiodide chain composed of $\mathrm{I}_3^-$ units. The $\mathrm{I}_3^-$ chain is modulated along the chain direction, as indicated by the x-ray diffuse line originating in the anion lattice. The splitting of the Raman spectra detecting iodide chains below 150 K suggests a small structural change in the anion lattice.

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