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Antiferromagnetic ordering of the incommensurate organic superconductor (MDT-TS)(AuI$_2$)$_{0.441}$ with a high spin-flop field

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The magnetic torque and high-pressure transport properties of the incommensurate organic superconductor (MDT-TS)(AuI$_2$)$_{0.441}$ are investigated, where MDT-TS is 5H-2-(1,3-disenlenol-2-yldene)-1,3,4,6-tetraselenafulvalene. The magnetic torque provides unquestionable evidence of an antiferromagnetic ordered state with a high spin-flop field of 6.9 T at ambient pressure. Hydrostatic pressure suppresses this insulating state and induces superconductivity, where the superconducting transition temperature rises to the maximum, 4.9 K at 1.27 GPa; the superconducting phase exists between 1.0 and 1.8 GPa above 1.5 K.

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I. INTRODUCTION

In the materials with strongly correlated electrons such as the high-$T_c$ superconductors,\textsuperscript{1} heavy fermion compounds,\textsuperscript{2} and organic molecular crystals,\textsuperscript{3–6} the superconducting (SC) phases appear in the vicinity of the antiferromagnetic (AF) state. In view of the current theoretical models, magnetism bordering on an SC phase is quite important for the state of these organic superconductors.\textsuperscript{3–6} The ground state depends not only on physical pressure but also on the change of the anion $X$ (chemical pressure).

By contrast, an ambient-pressure organic superconductor (MDT-TSF)(AuI$_2$)$_{0.436}$, where MDT-TSF is methylenedithio-tetraselenafulvalene [Fig. 1(a)], has uniform donor stacking without dimerization.\textsuperscript{16} This superconductor shows an incommensurate anion structure and unique Fermi surface reconstruction by the incommensurate anion potential.\textsuperscript{19–21} The incommensurate anion potential effect on the electronic states appears in the heat capacity at the superconducting transition.\textsuperscript{22}

The AuI$_2$ salt of the sulfur analog MDT-TS [Fig. 1(a)] is represented as (MDT-TS)(AuI$_2$)$_{0.441}$, and has basically the same incommensurate crystal structure as the selenium ana-

![FIG. 1. (a) MDT-TSF molecule. (b) Crystal structure projected along the molecular long axis and (c) projection onto the bc plane of (MDT-TS)(AuI$_2$)$_{0.441}$. $t_s$, $t_p$, and $t_{p2}$ in (b) are crystallographically independent transfer integrals.](Image)
log. This compound has a uniform donor stacking along the a axis and the donors form a conducting sheet on the ab plane [Figs. 1(b) and 1(c)]. The anions form chains running parallel to the donor stacks, and the anion periodicity is incommensurate to the donor spacing. Consequently, the noninteger composition, \((\text{MDT-TS})\text{(AuI}_2\text{)}_{0.441}\), has been determined from the ratio of the donor lattice \((a=3.992(3) \text{ Å})\) and the anion lattice \((a'=9.045(6) \text{ Å})\) as \(a'/a=0.4413(3)\).\(^{23}\) As a result, the charge transfer degree from the donor to anion is 0.4413(3) electrons per a donor molecule. The resulting energy band filling is 0.7764, and different from the usual 3/4- and 1/2-filling. The Fermi surface is two-dimensional owing to the considerable interchain interaction. This compound, however, shows a metal-insulator (MI) transition at low temperatures, and shows superconductivity under high pressure.\(^{23,24}\) The magnetic susceptibility of the present compound gradually increases with decreasing temperature in the metallic region. The magnetic susceptibility exhibits anisotropic behavior below 50 K, which suggests an AF ordering, but a spin-flop transition is not observed for magnetic fields up to 5 T.\(^{24}\) It should be mentioned that \(\alpha\)-\((\text{ET})_2\text{KHg(SCN)}_4\), whose ground state is a charge density wave state, shows anisotropic behavior of the magnetic susceptibility.\(^{25-27}\) Therefore, it is important to observe a spin-flop transition in \((\text{MDT-TS})\text{(AuI}_2\text{)}_{0.441}\) to verify the antiferromagnetic ground state.

The present paper reports magnetic torque measurements, which demonstrate the antiferromagnetic state with the high spin-flop field \(\mu_0H_s=6.9 \text{ T}\) and the high Néel temperature \(T_N=50 \text{ K}\), where \(\mu_0\) is the vacuum magnetic permeability. The phase diagram is extended to higher pressures using the high-pressure transport results, and maximum \(T_c\) is determined.

II. EXPERIMENT

Single crystals were prepared by electrocrystallization.\(^{23}\) For the magnetic torque measurements, the sample \((\sim30 \text{ µg/crystal})\) placed on a microcantilever for atomic force microscopy was mounted on a one-axis rotator in a cryostat in a 15 T superconducting magnet, and was cooled to 1.7 K.\(^{28}\) Uncertainty in the alignment of the field relative to the crystal axes is a few degrees. The high-pressure resistivity measurements were carried out by a clamped piston-cylinder cell consisting of a NiCrAl alloy inner cylinder and a BeCu outer shell with Daphne 7373 oil as a pressure-transmitting medium, and the sample was cooled to 1.5 K.\(^{29}\) The room-temperature-pressure value was determined by the resistance measurement of a Manganin wire with the pressure coefficient of 2.4%/GPa.\(^{30}\) Because the pressure is released by about 0.15 GPa between 300 K and 50 K, this value is subtracted from room-temperature values.\(^{31,32}\) The resistivity measurements were performed by the four-probe method along the a (intralayer) axis with ac current. Magnetic torque measurements were carried out at Tsukuba Magnet Laboratories, NIMS.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the magnetic torque curves of a piece of the single crystal at 1.7 K in various magnetic field directions. The field orientation as shown in the insets is defined by tilt angles \(\theta\) and \(\phi\), which are the angles tilted from b to c and a to c axes, respectively. The red lines in (a) are the fitted results.

![Magnetic torque curves](image-url)
The magnetic torque $\tau$ for a uniaxial antiferromagnet is expressed by the following equations.35–38

$$\tau = \frac{1}{2} (x_\perp - x_\parallel) \mu_0 H^2 \sin 2\theta \frac{\sin 2\theta}{\sqrt{\lambda^2 - 2\lambda \cos 2\theta + 1}}$$

(1)

$$\lambda = \left( \frac{H}{H_{df}} \right)^2$$

(2)

$$H_{df} = \sqrt{\frac{2K_u}{\mu_0 (x_\perp - x_\parallel)}}$$

(3)

where $x_\parallel$ and $x_\perp$ are the spin susceptibilities parallel and perpendicular to the easy axis, respectively, $H$ is the external magnetic field, $\theta$ is the angle between the applied field and the easy axis, $H_{df}$ is the spin-flop field, and $K_u$ is the anisotropy energy. By fitting to these equations, we obtain the spin-flop field as $\mu_0 H_{df} = 6.9$ T. We can estimate $K_u = 1.4 \times 10^{-1}$ J/mol at 1.7 K, where we define 1 mol as 100 g. The maximum midpoint (onset) $T_c = 4.9$ K (6.2 K) at 1.27 GPa, and $T_c$ decreases with $dP/dT \sim -6$ K/GPa above this pressure value. This decreasing rate is significantly smaller than those of other organic superconductors; $\beta'-(ET)_2$SF$_5$CF$_2$SO$_3$ has $-13.4$ K/GPa, and $\kappa-(ET)_2$Cu(NCS)$_2$ shows $-38.4$ K/GPa.39

Figure 5 shows the $T$-$P$-$H$ phase diagram of (MDT-TS)(AuI)$_2$ based on the transport and the magnetic measurements. The triple point bordering on insulator, metal, and superconductor, exists at about $P = 1.22$ GPa and $T_c = 4.5$ K in the $T$-$P$ plane. Below this pressure, the superconducting phase exists under the insulating phase.40 This is the same as those of $\kappa-(ET)_2$Cu[N(CN)$_2$]Cl $\beta'-(ET)_2$ICl$_2$,41 and (TMTSF)$_2$AsF$_6$.42 For $\kappa-(ET)_2$Cu[N(CN)$_2$]Cl, the NMR and ac susceptibility measurements under helium gas pressure have shown that the AF phase coexists with the SC phase in such a pressure region.43 The present MDT-TS salt seems to have a coexistence region of the AF and SC phases, as well. The highest $T_c$ appears around 50 K.

The resistivities under various pressures are shown in Fig. 4. At ambient pressure, the resistivity decreases with decreasing temperature and increases below $T_p = 85$ K. The metal-insulator transition temperature $T_{MI}$ is determined from the peak of $d(ln \rho)/d(1/T)$ as $T_{MI} = 50$ K at ambient pressure. $T_p$ and $T_{MI}$ shift to lower temperatures as the pressure increases, and the resistivities drop to the noise level above $P_c = 1.05$ GPa below onset $T_c = 4.3$ K (midpoint) $T_c = 3.2$ K. The resistance peak observed above 1.05 GPa corresponds to the superconducting onset $T_c$. The resistance peak is suppressed with increasing pressure, and $T_c$ increases with increasing pressure. At 1.27 GPa, the resistance peak vanishes and the normal Fermi liquid-like behavior appears. This decreasing rate is significantly smaller than those of other organic superconductors; $\beta'-(ET)_2$SF$_5$CF$_2$SO$_3$ has $-13.4$ K/GPa, and $\kappa-(ET)_2$Cu(NCS)$_2$ shows $-38.4$ K/GPa.39

FIG. 3. (Color online) Magnetic torque curves at $\theta = 1.0^\circ$ under various temperatures.

FIG. 4. (Color online) Temperature dependence of the resistivities under various pressures. The results below 1.19 GPa are the previous work.44

FIG. 5. (Color online) Phase diagram of (MDT-TS)(AuI)$_2$ based on the transport and the magnetic measurements. The solid and dotted lines are guides to the eye.
slightly above the triple point pressure not only in the MDT-TS salt but also in the above ET and TMTSF salts.

Although the present phase diagram resembles that of (TM)2X3, T_M and T_N of the present compound are about four times higher than those of (TM)2X. The magnetic insulating state below T_M=50 K is not a simple antiferromagnetic state with alternate spins such as β’-(ET)2ICl2, because each molecule or dimer does not have one electron. In this sense, the insulating state is regarded as a kind of SDW state. In contrast to (TM)2X, however, the electronic state of the present compound is two dimensional, and the Fermi surface does not nest. Yoshioka et al. have shown the possibility of MI transition in organic conductors with noninteger carrier number based on the one-dimensional extended Hubbard model, where donor carriers are slightly deviated from quarter filling and under an incommensurate periodic potential from anions. They have pointed out that the incommensurate Mott insulating state can be generated by the anion potential, δ, and the ratio between the on-site Coulomb repulsion and the nearest-neighbor transfer integral, U/t, without the nearest-neighbor Coulomb repulsion, i.e., V=0. The present experimental results do not give any information about the microscopic magnetic structure, i.e., the periodicity of the spin arrangement. Therefore, the mechanism of the MI transition of the present compound is unclear. Neutron diffraction and x-ray magnetic diffraction measurements are potential tools to clarify this important point, if the small sample size is overcome. For the heavy fermion compounds, CeRhIn5 shows an incommensurate AF ordering, in which the periodicity of the spin arrangement is determined by a neutron diffraction, and an SC phase appears under high pressure. The incommensurability of the spin arrangement slightly changes with increasing pressure. Although the SC phase exists under the AF phase in CeRhIn5, as well, the AF phase is not an insulator but a metal.

Table I lists the characteristic parameters of (MDT-TS)(Au2)0.441, β’-(ET)2ICl2, (TM)2AsF6, and (TMTTF)2Br.

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<tr>
<th>Compound</th>
<th>T_N (K)</th>
<th>μ_2H_d (T)</th>
<th>K_u (J/mol)</th>
<th>T^max (K)</th>
<th>P (GPa)</th>
<th>Band filling</th>
<th>Ground state</th>
<th>Tc (K)</th>
</tr>
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<tr>
<td>(MDT-TS)(Au2)0.441</td>
<td>50</td>
<td>6.9</td>
<td>1.4 × 10^{-1}</td>
<td>4.9</td>
<td>1.27</td>
<td>0.7764(2)</td>
<td>AFI</td>
<td>13</td>
</tr>
<tr>
<td>β’-(ET)2ICl2</td>
<td>22</td>
<td>1.1</td>
<td>5.4 × 10^{-3}</td>
<td>13.4</td>
<td>8.2</td>
<td>effective 0.5</td>
<td>AF Mott</td>
<td>12.6</td>
</tr>
<tr>
<td>(TM)2AsF6</td>
<td>12</td>
<td>0.45</td>
<td>1.5 × 10^{-4}</td>
<td>1.26^a</td>
<td>1.2</td>
<td>0.75</td>
<td>C-SDW</td>
<td>0.42</td>
</tr>
<tr>
<td>(TMTTF)2Br</td>
<td>13</td>
<td>0.42</td>
<td>–</td>
<td>2.6</td>
<td></td>
<td>0.75</td>
<td>C-SDW</td>
<td></td>
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*Tc is defined as the intersection of the extrapolated normal resistivity curve with the tangent drawn through the inflexion point in Ref. 44.

In summary, the incommensurate organic conductor (MDT-TS)(Au2)0.441 shows an antiferromagnetic ordering with a high Néel temperature (T_N=50 K) and a high spin-field pressure (μ_2H_d=6.9 T) at ambient pressure. Although the highest T_c (midpoint T_c=4.9 K) appears at P=1.27 GPa, T_c is much lower than that of β’-(ET)2ICl2 in spite of the high Néel temperature, a large spin-field, and anisotropy energy.

IV. CONCLUSION

In summary, the incommensurate organic conductor (MDT-TS)(Au2)0.441 shows an antiferromagnetic ordering with a high Néel temperature (T_N=50 K) and a high spin-field pressure (μ_2H_d=6.9 T) at ambient pressure. Although the highest T_c (midpoint T_c=4.9 K) appears at P=1.27 GPa, T_c is much lower than that of β’-(ET)2ICl2 in spite of the high Néel temperature, a large spin-field, and anisotropy energy.

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