

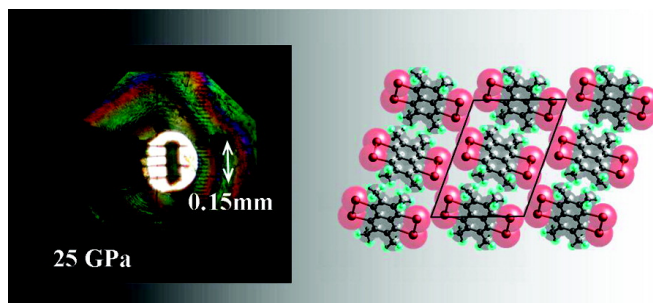
Communication

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## Electrical Resistivity of Tetramethyltetratelluronaphthalene Crystal at Very High Pressures — Examination of the Condition of Metallization of $\pi$ Molecular Crystal

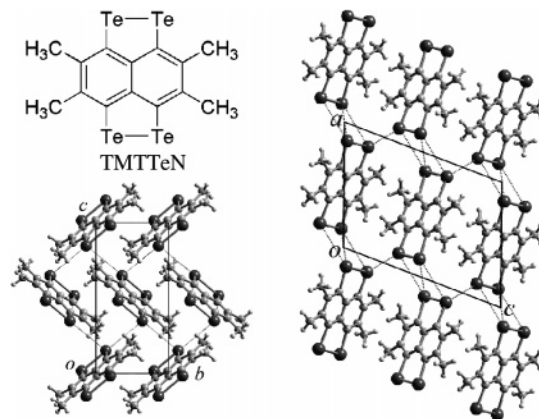
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Before the discovery of the first single-component molecular metal [Ni(tmdt)<sub>2</sub>] (tmdt = trimethylenetetrafulvalenedithiolate),<sup>1</sup> carrier generation by charge transfer between molecules forming conduction bands and other chemical species was considered to be indispensable for developing molecular metals. Consequently, more than two chemical species were needed to develop molecular metals. The first organic metal, (TTF)(TCNQ),<sup>2</sup> and the first organic superconductor, (TMTSF)<sub>2</sub>PF<sub>6</sub>,<sup>3</sup> are typical examples (TTF = tetrathiafulvalene; TCNQ = tetracyanoquinodimethane; TMTSF = tetramethyltetraselenafulvalene).

Crystals consisting of a single kind of  $\pi$  molecules (“single-component  $\pi$  molecular crystal”), such as naphthalene or anthracene, are insulators because of the large energy gap between the fully occupied HOMO band and the completely vacant LUMO band. However, even such systems become metallic if the HOMO and LUMO bands can be energetically overlapped. There will be two possible ways to realize the overlapping of the HOMO and LUMO bands. One is the large enhancement of the bandwidth by applying extremely high pressures (“the first way”). The other is the strong reduction of the HOMO–LUMO gap by a suitable molecular design of the constituent molecules (“the second way”). In fact, we have succeeded in developing the first single-component molecular metal, [Ni(tmdt)<sub>2</sub>], by obtaining a molecule with an extremely small HOMO–LUMO gap and fairly large intermolecular interactions (the second way).<sup>1,4</sup> On the other hand, it is well-known that typical inorganic semiconductors such as Si and Ge can be metallized by applying a high pressure.<sup>5</sup> At first sight, it might be assumed that similar pressure-induced metallization can easily occur in a molecular crystal as well because of its large compressibility (the first way). However, in the case of the molecular crystal, the situation is not so simple. The HOMO–LUMO gap is determined by the strong intramolecular interactions, while the bandwidth is determined by relatively weak intermolecular interactions. Consequently, it may be roughly stated that, in order to realize the overlapping of the HOMO and LUMO bands, the intermolecular interactions must be enhanced to be comparable to the intramolecular interactions. However, this situation is very abnormal for the molecule. If the intermolecular interactions become comparable to the intramolecular interactions, it will mean that the molecular structure cannot be closed. Therefore, it might be assumed that the pressure-induced metallization of single-component molecular crystals will be difficult to achieve if the stable molecular structure is not broken.<sup>6</sup> The best example to illustrate the pressure-induced metallization of a molecular crystal is the iodine crystal. It has been reported that iodine molecules undergo molecular



**Figure 1.** (a) Crystal structure of TMTTeN viewed along the *a* and *b* axes. The dotted lines are the short Te...Te contacts (<4.40 Å).

dissociation into an atomic state at around 20 GPa, at which the iodine crystal becomes a monoatomic metal and superconductor.<sup>7,8</sup> In order to examine the condition of metallization of  $\pi$  molecular crystals,<sup>9</sup> we have tried to measure the resistivity of a crystal of *peri*-ditellurium-bridged  $\pi$  molecules, tetramethyltetratelluronaphthalene (TMTTeN) (2,3,6,7-tetramethylnaphtho[1,8-*cd*:4,5-*c'*-*d'*]bis-[1,2]ditellurole), up to a very high pressure.

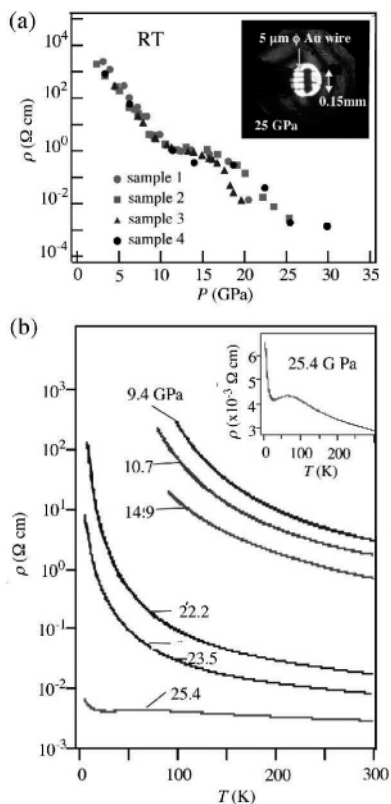
Several years before, we reported the four-probe resistivity measurements performed on a triclinic crystal of TMTTeN with the crystal solvent (CS<sub>2</sub>), TMTTeN(CS<sub>2</sub>), up to 15 GPa.<sup>10,11</sup> We recently obtained thin plate crystals of new monoclinic modifications of TMTTeN crystal without the crystal solvent (Figure 1).<sup>12</sup> TMTTeN molecules are arranged regularly along the *b*-axis. There are intermolecular Te...Te contacts shorter than the corresponding van der Waals distance (4.40 Å). Hence, the monoclinic modification of TMTTeN appears to be a very suitable for examining the possibility of pressure-induced metallization of  $\pi$  molecular crystals.

In the high-pressure resistivity measurements, diamond anvils with a top surface diameter of 560–700  $\mu$ m were used. Standard four-probe resistivity measurements on fragile organic crystals at very high pressures have been considered to be extremely difficult. However, we succeeded in performing the resistivity experiments up to 30 GPa.<sup>13</sup> Figure 2a shows the pressure dependence of the room-temperature resistivity along the *b*-axis. At ambient pressure, the resistivity of the TMTTeN crystal was too high to be measured. When the pressure was increased up to 3 GPa, the color of the crystal changed from brown to black and the room-temperature resistivity reduced to  $2.5 \times 10^3 \Omega$  cm. The resistivity decreased smoothly with an increase in the pressure up to 10 GPa. However, the pressure dependence of the resistivity decreased between 10 and 16 GPa. These behaviors are approximately similar to those

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**Figure 2.** (a) Pressure dependence of the room-temperature resistivity of TMTTeN. The inset shows the crystal in the diamond anvil cell at approximately 25 GPa. (b) Temperature dependency of the resistivities at various pressures. The inset shows the resistivity decrease below 65 K at 25.4 GPa. The resistivity behavior at 30 GPa was not included because the diamond anvil was broken into pieces at around 100 K.

observed in the triclinic modification.<sup>10</sup> However, at around 20 GPa, the resistivity again decreased fairly rapidly, which suggests a change in the electronic structure of the crystal in this pressure region. The pressure dependence of the lattice constants of iodine<sup>7</sup> and  $[\text{Au}(\text{tmdt})_2]$ <sup>14</sup> showed that the unit cell volumes of these single-component molecular crystals decrease to approximately 75 and 63% of their initial volumes at 10 and 20 GPa, respectively. If a similar  $P$ - $V$  relation can be applied to the compression of the TMTTeN crystal, the energy gain of the TMTTeN molecule ( $-fP$  dV) can be roughly estimated as 6.8 eV/mol at 20 GPa. Since this value is approximately twice that of the C-C bond energy, it is possible that a significant change is induced in the electronic structure (even in the molecular structure).

As shown Figure 2b, the crystal exhibited a semiconducting behavior below 25 GPa throughout the temperature range examined. However, the apparent activation energy was reduced to only around 5 meV at 25.4 GPa. The room-temperature conductivity was 350 and 700  $\text{S cm}^{-1}$  at 25.4 and 30 GPa, respectively. To the best of our knowledge, all hitherto developed molecular conductors with a room-temperature conductivity higher than 300  $\text{S cm}^{-1}$  are metallic. However, the TMTTeN crystal was not metallized, at least up to 30 GPa, at around room temperature, though the metallic temperature dependence of the resistivity was observed at low temperatures (25–65 K) at 25.4 GPa. According to the above-mentioned  $P$ - $V$  relation, the unit cell volume will be decreased to approximately 60% of the initial volume at around 23 GPa. We

attempted to simulate very roughly the plausible molecular arrangement at high pressure on the basis of the assumption that the crystal is compressed while avoiding shortening of the shortest intermolecular contact as much as possible. It appears that an intermolecular Te...Te contact, comparable to a Te-Te bond (2.74–2.86 Å), appears when the unit cell volume is compressed to approximately 60% of the initial volume, which seems to be consistent with the expected change in the electronic structure at around 20 GPa.<sup>15</sup> As expected, the present resistivity measurements show the considerable difficulties involved in the pressure-induced metallization of a  $\pi$  molecular crystal.

In conclusion, we have succeeded in performing four-probe resistivity measurements of a TMTTeN crystal by using a diamond anvil high-pressure cell up to 30 GPa. The crystal was not metallized even though the room-temperature resistivity decreased to a very small value ( $1.5 \times 10^{-3} \Omega \text{ cm}$ ) and metal-like behavior began to appear at low temperatures at about 25 GPa.

**Supporting Information Available:** Result of the tight-binding band calculations on simulated high-pressure structure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) The lattice constants and  $R$ -values are:  $a = 10.130 \text{ \AA}$ ,  $b = 6.069 \text{ \AA}$ ,  $c = 13.549 \text{ \AA}$ ,  $\beta = 110.572^\circ$ ,  $V = 779.8 \text{ \AA}^3$ ,  $Z = 2$ , and  $R = 0.057$ . The crystal data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK (CCDC 670805) (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
- (14) The experimental procedure was essentially similar to the previously reported one (ref 10). Four gold wires with a diameter of 5  $\mu\text{m}$  were bonded to the crystal by gold paint and used as electric leads (see the inset of Figure 1). Inconel 625 was used as the metal gasket. Four parallel ditches with a 20–30  $\mu\text{m}$  width were grooved on the surface of the gasket by sharpened stainless steel needles. The typical size of the sample crystal was approximately  $0.17 \times 0.03 \times 0.02 \text{ mm}^3$ . The crystal was placed in the central hole of the gasket, and the four attached gold wires were placed on the four parallel ditches filled with a 1:1 mixture of alumina and epoxy adhesive (Araldite). A mixture of fluorinert 3M, FC70, and FC72 was used as the pressure medium. The pressure was determined by the ruby fluorescence method at room temperature. The calibration of the pressure at lower temperatures was not made.
- (15) We recently performed the high-pressure X-ray structure analysis of the single-component antiferromagnetic metal  $[\text{Au}(\text{tmdt})_2]$  up to 11 GPa, which will be reported in the near future.
- (16) A simple tight-binding band calculation suggested that the TMTTeN crystal is not metallized even in such a situation.

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