Electrical Properties of Single-Component Molecular Crystals

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Since the discovery of the first single-component molecular metal, [Ni(tmdt)$_2$] (tmdt = trimethylenetetrathiafulvalenedithiolate), many analogous systems consisting of the transition metal complex molecules with similar extended-TTF type ligands were developed. However, the single-component molecular supercoductor has not been developed yet. We have tried to prepare and characterize new analogous systems. The trial to examine the condition to metallize the insulating crystal of planar π donor molecule was made by using diamond anvil high-pressure cell.

1. Resistance Measurements of Microcrystals of Single-Component Molecular Metals Using Finely Patterned Interdigitated Electrodes

One of the largest problems in the studies on single-component molecular metals is the difficulties in the growth of sufficiently large single crystals. Therefore almost all the resisitivity measurements ever made were performed on compacted crystalline powder pellets, which prevent to see the intrinsic resistivity behavior of the system. Recently, we have made the two-probe resisitivity measurements on the as-grown polycrystalline samples of [Au(tmdt)$_2$] (tmdt = trimethylenetetrathiafulvalenedithiolate) using finely patterned interdigitated electrodes and confirmed the system to be antiferromagnetic molecular metal with unprecedentedly high magnetic transition temperature (T_N = 110 K). We used the commercially available gold or platinum electrodes with gap between interdigitated electrodes was 5 µm and the width of electrodes was 10 µm. The microcrystals were grown on the interdigitated electrodes electrochemically from the acetonitrile solution containing (Me$_4$N)[Au(tmdt)$_2$] and (n-Bu$_4$N)PF$_6$. The resistivity measurements showed metallic behavior down to 3 K where the resistance ratio ρ(3 K)/ρ(300 K) was 0.4. Despite of large decrease in the susceptibility at T_N suggesting the disappearance of a considerably large part of the Fermi surface, the resistivity showed no distinct anomaly around 110 K. This work was made under the collaboration with Dr. Hishashi Tanaka (AIST), Prof. Madoka Tokumoto (National Defense Academy) and Prof. Akiko Kobayashi (Nihon University).

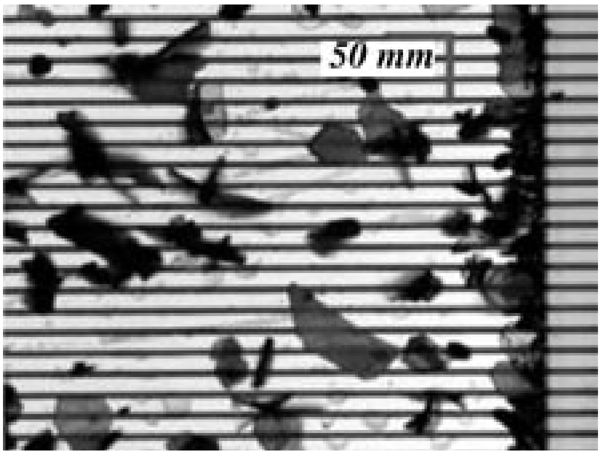

Figure 1. Microcrystals grown on interdigitated electrodes.

2. Structures and Physical Properties of Highly Conducting Single-Component Molecular Conductors Substituted with Selenium Atoms, [M(tmstfdt)$_2$] (M = Ni and Au, tmstfdt = trimethylenediselenadithiafulvalenedithiolate)

With the aim of obtaining the single-component molecular metals with larger intermolecular interactions, that is, stronger metallic properties, we have tried to prepare [M(tmstfdt)$_2$] (M = Ni, Au) with Se-containing extended-TTF ligands, tmstfdt. Microcrystals of [M(tmstfdt)$_2$] were grown by electrochemical oxidation of $(Me_4N)_n$[M(tmstfdt)$_2$] (n = 1 (Au), 2 (Ni)) in the presence of tetra-n-butylammonium perchlorate in THF or acetonitrile. The crystal structures of [M(tmstfdt)$_2$] (M = Ni, Au) were determined by synchrotron radiation X-ray powder diffraction experiments. The crystals [Ni(tmstfdt)$_2$] and [Au(tmstfdt)$_2$] are isostructural to each other and have very simple triclinic unit cells with only one molecule on the lattice point. Although resistivity measurements were made on compressed polycrystalline pellet samples, the room temperature resistivities were very high (ρ(RT) = 10^{-2} Ω cm (Ni), 10^{-1} (Au)). Furthermore, [Ni(tmstfdt)$_2$] showed metallic behavior down to about 50 K and kept high conductivities even at 4.2 K (ρ(RT) ≈ ρ(4 K)). That is, [Ni(tmstfdt)$_2$] is a new Se-containing single-component molecular metal. On the other hand, the resistivity of [Au(tmstfdt)$_2$] increased slowly with lowering temperature. Magnetic measurements indicated Pauli paramagnetic behavior for [Ni(tmstfdt)$_2$] and antiferromagnetic transition below 10 K for [Au(tmstfdt)$_2$]. This work were made under the collabolation with Dr. Emiko Fujiwara (the University of Tokyo) and Akiko Kobayashi (the University of Tokyo and Nihon University).

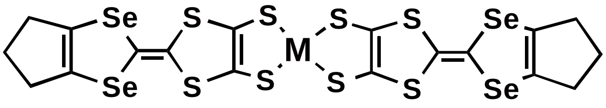

Figure 2. M(tmstfdt)$_2$, M = Ni, Au.

3. Possibility of Metallization of π Molecular Crystal at High Pressure

It may be said that the science on the molecular conductors was started by the pioneer works by Eley, Vartanyan, Akamatu and Inokuchi around the middle of 20 century, who examined the conducting properties of the crystals of neutral π molecules such as phthalocyanine and condensed aromatic hydrocarbons. Since then an extremely large progress has been achieved in the field of molecular conductors. The first one-dimensional organic metal, (TTF)(TCNQ) and the first organic superconductor, $(TMTSF)_2PF_6$ were reported in 1973 and 1980, respectively and through the examination of these systems and analogous molecular conductors, the requirements for the design of molecular metals became clear. That is, (1) the formation of conduction band by suitable molecular arrangement and (2) the carrier generation by charge transfer (CT) between the molecules forming conduction band and other chemical species were found to be two essential requirements. Due to the large success in the development of "*CT-type* molecular metals and superconductors," almost all the chemists seemed to believe until recently that the crystal consisting of single kind of molecule could not be highly conducting at least at ambient pressure. However we have succeeded to develop the first single-component molecular metal in 2001 by designing the transition metal complex molecule with extremely small HOMO-LUMO gap and fairly large intermolecular interactions. It may be imagined that more straightforward way to metallize the single-component molecular crystal will be to apply extremely high pressure.

We have recently examined the possibility of metallization of the crystal of π donor molecule tetramethyltetrateluronaphthalene (TMTTeN) up to 30 GPa by performing high-pressure four-probe resistivity measurements using diamond anvil cell (DAC). The crystal of TMTTeN has monoclinic lattice with space group $P2_1/c$ and the lattice constants of a = 10.130 Å, b = 6.069, c = 13.549, β = 110.572°, V = 779.8 Å^3, Z = 2. The room-temperature resistivity (ρ(RT)) decreased smoothly with increasing pressure at P < 10 GPa, almost constant at 11 < P < 16 GPa and decreased again at 17 < P < 25 GPa. ρ(RT) became as small as 1.4×10^{-3} Ω cm at 30 GPa. To our best knowledge, all the hitherto reported molecular conductors with ρ(RT) smaller than 10^{-2} Ω cm are metallic at around room temperature. However, TNTTeN was not metallic at least around room temperature. These results seem to support our conjecture that it is very difficult to metallize the crystal without destroying the molecular structure.

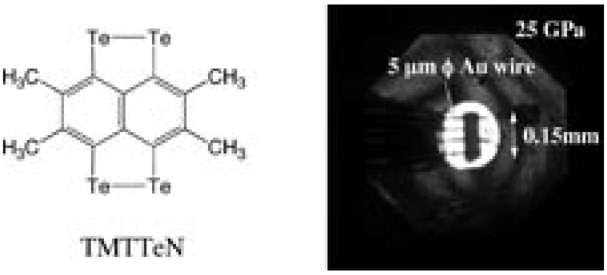

Figure 3. TMTTeN crystal put in the hole of metal gasket of DAC for 4-probe resistivity experiments.

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