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Metallization of the Single Component Molecular Semiconductor $[Ni(ptdt)_2]$ under Very High Pressure

Hengbo Cui,[†] James S. Brooks,*[,†] Akiko Kobayashi,[‡] and Hayao Kobayashi[‡]

Department of Physics and National High Magnetic Field Laboratory, Florida State University,
Tallahassee Florida 32310, and Department of Chemistry, College of Humanities and Sciences, Nihon University,
Tokyo 156-8550, Japan

Received February 27, 2009; E-mail: brooks@magnet.fsu.edu

Since the discovery of the first organic one-dimensional metal (TTF)(TCNQ) (TTF = tetrathiafulvalene; TCNQ = tetracyanoquinodimethane)[1] and especially the discovery of the first organic superconductor $(TMTSF)_2PF_6$ (TMTSF = tetramethyltetraselenafulvalene),[2] a tremendous number of organic metal and superconductors have been synthesized.[3] However, to this point, only charge transfer complexes of donor−acceptor compounds produced molecular metals (and superconductors) under ambient conditions. A breakthrough came with the synthesis of the first three-dimensional single component molecular metal of $[Ni(tmdt)_2]$ $(Ni(S_6C_9H_6)_2$; tmdt = trimethylenetetrathiafulvalenedithiolate).[4,5] It is expected that, in organic molecular materials, where the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) can overlap energetically, metallization can be realized. Although electrical resistivity measurements at high pressures above 10 GPa are difficult, we recently succeeded in carrying out systematic four-probe measurements on the single component molecular crystal TMTTeN (tetramethyltetratelluronaphthalene) up to 30 GPa.[6] Single crystal TMTTeN is an insulator at ambient pressure, and although the room-temperature resistivity was greatly reduced by 25.4 GPa, only a small region (60−25 K) of metal-like behavior was observed.

Considering the close resemblance between the molecular structure of $[Ni(tmdt)_2]$ and $[Ni(ptdt)_2]$ $(Ni(S_8C_9H_6)_2$ (see Figure 1a); ptdt = propylenedithiotetrathiafulvalenedithiolate) and the existence of many organic semiconductors exhibiting pressure-induced metallization at low pressures (e.g., <1 GPa), $[Ni(ptdt)_2]$ will be expected to be easily converted to metal by pressure. However, it was reported that $[Ni(ptdt)_2]$ remains a semiconductor up to 7.2 GPa.[7] In this work, the critical pressure needed to metallize $[Ni(ptdt)_2]$ was successfully determined by improving the technique of diamond anvil cell (DAC) high pressure resistivity measurements.

Figure 1a and 1b show the molecular and crystal structures of $[Ni(ptdt)_2]$ have a large room temperature conductivity (~7 S cm^{-1}) compared with other molecular conductors, and the simple tight-binding band structure calculation shows that very small electron and hole pockets are present at the Fermi surface.[7] However, as mentioned above, four terminal resistivity measurements show the temperature dependence of resistivity is still semiconducting even up to 7.2 GPa. To achieve metallic $[Ni(ptdt)_2]$ there are two problems that must be addressed. One is that organic samples are very soft and sensitive to uniaxial pressure, and the pressure needs to be hydrostatic. Generally, liquid pressure media will transform to a solid under high pressure, causing the pressure to be nonuniform (uniaxial) at the surface of a sample. Some liquefied gases like Ar or He can enhance the hydrostatic condition, but the loading of a DAC with liquefied gas is not practical in our method. The other problem, of course, is that the applied pressure must be large enough to reach metallization. Very recently, we improved the DAC high pressure resistivity measurement technique and found a method to control and enhance the hydrostatic pressure condition. In this procedure, after the electrical contacts are made to the sample, the sample is encapsulated in a thin layer of alumina−reinforced epoxy. The encapsulation greatly decreases the effects of uniaxial strains on the sample.

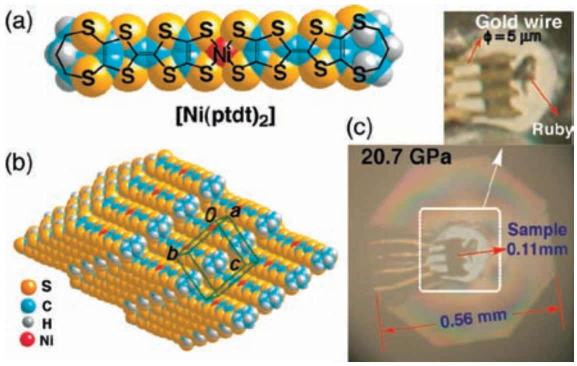

Figure 1. (a) Molecular structure of $[Ni(ptdt)_2]$. (b) Molecular packing of $[Ni(ptdt)_2]$. (c) A picture of a sample at 20.7 GPa assembled in a DAC.

Since the inner diameter of the gasket shrinks with pressure, the sample space is limited to less than 0.15 mm. Here we used a 0.11 × 0.05 × 0.02 mm^3 size sample, and 5 μm gold wires were attached to the sample with gold paint and placed in the sample chamber of the DAC (Figure 1c). The diamond anvils had a top surface diameter of 0.56 mm, and Inconel 625 was used as the metal gasket. To avoid having gold wires cut by the edge of the diamond during the pressurizing process, we recessed the wires into insulated grooves in the gasket. A hard stainless steel needle was used to make approximately 20 μm wide and 20 μm deep grooves in the gasket, which were then filled with a mixture of alumina and epoxy. The mixture was also used to encapsulate the sample and wire assembly. Daphne Oil 7373 is used for the pressure medium, and the pressure was determined at room temperature by monitoring the shift of ruby fluorescence R_1 lines. Two experiments were performed. For sample 1, we pressurized the sample without a protective layer (Figure 2a), and for samples 2, 3, and 4 we employed the epoxy encapsulation method to reduce uniaxial effects (Figure 2b and 2c).

The less hydrostatic pressure measurement (sample 1) was performed to 20.8 GPa as shown in Figure 2a. The pressure dependence of resistivity at room temperature (inset of Figure 2a) is not monotonic but has alternating minima and maxima with increasing pressure. The low pressure behavior (<7.2 GPa) is consistent with that of previous work.[7] Considering the "crossing-

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[†] Florida State University.
[‡] Nihon University.

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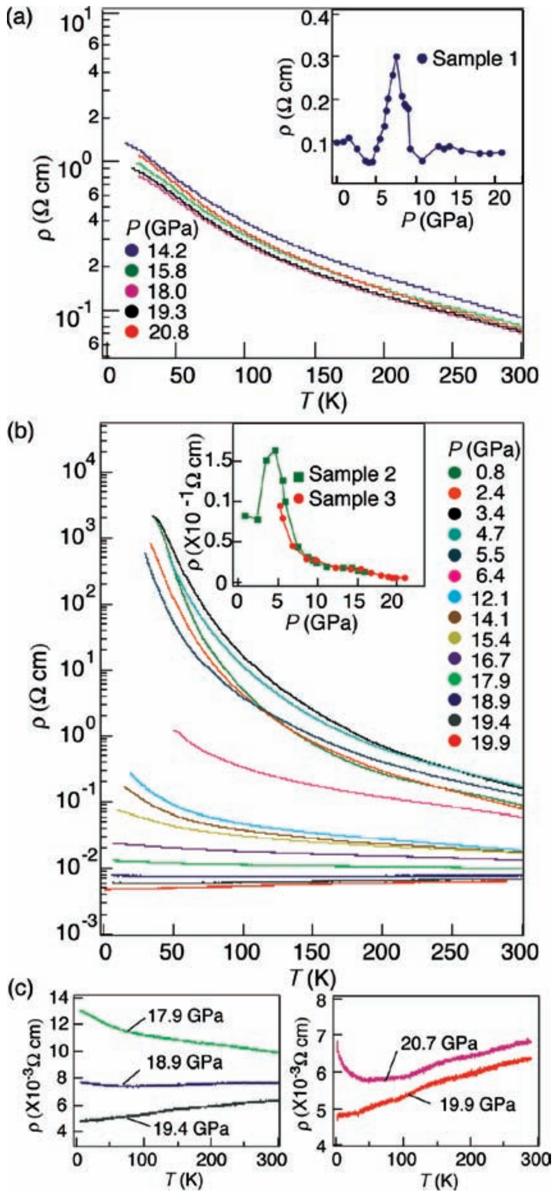

Figure 2. Temperature and pressure dependences of the resistivity of [Ni(ptdt)$_2$] (a) under less hydrostatic conditions (sample 1) and (b) under more hydrostatic conditions (sample 2 below 5.5 GPa, sample 3 between 12.1 to 20.7 GPa, and sample 4 at 6.4 GPa). The insets are temperature dependences of the resistivities at room temperature. (c) Details of higher pressure data. Sample 3 is completely metallic at 19.9 GPa, but semiconducting behavior emerges again at 20.7 GPa.

band nature" of [Ni(ptdt)$_2$], where HOMO−LUMO interactions tend to produce an energy gap,[7,8] the large increase of the room temperature resistivity near 7.5 GPa suggests a crucial role of HOMO−LUMO interactions around this pressure region. In the pressure range 14.2 to 20.8 GPa, the resistivity was almost pressure independent and shows semiconducting behavior (Figure 2a).

The more hydrostatic case for samples 2 and 3 is shown in Figure 2b and 2c. The inset of Figure 2b shows the pressure dependence of the room temperature resistivity. The resistivity decreases with pressure up to ~2.4 and ~4.6 GPa; the resistivity has a maximum value that is two times larger than that at ambient pressure. This behavior was not observed in previous work.[7] We believe this is caused by the more hydrostatic pressure condition in the present case. For a pressure up to 19.8 GPa, the room temperature resistivity is ten times less than the zero pressure resistivity. The two encapsulated samples (2 and 3) exhibit similar behavior (an increasing contact resistance of sample 2 precluded measurements above 5.5 GPa). As shown in Figure 2c, at low pressure (<18 GPa) the temperature dependence of resistivity is semiconducting. At 18.9 GPa, metallic behavior starts to appear from room temperature down to 70 K, but at lower temperature the resistivity increases again. Complete metallization (over the entire temperature range to 1 K) occurs at 19.8 GPa. However, at 20.7 GPa, a metal-semiconductor transition appearsat ~40 K (see Figure 2c).

In conclusion, by using a newly improved technique for DAC four-probe resistivity measurement, we successfully metalized the single component organic crystal [Ni(ptdt)$_2$] which provides a new example of a single component molecular crystal showing pressure-induced metallization. However, the critical pressure (~19 GPa) is unexpectedly high. These results indicate that the crystal retains the "crossing-band nature" up to very high pressure.

Acknowledgment. We would like to thank Dr. S. Tozer of NHMFL, for use of the ruby fluorescence system. This work was supported by NSF DMR-0602859 and DMR- 0654118 and in part by Grant-in-Aid for Scientific Research of Ministry of Education, Culture, Sports, Science and Technology, Japan.

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JA901553Z