Pressure-Induced Metallic Conductivity in the Single-Component Molecular Crystal [Ni(dmit)$_2$]

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Keywords: High-pressure chemistry / Diamond anvil cell / Molecular metals / Nickel / S ligands

Given that a molecular system has a soft lattice, high-pressure applications are effective ways to discover new single-component molecular metals and superconductors. In this study, we measured the high-pressure electrical resistivity of a single-component molecule crystal of [Ni(dmit)$_2$] (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) up to 25.5 GPa by using a newly developed diamond anvil cell technique that generates high-quality hydrostatic pressures. We successfully observed the metallic state over a wide temperature range above 15.9 GPa. Two different band calculation methods, tight-binding calculations coupled with the interatomic repulsion model and ab initio DFT calculations, indicated that 2D and 3D Fermi surfaces appear under high pressures.

Introduction

One of the first lessons in physics at school is that molecular materials are insulators, and thus, rendering a crystal of one of these molecular materials electrically conducting has been of major importance. In the early 1970s, the idea of partially depopulating the highest occupied molecular orbital (HOMO) or partially populating the lowest unoccupied molecular orbital (LUMO) in planar $\pi$-conjugated molecules consisting of chalcogen heterocycles was attempted in the syntheses of charge-transfer salts. This opened the field, and not only was metallic conductivity observed at very low temperatures but superconductivity was ultimately put into evidence, first under pressure and later at ambient pressure. Such materials are not single-component anymore, but they contain other cations or anions and sometimes solvents (even water). Yet the idea of finding metallic conductivity and superconductivity in neutral molecules did not fade away. A breakthrough came with an idea that was developed through experience, that lengthening the planar molecules with more chalcogen heterocycles, and the synthesis of [Ni(tmdt)$_2$] $\{Ni(S_6C_9H_6)H_2\}$, tmdt = trimethylenetetrathiafulvalenedithiolate, for which on each side of the nickel atom is three sulfur heterocycles with a trimethylene unit capping the end. This was the first ambient-pressure single-component molecular metal with a Fermi surface that was characterized experimentally and theoretically. Thus, it was anticipated that by increasing the number of sulfur heterocycles by one (from three to four on each side) in [Ni(ptdt)$_2$] $\{Ni(S_8C_9H_6)H_2\}$, ptdt = propylenedithiotetrafulvalenedithiolate, a metallic state would be stabilized at ambient pressure. However, this was not case, and a metallic state was observed only above 19 GPa.[2] Recently, Oakley and co-workers found metallization of the insulating bis(thiaselenazolyl) radical dimer (C$_6$N$_3$S$_2$Se$_2$H$_4$)$_2$, which has no extended sulfur heterocycles, under pressure of 5 GPa. From studies of the crystal structures under pressure and from DFT calculations they associated the transformation with a change from $\sigma$ to $\pi$ interaction between the Se atoms within the dimer.[3] In addition, the single-component semiconductor [Au(Et-thiazdt)$_2$] (Et-thiazdt = N-ethyl-1,3-thiazoline-2-thione-4,5-dithiolate), which contains small chelating parts with ethyl groups pointing out of the molecular plane, was reported to turn metallic under a relatively low pressure of 2.1 GPa.[4] These results prompted us to expand the search for smaller molecules, and we decided to study neutral [Ni(dmit)$_2$] $\{Ni(S_5C_3)H_2\}$: dmit = 1,3-dithiole-2-thione-4,5-dithiolate, which is one of the most significant and fundamental components for molecular metals and superconductors. Numerous molecular conductors based on the anion radical of [Ni(dmit)$_2$] have been synthesized over the past three decades.[5] We therefore expected that metallization of neutral [Ni(dmit)$_3$] would be quite challenging and would provide important information on ligand design for single-component molecular conductors and eventually superconductors. Herein, we present the pressure dependence of sin-
gle crystals of [Ni(dmit)₂] and the energy band structure of the neutral compound under high pressures by using two different methods, ab initio DFT calculations and simple tight-binding calculations.

Results and Discussion

Single crystals of [Ni(dmit)₂] were freshly prepared from (nBu₄N)₂[Ni(dmit)₂] by I₂ oxidation. Figure 1 (a,b) shows the molecular and crystal structures. The [Ni(dmit)₂] molecules are stacked along the b axis, and the neighboring molecules are arranged in a zigzag form with a dihedral angle of 84.21°. The structure is the same as that previously reported by Valade et al.,[6] except that the a and c axes are exchanged. In this study, the quality of the crystal data was rather improved (R = 1.7%), and it was used for band calculations (see the Supporting Information). The room-temperature resistivity was 6 × 10⁻² S cm⁻¹, and the temperature-dependent resistivity showed semiconducting behavior with an activation energy of 0.14 eV.

Because a molecular system has a soft lattice and because its electronic structure is sensitive to pressure, an applied external high pressure can provide a longer list of new single-component molecular metals. Although a diamond anvil cell (DAC) is very useful for high-pressure measurements, the pressure generated by a DAC tends to be anisotropic and its effect is often different from that of hydrostatic pressure. The DAC technique developed by us can generate high-quality hydrostatic pressures and was applied to the present system. The temperature-pressure dependences of the resistivity are shown in Figure 2. The inset in Figure 2 (b) shows the pressure dependence of the resistivity of the six crystals at room temperature. With increasing pressure up to about 9 GPa, the resistivity rapidly decreased by more than three orders of magnitude, followed by a small increase around 13.2 GPa, and then decreased moderately. As shown in Figure 2 (a), in the low-pressure region (<8 GPa), the temperature dependence of the resistivity showed semiconducting behavior. Around 8 GPa, weak metallic behavior began to appear in the high-temperature region (300–250 K). However, this metallic state was slightly unstable. At 8.3 GPa, the resistivity turned semiconducting with a very small activation energy (=1 meV) over the whole temperature region. Interestingly, at 10.3 and 11.6 GPa, the resistivity showed metallic behavior in the low-temperature regions of 40–11 and 80–16 K, respectively. Such metal-like behavior in the low-temperature region was also observed in an organic single-component crystal tetramethyltetraluronaphthalene (TMTTeN) under 25.4 GPa,[7] which suggests that this kind of metallic behavior is somewhat common in single-component materials under high pressures. Subsequent application of pressure up to 13.2 GPa removed the low-temperature metallic behavior, and the system remained metallic down to 47.5 K under 15.9 GPa. A tiny upturn in the resistivity was observed; however, the resistivity at the lowest temperature (3.4 K) was as low as the room-temperature resistivity. Above 15.9 GPa, the system exhibited essentially the same behavior and the upturn slightly shifted down to roughly 35 K and the room-temperature resistivity increased to 140 S cm⁻¹ at 25.5 GPa.

In most single-component molecular metals, extended tetrathiafulvalene (TTF)-type ligands are used to favor sizeable intermolecular transfer integrals between the frontier orbitals, which thus forms a large bandwidth. In the molecular conducting system, not only the bandwidth, but also
the effective on-site Coulomb repulsion energy plays an important role.[8] In general, small ligands are not suitable to gain a large bandwidth and reduce Coulomb interactions, which makes the metallic state unstable. Often, the superconducting phase is next to the insulating phase, and a strongly stabilized metallic state does not appear to meet the requirements for the superconducting transition.[9] Considering that high pressures can enlarge the bandwidth, systematic bandwidth control for semiconductors by high pressures could be an effective way to discover new superconductors. Successful metallization of the simple and small neutral molecule [Ni(dmit)₂] gives a good example of a small ligand yielding metallic conduction and has inspired us to further investigate new single-component metallic metals with smaller ligands.

Under high pressures, overlap between the HOMO band and the LUMO band would cause the single-component molecular system to be in the metallic state. To understand the pressure-induced metallic behavior in detail, we employed two different theoretical techniques to investigate the atomic and electronic structures of the [Ni(dmit)₂] molecular crystal under different pressures.

The first one was the ab initio DFT method within the generalized gradient approximation (GGA). Ab initio DFT is a very powerful tool for understanding the electronic states under high pressures. Recently, there have been several reports showing that the ab initio DFT method can provide reliable structural parameters and the electronic structures of molecular crystals at high pressures. DFT methods are known to have difficulties in expressing weak van der Waals interactions and pressure-induced phase transitions.[10] Nevertheless, many experimental results of the interesting pressure effects on molecular crystals have been clarified by such theoretical methods. Using the plane-wave basis set with the ultrasoft pseudopotential technique,[11] we optimized the cell parameters as well as the internal coordinates of [Ni(dmit)₂] at several given hydrostatic pressures up to 20 GPa. We found that the electronic structure significantly changed upon applying pressure. First, the electronic structure at ambient pressure, calculated with the experimental atomic positions, showed a semiconducting band structure with an indirect band gap of 0.48 eV (see Figure S1a, Supporting Information). This is consistent with the experimental result in Figure 2 (a), which indicates that the system is semiconducting over the whole temperature region. Note that the experimental energy gap estimated from the temperature dependence of the resistivity was 0.24 eV. In contrast, the band structure at 16 GPa shows a metallic character because the LUMO and HOMO bands overlap, as shown in Figure 3 (a). The Fermi surface consists of small pockets (blue color) and a relatively complicated cylinder shape (purple color, Figure 3, b). The calculated band structures at 18 and 20 GPa are similar to that at 16 GPa (see Figures S1b,c). These results obtained by assuming the hydrostatic condition are in good agreement with the resistivity measurements for which metallic behavior was observed over a wide temperature range above 15.9 GPa.

The second method was tight-binding calculations coupled with the interatomic repulsion model.[11] Simple tight-binding band calculations based on the extended Hückel method are quite useful for the description of energy bands in the vicinity of the Fermi level for molecular conductors.[6] However, this semiempirical method requires structural parameters, and it is not easy to obtain structural data under high pressures. It has been reported that the cell volume of [Au(tmdt)₂] at 10.7 GPa was about 75% of that at ambient pressure.[12] The molecular arrangement in the unit cell with volume 71% of the initial volume (which corresponded with that at about 16 GPa; see Figure S2a) was obtained on the assumption that the molecules behave as rigid bodies and are packed as far as possible in such a way as to avoid an increase in the interatomic repulsion between neighboring molecules. The unit cell parameter of the a, b, and c axes were reduced to 95.5, 81.9, and 90.7%, respectively. In contrast, the results of the full structural optimization by the ab initio DFT calculations with GGA at 16 GPa showed that these three axes were reduced to 90.8, 89.9, and 85.9%, respectively (see Figure S2b). As shown in Figure 3 (c), the band structure around the Fermi level is nearly similar to that in Figure 3 (a). A small 3D (purple color) and two small 2D (red with blue color) Fermi surfaces appear, which is consistent with a metallic state under high pressures. Although there are quantitative differences, both calculations indicate the existence of 3D and 2D Fermi surfaces under high pressures. In particular, the 3D character of the high-pressure band structure would originate from intermolecular interactions through terminal thioether groups in the dmit ligand. Under 16 GPa, the intermolecular overlap integral along the c axis in the tight-binding calculations is 5.14 × 10⁻³, which is comparable to the largest overlap integral within the ab plane (16.0 × 10⁻³; see Figure S3 and Tables S1 and S2).
Conclusions

By DAC four-probe resistivity measurements, we successfully demonstrated the metallic state in the single-component molecular crystal \([\text{Ni(dmit)}_2]\) under high pressures. Our results expanded the possibilities of simple and small ligands for the construction of single-component metals. Both the ab initio DFT method and the tight-binding method based on the interatomic repulsion model gave a similar energy-band structure under high pressures. The ab initio DFT calculations assuming hydrostatic conditions explained well the experimental results obtained by our DAC technique that provided high-quality hydrostatic pressures. In contrast, the simple tight-binding method properly extracted the essence of the band structure. In particular, the characteristics of the dmit ligand with terminal thio-ketone groups were demonstrated by the 3D nature of the high-pressure band structure.

Experimental Section

General Procedure: Black needle-shaped single crystals of \([\text{Ni(dmit)}_2]\) were freshly prepared from \((n\text{Bu}_4\text{N})_2[\text{Ni(dmit)}_2]\) by I\(_2\) oxidation. An acetone solution (20 mL) of \((n\text{Bu}_4\text{N})_2[\text{Ni(dmit)}_2]\) (20 mg) was poured into H-shaped glass cells, and then acetic acid (5 mL) and I\(_2\) (100 mg) were added to the different sides of the cell. Slow diffusion under non-vibration conditions for 2 weeks at room temperature gave black needles. Crystal-structure determination for \([\text{M(dmit)}_2]\) was performed with a Rigaku Mercury CCD AFC10 system with monochromated Mo-K\(\alpha\) radiation at room temperature. Six single crystals with an average size of 0.11 \(\times\) 0.03 \(\times\) 0.01 mm\(^3\) were used for the high-pressure measurements. The sample was mounted in the DAC by using the same technique as that used for \([\text{Ni(ptdt)}_2]\).\(^{[2]}\) The sample was encapsulated with a mixture of epoxy and alumina. As shown in Figure 1 (c), the diamond culet size was 0.56 mm. Tension annealed SUS301 was used for samples 1–5, whereas Inconel 625 was used for sample 6. Electrical contacts were obtained by attaching four 5 \(\mu\)m gold wires with gold paint, and the four-probe DC method was used for all measurements. Daphne Oil 7373 was used as the pressure-transmitting medium. The pressure was determined by the shift in the ruby fluorescence \(R_1\) lines at room temperature. In the extended Hückel molecular orbital calculations, the parameter sets of atomic orbitals reported by Komiyama et al.\(^{[13]}\) were used.

Supporting Information (see footnote on the first page of this article): Structural information of \([\text{Ni(dmit)}_2]\); band structures obtained by ab initio DFT calculations; full structural optimization results by tight-binding calculations coupled with the interatomic repulsion model and by ab initio DFT calculations with GGA; molecular arrangement and overlap integrals between the frontier molecular orbitals.

Acknowledgments

Numerical calculations in this work were partly performed by using the facilities of the RIKEN Integrated Cluster of Clusters (RICC) and the numerical materials simulator at the National Institute for Materials Science (NIMS). This work was partially supported by the Japan Society for the Promotion of Science (JSPS) through a Grant-in-Aid for Scientific Research (S) (grant number 22224006).

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