

Structure Phase Transition and Electrical Properties of a Single-component Molecular Crystal $[\text{Ni}(\text{ddds})_2](\text{ddds}=\text{5,6-dihydro-1,4-dithiin-2,3-diselenolate})$ under High Pressure

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In the development of single-component molecular conductors, metal dithiolene complexes, with a small energy gap (~ 0.5 eV) between HOMO and LUMO, have formed an important category [1,2]. On the other hand, molecular crystals have a soft lattice, and thus an application of pressure to insulating single-component molecular crystals is very efficient way to discover new single-component molecular metals/superconductors. Indeed, we have modified the four-probe resistivity measurement technique by using a Diamond Anvil Cell (DAC), and successfully found that insulating $[\text{Ni}(\text{ptdt})_2]$ (ptdt = propylenedithiotetrathiafulvalenedithiolate) [3], $[\text{Cu}(\text{dmdt})_2]$ (dmdt = dimethyltetrathiafulvalenedithiolate) [4] turned metallic at 19.4 GPa and 4.7 GPa, respectively. Recently, we also found that a single-component molecular superconductor based on metal dithiolene complex $[\text{Ni}(\text{hfdt})_2]$ (hfdt = bis(trifluoromethyl)tetrathiafulvalenedithiolate) at 8 GPa ($T_c = 5.5$ K) [6]. However, not only large-sized single-component molecular crystals, but also small-sized single-component molecular crystals could be good candidates for single-component molecular metals. Recently, Lorcy and coworkers found that the small-sized gold dithiolene complex $[\text{Au}(\text{Me-thiazdt})_2]$ (N-Methyl-1,3-thiazoline-2-thione-4,5-dithiolate) [6] showed metallic behavior at ambient pressure. Its analogs $[\text{Au}(\text{Et-thiazdt})_2]$ with the ethyl substitution [7], $[\text{Au}(\text{Et-thiazds})_2]$ with the Se substitution [8], and the most basic metal dithiolene complex $[\text{Ni}(\text{dmit})_2]$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) [9] are reported to become metallic at 1.3 GPa, 0.6 GPa, and 15.9 GPa, respectively. Moreover, in single-component molecular conductors that meet several conditions, the HOMO band and LUMO band can touch at a single point to form a Dirac fermion system. We have employed *ab initio* density functional theory (DFT) calculations for single-component molecular crystal $[\text{Pd}(\text{dddt})_2]$ (dddt = bis(5,6-dihydro-1,4-dithiin-2,3-dithiolate) that exhibits temperature-independent resistivity at 12.6 GPa. The result indicates that Dirac cones emerge in $[\text{Pd}(\text{dddt})_2]$ under high pressure. Here, we report the crystal structure and the pressure dependent resistivity of $[\text{Ni}(\text{ddds})_2]$ (ddds = 5,6-dihydro-1,4-dithiin-2,3-diselenolate).

Black needle-shaped single crystals of $[\text{Ni}(\text{ddds})_2]$ were prepared by electrochemical oxidation of $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Ni}(\text{ddds})_2]$ in acetonitrile

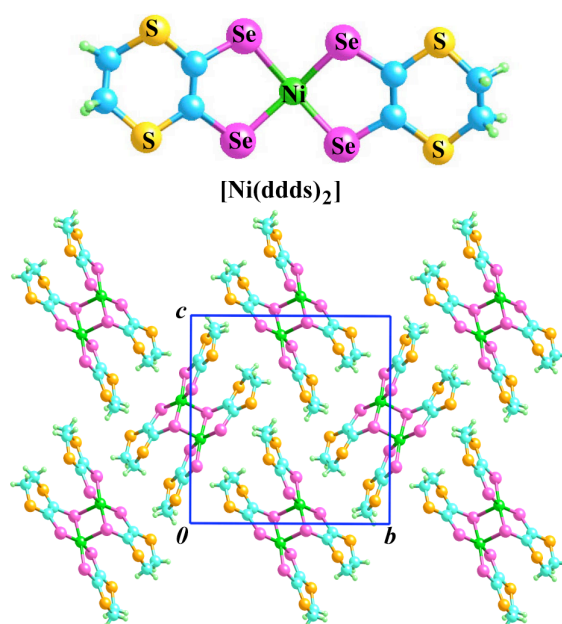


Figure 1 Molecular and crystals structure of trimer structure $[\text{Ni}(\text{ddds})_2]$.

with tetrabutylammonium perchlorate as a supporting electrolyte. As shown in Fig. 1, two Ni(ddd)s₂ molecules are strongly dimerized, and are stacking along the *a* axis. Within the dimer, the central Ni atom is connected to the Se atom in the adjacent molecule with a bond length of 2.496 Å. The dimers are packed perpendicular to each other and make a checkerboard type arrangement.

Figure 2 shows the temperature dependent of resistivity under various pressures for [Ni(ddd)s₂]. The system was insulating at 1.9 GPa, and room-temperature conductivity (σ_{rt}) and activation energy (E_a) were $8 \times 10^{-4} \text{ S cm}^{-1}$ and 203 meV, respectively. With increasing pressure, resistivity and E_a rapidly decreased. At 10.8 GPa, σ_{rt} reached up to 3 S cm^{-1} and the temperature dependence of resistivity was semiconducting with E_a of 20 meV. However, at higher pressure, both resistivity and E_a remained almost pressure-independent, and σ_{rt} and E_a were 10 S cm^{-1} , and 19 meV, respectively. The single crystal structure analysis under high pressure was performed in synchrotron radiation facility. Interestingly, a structural transition was found at high pressure, and the intermolecular Ni-Se bond at ambient pressure disappeared and new Ni-Ni bonds were formed (see Fig. 3).

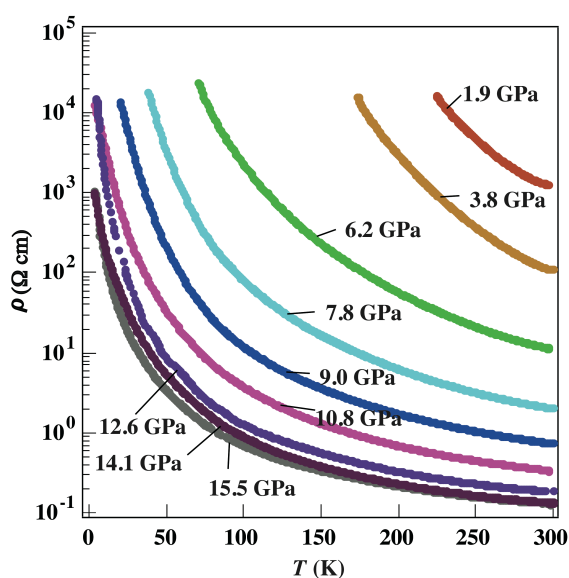


Figure 2 Temperature and pressure dependences of the resistivity of [Ni(ddd)s₂].

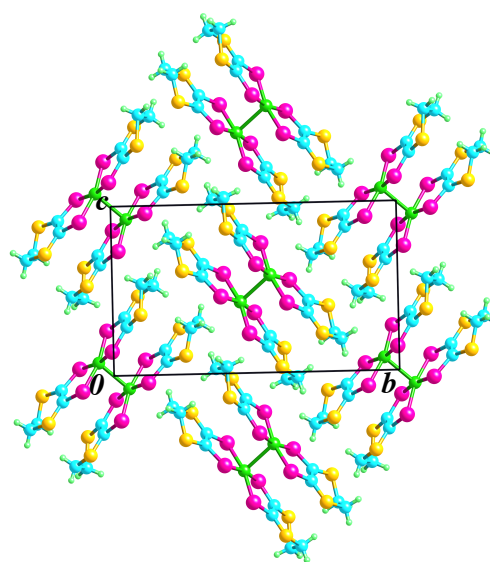


Figure 3 High pressure crystal structure of [Ni(ddd)s₂].

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