X-ray and optical studies of one-dimensional bis(dimethylglyoximato)Pd(II), Pd(dmg)\(_2\) at high pressures

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Abstract. By use of synchrotron radiation, powder x-ray diffraction of one-dimensional bis(dimethylglyoximato)Pd(II), Pd(dmg)\(_2\) has been studied at high pressures. The lattice constants with an orthorhombic structure for Pd(dmg)\(_2\) decreased with increasing pressure up to 10 GPa. The rate of the decrease of the \(b\)-axis was lower than that of the \(a\)-axis above 3 GPa. The \(c\)-axis is very compressible. A Pd-Pd distance along the \(c\)-axis abruptly decreased from 3.255 Å at ambient pressure to 2.82 Å at 7.4 GPa. A bulk modulus was estimated from the volume vs. pressure curve fitted by a Birch equation of state. The bulk modulus and its derivative of Pd(dmg)\(_2\) were 9.9(7) GPa and 9.2(8). This complex is a very compressible compound. The electronic absorption spectra of a thin film of Pd(dmg)\(_2\) have been investigated at high pressures. The 4\(d\)-5\(p\) transition bands rapidly shifted to lower energy region with increasing pressure. This optical transition energy decreased linearly with decreasing Pd-Pd distance. The optical property of Pd(dmg)\(_2\) shows the one-dimensional character in the 0-6 GPa region.

1. Introduction

The resistivity of one-dimensional bis(dimethylglyoximato)Pt(II), Pt(dmg)\(_2\) drastically decreases with increasing pressure and reaches the minimum at around 6.5 GPa, and then slowly increases with increasing pressure above this pressure [1]. The insulator-to-metal-to-insulator (IMI) transitions for Pt(dmg)\(_2\) occur at high pressures [2]. The pressure-induced absorption band has been found for Pt(dmg)\(_2\) [3]. On the other hand, the resistivity of Ni(dmg)\(_2\) decreases abruptly with increasing pressure from 10\(^{15}\) Ωcm at 1atm to about 50 Ωcm at 23 GPa [4]. This complex shows semiconductive behavior at high pressures.

A crystal structure of Ni(dmg)\(_2\) and Pt(dmg)\(_2\) is orthorhombic, space group \(Ibam\) [5, 6]. Both complexes crystallize in linear metal chain columnar structures. Powder x-ray diffraction of M(dmg)\(_2\) (M = Ni and Pt) has been studied with synchrotron radiation at high pressures [2, 4]. The M-M distances along the one-dimensional chains (the \(c\)-axis) for both complexes decrease rapidly with increasing pressure. The bulk moduli estimated from the volume vs. pressure curves are 8.0 GPa for Ni(dmg)\(_2\) and 10 GPa for Pt(dmg)\(_2\) [2, 4]. The one-dimensional Pd complexes show the interesting pressure-sensitive optical properties [7, 8]. Figure 1 exhibits the crystal structure of Pd(dmg)\(_2\). This structure is isostructural with M(dmg)\(_2\) (M = Ni and
Pd(dmg)$_2$ has the columnar structures along the needle axis. The columns are formed by square planar complex molecules with a Pd-Pd distance of 3.251 Å in a direction of the stack [9]. By use of synchrotron radiation, we have studied powder x-ray diffraction and absorption spectra of Pd(dmg)$_2$ up to 10 GPa at room temperature. In this report, the relationship between structure and optical property of Pd(dmg)$_2$ is discussed.

Figure 1. Crystal structure of Pd(dmg)$_2$.

2. Experimental details
Pd(dmg)$_2$ was prepared from an aqueous solution of K$_2$PdCl$_4$ and a hot alcoholic solution of dimethylglyoximes [8]. This complex is characterized by powder x-ray diffraction using CuK$_\alpha$ radiation and silicon as a standard. All diffraction lines were indexed in the structure. The values of the lattice constant obtained for Pd(dmg)$_2$ agree with almost the results of the single crystal diffraction data [9].

Using synchrotron radiation, powder x-ray diffraction of Pd(dmg)$_2$ was studied with a diamond-anvil cell and an imaging plate up to 10 GPa at room temperature [2, 4]. The incident beam was monochromatized by Si(111) double crystals. The x-ray beam with a wavelength of $\lambda = 0.6184$ Å was collimated to 40 $\mu$m in diameter. High-pressure diffraction experiments were performed at the beam line (BL-18C) of the KEK Photon Factory in Tsukuba. The pressure in a diamond-anvil cell was determined from a pressure shift in the sharp R-line fluorescence spectrum of ruby. The measurement of x-ray diffraction was carried out under hydrostatic conditions because the 4:1 methanol-ethanol solution used as pressure medium was solidified at around 10 GPa.

The absorption spectra of the thin film of Pd(dmg)$_2$ were measured with the diamond-anvil cell up to 10 GPa at room temperature. The optical system comprised a standard microscope and a spectrophotometer with an associated photodetection system. The thin film of this complex was prepared by evaporation onto the surface of the diamond-anvil in high vacuum. The thickness of the evaporated film is about 1500 Å. Fluorinert was used as the hydrostatic pressure fluid.

3. Results and discussion
Figure 2 shows powder x-ray diffraction patterns of Pd(dmg)$_2$ at high pressures. Two very strong diffraction lines, 110 and 200, of the complex are observed in the low angle region. However, both strong lines are cut in fig. 2 because there are many weak diffraction lines in the high-angle region. These diffraction lines shift to the high-angle region with increasing pressure. Each line
sho
| the different pressure shift. The d-value of the 002 line agrees with the Pd-Pd distance in
| the linear metal chains. This line is very sensitive to pressure. The intensity of the diffraction
| lines decreases and the width broaden with increasing pressure. The x-ray diffraction pattern
| of Pd(dmg)$_2$ does not change essentially at high pressures. Thus, the phase transition is not
| observed up to 10 GPa. When pressure is reduced from 10 GPa to the ambient pressure, the
| diffraction pattern at normal pressure appears again at room temperature. This behavior is
| completely reversible.

Figure 3 shows the ratio of lattice constants for Pd(dmg)$_2$ at high pressures. As shown in
fig. 1, the crystal structure of the complex is anisotropic. The lattice constants monotonically
decrease with increasing pressure. However, the rate of the decrease of the $b$-axis is lower than
that of the $a$-axis above 3 GPa. The lattice constants along $a$- and $b$- axes are not sensitive to
pressure compared with that along the $c$-axis. On the other hand, the $c$-axis is very compressible.

Figure 4 shows the relative cell volume ($V / V_0$) vs. pressure curve for Pd(dmg)$_2$. The cell
volume monotonically decreases with increasing pressure up to 10 GPa. The experimental data
can be fitted by a Birch equation of state [10]:

$$ P = \frac{3}{2} B_0 \left\{ \left( \frac{V}{V_0} \right)^{-\frac{7}{3}} - \left( \frac{V}{V_0} \right)^{-\frac{5}{3}} \right\} \left[ 1 - \frac{3}{4} \left( 4 - B'_0 \right) \left( \frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right], $$

(1)

where $B_0$ is the bulk modulus, $B'_0$ its first pressure derivative, $V$ the volume, and $P$ the pressure.
A least-squares fit to the data of Pd(dmg)$_2$ gives the following values: $B_0 = 9.9(7)$ GPa and
$B'_0 = 9.2(8)$. In the previous papers, we have reported that the bulk modulus of Ni(dmg)$_2$ and
Pt(dmg)$_2$ is 8.0(4) GPa and 10.0(5) GPa, respectively [2, 4]. Ni(dmg)$_2$ is slightly compressible
compared with Pd(dmg)$_2$ and Pt(dmg)$_2$. Powder x-ray diffraction of anthracene, tetracene and
pentacene has been studied at high pressures [11, 12]. The volume vs. pressure curves are
obtained for these oligoacenes. The bulk modulus is estimated from the $V$-$P$ curves fitted by a
Murnaghan equation of state. The magnitude of the bulk modulus is 8.4 GPa for anthracene, 9.0
GPa for tetracene and 9.6 GPa for pentacene [10]. These values of the aromatic hydrocarbons
are almost same for those of M(dmg)$_2$ (M = Ni, Pd and Pt). In the crystalline state of M(dmg)$_2$,
Figure 4. Relative cell volume ($V / V_0$) vs. pressure curve for Pd(dmg)$_2$.

Figure 5. Absorption spectra of the thin film of Pd(dmg)$_2$ at high pressures.

There is the metal-metal bond in the linear metal chains along the c-axis. We have found the short contacts between C and O atoms of adjacent molecules of M(dmg)$_2$ [6]. It is very interesting that the bulk modulus of M(dmg)$_2$ almost agrees with that of the aromatic crystals bound by the van der Waals force.

Figure 5 shows the absorption spectra of the thin film of Pd(dmg)$_2$ at high pressures. The absorption bands are located at around 290 and 461 nm at ambient pressure. The 290 nm band is ascribed to $\pi-\pi^*$ transition in the ligand. The 461 nm band is due to the $4d-5p$ transition, and rapidly shifts to the lower energy region up to 6 GPa. The polarization of the $4d-5p$ transition is parallel to the c-axis with the Pd-Pd bond [13]. The $d_{z^2}$ and $p_z$ orbitals extend in the direction of the c-axis. Since the Pd-Pd distance abruptly decreases with increasing pressure, the $d-p$ band shows the large pressure shift.

Figure 6 shows the optical transition energy of the $d-p$ band plotted as a function of the Pd-Pd distance for Pd(dmg)$_2$. This energy of this complex decrease linearly with decreasing Pd-Pd distance.
distances. Thus, the high-pressure optical behavior of Pd(dmg)$_2$ shows the one-dimensional character in the 0-6 GPa region. The Pd-Pd distance along the linear chains for Pd(dmg)$_2$ is 2.9 Å at around 6 GPa. The resistivity of Pd(dmg)$_2$ decreases monotonically with increasing pressure up to 22 GPa. The lowest resistivity of this complex is about 50 Ωcm at around 22 GPa [14]. Pd(dmg)$_2$ does not show metallic behavior though the Pd-Pd distance is much lower than 2.9 Å. In contrast, the Pt-Pt distance within the metal chain becomes below 2.9 Å at around 5.0 GPa. This distance almost agrees with the Pt-Pt spacing of the one-dimensional metal, K$_2$Pt(CN)$_4$Br$_{0.3}$·3H$_2$O. Therefore, the insulator-to-metal transition of Pt(dmg)$_2$ occurs at around 5 GPa [1, 2]. Bella et al. have studied the molecular orbitals of Pd(dmg)$_2$ and Pt(dmg)$_2$ molecules by ab initio LCAO-MO SCF calculations [15]. The top of the valence band of Pt(dmg)$_2$ consists of the 9$\alpha_g$ molecular orbital ($d_{z^2}$ character, metal-based molecular orbital) at ambient pressure. In contrast, the highest lying occupied molecular orbitals (HOMO) of Pd(dmg)$_2$ molecule consists of the 3$b_{3g}$ orbital (ligand-based molecular orbital). The energy level of the 9$\alpha_g$ orbital is lower than that of the 3$b_{3g}$ orbital. The top of the valence band of Pd(dmg)$_2$ is different from that of Pt(dmg)$_2$ at normal pressure. Further, we have found that Pt(dmg)$_2$ shows the pressure-induced absorption band at around 540 nm above 6.2 GPa [1-3]. These results suggest that the electronic states of Pd(dmg)$_2$ essentially differ from those of Pt(dmg)$_2$ at high pressure. The bulk moduli for M(dmg)$_2$ [M = Ni, Pd and Pt] are almost same. The anomalous electrical and optical behavior of Pt(dmg)$_2$ may mainly be explained in terms of the large spatial extent of the outer $d$ and $p$ orbitals in Pt atoms.

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