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Compression behavior of the delafossite-type metallic oxide $PdCoO_2$ below 10 GPa

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Abstract

The compression behavior of delafossite-type metallic oxide $PdCoO_2$ below 10 GPa has been investigated by in situ high pressure X-ray diffraction measurement using synchrotron radiation. It is found that the delafossite-type structure of $PdCoO_2$ is stable below 10 GPa. It should be noted that compression behavior of $PdCoO_2$ is anisotropic. Pressure dependence of the lattice parameters indicates that the a-axis is more compressible than the c-axis. The lattice parameter ratio c/a in the hexagonal unit increases with increasing pressure. The calculated zero-pressure bulk modulus is 224 GPa. It is found that the above characteristic compression behaviors of $PdCoO_2$ are the same as those of the delafossite $CuFeO_2$. The compressibilities of the a-axis of both $PdCoO_2$ and $CuFeO_2$ are highly different although those of the c-axis are almost the same.

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Keywords: A. Delafossite-type oxide; A. Metallic oxide; D. Compressibility; D. Anisotropy; E. High pressure

1. Introduction

High pressure research is one of the important ways to investigate fundamental properties and high pressure behaviors of materials. Since many perovskite-type oxides exist and are interesting from various kinds of academic viewpoints such as solid state physics and chemistry, earth science and so on, a lot of high pressure researches have been reported. On the other hand, there are also a lot of delafossite-type oxides (Fig. 1) [1–4] and they have attractive physical properties, such as frustrated magnetism, metamagnetism [5–8], metallic oxide having considerably low electrical resistivity [4,9–12], transparent conductor [13–16] and so on. However, there are only a few reports of high-pressure researches of the delafossite-type oxides [17,18]. Zhao et al. reported X-ray diffraction results of $CuFeO_2$ under high pressure up to 10 GPa at room temperature, which is one of typical delafossite-type semiconductive antiferromagnetic oxides. They reported interesting results of compression behavior of the cell parameters, such as a remarkable anisotropic compression of the unit cell and an increase of the cell parameter ratio c/a with increasing pressure.

Most of the delafossite-type oxides are ionic semiconductors [19]. $CuFeO_2$ reported before is one of typical oxides in this class. On the other hand, there are a few metallic delafossite-type oxides [4,9–12]. The typical one in this class is $PdCoO_2$. It shows anisotropic metallic temperature dependence of electrical resistivity in the directions parallel and perpendicular to the c-axis [9]. In this manuscript, compression behavior of metallic $PdCoO_2$

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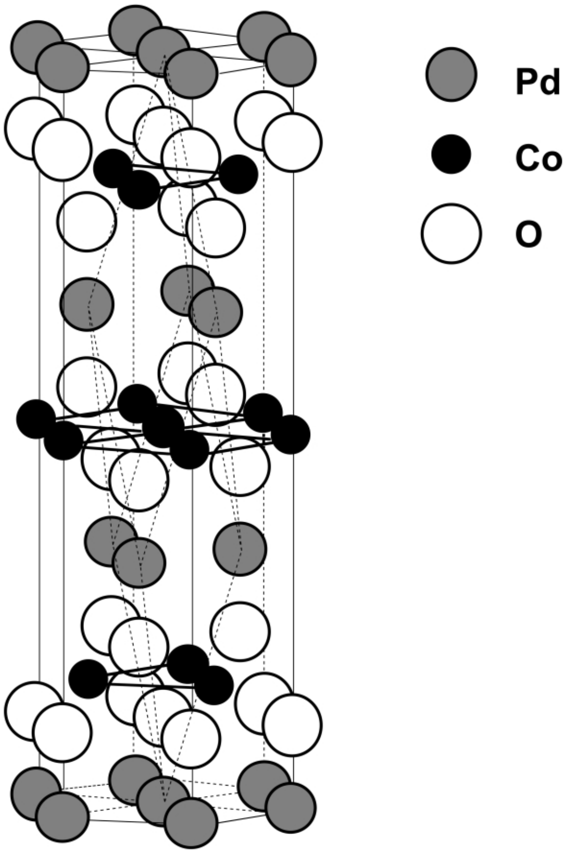

Fig. 1. Crystal structure of $PdCoO_2$.

under high pressure up to 10 GPa at room temperature are described and compared with $CuFeO_2$ reported before.

2. Experimental procedure

$PdCoO_2$ single crystals were grown using the metathetical reaction. Powders of reagent grade (purity 99.9%) $PdCl_2$ and CoO (Kokusan Chem. Co.) were well mixed in accordance with the chemical reaction,

$$PdCl_2 + 2CoO\varnothing PdCoO_2 + CoCl_2 \quad (1)$$

Mixed powder was sealed in an evacuated silica tube and then it was heated in a furnace at 700 °C for 40 h. After cooling, single crystals were obtained by leaching out of the cobalt chloride as a by-product with ethanol or distilled water. Typical size of the grown crystals is about 0.6 mm × 0.6 mm × 0.1 mm. The details of crystal growth and characterization results have been reported elsewhere [10,20]. Powder for a specimen for an X-ray diffraction experiment was prepared by crashing single crystals gently in a mortar.

High pressure X-ray diffraction studies were performed using a lever and spring-type diamond anvil (culet size: 600 μm in diameter) apparatus [21] and stainless steel gasket (gasket hole: about 200 μm in diameter).

A fine powdered specimen was placed in the gasket hole. A fluid mixture of methanol and ethanol with the volume ratio 4:1 was used as a pressure medium to realize the hydrostatic condition. The pressure was measured using the ruby fluorescence technique. Some small ruby chips were arranged on the surface of the sample.

High resolution angle dispersive X-ray diffraction experiments were carried out using the synchrotron radiation at the Photon Factory, National Laboratory for High Energy Physics (KEK) in Tsukuba. A monochromatized X-ray of wavelength 0.6888 Å was collimated to a thin beam (50 μm × 50 μm). The diffracted X-ray was detected by an imaging plate (IP). In order to obtain high resolution and accuracy, the IP detector was placed about 320 mm apart from the sample.

The X-ray intensities recorded in each pixel of the IP were measured by a laser-scanning reader and converted into two-dimensional digital intensities data. These data were then integrated along a polar axis which coincided with the Debye rings observed on the IP, and the powder diffraction intensities were obtained as a function of 2θ angle. An exposure time was about 1 h. The details of the data analysis was described elsewhere [22]. The X-ray diffractions were taken at five pressures: 2.4, 4.5, 7.3, 10.5 GPa and ambient pressure after recovered.

3. Results and discussion

Fig. 2 shows X-ray diffraction patterns of $PdCoO_2$ below about 10 GPa. No changes are observed in the pressure dependence of the X-ray diffraction pattern and all of the diffraction patterns correspond to the delafossite-type. This indicates that the delafossite structure of $PdCoO_2$ is stable up to about 10 GPa as well as $CuFeO_2$ reported before [17, 18]. The observed d-values (spacing) were calculated by fitting each diffraction peak using the Gausian formula. The cell parameters a and c in the hexagonal unit were calculated using these calculated d-values and are tabulated in Table 1. Volume V and ratio c/a are also tabulated in Table 1. Fig. 3 shows the pressure dependence of cell parameters. The results of $CuFeO_2$ reported before are also plotted to

Table 1
Lattice parameters a, c, volume, V and ratio, c/a of $PdCoO_2$ at each measured pressure at room temperature

Pressure (GPa)	a (Å)	c (Å)	V (Å^3)	c/a
Ambient pressure	2.8299(3)	17.741(1)	123.04(2)	6.2691
2.4	2.8162(3)	17.718(1)	121.69(2)	6.2908
4.5	2.8063(3)	17.688(1)	120.63(2)	6.3030
7.3	2.7914(5)	17.654(2)	119.12(4)	6.3244
10.5	2.776(2)	17.61(1)	117.5(2)	6.344

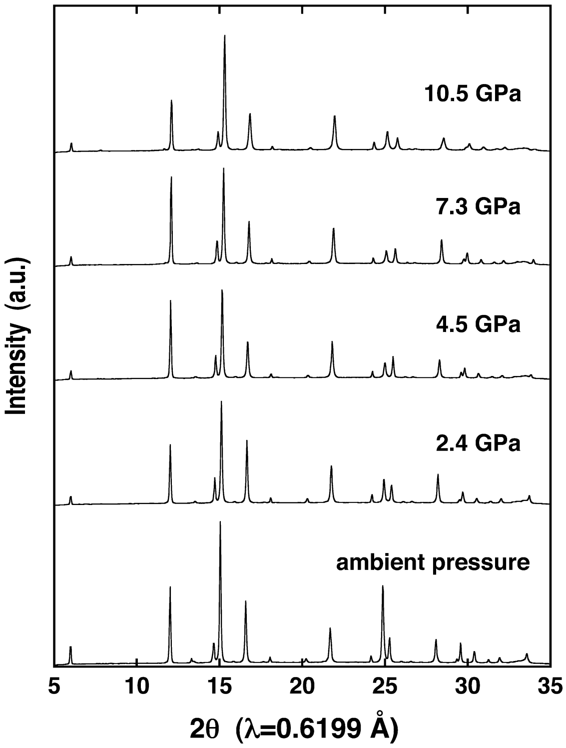

Fig. 2. Pressure change of X-ray diffraction pattern of $PdCoO_2$.

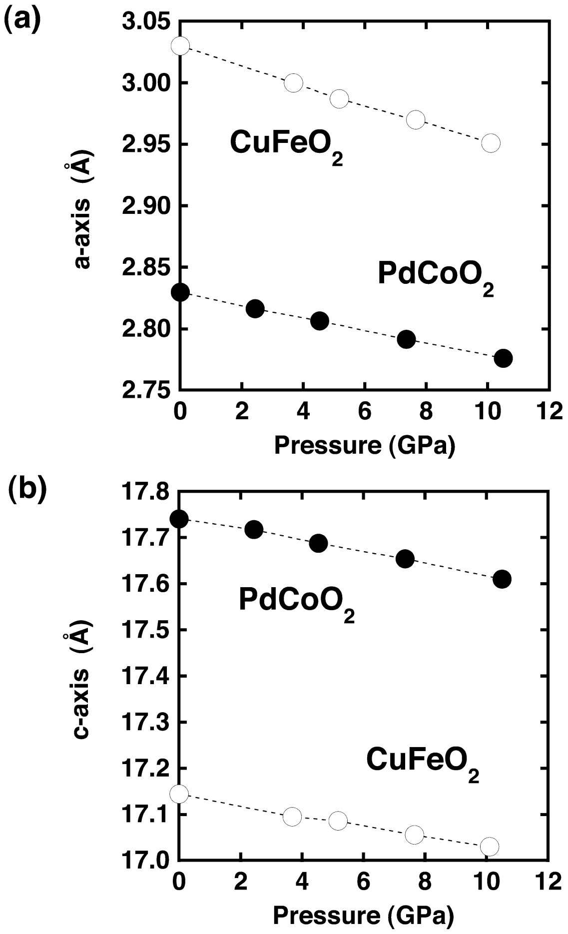

Fig. 3. Pressure dependence of lattice parameters a and c in the hexagonal unit of $PdCoO_2$ (solid circles). Results of $CuFeO_2$ are also plotted (open circles) to compare. (a) Lattice parameter of the a-axis, (b) lattice parameter of the c-axis. Errors in the lattice parameters are less than the size of the data points.

compare. Both lattice parameters decrease monotonically with increasing pressure. This means that the delafossite structure in $PdCoO_2$ has no drastic change below 10 GPa as well as $CuFeO_2$. It is interesting that the a-axis parameters of $PdCoO_2$ below 10 GPa are smaller than that of $CuFeO_2$ but that the c-axis parameters are larger. Fig. 4 shows the pressure dependence of cell parameters normalized by parameters at ambient pressure, in which data of $CuFeO_2$ reported before are also plotted to compare. It is found that the pressure gradient of the normalized cell parameter a/a_0 is much larger than that of the normalized cell parameter c/c_0. The a-axis is about 2.5 times more compressible than the c-axis. This means that the delafossite structure of $PdCoO_2$ has a remarkable anisotropic compression behavior as well as $CuFeO_2$, as shown in the Figure. It is interesting that $PdCoO_2$ has a less anisotropic compression behavior than $CuFeO_2$ of which the a-axis is about 3.9 times more compressible than the c-axis. It should be noted that compressibility of the c-axis of both $PdCoO_2$ and $CuFeO_2$ are almost the same in contrast to the difference compressibility of the a-axis between them. This means that stacking of hexagonal layers along c-axis of delafossite-type oxides are quite dense and so does not depend on the oxides. In other words, the anisotropic compression behavior of the delafossite-type structure depends mainly on the compressibility of the a-axis (or a-plane). In order to expose the anisotropic compression behavior more clearly, the pressure dependence of the ratio c/a in cell parameters is shown in Fig. 5 where data of $CuFeO_2$ reported before are also plotted to compare. It should be noted that the ratio c/a of $PdCoO_2$ increases with increasing pressure. This means that the hexagonal delafossite-type structure of $PdCoO_2$ becomes more anisotropic with increasing pressure. The c/a value at 10 GPa of $PdCoO_2$ is 1.13% larger than that at ambient pressure, while that of $CuFeO_2$ is 2.01% larger. This means that the hexagonal structure of $CuFeO_2$ becomes much more anisotropic with increasing pressure than that of $PdCoO_2$.

Fig. 6 shows pressure dependence of normalized volume, so-called compression curve, in which data of $CuFeO_2$ reported before are also plotted to compare. A monotonous decrease is observed with increasing pressure. The zero-pressure bulk modulus was calculated by fitting V/V_0, to the

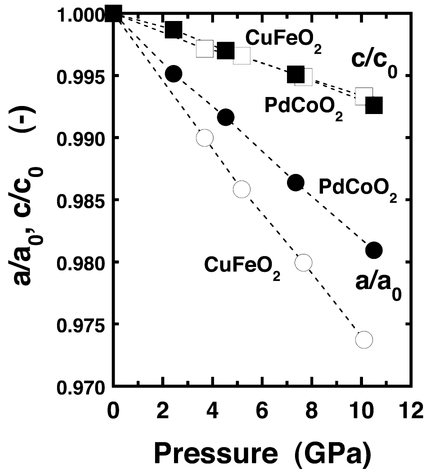

Fig. 4. Pressure dependence of lattice parameters normalized at ambient pressure a/a_0 and c/c_0 of $PdCoO_2$ (solid circles and squares). Results of $CuFeO_2$ are also plotted (open circles and squares) to compare.

following Birch–Murnaghan equation:

$$P = (3/2)B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}] \times \{1 + (3/4)(B_0{}' - 4)[(V/V_0)^{-2/3} - 1]\} \quad (2)$$

Here, B_0 and $B_0{}'$ are the zero-pressure bulk modulus and its pressure derivative, respectively. The solid line in Fig. 6 is obtained by the fitting of the equation. The calculated zero-pressure bulk modulus and its pressure derivative of $PdCoO_2$ are $B_0 = 224 \pm 2$ GPa and $B_0{}' = 0.7 \pm 0.5$. The zero-pressure bulk modulus of $CuFeO_2$ is $B_0 = 156 \pm 2 \times$ GPa [17,18] and smaller than that of $PdCoO_2$. These results indicates clearly that $PdCoO_2$ is less compressible.

From these results mentioned above, characteristics of compression behaviors of $PdCoO_2$ below 10 GPa are summarized as below:

1. Delafossite structure is stable and there is no structural transition.

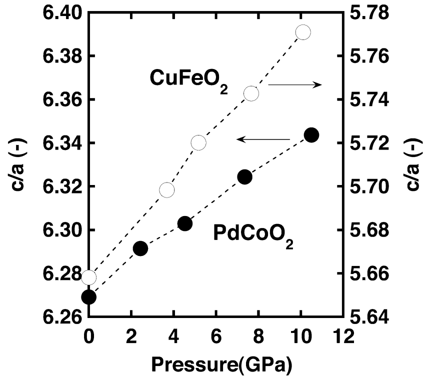

Fig. 5. Pressure dependence of a ratio c/a of lattice parameters of $PdCoO_2$ (solid circles). Results of $CuFeO_2$ are also plotted to compare (open circles).

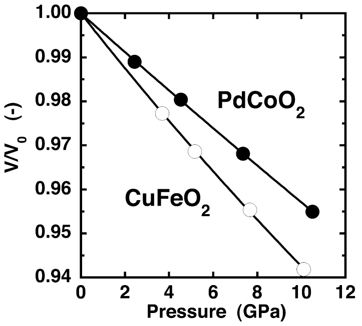

Fig. 6. Pressure dependence of volume normalized at ambient pressure V/V_0 of $PdCoO_2$ (compression curve) (solid circles). Results of $CuFeO_2$ are also plotted (open circles) to compare. The solid line is the fitting of the Birch–Murnaghan equation. Errors in V/V_0 are less than the size of the data points.

2. Lattice parameters, a and c are monotonously decrease with increasing pressure.
3. The structure has a remarkable anisotropic compression behavior.
4. The structure becomes more anisotropic with increasing pressure.

These characteristic compression behaviors of $PdCoO_2$ are qualitatively same as those of $CuFeO_2$. This suggests that they are common characteristics in the delafossite-type oxides.

As a matter of course, there are quantitative differences between them, as mentioned above. The distinguished difference is the compressibility of the a-axis although that of the c-axis is almost same. As mentioned in the introduction, $PdCoO_2$ is a metal, while $CuFeO_2$ is a semiconductor. Layers of the monovalent Pd or Cu ions play an important role to decide the electronic states i.e. electrical properties [3,4,11,23,24]. In the case of $PdCoO_2$, a distance between Pd–Pd ions in the monovalent Pd layer, which is same as the a-axis lattice parameter, is about 2.83 Å at ambient pressure and about 2.78 Å at about 10 GPa. These are close to that of the fcc Pd metal, 2.75 Å, resulting in the metallic properties. On the other hand, a distance between Cu–Cu ions in the $CuFeO_2$ is about 3.03 Å at ambient pressure and still about 2.95 Å at about 10 GPa. These are quite longer than that of the fcc Cu metal, 2.56 Å. If the Cu–Cu distance (a-axis parameter) of $CuFeO_2$ changes above 10 GPa in accordance with the results of Fig. 3, it approaches to that of fcc Cu metal and $CuFeO_2$ may shows a transition from semiconductor to metal (or semi-metal) at several dozens GPa or more. Since $CuFeO_2$ is an interesting semiconducting and antiferromagnetic oxide at ambient pressure, it is also interesting to investigate pressure effects on temperature dependence of electrical resistivity and magnetic susceptibility.

Finally, high interests are remained in the compression behaviors of another delafossite-type oxides such as $HCrO_2$, $CuAlO_2$, $PtCoO_2$, $CuYO_2$, $AgNiO_2$, $HgCaO_2$ and so forth.

Furthermore, the compression behavior of these oxides above 10 GPa is an interesting research target in terms of the structural anisotropy and anisotropic compression in comparison with pressure effects on physical properties.

4. Conclusion

Compression behaviors of delafossite-type metallic oxide $PdCoO_2$ below 10 GPa have been investigated by the in situ high pressure X-ray diffraction measurement using the synchrotron radiation. It is found that the delafossite-type structure of $PdCoO_2$ is stable and that it shows no drastic structural change below 10 GPa. The compression behavior of $PdCoO_2$ is anisotropic, that is, the *a*-axis is more compressible than the *c*-axis. The lattice parameter ratio *c*/*a* of $PdCoO_2$ in the hexagonal unit increases with increasing pressure. This means that the structure becomes more anisotropic with pressure. The zero-pressure bulk modulus of $PdCoO_2$ calculated using the compression curve is $B_0 = 224 \pm 2$ GPa. It is found that these characteristic compression behaviors of $PdCoO_2$ are same as those of the delafossite $CuFeO_2$. It should be noted that compressibilities of the *a*-axis of both $PdCoO_2$ and $CuFeO_2$ are highly different although those of the *c*-axis are almost the same.

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