

## Electronic Structure of Delafossite-Type Metallic Oxide PdCoO<sub>2</sub>

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The electronic structure of metallic oxide PdCoO<sub>2</sub> has been investigated by photoemission and inverse photoemission spectroscopies. It is found that the finite density of states at the Fermi level in the spectra is observed at the low photon energy where the ionization cross-section of Pd 4d increases with decreasing photon energy. Resonant photoemission spectra of PdCoO<sub>2</sub> at photon energies near the Co 3p to 3d and Pd 4p to 4d absorption thresholds, indicate no density of states at the Fermi level in the partial density of states of Co 3d, and finite density of states at the Fermi level in the partial density of states of Pd 4d, respectively. These results indicate that the main contribution to the density of states at the Fermi level is Pd 4d and that the low resistivity of PdCoO<sub>2</sub> is attributable to the itinerancy of the Pd 4d electrons.

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### 1. Introduction

Since the two-dimensional Cu–O planes play an important role in the high- $T_c$  cuprate superconductors, materials with such low dimensional structures are attractive in their exotic physical properties. Thus, oxides having the two-dimensional triangular-lattice structure become next important targets. Delafossite-type oxides  $MM'O_2$  are one of these materials. They have a crystal structure with the space group  $R\bar{3}m$ , as shown in Fig. 1. The structure consists of respective hexagonal layers of M, M' and O with M at (0, 0, 0), M' at (1/2, 1/2, 1/2) and two O at (1/9, 1/9, 1/9) and (-1/9, -1/9, -1/9), which stack in the sequence of A–B–C [A(M), A(O), B(M'), C(O), C(M), C(O), A(M'), etc.] to form a layered triangular lattices.

The delafossite-type oxides have been mainly investigated from the viewpoint of frustrated magnetism because most of them are semiconductive antiferromagnets.<sup>1–3)</sup> On the other hand, there are only a few metallic delafossite-type oxides. Shannon *et al.* had reported the first studies on the metallic delafossite-type oxides.<sup>4–6)</sup> They reported that PdCoO<sub>2</sub> and PtCoO<sub>2</sub> had the lowest electrical resistivity at room temperature among conductive oxides in the normal state. Tanaka *et al.* has recently investigated the physical properties and crystal chemistry of PdCoO<sub>2</sub>.<sup>7–9)</sup> They reported anisotropic metallic temperature dependence of electrical resistivity below 300 K in the directions parallel and perpendicular to the *c*-axis. The electrical resistivities perpendicular to the *c*-axis at 16 K and 260 K were 0.55  $\mu\Omega\text{cm}$  and 4.69  $\mu\Omega\text{cm}$ , respectively. Compared to ReO<sub>3</sub> ( $\sim 10 \mu\Omega\text{cm}$  at room temperature<sup>10)</sup>) which is one of famous oxide conductors, one can recognize low electrical resistivity of PdCoO<sub>2</sub>.

They also clarified that Pd and Co ions in PdCoO<sub>2</sub> were monovalent Pd<sup>1+</sup> and trivalent low-spin state of Co<sup>3+</sup>, respectively, by the Co 2p X-ray absorption and Pd 3d X-ray photoe-

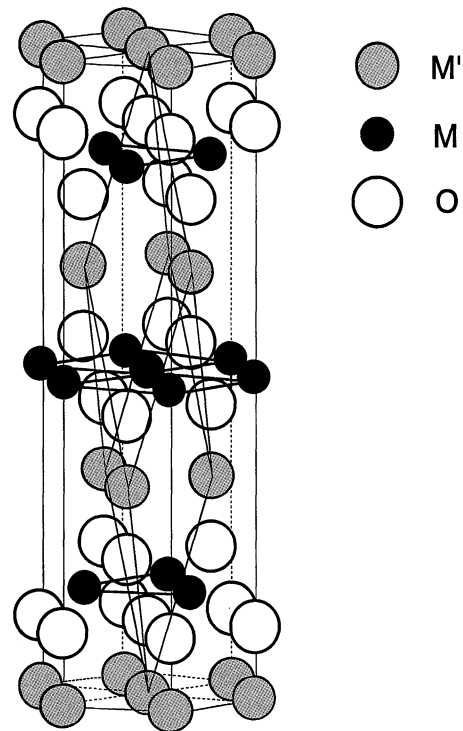


Fig. 1 Crystal structure of delafossite-type oxide  $MM'O_2$ .

mission spectroscopies. Thus, Pd is in the site of the linear O–Pd–O chain with an electronic configuration of monovalent Pd<sup>1+</sup>. Co is in an octahedral site with trivalent low-spin state of Co<sup>3+</sup>. In other words, PdCoO<sub>2</sub> structure is constructed by two-dimensional layers with the edge-linked CoO<sub>6</sub> octahedra connected by the O–Pd–O dumb-bells. As a results, on the basis of the ligand field theory, they suggested that the metallic behavior of PdCoO<sub>2</sub> was attributable to a half-filled band formed by s-d hybridized orbitals originated from the mono-

valent Pd ions and coordinated oxygens.

In order to clarify the origin of the metallic behaviors of PdCoO<sub>2</sub>, it is crucial to clarify the electronic structure. It is well known that the photoemission spectroscopy is powerful to study electronic structure of materials. Higuchi *et al.* reported the first study of photoemission spectroscopies on PdCoO<sub>2</sub>.<sup>11)</sup> They suggested no or extremely low density of states at  $E_F$ , like a “pseudogap”. This was inconsistent with the lowest metallic electrical resistivity of PdCoO<sub>2</sub>. Accordingly, in this study the more detailed study on the electronic structure around  $E_F$  of PdCoO<sub>2</sub> are investigated by the photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES), and clarifies the origin of the metallic electrical resistivities.

## 2. Experimental Procedure

PdCoO<sub>2</sub> single crystals were grown using the metathetical reaction.<sup>4–8)</sup> Powders of reagent grade (purity 99.9%) PdCl<sub>2</sub> and CoO (Kokusai Chem. Co.) were well mixed in accordance with the chemical reaction,



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.

Crystals were characterized by an optical microscope, a scanning electron microscope (SEM) with an electron probe microanalyzer (EPMA) and an X-ray precession camera. Chemical composition was determined by the inductively coupled plasma spectroscopy (ICP) and thermo-gravimetry (TG) with differential thermal analysis (DTA). TG-DTA was performed under H<sub>2</sub>/He (10/90%) atmosphere in order to determine the content of oxygens reducing PdCoO<sub>2</sub> to metal Pd and Co. Lattice parameters were determined by an X-ray powder diffraction measurements (XPD). Electrical resistivities were measured by a conventional four-probe DC method from 12 and 300 K.

Photoemission spectroscopy measurement was carried out at undulator beamline BL-19B at the Photon Factory of the High Energy Accelerator Research Organization, Tsukuba in Japan. Synchrotron radiation from the undulator was monochromatized using a grating monochromator. The resolution of about  $\Delta E/E = 5000$  at  $h\nu = 400$  eV and high photon flux of about  $10^{12}$ – $10^{13}$  photons/s were reached with the spot size of 100  $\mu\text{m}$ .<sup>12)</sup> Photoelectron energies were measured with an electrostatic hemispherical analyzer whose radius was 100 mm.

IPES measurement was carried out at the Institute for Solid State Physics, University of Tokyo. A filament cathode-type electron gun was used for the excitation source. The kinetic energy ( $E_K$ ) of the electron was calibrated by the electron energy analyzer. IPES was measured by the soft-X-ray emission spectrometer. The total energy resolution of the experimental system was about 0.6 eV at  $E_K = 80$  eV.

The sample was scraped *in-situ* with a diamond file in a vacuum of  $1.33 \times 10^{-8}$  Pa in order to obtain clean surface. The measurements were carried out at 90 K. The position of  $E_F$  was determined by measuring the spectra of Au.

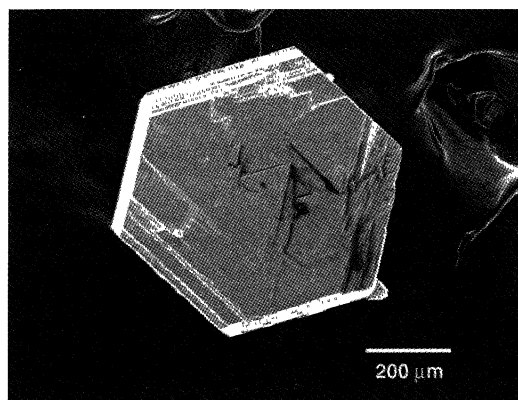


Fig. 2 SEM photograph of grown single crystal of PdCoO<sub>2</sub>.

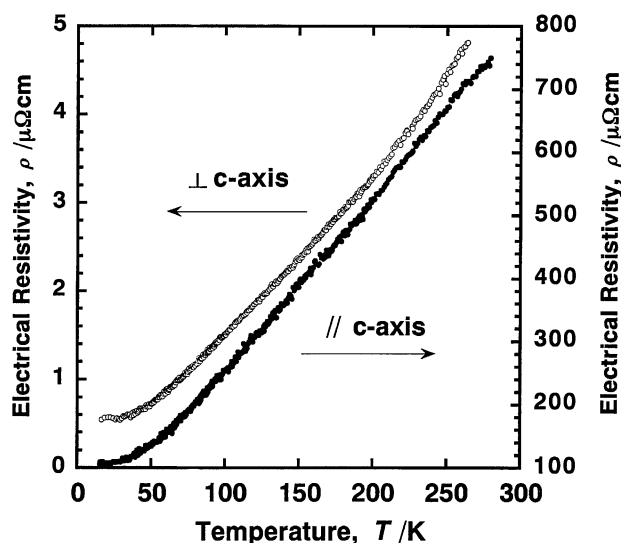


Fig. 3 Temperature dependence of electrical resistivity parallel and perpendicular to the  $c$ -axis.

## 3. Results and Discussion

Figure 2 shows a SEM photograph of typical PdCoO<sub>2</sub> single crystal. Crystals show silvery metallic lustre and have a form of well-habited polyhedral shape. The X-ray precession diffraction showed sharp spots, indicating high crystallinity of the grown crystals. The analyzed chemical composition of the crystal was Pd : Co : O = 1 :  $0.998 \pm 0.002$  :  $1.98 \pm 0.02$ . Lattice parameters were determined to be  $a = 0.28317$  nm and  $c = 1.7740$  nm.

Figure 3 shows temperature dependence of electrical resistivity parallel and perpendicular to the  $c$ -axis. They decrease with decreasing temperature anisotropically and then tend to be slightly saturated below about 40 K in both directions. These are typical temperature dependence of metals, indicating that PdCoO<sub>2</sub> is metallic. The detailed results of characterization and physical properties were reported elsewhere.<sup>7,8)</sup>

Figure 4 shows PES and IPES spectra measured at  $h\nu = 63, 80$  and  $100$  eV. The feature A indicates an occupied Co 3d state. The feature C indicates a hybridization state of Co 3d and O 2p states. The feature D at  $\sim 10$  eV, which is assigned to be a Co 3d satellite structure, is not predicted by a one-electron band calculation<sup>13,14)</sup> and is often taken to be a signal

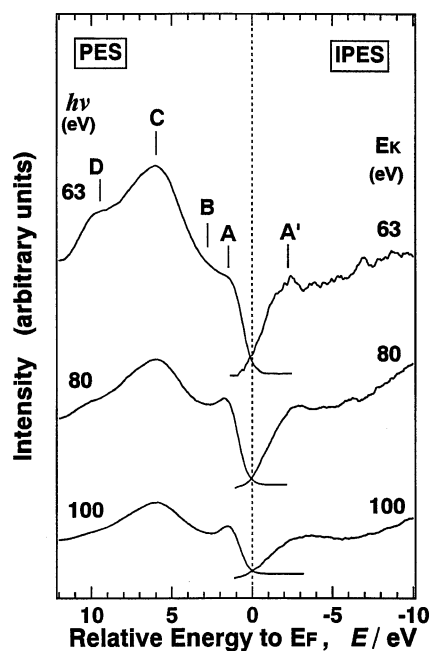


Fig. 4 Photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) spectra of PdCoO<sub>2</sub> measured at  $h\nu = 63, 80$  and  $100$  eV.

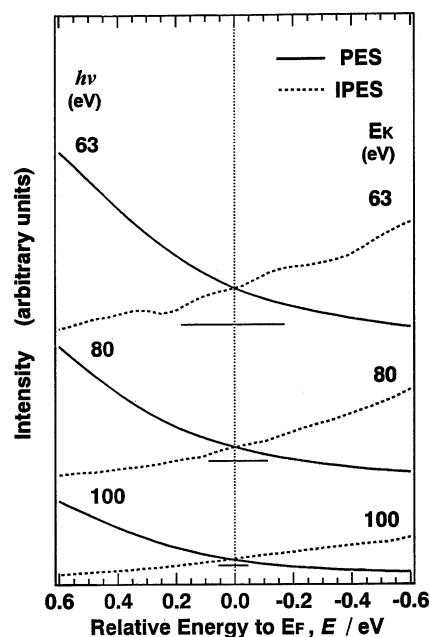


Fig. 6 Detailed PES and IPES spectra around the Fermi level ( $E_F$ ) of PdCoO<sub>2</sub>.

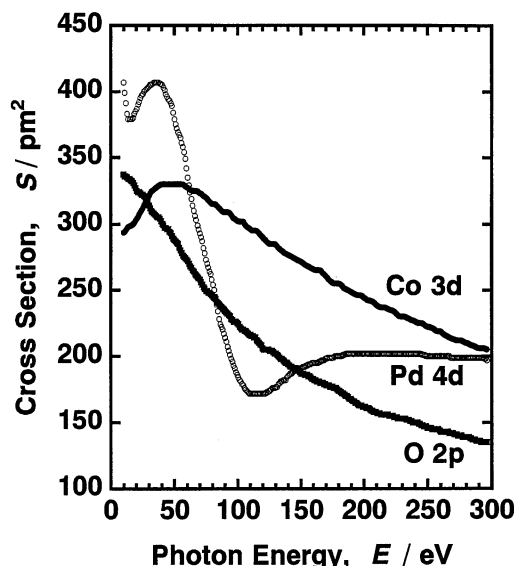


Fig. 5 Photon energy dependence of cross sections of Co 3d, Pd 4d and O 2p.<sup>15)</sup>

of strong correlation effects. On the other hand, the feature B indicates Pd 4d. In the IPES spectra, the abscissa is the energy above  $E_F$  that is calibrated by the Fermi edge of gold. The feature A' is an unoccupied Co 3d state.<sup>11)</sup>

It should be noted that the feature B becomes stronger with decreasing photon energy from 100 to 63 eV. This is attributable to the drastic increase of the ionization cross-section of Pd 4d with decreasing the photon energy, as shown in Fig. 5.<sup>15)</sup> It should be also noted that the density of state at  $E_F$  increases with decreasing the photon energy as well as the feature B.

Figure 6 shows the detailed PES and IPES spectra around  $E_F$ . The increase of the density of states at  $E_F$  with decreasing the photon energy can be also clearly observed in this figure. The spectra of  $h\nu = 100$  eV and  $E_K = 100$  eV almost give

the density of states of Co 3d and O 2p because there is a Cooper-minimum of Pd 4d around  $h\nu = 100$  eV (Fig. 5). It is found that there is no density of states around  $E_F$  in this spectra. These spectra remind us as if there is a pseudogap at  $E_F$  in the electronic structure of PdCoO<sub>2</sub>, as reported in the previous manuscript.<sup>11)</sup> However, a large density of states was observed at  $E_F$  as the photon and electron energies decrease. The apparent Fermi edge is not observed in this excitation energy. Considering the photon and electron energies dependence of the ionization cross-section (Fig. 5), these spectra indicate that the main contribution to the density of states is Pd 4d.

Figure 7 shows resonant photoemission spectra of PdCoO<sub>2</sub> at the photon energies near the Co 3p to 3d and Pd 4p to 4d absorption thresholds. It is found that the spectrum of the difference between on- and off-resonances in the resonant photoemission spectra of Co 3p, which corresponds to the partial density of states of Co 3d, has no density of states at  $E_F$ . On the other hands, finite density of states at  $E_F$  is apparently observed in the difference spectrum of Pd 3p, which corresponds to the partial density of states of Pd 4d. These results are consistent with the PES-IPES results mentioned above and also indicate that the main contribution to the density of states is Pd 4d.

The spectroscopic results indicate that there is no pseudogap at  $E_F$  in the electronic structure of PdCoO<sub>2</sub>. This is consistent with the metallic electrical resistivity of PdCoO<sub>2</sub>. In addition, it is concluded that the origin of the low electrical resistivity of PdCoO<sub>2</sub> is attributable to the itinerancy of the Pd 4d electrons.

It is interesting to compare to pure metal Pd which has also itinerant electrons. The pure metal Pd is a well-known nearly weak ferromagnet which has itinerant electrons correlated among them. Therefore, the electronic specific coefficient of Pd is enhanced to be  $9.48$  mJ/K<sup>2</sup>mol.<sup>16)</sup> On the other hand, that of PdCoO<sub>2</sub> in this study is  $4.14$  mJ/K<sup>2</sup>mol.<sup>9)</sup> This

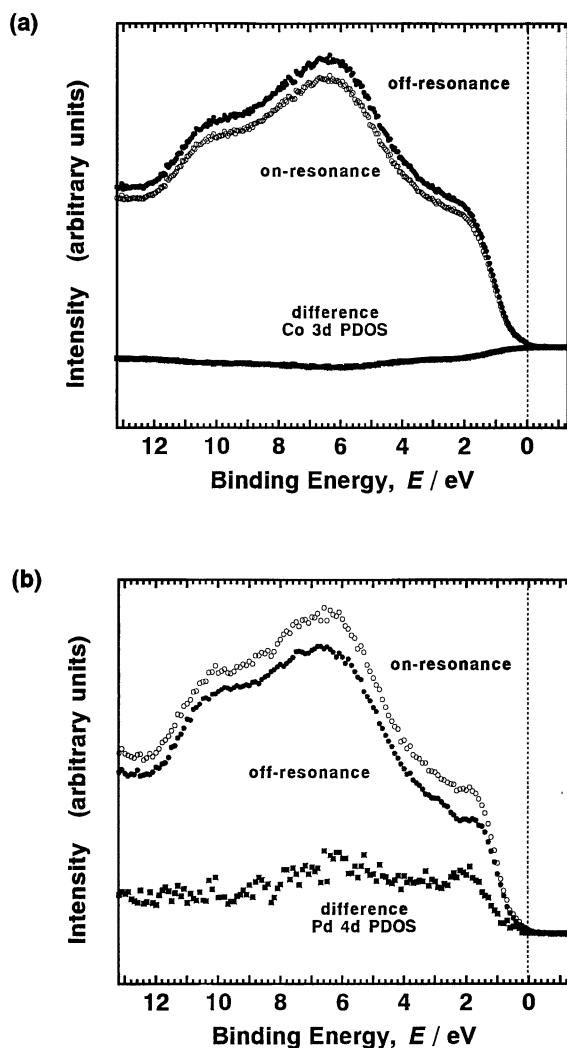


Fig. 7 Resonant photoemission spectra of PdCoO<sub>2</sub> at the photon energies. Difference spectra indicates partial density of states (PDOS) of Co 3d (a) and Pd 4d (b), respectively. (a) near the Co 3p to 3d absorption thresholds, (b) near the Pd 4p to 4d absorption thresholds.

is smaller than that of Pd. Accordingly, the electron correlation in PdCoO<sub>2</sub> is weak compared to that in pure metal Pd. This is interesting because Pd atoms in PdCoO<sub>2</sub> forms two-dimensional layers in the structure.

#### 4. Conclusion

The electronic structure of metallic oxide PdCoO<sub>2</sub> has been investigated by the photoemission and inverse photoemission spectroscopies. It is found that the feature corresponding to the Pd 4d becomes stronger in the spectrum with decreasing the photon energy. This is attributable to the rapid increase

of the ionization cross-section with decreasing the photon energy. It is also found that the finite density of states at the Fermi level is observed at the low photon energy. The resonant photoemission spectra of PdCoO<sub>2</sub> at the photon energies near the Co 3p to 3d and Pd 4p to 4d absorption thresholds indicate no density of states at  $E_F$  in the partial density of states of Co 3d, and finite density of states at  $E_F$  in the partial density of states of Pd 4d, respectively.

These results indicate that there is no pseudogap at the  $E_F$  in the electronic structure of PdCoO<sub>2</sub> and that the main contribution to the density of states is Pd 4d. Accordingly, it is concluded that the origin of the low resistivity of PdCoO<sub>2</sub> is attributable to the itineracy of the Pd 4d electrons.

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