

## Unoccupied Electronic State of Delafossite-Type PdCoO<sub>2</sub> Single Crystal Probed Using Inverse Photoemission Spectroscopy

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The unoccupied electronic state of delafossite-type PdCoO<sub>2</sub> has been studied using inverse-photoemission spectroscopy (IPES). The Fermi edge and the unoccupied density-of-state (DOS) at the Fermi level ( $E_F$ ) are not observed in the IPES spectrum measured at the incidence electron energy ( $E_K$ ) of 100 eV, which corresponds to the Cooper minimum of Pd 4*d*. The finite DOS at  $E_F$  is observed in the IPES spectra measured at the lower  $E_K$ , which the ionization cross section of Pd 4*d* increases. These findings indicate that the Pd 4*d* electron is closely related to the low electrical resistivity of PdCoO<sub>2</sub>.

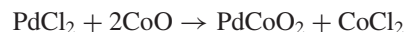
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The delafossite-type oxides have mainly been investigated from the viewpoint of frustrated magnetism because most of them are semiconductive antiferromagnates.<sup>1–3)</sup> On the other hand, there are only a few metallic delafossite-type oxides, such as PdCoO<sub>2</sub> and PtCoO<sub>2</sub>.<sup>4–6)</sup> PdCoO<sub>2</sub> has a characteristic structure constructed of two-dimensional layers with the edge-linked CoO<sub>6</sub> octahedra connected by O–Pd–O dumbbells.<sup>7–11)</sup> The Co<sup>3+</sup> ions in the octahedral site of PdCoO<sub>2</sub> are in a nonmagnetic low-spin state. Hasegawa and co-workers have reported that PdCoO<sub>2</sub> exhibits a metallic temperature dependence of electrical resistivity below 300 K in the directions parallel and perpendicular to the *c*-axis.<sup>9,11)</sup> The electrical resistivities perpendicular to the *c*-axis at 16 and 260 K were 0.55 and 4.69 μΩcm, respectively. The electrical resistivity of PdCoO<sub>2</sub> is lower than that of ReO<sub>3</sub> (~10 μΩcm at 300 K), which is a well known oxide conductors. In recent resonant-photoemission studies, it has been reported that the low electrical resistivity of the density-of-state (DOS) of Pd 4*d* electrons is at the Fermi level ( $E_F$ ).<sup>12–14)</sup> The same situation might also be expected in the unoccupied electronic state.

In this study, the unoccupied electronic state of PdCoO<sub>2</sub> has been studied using inverse-photoemission spectroscopy (IPES). IPES is a powerful technique for investigating the unoccupied electronic structure in the surface state. However, the number of experimental IPES studies of 3*d* transition metal oxides is very few. For this reason, IPES has a weak detecting coefficient and bad resolution. To resolve these problems, we have used a grating with a groove density of 300 lines/mm and a Cs-coated multichannel detector in the soft-X-ray emission spectrometer of IPES system. Thus, we have demonstrated that the Pd 4*d* electron is closely related to the low resistivity of PdCoO<sub>2</sub>, as was previously observed in the resonant-photoemission study.<sup>12,13)</sup>

PdCoO<sub>2</sub> single crystal was grown using the metathetical reaction. 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 crystal was obtained by leaching out the cobalt chloride as a by-product with ethanol or distilled water. A typical side of the grown crystal is approximately 0.6 × 0.6 × 0.1 mm. The details of crystal growth and characterization results have been reported in refs. 7,9 and 11.

The IPES measurements were 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 of the electron was calibrated using an electron energy analyzer. The IPES spectra were measured using a soft-X-ray emission spectrometer, which covers a wide photon energy range from 30 to 800 eV. The spectrometer used Rowland circle geometry that consists of a grating with a groove density of 300 lines/mm and Cs-coated multichannel detector.<sup>15)</sup>

The single crystal was scraped in situ with a diamond file in a vacuum of 4.0 × 10<sup>−10</sup> Torr in order to obtain a clean surface. The measurement temperature was carried out at 30 K. The total resolution of the experimental system was approximately 0.5 eV at the incident electron energy ( $E_K$ ) = 100 eV.

Figure 1(a) shows the excitation energy dependence of the IPES spectra of PdCoO<sub>2</sub>. The abscissa represents the energy above  $E_F$  that was calibrated by the Fermi edge of Au. The intensity of both spectra is normalized by sample current and measurement time. The experimentally determined  $E_F$  is located at the bottom of the conduction band because the sample used in this study has metallic conductivity. A prominent feature  $\alpha$  is observed at ~2.1 eV. The PES spectrum measured at  $E_K$  = 100 eV reflects the unoccupied DOS of the Co 3*d* and O 2*p* states, since the ionization cross section of Pd 4*d* has the Cooper minimum at  $E_K$  = 100 eV.<sup>16)</sup> The intensity of the feature  $\alpha$  increases in the IPES spectra measured at  $E_K$  below 100 eV, for which the

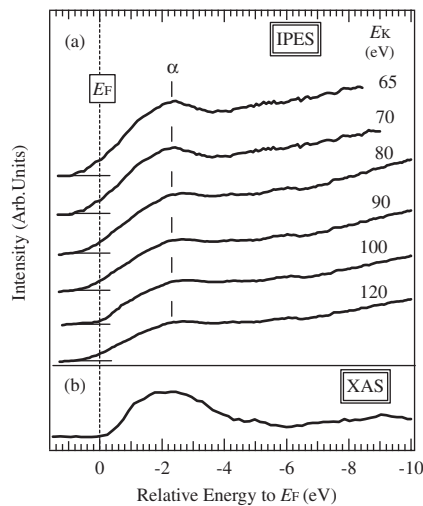


Fig. 1. (a) IPES spectra of PdCoO<sub>2</sub> measured at various kinetic energies of the electron ( $E_K$ ). The abscissa is the energy above Fermi level ( $E_F = 0$ ). (b) O 1s XAS spectrum of PdCoO<sub>2</sub>.

cross sections of Co 3d and Pd 4d increase.

As a reference, the O 1s X-ray absorption (XAS) spectrum of PdCoO<sub>2</sub> is also shown in Fig. 1(b). The dipole selection rule indicates that the O 1s XAS spectrum corresponds to transitions into a O 2p character hybridized with the unoccupied Co 3d or Pd 4d states.<sup>17)</sup>  $E_F$  of the XAS spectrum is determined from the binding energy of the O 1s photoemission peak. The peak position of the XAS spectrum is in agreement with that of the IPES spectra.

Here, we note the DOS at  $E_F$ . The Fermi edge and the unoccupied DOS at  $E_F$  are not observed in either the IPES spectrum measured at  $E_K = 100$  eV or the XAS spectrum. These findings indicate that the Co 3d and O 2p electrons are not related to the low resistivity of PdCoO<sub>2</sub>. The  $E_K$  dependences of the intensities of the feature  $\alpha$  and  $E_F$  are shown in Fig. 2. These curves are obtained by plotting the intensities against  $E_K$ , and correspond to the constant final state (CFS). The intensity of the feature  $\alpha$  increases with decreasing incident electron energy. However, the intensity of  $E_F$  has a minimum at  $E_K = 100$  eV and increases with decreasing  $E_K$  below 100 eV. This behavior is in agreement

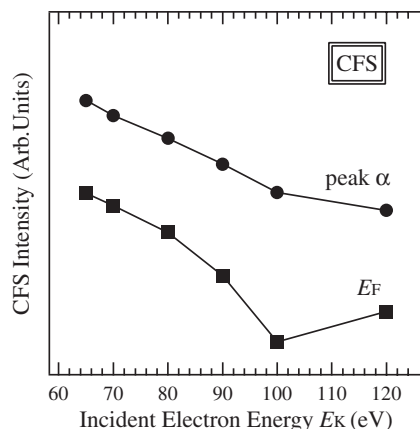


Fig. 2. CFS intensities as a function of  $E_K$  of  $E_F$  (closed square) and peak  $\alpha$  (closed circle) estimated from Fig. 1.

with the result of the ionization cross section of the Pd 4d state.<sup>16)</sup> A similar situation has also been observed in the resonant-photoemission spectra on the same sample.<sup>12,13)</sup>

The above results indicate that the Pd 4d electron contributes to the low electrical resistivity of PdCoO<sub>2</sub>. In term of crystal structure, Pd is on the site of the linear O–Pd–O chain with an electronic configuration of monovalent Pd<sup>1+</sup> and Co is an octahedral site with a trivalent low-spin state of Co<sup>3+</sup>.<sup>9,13)</sup> On one hand, the 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 dumbbells. As a result, on the basis of the ligand field theory, the metallic behavior of PdCoO<sub>2</sub> might be due to a half-filled band formed by *s*–*d* hybridized orbitals originated from the monovalent Pd ions and coordinated oxygens, although the contribution of the *s*-orbital has not been clarified in this study.

In conclusion, we have studied the unoccupied electronic state of PdCoO<sub>2</sub> using IPES. The Fermi edge and DOS at  $E_F$  are not observed in either the IPES spectrum measured at  $E_K = 100$  eV or the O 1s XAS spectrum. However, the unoccupied DOS at  $E_F$  is observed in the IPES spectra measured at low  $E_K$ , which the ionization cross section of Pd 4d increases. These results indicate that the Pd 4d electron is related to the low electrical resistivity of PdCoO<sub>2</sub>.

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- 1) M. Mekata, N. Yaguchi, T. Takagi, S. Mitsuda and H. Yoshizawa: *J. Magn. Mater.* **104–107** (1992) 823.
- 2) S. Mitsuda, M. Mase, T. Uno, H. Kitazawa and H. A. Katori: *J. Phys. Soc. Jpn.* **69** (2000) 33.
- 3) M. Hasegawa, M. I. Batrashedevich, T. R. Zhao, H. Takei and T. Goto: *Phys. Rev. B* **63** (2001) 184437.
- 4) R. D. Shannon, D. B. Rogers and C. T. Prewitt: *Inorg. Chem.* **10** (1971) 713.
- 5) C. T. Prewitt, R. D. Shannon and D. B. Rogers: *Inorg. Chem.* **10** (1971) 719.
- 6) D. B. Rogers, R. D. Shannon, C. T. Prewitt and J. L. Gillson: *Inorg. Chem.* **10** (1971) 723.
- 7) M. Tanaka, M. Hasegawa and H. Takei: *J. Phys. Soc. Jpn.* **65** (1996) 3973.
- 8) M. Tanaka, M. Hasegawa and H. Takei: *J. Cryst. Growth* **173** (1997) 440.
- 9) M. Tanaka, M. Hasegawa, T. Higuchi, T. Tsukamoto, Y. Tezuka, S. Shin and H. Takei: *Physica B* **245** (1998) 157.
- 10) M. Hasegawa, M. Tanaka and H. Takei: *J. Cryst. Growth* **226** (2001) 277.
- 11) M. Hasegawa, I. Inagawa, M. Tanaka, I. Shirotani and H. Takei: *Solid State Commun.* **121** (2002) 203.
- 12) T. Higuchi, T. Tsukamoto, M. Tanaka, H. Ishii, K. Kanai, Y. Tezuka, S. Shin and H. Takei: *J. Electron Spectrosc. Relat. Phenom.* **92** (1998) 71.
- 13) M. Hasegawa, T. Higuchi, M. Tanaka, T. Tsukamoto, S. Shin and H. Takei: *Mater. Trans.* **42** (2001) 101.
- 14) T. Higuchi, D. Baba, Y. Yokoyama, M. Hasegawa, H. Takei, A. Fukushima, S. Shin and T. Tsukamoto: *Jpn. J. Appl. Phys.* **42** (2003) 5698.
- 15) K. Kanai and S. Shin: *J. Electron Spectrosc. Relat. Phenom.* **117–118** (2001) 383.
- 16) J. J. Yeh and I. Lindau: *Atomic Data Nucl. Data Tables* **32** (1993) 1.
- 17) T. Higuchi, S. Nozawa, T. Tsukamoto, H. Ishii, R. Eguchi, Y. Tezuka, S. Yamaguchi and S. Shin: *Phys. Rev. B* **66** (2002) 153105.