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Orbital character of the conduction band of delafossite $PdCoO_2$ studied by polarization-dependent soft x-ray absorption spectroscopy

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We present the x-ray absorption spectra that show the Co valence state and the orbital character of the conduction band of delafossite $PdCoO_2$. The Co $2p$ x-ray absorption spectra of $PdCoO_2$ and $PtCoO_2$ show that the Co ions have the trivalent low-spin configuration. The polarization-dependent O $1s$ absorption spectra reveal that the unoccupied density of states (DOS) near the Fermi level consists mainly of the Pd $4d_{3z^2-r^2}$ states. The experimental O $2p_z$ partial DOS (PDOS) is extracted from the polarization-dependent O $1s$ spectra and is compared with the theoretical PDOS by the local-density approximation, showing a good agreement. These observations provide a consistent picture on the origin of the good conductivity of the delafossite oxides.

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Metallic conductivity of delafossites was first reported in $PdCoO_2$ and $PtCoO_2$ by Shannon *et al.*,[1–3] which has attracted much interest in that most of delafossite oxides are magnetically frustrated semiconductors. After a decade, the reinvestigation of the transport properties of $PdCoO_2$ found that the in-plane resistivity of the oxide at room temperature is the lowest in normal-state oxides and is even lower than that of Pd metal.[4,5] Another intriguing feature of $PdCoO_2$ is the anisotropy in the conductivity. Because delafossites have a layered structure, there is an intrinsic reason for the anisotropy. However, in the cases of $PdCoO_2$ and $PtCoO_2$, the anisotropy measured by the ratio of the in-plane ($\rho_\parallel$) to out-of-plane conductivity ($\rho_\perp$) is as large as ~150. It is unlikely that the large anisotropy arises from the two-dimensional structure only.

The succedent studies have mainly focused on the origin of the anisotropic good conductivity.[6–8] Tanaka *et al.*[6] have noted that their photon energy-dependent photoemission spectra have no spectral weight at the Fermi level when the photon energy is ~100 eV, which corresponds to the Cooper minimum of the Pd $4d$ orbitals. Thus, the density of states (DOS) at the Fermi level is attributed to the Pd $4d$ states, and so-called s-d hybridization model has been proposed in order to explain the anisotropic conductivity. Their model is based on the monovalent Pd ions and trivalent low-spin Co ions, which are inferred by photon energy-dependent photoemission spectroscopy and Co $2p$ x-ray absorption spectroscopy (XAS), respectively. However, their reported spectra do not seem to fully support their arguments because of the impurities in their polycrystalline samples. Recently, an angle-resolved photoemission spectroscopy (ARPES) study has been reported to explain the anisotropic high conductivity of the $PdCoO_2$,[8] in which an explicit connection between the electronic structure and the in-plane conductivity was demonstrated. The dispersion of the band crossing the Fermi level was observed by ARPES and was compared with the theoretical band structure calculated by the local-density approximation (LDA) method, confirming that the conduction band has mostly Pd $4d$ characters. The ARPES study gives a consistent band structure with the recently reported *ab initio* calculation result by Eyert *et al.*[9]

At present, most of the main issues on the $PdCoO_2$ are thought to be resolved by the ARPES study. However, ARPES observes only the occupied states of the electronic structure, so experimental information on the unoccupied states needs providing as complementary evidence for the physical properties of the $PdCoO_2$. Here, we present high-resolution x-ray absorption spectra of $PdCoO_2$ at O K and Co L edges in order to supply spectroscopic evidence for the monovalent Pd ions and trivalent low-spin Co ions in delafossite $PdCoO_2$. Our x-ray absorption spectra clarify that the conduction band has Pd $4d_{3z^2-r^2}$ character.

The single crystals of $PdCoO_2$ were obtained from the same sample batch reported in the ARPES study.[8] The single crystals of $PtCoO_2$ were synthesized by the metathetical reaction method as described in the Ref. 4. The obtained crystals are silvery hexagonal plates as small as ~0.1 mm in diameter. The single phase was checked by x-ray diffraction. The x-ray absorption experiments were performed on undulator beam line 2A at the Pohang Light Source. In the case of $PdCoO_2$, the crystals were cleaved *in situ* by the top post method under the pressure of $\sim 5.0 \times 10^{-10}$ Torr and at the temperature of 80 K. Due to the two-dimensional structure of the crystals, the cleaved surface was shinny and well ori-

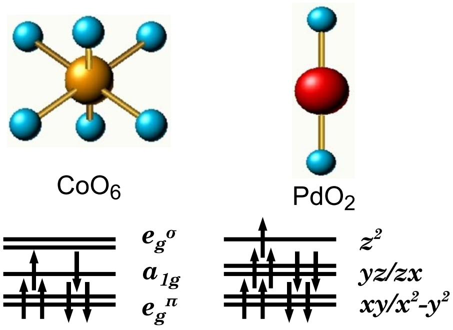

FIG. 1. (Color online) (Left) CoO_6 cluster and the energy level diagram of Co 3*d* states in delafossite $PdCoO_2$. (Right) PdO_2 cluster and the energy diagram of Pd 4*d* states.

ented. In the case of $PtCoO_2$, no surface preparation was carried out due to the small size of the samples. The photon energy resolution was set to ~0.2 eV. All the absorption spectra were recorded in the total electron yield mode and were normalized by the incident photon flux.

The crystal structure of $PdCoO_2$ ($PtCoO_2$) consists of a triangular CoO_2 layer and a triangular PdO_2 (PtO_2) layer. The two layers are stacked up alternately, sharing all the oxygen ions. In the CoO_2 layer, a Co ion is in the center of a trigonally distorted oxygen octahedron as shown in Fig. 1. The octahedron shares its edges to form the triangular lattice. A Pd (Pt) ion sits on each oxygen ion of the triangular lattice, linking two CoO_2 layers along the normal direction as shown in Fig. 1. The energy level of the Co 3*d* states under a crystal electric field with D_{3d} symmetry splits into three groups, namely, double e_g^{π}, single a_{1g}, and double e_g^{σ} from low- to high-energy level. If we assume that the Co ions are trivalent with the low-spin configuration, the six *d* electrons fully occupy the e_g^{π} and a_{1g} states. The PdO_2 dumbbell can be regarded as a limiting case of a tetragonally distorted octahedron. In that case, the fivefold degenerated Pd 4*d* orbitals split into d_{xy/x^2-y^2}, $d_{yz/zx}$, and $d_{3z^2-r^2}$ states. Thus, a monovalent Pd ion has nine *d* electrons with one $d_{3z^2-r^2}$ hole in the 4*d* orbitals. One noticeable feature is that the $d_{3z^2-r^2}$ hole in the Pd ions is directionally anisotropic while the fully empty e_g^{σ} holes in the Co ions are isotropic in the absorption signals. This contrastive feature will be exploited in the analysis of our XAS spectra.

The *d* electron configuration of the Co ions in $PdCoO_2$ and $PtCoO_2$ is definitely determined by Co 2*p* XAS. The XAS spectra of $PdCoO_2$ with photon polarization vector parallel to the *ab* plane ($E \parallel ab$) and *c* axis ($E \parallel c$), respectively, are presented in Fig. 2 together with the spectra of $LaCoO_3$, $PtCoO_2$, and CoO as reference data. The XAS spectra of $LaCoO_3$ and CoO are taken from the literatures.[10,11] The two XAS spectra of $PdCoO_2$ show a very similar shape to that of $LaCoO_3$. Since $LaCoO_3$ is taken as a typical material that has trivalent low-spin Co ions ($3d^6$, $S=0$), the similar spectral shape indicates that a Co ion in $PdCoO_2$ is also trivalent with the low-spin configuration. A Co 2*p* XAS spectrum of $PdCoO_2$ was reported in the previous study,[6] but it looks different from ours due to the existence of divalent Co impurities in their polycrystalline samples. The XAS spectrum of $PtCoO_2$ looks similar to those of $PdCoO_2$ except for the low photon energy part of the L_3 region. We attribute this low photon energy structure as Co^{2+} impurities, possibly originating from $CoCl_2$. As we described above, the crystal size of $PtCoO_2$ is too small, so the measurements were not performed on cleaved surfaces. In addition, the synthesis method produces $CoCl_2$ as a by product, which is not completely removed on the surfaces of the small crystals. If we subtract the $PdCoO_2$ spectrum from that of $PtCoO_2$, a typical XAS spectrum of high-spin Co^{2+} ion is obtained as shown in Fig. 2. Comparison with the CoO spectrum, which corresponds to a high-spin d^7 configuration, confirms this conjecture.

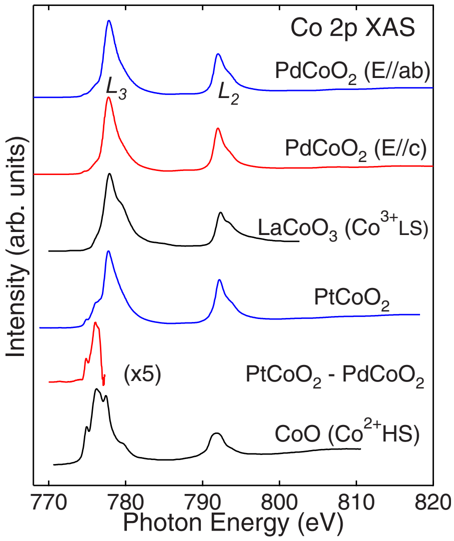

FIG. 2. (Color online) Co 2*p* XAS spectra of $PdCoO_2$ and $PtCoO_2$.

Further, the insensitivity of the spectral shape to the polarization direction supports the trivalent low-spin configuration of the Co ions. Generally, the *d* orbital anisotropy is well probed with polarized x rays, but it is not applicable to the case of an isotropic hole distribution. The linearly polarized absorption intensity from a 2*p* core state to an empty *d* state is proportional to the number of *d* holes projected to the polarization axis. The projected *d* orbital charge distributions are given by $4(1-\frac{7}{4}Q_{\alpha}^{i})$.[12] Here, α is the photon polarization direction ($=x$, y, or z) and $Q_{\alpha}^{i}=\langle d_i|Q_{\alpha\alpha}|d_i\rangle$, where $i=xy$, yz, zx, x^2-y^2, or $3z^2-r^2$, and $Q_{\alpha\beta}=\delta_{\alpha\beta}-3r_{\alpha}r_{\beta}/r^2$ is the symmetric quadrupole tensor with zero trace. The fully empty e_g^{σ} states under D_{3d} symmetry of a trigonally distorted CoO_6 cage are represented by $\frac{1}{\sqrt{2}}(|d_{x^2-y^2}\rangle \pm i|d_{3z^2-r^2}\rangle)$ in the local coordinate system.[13] Then, the absorption coefficient probed with $x(y)$-polarized photons is proportional to $2(1-\frac{7}{4}Q_{x(y)}^{x^2-y^2})+2(1-\frac{7}{4}Q_{x(y)}^{3z^2-r^2})=3+1$. Likewise, the coefficient for z polarization is $2(1-\frac{7}{4}Q_{z}^{x^2-y^2})+2(1-\frac{7}{4}Q_{z}^{3z^2-r^2})=0+4$. That is, the absorption coefficient of the fully empty e_g^{σ} states is isotropic, and the absorption spectra do not give any difference for this d^6 low-spin case.

On the contrary, O 1*s* XAS spectra exhibit significant polarization dependence which can be exploited to extract the orbital character of the conduction band of $PdCoO_2$. In the inset of Fig. 3, wide range absorption spectra with $E \parallel ab$ (red

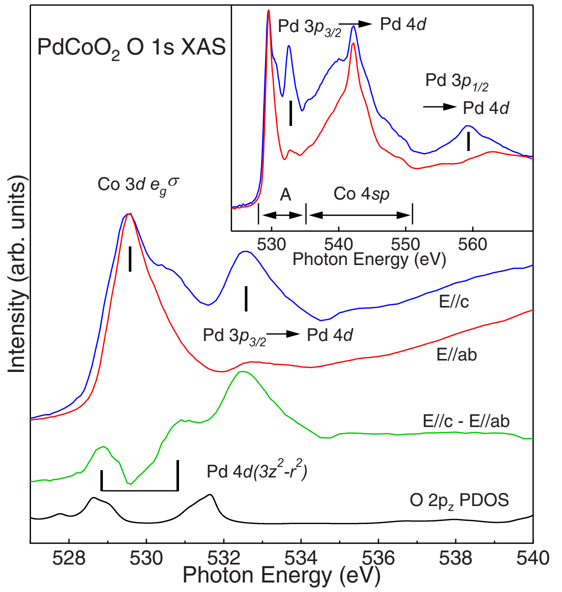

FIG. 3. (Color online) Polarization-dependent O 1s XAS spectra of PdCoO$_2$.

lower line) and $E \| c$ (blue upper line) are displayed. In this energy range, the Pd $3p \rightarrow$ Pd $4d$ absorption peaks (black vertical bars) at 532 and 560 eV are also observed. Apart from the Pd $3p \rightarrow 4d$ peaks, the spectra are divided into two regions, namely, Co $3d$/Pd $4d$ region, denoted as A, and Co $4sp$ region. In Fig. 3, a closeup view of region A (blue and red lines) is presented together with the difference spectrum (green line), and the theoretical O $2p_z$ partial density of states (PDOS) calculated by the LDA method (black line). The PDOS is broadened with a Lorentzian of 0.3 eV in full width at half maximum to simulate a core-hole lifetime effect. The two absorption spectra, $E \| ab$ and $E \| c$, commonly show a large peak at 530 eV, which are assigned to Co $3d$ e_g^σ states. However, a moderate difference between the two spectra is observed around the e_g^σ peak. To see the difference more clearly, we subtract the $E \| ab$ spectrum from the $E \| c$ spectrum and obtain the difference spectrum. This approximately removes the DOS of the Co $3d$ e_g^σ orbitals in the spectrum.

The isotropy of the polarization-dependent O 1s XAS spectra for the fully empty e_g^σ states can be checked as follows. Since O 1s absorption spectroscopy uses the absorption process from O 1s to O 2p states, the empty d states are observed through the hybridization between O 2p and transition metal d orbitals. For a given polarization mode, the absorption intensity is proportional to the sum of square of the polarization direction component of all overlap integrals between p and d orbitals. The orbital geometries for a CoO$_6$ octahedron in the local coordinate system is shown in Fig. 4. Using a symmetry argument, it is easily checked that $d_{x^2-y^2}$ hole has nonzero overlap integrals with p_x^1 and p_y^2, and $d_{3z^2-r^2}$ with p_x^1, p_y^2, and p_z^3. Here, the superscript refers the oxygen number in Fig. 4. Then, the square sum of the integrals projected to the polarization direction is $|\langle p_x^1|H|d_{x^2-y^2}\rangle|^2 + |\langle p_x^1|H|d_{3z^2-r^2}\rangle|^2$ for $E \| ab$ and $\frac{2}{3}|\langle p_x^1|H|d_{x^2-y^2}\rangle|^2 + \frac{1}{3}|\langle p_z^3|H|d_{3z^2-r^2}\rangle|^2 + \frac{2}{3}|\langle p_x^1|H|d_{3z^2-r^2}\rangle|^2$ for $E \| c$, respectively.

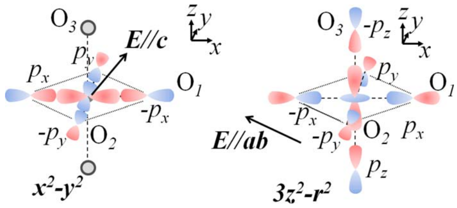

FIG. 4. (Color online) Co 3d-O 2p bonded orbital geometries in a CoO$_6$ octahedron.

The equality of the two square sums is easily obtained if $|\langle p_z^3|H|d_{3z^2-r^2}\rangle|^2 = |\langle p_x^1|H|d_{x^2-y^2}\rangle|^2 + |\langle p_x^1|H|d_{3z^2-r^2}\rangle|^2$, which can be confirmed by the threefold symmetry along the (111) direction. Although we evaluate the integrals under O_h symmetry for convenience, the result also holds for D_{3d} symmetry because we do not use higher symmetry properties than those of D_{3d}. For more general cases, the interatomic matrix elements table can be referred.[14]

Meanwhile, the Pd $4d_{3z^2-r^2}$ state has two large lobes along the z direction, so the nonzero overlap integrals exist only in the $E \| c$ mode. Note that here the global coordinate system ($z \| c$) is used and that there is no in-plane oxygen in the PdO$_2$ case. Thus, the difference curve can be approximately regarded as the Pd 4d states projected to the O $2p_z$ orbitals. The difference curve shows a two-peak structure near 530 eV, which is assigned to the $d_{3z^2-r^2}$ state. This assignment gives a good agreement with the theoretical band calculation result. The two-peak structure in the O $2p_z$ PDOS is very similar to the measured difference curve. The large spectral increase of the Pd $3p_{3/2,1/2} \rightarrow 4d$ absorption peaks from $E \| ab$ to $E \| c$ also supports our interpretation. In the $3p \rightarrow 4d$ absorption process, the exactly same argument for the anisotropy of the absorption signal to the $2p \rightarrow 3d$ process is applicable. In the Pd 3p case, only $d_{3z^2-r^2}$ hole remains in a Pd ion, so there is a large hole anisotropy for the photon polarization direction in the absorption spectra.[12] Although the overlap of the two absorption edges keep us from analyzing the XAS spectra quantitatively, all the spectroscopic features presented in this work confirm that the Co ions of the delafossite PdCoO$_2$ are trivalent with the low-spin configuration and that the orbital character of the conduction band is Pd $4d_{3z^2-r^2}$ state. These observations are consistent with the recent ARPES study on the electronic structure of the PdCoO$_2$, and provide complementary evidence for the origin of the good conductivity of the delafossite oxides.

In summary, we present the polarization-dependent soft XAS spectra which reveal the orbital character of the conduction band of delafossite PdCoO$_2$. The Co 2p XAS spectra show that the Co ions have the trivalent low-spin configuration. The O $2p_z$ PDOS is extracted from the polarization-dependent O 1s spectra and is compared with the theoretical PDOS by the LDA calculation, showing a good agreement. These observations give a consistent picture on the origin of the good conductivity of PdCoO$_2$ and PtCoO$_2$.

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