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Electronic structure of Ca_3CoXO_6 (X=Co, Rh, Ir) studied by x-ray photoemission spectroscopy

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We have obtained Co 2p, Rh 3d, Ir 4f, and valence-band x-ray photoemission spectra of $Ca_3Co_2O_6$, Ca_3CoRhO_6, Ca_3CoIrO_6, and Sr_3ZnIrO_6 in order to determine the valence states of Co. The spectral features are consistent with the picture that Co is in the trivalent state at both trigonal prismatic and octahedral sites with high- and low-spin states, respectively, in $Ca_3Co_2O_6$, whereas Co is in the high-spin Co^{2+} state for Ca_3CoRhO_6 and Ca_3CoIrO_6. This conclusion resolves a recent controversy regarding the valence and spin states of Co in $Ca_3Co_2O_6$ and Ca_3CoRhO_6. This is the first x-ray photoemission spectroscopic study of this family of oxides.

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Recently, Co containing spin-chain compounds, e.g., Ca_3MXO_6 (M=Co, X=Co, Rh, and Ir), obtained from the K_4CdCl_6-derived rhombohedral structure, have been attracting a lot of attention due to many exotic features exhibited by them in their properties (see, for instance, Refs. 1–25). These compounds are characterized by the presence of M-X spin chains running along the c direction intervened by Ca ions, with a (distorted) trigonal prismatic and octahedral coordination around M and X, respectively. The compound $Ca_3Co_2O_6$ is also found to be characterized by large thermopower and therefore there are discussions in the literature about the applicability of this compound or its derivatives for thermoelectric applications.[12]

A survey of the current literature, which can be found in Ref. 19, suggests that there is a dispute, particularly aroused by a report of Vidya *et al.*,[17] on the nature of valence/spin states of Co in $Ca_3Co_2O_6$, broadly speaking, between two possibilities: (i) Co at both the sites is trivalent,[3,18] (ii) Co exists in the high-spin 2+ and low-spin 4+ states (since the octahedral coordination in this compound is known to favor the low-spin state, according to crystal-field calculations).[17]

In order to enable further understanding of this compound, particularly for any theoretical framework, it is crucial to resolve this issue. Recently, ^{59}Co NMR measurements were performed[19] keeping this issue in mind, and the results established that Co is in the high- and low-spin d^6 configurations at the M and X sites, respectively, at least below 15 K. However, the NMR signal could not be observed at higher temperatures and there is an urgent need to explore whether there is a change in the valence/spin state of Co (favoring the second alternative) as the temperature is increased, as often discussed in perovskite-based cobaltites.

A survey of the literature for Ca_3CoRhO_6 suggests that there are similar disputes in this compound as well. While the magnetic susceptibility data[20] indicates a divalent state for the Co site, the neutron-diffraction experiment[23] and band calculations[18] appear to favor the trivalent (high-spin) state. Similar to $Ca_3Co_2O_6$, Ca_3CoRhO_6 has two possibilities: (i) Co and Rh are trivalent, (ii) Co exists in the high-spin 2+ state and Rh in the low-spin 4+ state.

In order to address these issues in the high-temperature range of these compounds, we have performed photoemission measurements at room temperature. The results for $Ca_3Co_2O_6$ conclusively establish that Co is indeed in the trivalent state favoring the first possibility, even at 300 K, thereby resolving the major controversy. On the other hand, the photoemission data for Ca_3CoRhO_6 indicate that Co is in the divalent state favoring the second possibility. We have in addition carried out similar measurements on Ca_3CoIrO_6,[10,11] as well as on Sr_3ZnIrO_6, as suitable reference materials, since it is known that Co (Zn) and Ir are in the 2+ and 4+ states in Ca_3CoIrO_6 and Sr_3ZnIrO_6.[24,25]

Polycrystalline samples were synthesized by a solid-state reaction[8] and characterized by x-ray diffraction to be single phase. The photoemission spectroscopy measurements for Ca_3CoXO_6 (X=Co, Rh and Ir) were performed at room temperature using a JPS9200 spectrometer equipped with a monochromatized Al $K\alpha$ x-ray source ($h\nu$=1486.6 eV). The total-energy resolution was ~0.6 eV. The pressure of the spectrometer was $\sim 8\times 10^{-10}$ mb during the measurements. The polycrystalline samples were fractured *in situ* in order to obtain clean surfaces. All photoemission data were collected within 24 h after fracturing. The photoemission spectroscopy for Sr_3ZnIrO_6 has been performed at room temperature using a custom built multitechnique VSW electron spectrometer with a resolution of 0.5 eV and a vacuum of $\sim 8\times 10^{-10}$ mb.

The high-spin Co^{2+} state is known to result in an intense satellite structure in the Co 2p XPS spectrum.[26] The main peak at ~780 eV and the satellite structure at ~787 eV are

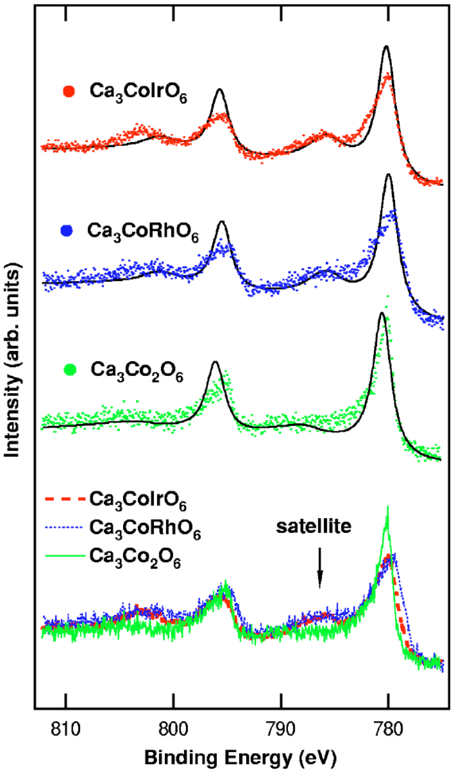

FIG. 1. Co $2p$ photoemission spectra of $Ca_3Co_2O_6$, Ca_3CoRhO_6, and Ca_3CoIrO_6. The calculated spectra are shown by solid curves. The Co $2p$ spectra of Ca_3CoRhO_6 and Ca_3CoIrO_6 are overlaid with that of $Ca_3Co_2O_6$ to show the difference in the satellite region.

derived from charge-transfer-type screening on the Co $2p$ core hole. The main and satellite peaks correspond to the well screened and poorly screened final states, respectively. In contrast to the Co^{2+} state, the satellite structure of the Co $2p$ XPS spectrum for the Co^{3+} state has only a small intensity.[26–28] The difference arises from an enhanced screening in the case of Co^{3+} due to a larger Co $3d$–O $2p$ hopping strength and a smaller charge-transfer energy compared to those for the Co^{2+} state.[26,29,30] Therefore the Co $2p$ XPS spectrum is very useful to distinguish the two possibilities: M and X are trivalent or M exists in the high-spin 2+ state and X in the low-spin 4+ state.

Figure 1 shows the Co $2p$ XPS spectra of $Ca_3Co_2O_6$, Ca_3CoRhO_6, and Ca_3CoIrO_6. The Co $2p$ XPS spectra of Ca_3CoRhO_6 and Ca_3CoIrO_6 show intense satellite structures that are very similar to that of CoO with the high-spin Co^{2+} configuration and are very different from that of $LiCoO_2$ with the low-spin Co^{3+} configuration.[26,27] This result indicates that Ca_3CoRhO_6 and Ca_3CoIrO_6 have the high-spin Co^{2+} species. On the other hand, the satellite structure is not visible at all in $Ca_3Co_2O_6$ as shown in Fig. 1. The apparent absence of the satellite shows that $Ca_3Co_2O_6$ has no high-spin Co^{2+} site and consists solely of Co^{3+}. These observations for the Co $2p$ spectra indicate that the prismatic Co site is in the Co^{2+} high-spin configuration in both Ca_3CoRhO_6 and Ca_3CoIrO_6. In contrast, $Ca_3Co_2O_6$ consists of Co^{3+} ions only.

In order to confirm this conclusion, we have performed configuration-interaction (CI) calculations on the prismatic and octahedral CoO_6 cluster models. We have followed the conventional CI method that has been widely used to analyze photoemission spectra of transition-metal oxides.[26,29,30] In the CI approach, the ground state is expressed by a linear combination of d^n, $d^{n+1}L$, $d^{n+2}L^2$, etc., where L denotes a hole at the O $2p$ level. The values of n are 6 and 7 for the Co^{3+} and Co^{2+} cases, respectively. The energy difference between d^n and $d^{n+1}L$ is given by charge-transfer energy Δ and that between $d^{n+1}L$ and $d^{n+2}L^2$ by $\Delta+U$, where U is the Coulomb repulsion energy between the Co $3d$ electrons. The final states are expressed by linear combinations of cd^n, $cd^{n+1}L$, $cd^{n+2}L^2$ etc., where c denotes a hole at the Co $2p$ core level. The energy difference between cd^n and $cd^{n+1}L$ is given by $\Delta-Q$ and that between $cd^{n+1}L$ and $cd^{n+2}L^2$ by $\Delta-Q+U$ where Q is the Coulomb energy between the Co $2p$ core hole and the Co $3d$ electron. Here, the ratio U/Q is fixed at ~0.7. The transfer integrals between cd^n and $cd^{n+1}L$, etc., are expressed by $(pd\sigma)$ and $(pd\pi)$ with the ratio $(pd\sigma)/(pd\pi)$ of -2.16. As a consequence, the Co $2p$ spectrum can be calculated with the three adjustable parameters Δ, U, and $(pd\sigma)$. As shown in Fig. 1, the calculated spectra can explain the satellite structure observed in Ca_3CoRhO_6 and Ca_3CoIrO_6. The obtained parameters are $\Delta=5.0$ eV, $U=6.5$ eV, $(pd\sigma)=-1.2$ eV for Ca_3CoRhO_6 and $\Delta=5.0$ eV, $U=6.5$ eV, $(pd\sigma)=-1.1$ eV for Ca_3CoIrO_6. These values are reasonable for Co^{2+} oxides. On the other hand, it is almost impossible to fit the Co $2p$ spectrum of $Ca_3Co_2O_6$ by adjusting the parameters since it has the contributions from the two different Co sites. Here, we estimate $(pd\sigma)$ for the two Co sites using Harrison's rule. Also we employ typical Δ value for Co^{3+} oxides.[26,29,30] Using the parameter sets of $\Delta=2.0$ eV, $U=6.5$ eV, $(pd\sigma)=-1.7$ eV for the octahedral site (low-spin Co^{3+}) and $\Delta=2.0$ eV, $U=6.5$ eV, $(pd\sigma)=-1.3$ eV for the prismatic site (high-spin Co^{3+}), the calculated Co $2p$ spectrum agrees well with the experimental result as shown in Fig. 1.

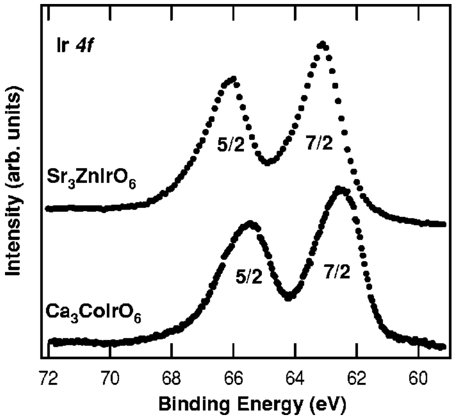

FIG. 2. Ir $4f$ photoemission spectra of Ca_3CoIrO_6 and Sr_3ZnIrO_6.

Figure 2 shows the Ir $4f$ XPS spectra of Ca_3CoIrO_6 and Sr_3ZnIrO_6. Since Sr and Zn are definitely divalent, Ir in Sr_3ZnIrO_6 must be tetravalent or Ir^{4+}. Therefore Sr_3ZnIrO_6 is a good reference sample to judge whether Ir is trivalent or tetravalent in Ca_3CoIrO_6. As shown in Fig. 2, the binding

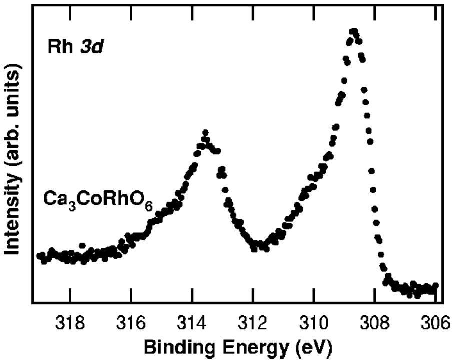

FIG. 3. Rh 3d photoemission spectra of Ca_3CoRhO_6.

energy of Ir $4f_{7/2}$ is 62.5 eV for Ca_3CoIrO_6 and is 63.1 eV for Sr_3ZnIrO_6. The valence-band spectrum of Sr_3ZnIrO_6 is shifted by $\sim$0.5 eV to the higher binding energy side compared to that of Ca_3CoIrO_6 (see below). The binding-energy shift in Sr_3ZnIrO_6 is probably caused by charging effect. After correction for the binding-energy shift, the Ir $4f_{7/2}$ binding energy of Sr_3ZnIrO_6 becomes $\sim$62.6 eV, a value which is very close to the Ir $4f_{7/2}$ binding energy of Ca_3CoIrO_6. This result suggests that Ir in Ca_3CoIrO_6 also has Ir^{4+}. This argument with the Ir 4f spectra naturally leads us to the conclusion that the octahedral Ir site has Ir^{4+} ions and, consequently, the prismatic Co site should be in Co^{2+} configuration. This result is consistent with the conclusion from magnetic susceptibility experiments.[10] Therefore comparison of the Ir^{4+} spectra between Ca_3CoIrO_6 and Sr_3ZnIrO_6 also supports the valence states obtained from the Co 2p spectra. Figure 3 shows the Rh 3d XPS spectra of Ca_3CoRhO_6. The Rh $3d_{5/2}$ binding energy of Ca_3CoRhO_6 (308.7 eV) is much higher than that of Rh_2O_3 (308.2 eV) and is rather close to that of RhO_2 (308.5 eV).[31] This result also suggests that the valence state of the octahedral Rh site should be far away from 3+, which means that Rh is 4+. A higher binding energy compared to RhO_2 also should not be taken as an indication for a still higher valence, as this yields an unphysical valence for Co (close to 1+). This conclusion that is consistent with that from the Co 2p spectra.

Figure 4 shows the valence-band XPS spectra of $Ca_3Co_2O_6$, Ca_3CoRhO_6, Ca_3CoIrO_6, and Sr_3ZnIrO_6. Since the photoionization cross sections of the Rh 4d and Ir 5d orbitals are much larger than that of the Co 3d orbital at photon energy of 1486.6 eV, the valence-band spectra of Ca_3CoRhO_6, Ca_3CoIrO_6, and Sr_3ZnIrO_6 are dominated by contributions from the octahedral Rh or Ir sites. On the other hand, in the valence-band spectrum of $Ca_3Co_2O_6$, contributions from the octahedral Co site are comparable to those from the prismatic Co site. The energy splitting between structures A and B in Ca_3CoIrO_6 and Sr_3ZnIrO_6 is larger than that between structures A'' and B'' in $Ca_3Co_2O_6$. Structures A (A'') and B (B'') can be assigned to the antibonding and bonding bands of the Ir 5d (Co 3d) and O 2p orbitals. The energy splitting becomes smaller in going from Ca_3CoIrO_6 to Ca_3CoRhO_6 to $Ca_3Co_2O_6$ since the hybridization strength with the O 2p orbitals becomes smaller in going from Ir 5d to Rh 4d to Co 3d. Another important point is that sharp structures A, A', and A'' are rather intense and located just below the Fermi level in Ca_3CoXO_6 (X=Co, Rh, Ir). For typical low-spin compounds such as $LiCoO_2$, the valence-band XPS spectra commonly have a sharp and intense peak (with a width of $\sim$1.5 eV) just below the Fermi level that is assigned to the t_{2g} band fully occupied by electrons.[26] On the other hand, since the t_{2g} and e_g bands are partially occupied in the high-spin configurations, an antibonding band for a high-spin state consists of t_{2g} and e_g components and is not so sharp as that for the low-spin state. In addition, for the Co^{3+} case, while the low-spin ground state ($S=0$) has only the $S=1/2$ final state, the high-spin ground state ($S=2$) gives the $S=5/2$ and $S=3/2$ final states that are split by the exchange interaction. As a result, for the high-spin Co^{3+} state, one should have seen a much broader peak near the Fermi level, which is not observed. Therefore, for Ca_3CoXO_6 (X=Co, Rh, Ir), the existence of structures A, A', and A'' indicates that one of the Co and X sites should have a low-spin configuration in which the t_{2g} band is fully (or almost fully) occupied and the e_g band is fully unoccupied by electrons. Since it is well established that the prismatic M site is in the high-spin state, the above argument leads us to the conclusions that the Ir^{4+} and Rh^{4+} sites in Ca_3CoXO_6 (X=Rh, Ir) take the low-spin $d^5(t_{2g}^5)$ state and that the octahedral Co^{3+} site in $Ca_3Co_2O_6$ takes the low-spin $d^6(t_{2g}^6)$ state.

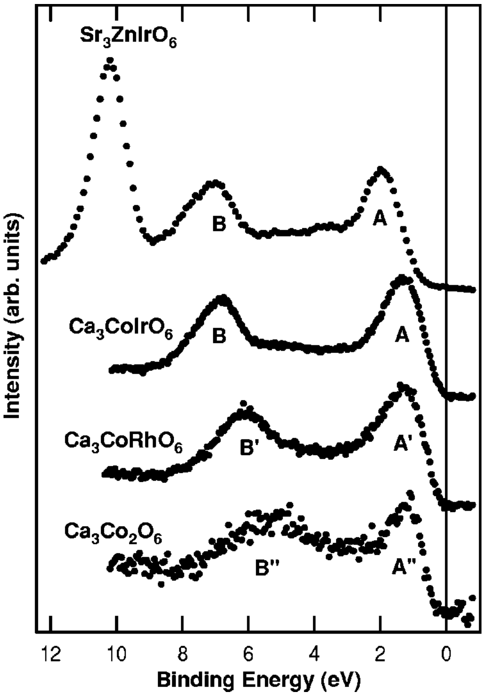

FIG. 4. Valence-band photoemission spectra of $Ca_3Co_2O_6$, Ca_3CoRhO_6, Ca_3CoIrO_6, and Sr_3ZnIrO_6.

In conclusion, we have studied the electronic structure of quasi-one-dimensional Co oxides Ca_3CoXO_6 (X=Co, Rh, Ir) using x-ray photoemission spectroscopy. The Co 2p spectra of Ca_3CoRhO_6 and Ca_3CoIrO_6 show intense satellite structure indicating that the prismatic Co site is in the high-spin Co^{2+} configuration. The Ir 4f and valence-band spectra of Ca_3CoIrO_6 and Sr_3ZnIrO_6 indicate that the octahedral Ir sites take the low-spin Ir^{4+} configuration in

Ca_3CoIrO_6. In contrast, the Co 2*p* and valence-band spectra of $Ca_3Co_2O_6$ show that $Ca_3Co_2O_6$ consists of Co^{3+} species and that one of the prismatic and octahedral sites should take the low-spin configuration. Considering the fact that some Co sites have considerable magnetic moment in $Ca_3Co_2O_6$, the prismatic Co and octahedral Co sites take the Co^{3+} high-spin and Co^{3+} low-spin configurations, respectively, in $Ca_3Co_2O_6$. The present results are able to resolve the issues on Co valence for $Ca_3Co_2O_6$ and Ca_3CoRhO_6 at least around 300 K.

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