Photoemission and x-ray-absorption study of misfit-layered (Bi,Pb)-Sr-Co-O compounds: Electronic structure of a hole-doped Co-O triangular lattice

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We present a photoemission and x-ray-absorption study of the misfit-layered (Bi,Pb)-Sr-Co-O compounds which have a Co-O triangular lattice with a mixed valence of Co$^{3+}$ and Co$^{4+}$. The valence-band photoemission as well as the O 1$s$ and Co 2$p$ x-ray absorption spectra indicate that Co$^{3+}$ and Co$^{4+}$ have the low-spin $t_{2g}^{5}$ and $t_{2g}^{4}$ configurations, respectively. The angle-resolved photoemission spectra show that the dispersion of the $t_{2g}$ feature is very small compared to its width at each angle, suggesting that the electron-lattice coupling energy is much larger than the kinetic energy of the $t_{2g}$ electrons and that the carriers in the Co-O triangular lattice are essentially polarons formed by Co$^{4+}$ in the nonmagnetic Co$^{3+}$ background.

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I. INTRODUCTION

Physical properties of hole-doped 3$d$ transition-metal oxides have attracted much attention since the discovery of high-$T_c$ superconductivity in Cu oxides\(^1\) and colossal magnetoresistance (CMR) in Mn oxides.\(^2\) Insights gained about these Cu and Mn oxides have triggered renewed interest in other strongly correlated materials, especially those that also reveal intriguing properties such as the mixed-valent Co oxides. (La,Sr)CoO$_3$, for example, shows an evolution from a nonmagnetic insulator (LaCo$^{3+}$O$_3$) to a ferromagnetic metal (SrCo$^{4+}$O$_3$).\(^3,4\) Theoretical\(^5\) and experimental\(^6-8\) studies strongly suggest that in the ferromagnetic (La,Sr)CoO$_3$, Co$^{3+}$, and Co$^{4+}$ have the intermediate-spin configurations of $t_{2g}^{5}e_{g}^{1}$ and $t_{2g}^{4}e_{g}^{1}$, respectively. In such a case, the $e_{g}$ electrons are relatively itinerant and give a double-exchange interaction between the localized $t_{2g}$ spins. In fact, the magnetization of (La,Sr)CoO$_3$ is as large as 2 $\mu_B$/Co which is consistent with the intermediate-spin state.

A decade ago, one of the variations of the mixed-valent Co oxides, namely, Bi$_2$Sr$_2$CoO$_4$, has been assigned to have the same structure as the Bi$_2$Sr$_2$CaCu$_2$O$_8$ superconductor.\(^9\) Accordingly, the Pb-doped (Bi,Pb)-Si-Co-O compound has also been considered to have the same structure.\(^10\) However, a recent structural study of Yamamoto et al.\(^11\) has shown that the (Bi,Pb)-Sr-Co-O system (including the Pb-undoped Bi-Sr-Co-O) has a misfit-layered structure isomorphous to [Bi$_{0.875}$Sr$_{0.125}$]$_2$(Co$_2$O$_2$)$_{1.82}$ recently reported by Legleny et al.\(^12\) They contain a two-dimensional CoO$_2$ triangular lattice (see Fig. 1) with Co$^{3+}$ and Co$^{4+}$ mixed valence. Interestingly, Tsukada et al. have found that the misfit-layered (Bi,Pb)-Sr-Co-O compound is a ferromagnetic metal below 4 K and shows a negative magnetoresistance.\(^13\) The magnetization of the (Bi,Pb)-Sr-Co-O compound is only $\sim 0.1$ $\mu_B$/Co which is much smaller than that of (La,Sr)CoO$_3$.\(^13\) The small magnetization in the (Bi,Pb)-Sr-Co-O system suggests that Co$^{3+}$ and Co$^{4+}$ are in the low-spin state. Therefore, the (Bi,Pb)-Sr-Co-O system would provide an opportunity to study the electronic structure of the Co$^{3+}$-like species in the low-spin (nonmagnetic) Co$^{3+}$ background. The electronic structure of the CoO$_2$ triangular lattice is interesting in the light of the large thermoelectric power found in the (Bi,Pb)-Sr-Co-O compounds.\(^14,15\) The NaCo$_2$O$_4$ compounds,\(^16\) the Ca$_3$Co$_4$O$_9$ compounds,\(^17,18\) all of which have the metallic CoO$_2$ triangular lattice in common as shown in Fig. 1.\(^19,20\)

In this paper, we present a photoemission and x-ray-absorption study of the misfit-layered Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O compounds and discuss the electronic structure of the hole-doped Co-O triangular lattice. We also make a comparison with the angle-resolved photoemission (ARPES) results from the layered CMR Mn oxide (La,Sr)$_3$Mn$_2$O$_7$\(^21\) and discuss the differences.

II. EXPERIMENTAL

Single crystals of the misfit-layered Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O compounds were prepared by a floating zone method and consist of the (Bi,Pb)SrO$_2$ rock-salt layer and the CoO$_2$ hexagonal layer as reported in the literature.\(^11,13\) The actual composition of the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O single crystals are Bi$_2$Sr$_2$CoO$_4$ and Bi$_3$Pb$_2$Sr$_2$Co$_2$O$_9$, respectively, which were measured by inductively coupled plasma atomic emission spectroscopy. Since the chemical composition of the Bi-Sr-Co-O compound is approximately given by [Bi$_{0.875}$Sr$_{0.125}$]$_2$(Co$_2$O$_2$)$_{1.82}$, the average valence of Co ions is expected to be $+3.33$.\(^12,13\) For the (Bi,Pb)-Sr-Co-O case, by assuming that the oxygen content is not changed by the Pb doping, the average valence of Co ions is estimated to be...
While the in-plane resistivity of the Bi-Sr-Co-O sample increases at low temperature and exceeds 100 mΩ cm at 4 K, that of the Bi,Pb-Sr-Co-O sample is smaller than 10 mΩ cm at 4 K and shows a metallic behavior in almost whole temperature region.

X-ray photoelectron spectroscopy (XPS) experiments were carried out in a Vacuum Generators (VG) Surface Science X-probe spectrometer unit, equipped with a small spot (150–1000 µm) Al-Kα source (hν = 1486.6 eV) monochromatized by a VG twin-crystal monochromator, and with a hemispherical electron energy analyzer with multichannel detection system. The XPS overall energy resolution was 0.5 eV, as determined using the Fermi cutoff of a Ag reference sample. The zero of the binding energy scale was given by the Fermi level of this Ag reference. ARPES measurements were done using a VG He discharge lamp and a VG hemispherical electron analyzer installed on a two-axis goniometer. The acceptance angle of the analyzer was 2° and the energy resolution was set to 0.50 meV. X-ray absorption spectroscopy (XAS) were performed using the helical undulator beamline ID12B of the European Synchrotron Radiation Facility in Grenoble. The degree of circular polarization was 92%. For the XPS, ARPES, and XAS measurements, the samples were cleaved in situ under ultra-high vacuum conditions of low 10−10 Torr. All the spectra were taken at room temperature. The cleanliness of the surfaces was checked by the lack of the contamination/degradation-related feature on the higher binding energy side in the O 1s XPS spectra and the feature at ~9.5 eV in the ARPES spectra.

III. RESULTS AND DISCUSSION

A. XPS

Figure 2 shows the O 1s core-level XPS spectra of the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O samples. The difference between the O 1s binding energies is less than 0.1 eV. In the (La,Sr)CoO3 system, the O 1s binding energy is lowered by ~0.4 eV in going from LaCoO3 to La0.5Sr0.5CoO3 and by ~0.1 eV in going from La0.8Sr0.2CoO3 to La0.4Sr0.6CoO3. The binding energy shift of ~0.4 eV between LaCoO3 and La0.5Sr0.5CoO3 is attributed to the shift of the chemical potential across the band gap of LaCoO3. The binding energy shift between the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O compounds is small because the Bi-Sr-Co-O sample is already hole doped and the chemical potential is pinned near the top of the valence band in both compounds. This picture is also supported by the valence-band spectra presented in the following paragraphs. The lack of the contamination/degradation-related feature, which is expected at ~532 eV, indicates the good quality of the surface.

The Co 2p XPS spectra are shown in Fig. 3. The binding energy of the Co 2p3/2 main peak is ~779.0 eV. The charge-transfer satellite of the Co 2p3/2 peak is located at ~789.0 eV. The degree of circular polarization was ~92%. For the XPS, ARPES, and XAS measurements, the samples were cleaved in situ under ultra-high vacuum conditions of low 10−10 Torr. All the spectra were taken at room temperature. The cleanliness of the surfaces was checked by the lack of the contamination/degradation-related feature on the higher binding energy side in the O 1s XPS spectra and the feature at ~9.5 eV in the ARPES spectra.

FIG. 1. (a) A schematic picture of the CoO2 triangular lattice. The shaded circles indicate Co ions centered at the CoO6 octahedra sharing their edges. (b) The first Brillouin zone of the (Bi,Pb)SrO2 rock-salt layer (thick solid line) and that of the hexagonal CoO2 layer (thick dotted line). The Γ, X, Y, and M points are shown for the (Bi,Pb)SrO2 layer and the K and M points are shown for the hexagonal CoO2 layer. The arrows indicate the ΓY and ΓM directions of the (Bi,Pb)SrO2 rock-salt layer along which the ARPES data were taken.

FIG. 2. O 1s core-level XPS spectra of the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O samples.

The binding energy shift of ~0.4 eV between LaCoO3 and La0.5Sr0.5CoO3 is attributed to the shift of the chemical potential across the band gap of LaCoO3. The binding energy shift between the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O compounds is small because the Bi-Sr-Co-O sample is already hole doped and the chemical potential is pinned near the top of the valence band in both compounds. This picture is also supported by the valence-band spectra presented in the following paragraphs. The lack of the contamination/degradation-related feature, which is expected at ~532 eV, indicates the good quality of the surface.

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FIG. 3. Co 2p core-level XPS spectra of the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O samples.
electronic-structure parameters such as the charge-transfer energy are expected to be similar to those for (La,Sr)CoO$_3$.

The valence-band XPS spectra are shown in Fig. 4 which are normalized using the intensity at $\sim$14 eV. Structure A at $\sim$1 eV can be assigned to the Co $t_{2g}$ states hybridized with the O 2$p$ states in the CoO$_2$ layer. The intensity of structure A is reduced in going from Bi-Sr-Co-O to (Bi,Pb)-Sr-Co-O, which is consistent with the fact that the Pb substitution introduces extra holes in the $t_{2g}$ states. Structures B, C, and D are derived from the O 2$p$ states hybridized with Co 3$d$ states in the CoO$_2$ layer and with the Bi(Pb) 6$s$/6$p$ states in the (Bi,Pb)SrO$_2$ rock-salt layer. As shown later, the ARPES data indicates that structures C and D are derived from the (Bi,Pb)SrO$_2$ layer and that structure B originates from the CoO$_2$ layer. Although the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O samples are expected to be hole doped, the Co $t_{2g}$ peak (structure A) remains sharp with a line shape very similar to that of LiCoO$_2$ and LaCoO$_3$ which have the low-spin $t_{2g}$ configuration.

Therefore, the photoemission spectra shown in Fig. 4 suggest that in the (Bi,Pb)-Sr-Co-O system the Co$^{3+}$ state remains in the low-spin $t_{2g}$ configuration even when the material is heavily hole doped, and that the spectral weight near the Fermi level is dominated by the $t_{2g}$ states. This situation is in contrast to (La,Sr)CoO$_3$ where the Co $t_{2g}$ peak collapses rapidly with hole doping.$^8$ It is known that in (La,Sr)CoO$_3$ hole doping induces the transition of the low-spin states to the intermediate-spin states and that the $e_g$ states are partially occupied near the Fermi level.$^5,6$ This transition is responsible for the rapid destruction of the $t_{2g}$ peak and the formation of the broad $e_g$ band near the Fermi level in (La,Sr)CoO$_3$.$^8$

Yamamoto et al. have reported that the Pb doping reduces the $b$-axis length of the (Bi,Pb)SrO$_2$ rock-salt layer from 5.4 to 5.2 Å. The structural change induced by the Pb doping could influence the electronic structure of the (Bi,Pb)SrO$_2$ layer. For example, a reduction of the Bi(Pb)-O bond length due to Pb doping may enhance the hybridization between the O 2$p$ and Bi(Pb) 6$s$/6$p$ states. In fact, the intensity of structures C and D from the (Bi,Pb)SrO$_2$ layer increases with the Pb doping, indicating that the O 2$p$ states in the (Bi,Pb)SrO$_2$ layer are indeed affected by the Pb doping. The doping also shifts the Bi 6$s$ and 4$f$ peaks towards higher binding energies by $\sim$0.3 eV.

**B. XAS**

Figure 5(a) shows the O 1$s$ XAS spectra of Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O taken at normal ($\theta=0^\circ$) and off-normal ($\theta=60^\circ$) incidence. $\theta$ is the angle between the Poynting vector of the circularly polarized light and the $z$ direction which is normal to the CoO$_2$ layer. The spectra are normalized and aligned at structure $\beta$. (c) Fitted results (thick curves) for the O 1$s$ XAS spectra using two Gaussians for structures $\alpha$ and $\beta$, and the tail of another Gaussian to represent the tail of structure $\gamma$. The thin curves indicate the Gaussian for structure $\alpha$, that for structure $\beta$, and the tail of structure $\gamma$.

FIG. 4. Valence-band XPS spectra of the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O samples.

FIG. 5. (a) and (b) O 1$s$ XAS spectra of the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O samples taken at normal ($\theta=0^\circ$) and off-normal ($\theta=60^\circ$) incidence. $\theta$ is the angle between the Poynting vector of the circularly polarized light and the $z$ direction which is normal to the CoO$_2$ layer. The spectra are normalized and aligned at structure $\beta$. (c) Fitted results (thick curves) for the O 1$s$ XAS spectra using two Gaussians for structures $\alpha$ and $\beta$, and the tail of another Gaussian to represent the tail of structure $\gamma$. The thin curves indicate the Gaussian for structure $\alpha$, that for structure $\beta$, and the tail of structure $\gamma$. 

**FIG. 5.** (a) and (b) O 1$s$ XAS spectra of the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O samples taken at normal ($\theta=0^\circ$) and off-normal ($\theta=60^\circ$) incidence. $\theta$ is the angle between the Poynting vector of the circularly polarized light and the $z$ direction which is normal to the CoO$_2$ layer. The spectra are normalized and aligned at structure $\beta$. (c) Fitted results (thick curves) for the O 1$s$ XAS spectra using two Gaussians for structures $\alpha$ and $\beta$, and the tail of another Gaussian to represent the tail of structure $\gamma$. The thin curves indicate the Gaussian for structure $\alpha$, that for structure $\beta$, and the tail of structure $\gamma$. 

**FIG. 5.** (a) and (b) O 1$s$ XAS spectra of the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O samples taken at normal ($\theta=0^\circ$) and off-normal ($\theta=60^\circ$) incidence. $\theta$ is the angle between the Poynting vector of the circularly polarized light and the $z$ direction which is normal to the CoO$_2$ layer. The spectra are normalized and aligned at structure $\beta$. (c) Fitted results (thick curves) for the O 1$s$ XAS spectra using two Gaussians for structures $\alpha$ and $\beta$, and the tail of another Gaussian to represent the tail of structure $\gamma$. The thin curves indicate the Gaussian for structure $\alpha$, that for structure $\beta$, and the tail of structure $\gamma$. 

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sharp peak in LiCoO\textsubscript{2} which is a typical low-spin Co\textsuperscript{3+} oxide.\textsuperscript{20} The O 1\textit{s} XAS spectra are normalized and aligned at structure \( \beta \) which would not be affected by the Pb doping if Co\textsuperscript{3+} and Co\textsuperscript{4+} have the low-spin configurations. The O 1\textit{s} spectra thus normalized are almost aligned between 540 to 565 eV indicating that the normalization procedure is reasonable. The uncertainty in the intensity normalization is less than 10\%. Structure \( \gamma \) is the transition from O 1\textit{s} to O 2\textit{p} which is mixed into the unoccupied Bi and Pb 6\textit{p} orbitals. The intensity of structure \( \gamma \) increases in going from Bi-Sr-Co-O to (Bi,Pb)-Sr-Co-O, indicating that the hybridization between the O 2\textit{p} and Bi(Pb) 6\textit{p} states is enhanced by the Pb doping. This would be consistent with the reduction of \( b \)-axis length induced by the Pb doping.\textsuperscript{11}

As shown in Fig. 5(b), the intensity of structure \( \alpha \) is dramatically enhanced in going from normal (\( \theta=0^\circ \)) to off-normal (\( \theta=60^\circ \)). In order to quantitatively analyze these data, we have fitted the O 1\textit{s} XAS spectra using two Gaussians for structures \( \alpha \) and \( \beta \), and the tail of another Gaussian to represent the tail of structure \( \gamma \). The results are plotted in Fig. 5(c), showing the good fit to the experimental data. The intensity ratio of structure \( \alpha \) at \( \theta=60^\circ \) to that at \( \theta=0^\circ \) is thus estimated to be 2.4\pm0.2 and 2.1\pm0.2 for Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O, respectively. Theoretically, the intensity of O 1\textit{s} XAS is determined by the dipole matrix element of the O 1\textit{s} transition. The transitions to the O 2\textit{p} states is enhanced by the Pb doping. This would be consistent with the reduction of the O 2\textit{p} states is enhanced by the Pb doping. Therefore, the intensity of structure \( \alpha \) does not necessarily reflect directly the hole concentration in the \( a_{1g} \) orbital. Another possibility is that the oxygen content is reduced by the Pb doping and, consequently, the number of holes in (Bi,Pb)-Sr-Co-O is close to that in Bi-Sr-Co-O.

Figure 6 shows the Co 2\textit{p} (\( L_{23} \)) XAS spectra of the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O samples taken at normal light incidence. The spectra are dominated by the 2\textit{p} core-hole spin-orbit coupling, which splits the spectra roughly into two parts, namely, the \( L_{3} \) (\( h\nu\sim780\) eV) and \( L_{2} \) (\( h\nu\sim795\) eV) regions, separated by about 15 eV. Since the effect of the core-hole potential is substantial in the Co 2\textit{p} XAS spectra compared to that in the O 1\textit{s} XAS spectra, the Co 2\textit{p} XAS final states are well described by the multiplet structure due to the Coulomb and exchange interactions between the Co 2\textit{p} core hole and the Co 3\textit{d} electrons, the spin-orbit interactions, and the crystal-field splittings of the Co 3\textit{d} subshell. The dipole selection rules make the spectra strongly to depend on the symmetry of the initial state of the Co ions. In a high-spin state, the exchange coupling between the core-hole and 3\textit{d} electrons tends to reduce the branching ratio \( I_{2}/(I_{3}+I_{2}) \) considerably from 1/3, where \( I_{2} \) and \( I_{3} \) are the intensities of the \( L_{2} \) and \( L_{3} \) peaks, respectively.\textsuperscript{28,29} The ratio \( I_{2}/(I_{3}+I_{2}) \) is ~0.3 in Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O. This value is close to 1/3 indicating that the Co ions mainly have the local low-spin state character. In fact, the line shape of the Co 2\textit{p} spectra are rather similar to the multiplet calculations starting from the low-spin ground states (the \( t_{2g}^{6} \) configuration for the Co\textsuperscript{3+} ion\textsuperscript{25} and the \( t_{2g}^{5} \) configuration for the Co\textsuperscript{4+} ion\textsuperscript{26}) and are very different from those for the intermediate-spin or high-spin ground states. Structures \( a \), \( b \), and \( c \) in the \( L_{3} \) region and structures \( d \) and \( e \) in the \( L_{2} \) region.

\begin{equation}
\begin{align*}
\frac{1}{2} \left[ \frac{2n_{a}+5n_{e}}{18} \right] \left( \cos^{2} \theta + 1 \right) + \frac{1}{2} \left[ \frac{4n_{a}+n_{e}}{9} \right] \sin^{2} \theta.
\end{align*}
\end{equation}

Here, \( n_{a} \) and \( n_{e} \) are the number of holes in the \( a_{1g} \) and \( e_{g} \) states, respectively. For \( n_{a}=1 \) and \( n_{e}=0 \), the intensity ratio is calculated to be 2.1 which agrees well with the experimental value. On the other hand, the intensity ratio is 1.2 for \( n_{a}=n_{e}=1 \) and is 0.8 for \( n_{a}=0 \) and \( n_{e}=1 \). Therefore, one can conclude that the holes are mainly located in the \( a_{1g} \) orbital. This situation is possible only when Co\textsuperscript{4+} has the low-spin \( t_{2g}^{6} \) configuration (four electrons in \( e_{g} \) orbit and one electron in \( a_{1g} \)). Here, it should be noted that the trigonal crystal field cannot explain why the \( a_{1g} \) orbital is higher in energy than the \( e_{g} \) orbitals because the CoO\textsubscript{6} octahedron is compressed along the \( z \) direction in Bi-Sr-Co-O as well as in Na CO\textsubscript{2}O\textsubscript{4}.\textsuperscript{11} On the other hand, the experimental result is consistent with the band structure calculation on NaCoO\textsubscript{2}O\textsubscript{4} (Ref. 27) which predicts that the holes mainly have the \( a_{1g} \) character. The intensity of structure \( \alpha \) is not changed in going from Bi-Sr-Co-O to (Bi,Pb)-Sr-Co-O although the additional holes are introduced by the Pb doping. However, since the Co\textsubscript{O} distance and the strength of the Co-O hybridization might be changed by the Pb doping, the intensity of structure \( \alpha \) does not necessarily reflect directly the hole concentration in the \( a_{1g} \) orbital.
Bi$_2$Sr$_2$CaCu$_2$O$_8$. Therefore, as discussed in the previous paragraphs, the Bi-Sr-Co-O compound is already hole-doped and has the Fermi level near the top of the valence band. The line shape of the $t_{2g}$ peak can be interpreted in terms of the single-electron excitation spectrum from the localized electron coupled with phonons. The centroid of the $t_{2g}$ feature corresponds to the bare electron-removal excitation without lattice relaxations and the intensity at the Fermi level is derived from the final states fully stabilized by the lattice relaxation, namely, the final states with zero phonons.

It is interesting to compare the present ARPES data with that of (La,Sr)$_3$Mn$_2$O$_7$ reported by Dessau et al. In (La,Sr)$_3$Mn$_2$O$_7$, although the ARPES features are broad and the spectral weight at the Fermi level is depleted, the centroid of the ARPES feature shows the substantial dispersion. Dessau et al. argue that the final state is dressed by phonon excitations ending up with the broad ARPES feature which can still have the large dispersion as predicted by the band dispensers and intensities in LiCoO$_2$ are very similar to those of Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O. This also indicates that the Co$_{3+}$ ions in Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O have the low-spin state.

**C. ARPES**

ARPES data taken at $h\nu = 21.2 \text{ eV}$ are shown in Fig. 7. The ARPES data in the left panel were taken approximately along the $\Gamma Y$ direction of the (Bi,Pb)SrO$_2$ layer and is the Co-Co direction of the Co-O triangular lattice as indicated in Fig. 1. The ARPES data taken at $\theta = 15^\circ$ is approximately located near the $Y$ point of the (Bi,Pb)SrO$_2$ layer. ARPES data along the $\Gamma M$ direction of the (Bi,Pb)SrO$_2$ layer are shown in the right panel of Fig. 7, where the momentum for $\theta = 21^\circ$ is approximately located near the $M$ point. The band dispersion and the relative intensity of structures C and D are in good agreement with those reported for Bi$_2$Sr$_2$CaCu$_2$O$_8$, indicating that structures C and D are derived from the surface (Bi,Pb)SrO$_2$ layer. On the other hand, there is no counterpart of structures A and B in Bi$_2$Sr$_2$CaCu$_2$O$_8$. Therefore, as discussed in the previous paragraphs, structures A and B can be attributed to the Co $t_{2g}$ and O 2$p$ states of the CoO$_2$ layer. In order to show the dispersion of these features, the second derivatives of the ARPES spectra are shown in Fig. 8. While structure A is almost dispersionless, structures B, C, and D have some dispersions, indicating that the observed spectrum at each angle is indeed angle resolved. Therefore, we can conclude that the angle-independent $t_{2g}$ feature is intrinsic to the hole-doped CoO$_2$ triangular lattice.

ARPES data near the Fermi level are plotted in Fig. 9. The $t_{2g}$ spectral feature is centered at $\sim 0.9 \text{ eV}$ and has the width of $\sim 1 \text{ eV}$. The width of the $t_{2g}$ feature at each angle is very large compared to the dispersion of its centroid both in Bi-Sr-Co-O and in (Bi,Pb)-Sr-Co-O. At each angle, the tail of the $t_{2g}$ feature reaches the Fermi level although the intensity at the Fermi level is considerably suppressed. As discussed in the previous paragraphs, structures $C$ and $D$ are in good agreement with those reported for (La,Sr)$_3$Mn$_2$O$_7$, although the ARPES features are broad and the intensity at the Fermi level is derived from the final states fully stabilized by the lattice relaxation, namely, the final states with zero phonons.

It is interesting to compare the present ARPES data with that of (La,Sr)$_3$Mn$_2$O$_7$ reported by Dessau et al. In (La,Sr)$_3$Mn$_2$O$_7$, although the ARPES features are broad and the spectral weight at the Fermi level is depleted, the centroid of the ARPES feature shows the substantial dispersion. Dessau et al. argue that the final state is dressed by phonon excitations ending up with the broad ARPES feature which can still have the large dispersion as predicted by the band dispersioners and intensities in LiCoO$_2$. The Co 2$p$ XAS spectrum of the typical low-spin Co$_{3+}$ oxide LiCoO$_2$ has five spectral features: their relative energies and intensities in LiCoO$_2$ are very similar to those observed in Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O. This also indicates that the Co$_{3+}$ ions in Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O have the low-spin state.

**FIG. 7.** ARPES spectra of the Bi-Sr-Co-O sample along the $\Gamma Y$ and $\Gamma M$ directions of the (Bi,Pb)SrO$_2$ layer. $\phi$ denotes an angle between the sample surface normal and the emission direction of the collected photoelectrons.

**FIG. 8.** Second derivatives of the ARPES spectra of the Bi-Sr-Co-O sample along the $\Gamma Y$ and $\Gamma M$ directions of the (Bi,Pb)SrO$_2$ layer. The bright regions labeled as A, B, C, and D correspond to the dispersive features.

**FIG. 9.** ARPES spectra of the Bi-Sr-Co-O and (Bi,Pb)-Sr-Co-O samples near the Fermi level along the $\Gamma Y$ and $\Gamma M$ directions of the (Bi,Pb)SrO$_2$ layer. The $\Gamma Y$ direction corresponds to the Co-Co direction of the Co-O triangular lattice. $\phi$ denotes an angle between the sample surface normal and the emission direction of the collected photoelectrons.
probably the difference between the square MnO$_2$ layer and the triangular CoO$_2$ layer to be small. In fact, a recent band-structure calculation for NaCoO$_2$ predicts that the $t_{2g}$ band width is very narrow in the CoO$_2$ triangular lattice.\textsuperscript{25} Probably, the difference between the square MnO$_2$ layer and the different CoO$_2$ layer originates from the difference between the metal-oxygen-metal bond angle as well as from the different involvement of the $e_g$ and $t_{2g}$ electrons. In the CoO$_2$ triangular lattice, the $t_{2g}$ band width is small compared to the electron-lattice interaction term. Consequently, the effect of the electron-phonon coupling would be strong enough to form small polaron in the ground state.

It is also interesting that the line shape of the $t_{2g}$ feature is not changed by hole doping as shown in Fig. 9. Probably, the coupling between the $t_{2g}$ electrons and the optical phonons in the (Bi,Pb)-Sr-Co-O system is strong and does not depend on the hole concentration. This is also consistent with the picture that the Co$^{3+}$ state induced by hole doping forms a kind of small polaron (Co$^{4+}$ embedded in the nonmagnetic Co$^{3+}$ background). Since spin and charge orderings are frustrated in the CoO$_2$ triangular lattice, the strongly renormalized polaron band has more chance to survive at low temperatures although the small polaron would be localized at very low temperature because of randomness. In future, the relationships between the small polaron picture and the ferromagnetism and the enhanced thermoelectric power should be studied experimentally and theoretically.

\textbf{IV. CONCLUSIONS}

We have studied the electronic structure of misfit-layered (Bi,Pb)-Sr-Co-O compounds which have a Co-O triangular lattice with a mixed valence of Co$^{3+}$ and Co$^{4+}$. The valence band XPS data shows that the $t_{2g}$ peak remains sharp with hole doping, indicating that Co$^{3+}$ has the low-spin $t_{2g}^5$ configuration and that the electronic states near the Fermi level are constructed from the $t_{2g}$ states. The low spin configuration is also confirmed by the Co 2p XAS data. In addition, the O 1s XAS study reveals that the holes are mainly located in the $a_{1g}$ orbital among the three $t_{2g}$ orbitals and that Co$^{4+}$ also has the low-spin $t_{2g}^5$ configuration. This situation is in sharp contrast to (La,Sr)CoO$_3$, in which Co$^{3+}$ and Co$^{4+}$ have the intermediate-spin configurations and the $e_g$ electrons, the physical properties of (Bi,Pb)-Sr-Co-O are dominated by the electron-lattice interaction. In fact, the broad and angle-independent $t_{2g}$ feature observed in ARPES is consistent with the single-electron excitation from the small and almost localized polaron.

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