Electronic Structure of $La_{1-x}Ca_xCoO_3$ (x = O, 0.5)

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Abstract

X-ray photoemission measurements of the core levels and valence electronic structure of $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$ high quality epitaxial films are presented. Shifts of the core levels and main valence band features are consistent with a doping-induced change in the chemical potential. Oxygen states are found to significantly contribute to a peak in the valence band at 1 eV binding energy, verifying earlier results of cluster calculations. A Fermi level crossing of this same band upon doping is observed, yielding a high Fermi level density of states in contrast to earlier measurements on polycrystalline $La_{1-x}Sr_xCoO_3$.

Interest in perovskites and related oxides in recent years has been stimulated by the discoveries of high temperature superconductivity in cuprates and colossal magnetoresistance in rare earth manganites. In the rare earth cobaltites, as in the manganites, hole doping induces a mixed population of + 3 and +4 transition metal ions, ferromagnetic ordering, and metallic conduction.[1] However, unlike the manganites, there is no Jahn-Teller effect in the cobaltites, making for an interesting comparison since the Jahn-Teller effect is thought to be the dominant contributor to colossal magnetoresistance in the manganites.[2] Consequently, the observed magnetoresistance in doped cobaltites[3-6] is orders of magnitude smaller than that of the manganites, though still sufficiently large at low temperature for possible use as magnetic field sensors.[7] The electronic structure of cobaltites is thus of interest from both the fundamental and practical viewpoints.

The electronic structure of $LaCoO_3$ has previous] y been measured with photoemission[8-12] and calculated with band structure and cluster method s.[9-11] Photoemission measurements on doped cobaltites arc limited to recent studies[13,14] of pol ycrystalline $La_{1-x}Sr_xCoO_3$ scraped in vacuum, which reported low Fermi level densities of states despite metallic conductivity. In this work, x-ray photoelectron spectroscopy (X PS) measurements of the core levels and valence bands of chemical] y-etched $La_{1-x}Ca_xCoO_3$ (x = O, 0.5) epitaxial films are presented, These choices of material and sample preparation result in several potential advantages. A doping level of x ≈ 0.5 eliminates any possible effects of chemical inhomogeneity, since the cations are ordered[15] for x = 0.S but form alkaline earth-rich ferromagnetic clusters in a rare earth-rich paramagnetic matrix[16-18] for x < 0.5. Ca is chosen as the dopant since La^{+3} and Ca^{+2} have virtually identical ionic radii,[19] thus eliminating any possible effect of localized lattice distortions near larger Sr^{+2} ions. Finally, the usc of chemically-etched epitaxial films minimizes spectral contributions from contaminant species, as may occur from grain boundaries in polycrystalline specimens, and also avoids the problem of scrape-induced surface damage which has been observed for superconducting cuprates.[20]

200 rim-thick $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$ epitaxial films were grown by pulsed laser deposit ion from stoichiometric targets onto $LaAlO_3$ (100) substrates at 700° C in 100 mTorr oxygen, followed by cooling in 500 Torr ox ygen. Some of the films received an additional anneal

in 1 atmosphere oxygen at 900" C for two hours. Epitaxy was confirmed with x-ray rocking curves. Films were also grown on $SrTiO_3$ (100) substrates, but film-substrate reactions were found to be significant. Details of the structural, magnetic, and electrical transport properties of the films arc described elsewhere.[6,21]

The films were cleaned with a nonaqueous etchant consisting of 0,5% Br_2 in absolute ethanol in the ultrahigh purity nitrogen atmosphere of a glove box which encloses the XPS load lock, This procedure minimizes exposure of the clean surface to reactive atmospheric gases such as water vaper and carbon dioxide and has yielded high quality surfaces for cuprate superconductors.[20] A 30s etch was sufficient for obtaining XPS spectra characteristic of high quality surfaces, in particular an O 1s signal with minimal intensity on the high binding energy side.[8,9,12,13,20] The XPS spectra were accumulated at room temperature on a Surface Science Spectra SSX-501 spectrometer with monochromatized Al K_α x-rays (1486.6 eV), photoemission normal to the film surface, and a base pressure of 5 x 10^{-10} Torr. The x-ray beam diameter was 150 μm for the core level measurements and 300 pm for the valence band measurements. The pass energy of the electron energy analyzer was **25** eV, yielding a peak full width at half maximum (FWHM) of 0.7 eV for a Au $4f_{7/2}$ signal.

The core level binding energies and the FWHM of the peaks for the $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$ epitaxial films measured in this work are summarized in Table I. For comparison, data from epitaxial films of the manganites $LaMnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ and the cuprate La_2CuO_4 are also summarized in Table I. The O 1s spectra measured from $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$ are compared in Fig. 1, which shows that hole doping results in broadening of the signal and a shift to lower binding energy by -0.5 eV. The observed FWHM of the low binding energy cobaltite O 1s signals in Fig.1 are significantly narrower than the values of 1.5- 1.7 eV for previously published O 1s spectra from polycrystalline $LaCoO_3$ scraped or heated in vacuum. .[8,9] The low intensities of the contaminant signals near 531eV in Fig. 1 are comparable to the earlier measurements and demonstrate the surface cleanliness obtained in this work. The binding energies of the cobaltite O

1s signals are comparable to those observed for cuprates, but lower than those of manganites (see Table I).

'The Ca 2p signal measured from $La_{0.5}Ca_{0.5}CoO_3$ is shown in Fig. 2 with the result of a least-squares fitting. The lack of a Ca carbonate signal near 347 eV, as well as the lack of a carbonate. signal in the C 1s region (not shown), is consistent with the low level of contaminant signals observed in the O 1s region. The binding energy of the $Ca 2p_{3/2}$ component in Fig. 2 is -1 eV lower than that observed for $La_{0.7}Ca_{0.3}MnO_3$ (see Table 1) and comparable to measurements from Ca-containing cuprate superconductors.[22] The Ca 2p signals from these materials differ in that the cuprate signals consist of two doublets, commonly attributed to occupation of inequivalent lattice sites with differing coordination to oxygens,[22] while the cobaltites and manganites exhibit signals which are well -represented by a single doublet, as shown in Fig. 2, reflecting a single chemical environment.

The 1.a 3d signals from $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$ in Fig. 3 are typical of la'3 compounds. [23,24] 'l'here is general agreement in the literature that the double peak structure of each spin-orbit split component reflects states with configurations $\underline{3d}^9 4f^0 L$ and $\underline{3d}^9 4f^1 \underline{L}$, where 1. denotes the oxygen ligand and underscoring denotes a hole, 1 lowever, there has been considerable debate about whether the f^1 configuration corresponds to the higher binding energy peaks, and hence an excitation resulting in an energy loss, or to well-screened lower binding energy states. These atomic-like models appear to be too simplistic and strong final state mixing of the f^0 and f^1 states has been reported,[25] with f^0 character (reflecting the initial state configuration) being dominant in the more intense peaks. While state mixing is recognized to be significant, for simplicity in the following discussion the dominant low binding energy signals will be referred to as the f^0 peaks and the higher binding energy signals will be referred to as the f^1 peaks.

The similarities of the f^1/f^0 intensity ratios and the f^1 - f^0 energy separations of -4-4.5 eV for several La perovskites and La_2O_3 have been previously reported.[9,23] The f^1/f^0 intensity ratios have been reported[26] to be larger (compared to ABO_3 perovskites) for the K_2NiF_4-t ype compounds La_2CuO_4 and La_2NiO_4. In this work, the f^1/f^0 intensity ratios are found to be nearly the same for

the cobaltites and manganites and larger for the cuprates, in agreement with the earlier measurements on polycrystalline samples,[9,23,26] and hole doping is found to have no significant effect on the f^1/f^0 intensity ratios for any of the materials studied here. The f^1 - f^0 energy separations in cuprates also have been reported to differ from those of ABO_3 perovskites, with values of 3.1 CV reported[24] for La_2CuO_4 and 5.3 CV for $La_{1.85}Ba_{0.15}CuO_4$.[27] In this work, the f^1 - f^0 energy separation of 4.3 eV is found to be the same for doped and undoped cobaltites, manganites, and cuprates. These differing results may be attributed to contaminants in the earlier measurements, as is evident in the large peak widths (e.g. La_2CuO_4 O 1s FWHM = 4.4 eV reported in Ref. 24, vs. 1.35 eV measured in this work) and high binding energy shoulders in the published O 1s and Ba 3d spectra.[24,27] Although hole doping appears to have no discernible effect on the f^1/f^0 intensity ratio and the f^1 - f^0 energy separation, the spectra in Fig. 3 do show a 0.5 eV shift to lower binding energy for the doped cobaltite. It is notable that this shift is in the same direction and magnitude as that observed in the O 1s spectra, suggesting a doping-induced change in the chemical potential.

The Co 2p signals from $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$ are shown in Fig, 4, scaled to the same $Co\,2p_{3/2}$ peak height to facilitate comparison of the line shapes. Doping results in a shift of the peak maximum to lower binding energy by 0.2 eV and a significant broadening of the signal, particularly on the high binding energy side. The Co 2p lineshape is determined by a multiplet of Co^{+3} states[9,10,12,13] and, in the case of hole doping, an additional multiplet of Co^{+4} states[10,13] which would occur at higher binding energy,'0 consistent with the spectra in Fig. 4. An earlier photoemission study of $La_{1-x}Sr_xCoO_3$ also reported[13] a broadening of the Co 2p signal for a doping level similar to that studied here (FWHM = 3.8 eV for x = O and 4,0 eV for x=O.4), though the peak widths for both doped and undoped samples are substantially larger and the change less than the observations in this work (FWHM = 2.4 eV for x = O and 3.2 eV for x = 0.5). The narrower linewidths observed here reflect the improved resolution obtained with monochromatized x-rays (the earlier study[13] used nonmonochromatic $Mg\,K_\alpha$ x-rays), and may also be partly attributable to high quality epitaxial films being measured in the present work, rather than polycrystalline samples

as were used in the earlier work. The large Co 2p widths previous] y reported may also account for the failure to observe binding energy shifts with hole doping, leading to the conclusion that doping results in no appreciable shift in the Fermi level.[13] In this work, the Co 2p signal of the doped cobaltite is observed at lower binding energy despite the additional Co^{+4} states at higher binding energy. Although the magnitude of the Co 2p shift is smaller than the corresponding O 1s and La 3d shifts, the Co 2p measurement is complicated by the hole-doped states and the multiplet nature of the signal, so that the Co 2p data is consistent with a change in the chemical potential.

The valence bands and shallow core levels measured from $LaCoO_3$ films are shown in Fig. S and are comparable to previous measurements[8-10, 12,13] which have used the same or similar photon energy as that used in this work. The Co 3d partial density of states is the dominant contributor to the valence band in these measurements due to the higher photoionization cross section. The notable exception is the peak closest to the Fermi level at 1 eV binding energy, which is characteristic of low spin Co^{+3} and which cluster calculations show[11] has dominant O 2p character, rather than the Co 3d character predicted from band structure calculations. [10] The significant contribution of oxygen states to this peak is demonstrated in Fig, 5, which shows an increase in the intensities of the O 2s and the 1 eV valence band peaks after a high temperature oxygen anneal, Oxygen annealing has no significant effect on the core level line shapes or binding energies, and changes similar to those in Fig. 5 are not observed for doped cobaltite films.

'The valence bands and shallow core levels of $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$ are compared in Fig. 6. Previous XPS and ultraviolet photoemission measurements[13,14] of polycrystalline $La_{1-x}Sr_xCoO_3$ showed that doping caused a shift of the feature near 5 CV to lower binding energy by 0.6 eV, a decrease in intensity of the 1 eV peak with no change in position, and a broadening of the spectral features which results in an increased (but still small) intensity at the Fermi level. The data in Fig. 6 also show a broadening of the spectral features, a decrease in intensity of the 1 eV peak, and a shift of the 5 eV peak to lower binding energy by 0.5 eV as a result of the doping. However, these data differ from previous measurements in clearly showing, in addition to a loss of intensity with doping, a shift of the 1 eV peak to lower binding energy by 0.5 eV which results in a large Fermi

level density of states, observations which are characteristic of a Fermi level crossing and consistent with the observed[6] metallic conductivity. In contrast, a smaller 1 eV peak is also observed in manganites which does not shift with hole doping and no significant intensity is observed at the Fermi level, consistent with the semiconducting conductivity observed[6] above the Curie temperature (260 K). The 0.5 eV shift of the main valence band features of the doped cobaltite is the same as the shifts observed in the core levels and is consistent with a doping-induced change in the chemical potential. However, the valence band does not rigidly shift, doping also clearly results in changes in the character and/or a redistribution of states.

In summary, XPS measurements of the core levels and valence electronic structure of $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$ epitaxial films have been presented, Shifts of the core levels and main valence band features are consistent with a doping-induced change in the chemical potential. A peak in the valence band at 1 eV binding energy has been demonstrated to have significant oxygen character, consistent with the results of cluster calculations. This same band exhibits features characteristic of a Fermi level crossing upon hole doping, yielding a high Fermi level density of states in contrast to previously published measurements.

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"l'able 1. Summary of core level binding energies (± 0.05 eV) and peak full widths at half maximum (in parentheses) for $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$ epitaxial films measured in this work. For comparison, the results of measurements on $LaMnO_3$, $La_{0.7}Ca_{0.3}MnO_3$, and La_2CuO_4 epitaxial films are also presented.

Material	La 3d$_{5/2}$	Ca 2p$_{3/2}$	Co 2p$_{3/2}$	O 1s
LaCoO$_3$	833.3		779.5 (2.4)	528.6 (1 .05)
La$_{0.5}$Ca$_{0.5}$CoO$_3$	832.8	345.15 (1.3)	779.3 (3.2)	528.15 (1.30)
LA'l110$_3$	833.75			529.2 (1 .0)
La$_{0.7}$Ca$_{0.3}$MnO$_3$	833.65	346.2 (1.1)		529.1 (1 .05)
La$_2$CuO$_4$	833.3			528.6 (1.35)

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Figure Captions

1. ('comparison of the O 1s spectra measured from chemically-etched epitaxial films of $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$.

2. 'I'he Ca 2p spectrum measured from $La_{0.5}Ca_{0.5}CoO_3$, together with the result of a least-squares fitting.

3. The La 3d spectra measured from $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$.

4. 'I'he Co 2p spectra measured from $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$, scaled to the same Co $2p_{3/2}$ peak heights to facilitate comparison of the line shapes.

5. 'I'he valence bands and the La 5p/O 2s shallow core level spectra measured from as-grown and oxygen-annealed $LaCoO_3$.

6. 'J'he valence bands and the Ca 3p/La 5p/O 2s shallow core level spectra measured from $LaCoO_3$ and $La_{0.5}Ca_{0.5}CoO_3$.

O 1s
—— LaCoO₃
– – – La0.5Ca0.5CoO₃

INTENSITY (arb. units)

BINDING ENERGY (ev)

LaCoO$_3$

—— AS-GROWN
- - - O$_2$ ANNEALED

La 5p

O 2s

Co 3d/O 2p

E$_F$

BINDING ENERGY (eV)

INTENSITY (arb. units)

0   5   10   15   20   25