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Electronic structure and spin-state transition of $LaCoO_3$

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We present soft-x-ray absorption spectra (XAS) of $LaCoO_3$ taken at different temperatures (80–630 K). The shape of the multiplets in the Co $2p$ XAS spectra conveys information on the symmetry and spin of the ground state. The O $1s$ XAS spectra are related to unoccupied metal bands through covalent mixing. The changes in the spectra taken at different temperatures provide information on the spin-state transition in this compound. At low temperature, 80 and 300 K, the material is in a highly covalent low-spin state. The main contribution to the ground state in this case is given by $t_{2g}^6(^1A_1)$ with an occupancy of 0.56. At higher temperature, 550 and 630 K, the results indicate a gradual transition to a mixed-spin state. The main contribution to the high-spin part of the mixture is given by $t_{2g}^4 e_g^2(^5T_2)$ with an occupancy of 0.71. There is no evidence of charge disproportionation in the temperature range 80–630 K. The O $1s$ XAS spectra reflect important changes in the unoccupied Co $3d$ bands across the spin-state transition.

I. INTRODUCTION

The purpose of this paper is to investigate the electronic structure and the spin-state transition of $LaCoO_3$ by means of soft-x-ray-absorption spectroscopy (XAS). Despite extensive work done in the past,[1-14] there are some basic questions concerning this compound which still require attention. These questions include, for instance, the precise spin state as a function of temperature and the ensuing changes in the electronic structure. We show below that XAS can successfully address some of these questions and provide additional information on related topics. In particular, we show that the material is in a low-spin state at low temperatures, in agreement with previous work, and that no charge disproportionation takes place in the temperature range 80–630 K, in contradiction with previous conclusions.

The spin state of transition-metal oxides with a $3d^6$ configuration is determined by the relative magnitude of two competing interactions. On the one hand, the exchange interaction J favors spin alignment (Hund's rule) and a high-spin ground state ($S=2$). In $LaCoO_3$, however, the crystal-field-splitting $10Dq$ is just large enough to quench these interactions stabilizing a low-spin ground state ($S=0$). What makes $LaCoO_3$ especially interesting is the fact that the energy difference between these two states is extremely small, of the order of kT, and the compound is observed to undergo a gradual low-spin to high-spin transition as the temperature is raised.

This peculiar spin-state transition has attracted considerable experimental attention on $LaCoO_3$.[1-14] Heikes, Miller, and Mazelsky reported magnetic and electric anomalies around 500 K and related these to changes in the magnetic moment per Co ion.[1] Blasse discussed the factors influencing the equilibrium of high-spin and low-spin Co^{3+} ions.[2] Naiman *et al.* estimated the effective magnetic moment from susceptibility measurements.[3] Jonker studied magnetic and semiconducting properties and proposed thermal excitation of high-spin Co ions in the temperature range 50–350 K.[4] Menyuk, Dwight, and Raccah found no evidence of magnetic order down to 4.2 K and attributed most of the anomalous low-temperature magnetic properties to the presence of an impurity phase.[5] Raccah and Goodenough measured x-ray diffraction, magnetic susceptibility, and electrical conductivity.[6] The conclusions were summarized by Goodenough:[7] (i) primary low-spin state at low temperatures, (ii) increase of the high-spin component in the interval 400–650 K, and (iii) long-range order of alternating high-spin and low-spin ions along the (111) direction above 650 K. Bhide *et al.* measured Mössbauer spectra, magnetic susceptibility, and electrical conductivity;[8] the interpretation of Mössbauer's results suggested charge disproportionation above 200 K; it is worth noting here the connection between an ordered charge disproportionation and a charge-density wave. Thornton and coworkers measured neutron diffraction, differential-thermal analysis, and electrical conductivity;[9,10] they failed to find evidence of long-range order except, possibly, at 650 K. Richter, Bader, and Brodsky measured electron-energy loss and ultraviolet and x-ray photoelectron spectra;[11] they indicated that the spin state at the surface might be different from that of the bulk. Conductivity measurements reported by Thornton *et al.* revealed a broad higher-order semiconductor to metal transition in the range 385–570 K,[12] which coincides with the increase of the high-spin component. Asai *et al.* measured polarized neutron scattering and observed a drastic decrease in the magnetic cross section below 150 K.[13] Thornton, Owen, and Diakun measured Co 1*s* x-ray-absorption spectra;[14] the differences in the spectra were interpreted in terms of calculated density of states.

Several theoretical models have been proposed to explain the spin-state transition of $LaCoO_3$.[15–19] Chesnut pointed out the importance of spin-lattice interactions in the singlet to triplet transition of related complexes.[15] Bari and Sivardière presented a two-sublattice model to account for the structural changes in $LaCoO_3$.[16] Kurzynski extended the model to include both static and dynamic strains.[17] Zimmermann and König included the effects of low-symmetry ligand fields and spin-orbit coupling.[18] Ramasesha, Ramakrishnan, and Rao reviewed the situation and proposed a two-phonon model where the spin states are mixed by the ion-cage mode.[19]

A survey of the experimental literature reveals important discrepancies and conflicting interpretations. These concern, in particular, the precise spin state as a function of temperature as well as the importance and temperature onset of charge disproportionation. In addition, very little is known about the changes in the electronic structure associated to the spin-state transition. These justify a thorough investigation of $LaCoO_3$ based on the use of direct spectroscopic techniques. In particular, XAS can provide very useful information because of its well-known site- and symmetry-selective character.[20,21] Moreover, the potential application of soft XAS to the study of phase-transition phenomena, as illustrated by the recent work on the metal-insulator transition of VO_2, deserves to be further investigated.[22]

II. EXPERIMENTAL DETAILS

The sample was a $LaCoO_3$ single crystal grown as follows: (i) stoichiometric proportions of La and Co acetates were spray-dry mixed, (ii) the mixture was calcined at 800 °C for 5 h and then pressed into a rod at 1000 kg/cm^2, (iii) the rod was calcined again at 1000 °C for 20 h, and (iv) the crystal was grown by zone melting in a floating-zone furnace at a speed of 2 mm/h. The sample was glued to a copper plate and heated by means of a filament placed inside a tungsten cage at the back part of the sample holder. The temperature was measured using a thermocouple placed beside the sample.

The XAS measurements were carried out at the National Synchrotron Light Source using the DRAGON monochromator.[23] The energy resolution of the monochromator was approximately 130 meV at the O 1*s* edge (530 eV) and around 270 meV at the Co 2*p* edge (780 eV). The energy scale was calibrated using the known peak positions of the O 1*s* and Cu 2*p* edges in CuO.[24,25] The base pressure in the chamber was 2×10^{-10} Torr. The spectra were collected in partial-electron yield in order to reject low-energy electrons coming from the heating device. The spectra were normalized to the maximum absorption intensity; an absolute normalization is not possible in partial-electron yield. The spectra were taken several times, illuminating different spots on the sample and alternating cycles of heating and cooling to ensure reproducibility; all the spectra could be successfully reproduced.

The x-ray photoelectron spectra (XPS) were measured using a commercial *top hat* X Probe from Surface Science Instruments. The base pressure in the chamber was 2×10^{-10} Torr. The x-ray source is a monochromatized Al $K\alpha$ line (1486.6 eV); the combined energy resolution was approximately 0.9 eV.

III. RESULTS AND DISCUSSION

A. Ground state

In a first approximation, the ground state of $LaCoO_3$ can be described in configuration-interaction terms as $|\Psi_{GS}\rangle=\cos\alpha|3d^6\rangle+\sin\alpha|3d^7\underline{L}\rangle$, where $\underline{L}$ denotes a ligand hole.[26–29] Higher-energy configurations are neglected because they contribute little in this compound, as discussed below. Both the symmetry of the ground state Γ_{GS} and the mixing angle α depend on the spin state of the Co ions.

The symmetry of each configuration can be determined by inspecting the Tanabe-Sugano diagrams and taking into account the different coupling possibilities.[30] The ground-state symmetry Γ_{GS} for low-spin Co^{3+} is $^1A_1$; the first ket is given by $|t_{2g}^6(^1A_1)\rangle$ and the second is of the form $|t_{2g}^6e_g^1(^2E)\otimes\underline{e}\rangle$, where $\underline{e}$ denotes a ligand hole of e_g symmetry. On the other hand, the overall Γ_{GS} for high-spin Co^{3+} is $^5T_2$, the first ket is given by $|t_{2g}^4e_g^2(^5T_2)\rangle$, and the second is a mixture of $|t_{2g}^5e_g^2(^4T_1)\otimes\underline{t}\rangle$ and $|t_{2g}^4e_g^3(^4T_1 \text{ or } ^4T_2)\otimes\underline{e}\rangle$, where $\underline{t}(\underline{e})$ denotes a ligand hole of $t_{2g}(e_g)$ symmetry. The coupling within the second kets must naturally yield Γ_{GS} in all cases.

The degeneracy of the high-spin state is lifted by spin-orbit interactions. In general, the 15-fold degenerate $^5T_2$ state is split in six irreducible representations of the cubic double group $A_1+E+2T_1+2T_2$. We assume in the $T=630$ K calculation below, that all these states are populated according to their respective degeneracies because the average splitting (approximately 0.074 eV) is of the order of kT (0.065 eV). This is achieved in the calculations by setting the 3*d* spin-orbit coupling to zero.

The mixing angle α can be determined by solving the secular equation for the Hamiltonian in this base and is given by

$$\tan(2\alpha)=-\frac{2T}{\Delta_{\text{eff}}}\,, \tag{1}$$

where T is the transfer integral and Δ_{eff} is the effective charge-transfer energy.[31] The transfer integral T is related to the Slater-Koster $pd\sigma$ and $pd\pi$;[32] the relationships in octahedral symmetry are $T_\sigma=\sqrt{3}pd\sigma$ and $T_\pi=2pd\pi$ $(T_\pi\approx-0.5T_\sigma)$. In the low-spin state, only e_g (σ bond) electrons can be transferred and T_{LS} is given by $2T_\sigma$. In the high-spin state, both e_g (σ bond) and t_{2g} (π bond) electrons can be transferred and T_{HS} is given by $(2T_\sigma^2+2T_\pi^2)^{1/2}$. These parameters, as well as the effective electron repulsion U_{eff}, can be estimated by interpolation and extrapolation of the values obtained for related compounds.[33] Here, U_{eff} and Δ_{eff} are defined with respect to the lowest-energy multiplet of each configuration.

For low-spin Co^{3+}, the estimations are $U_{\mathrm{eff}}\approx4\pm0.5$ eV, $\Delta_{\mathrm{eff}}\approx1\pm0.5$ eV, and $T_{\mathrm{LS}}\approx4\pm0.4$ eV. The $3d^6$ configuration occupancy estimated with these parameters is approximately 0.56. For high-spin Co^{3+}, the estimated values are $U_{\mathrm{eff}}\approx7\pm1$ eV, $\Delta_{\mathrm{eff}}\approx3\pm1$ eV, and $T_{\mathrm{HS}}\approx3.1\pm0.3$ eV. The occupancy of the main configuration in this case is $\cos^2\alpha\approx0.71$. The large occupancy of the $3d^6$ configuration in the high-spin state indicates a fairly ionic ground state. By contrast, the low-spin state must be considered largely covalent and this has important consequences. In particular, the $3d$ part of the ground state contains considerable ^2E character and this might be contributing to the Co $2p$ XAS spectra at low temperatures; see below.

The energy of the next excited configuration, $3d^8\underline{L}^2$, is given by $\Delta E=2\Delta_{\mathrm{eff}}+U_{\mathrm{eff}}$. This gives $\Delta E_{\mathrm{LS}}\approx6$ eV and $\Delta E_{\mathrm{HS}}\approx13$ eV; these values are large compared to Δ_{eff} for both spin states. The occupancy of this configuration is less than 0.20 for low-spin Co^{3+} and approximately 0.05 in the high-spin case. The relative values illustrate again the more covalent character of the low-spin state. The absolute contributions to the ground state are, however, relatively small, even for the low-spin state.

B. Co 2*p* XAS spectra

Figure 1 shows the experimental Co $2p$ XAS spectra of $\mathrm{LaCoO_3}$ taken at different temperatures. The spectra correspond to on-site transitions of the form $2p^63d^n\rightarrow2p^53d^{n+1}$ and present two groups of multiplets (roughly around 780 and 795 eV) split by the spin-orbit interaction of the Co $2p$ core level. The multiplets arise because the Coulomb and exchange interactions between the core hole and the valence electrons are large compared to the dispersion of the $3d$ bands. The Co $2p$ XAS spectra provide useful information on the electronic structure of $\mathrm{LaCoO_3}$, indicating (i) a low-spin state at low temperatures, (ii) a mixed-spin state at higher temperatures, and (iii) no charge disproportionation in the temperature range 80–630 K.

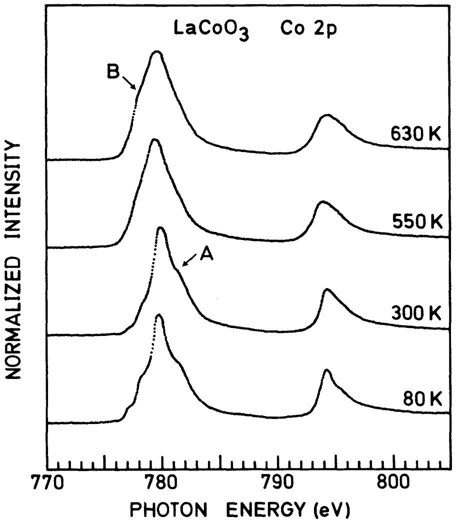

FIG. 1. Co $2p$ x-ray-absorption spectra of $\mathrm{LaCoO_3}$ taken at different temperatures. The spectra taken at higher temperatures (550 and 630 K) present two important changes, the absence of the shoulder at 781.5 eV (*A*) and the increased intensity around 778 eV (*B*).

The shape of the multiplets in the Co $2p$ spectra conveys information on the symmetry and spin of the ground state.[34,35] In fact, a comparison to atomic-multiplet simulations can be used as a diagnostic tool of the $3d$ part of the ground state.[36,37] The spectra taken at liquid nitrogen (80 K) and at room temperature (300 K) are quite similar. The features in the 300 K spectrum appear less well defined because of the larger phonon broadening. These low-temperature spectra correspond to low-spin Co^{3+} ions; this conclusion is supported by two facts. First, there is a close similarity to the Co $2p$ spectrum in a well-known low-spin Co^{3+} compound like $\mathrm{LiCoO_2}$.[38] Second, the spectra can be simulated by an atomic-multiplet calculation assuming a $t_{2g}^6(^1A_1)$ ground state with $10Dq=2.4$ eV. This is illustrated for the 300 K spectrum in Fig. 2(a).[39] The simulation reproduces fairly

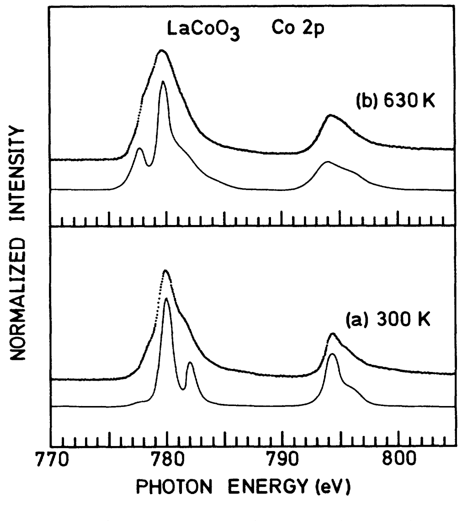

FIG. 2. Comparison between the experimental Co $2p$ x-ray-absorption spectra of $\mathrm{LaCoO_3}$ taken at 300 and 630 K (dots) and atomic-multiplet simulations (solid line). (a) The simulation is calculated assuming a low-spin $t_{2g}^6(^1A_1)$ ground state with $10Dq=2.4$ eV. (b) The simulation includes two mixed-spin contributions: the low-spin state described above and a high-spin $t_{2g}^4e_g^2(^5T_2)$ state with $10Dq=2.1$ eV.

well all major features, except for the shoulders around 778 eV. The agreement is considered acceptable for a highly covalent compound such as low-spin $LaCoO_3$. In fact, we cannot rule out completely the possible contribution to the spectra of excited configurations with different symmetries; see above.

On the other hand, the spectra taken at higher temperatures (550 and 630 K) present noticeable changes which cannot be attributed to phonon broadening. The absence of the shoulder at 781.5 eV (A) and the increased intensity around 778 eV (B) are particularly striking, see Fig. 1. These changes signal a modification of the symmetry and spin of the 3*d* part of the ground state at higher temperatures. Following the conclusions of previous work,[6,7] the 630 K spectrum is tentatively compared in Fig. 2(b) with the sum of two atomic-multiplet simulations, the low-spin $t_{2g}^6(^1A_1)$ state described above and a high-spin $t_{2g}^4e_g^2(^5T_2)$ state with $10Dq = 2.1$ eV. The simulation is considered satisfactory because it is able to reproduce qualitatively the main experimental changes. The high-temperature spectra are thus consistent with a mixed-spin state with a high-spin to low-spin ratio of approximately 1.[40]

Possible changes in the valence of the Co ions can be inferred from the chemical shifts in the Co 2*p* spectra.[41] The center of gravity of the multiplets in Fig. 1 remains approximately at the same energy regardless of the temperature. The absence of chemical shifts indicates that the average 3*d* count at the Co sites does not change. This contradicts the often-held idea that some charge disproportionation into Co^{2+} and Co^{4+} takes place in this oxide as the temperature is raised. Figure 3 shows atomic-multiplet simulations of the Co 2*p* XAS spectra for Co ions with different 3*d* counts, the calculations were performed using $10Dq = 2.1$ eV in all cases. The calculations provide additional evidence against charge disproportionation in $LaCoO_3$. Indeed, the presence of either Co^{2+} or Co^{4+} ions in the temperature range 80–630 K can be ruled out with confidence because the shape of the respective multiplets deviates too strongly from the experimental results shown in Fig. 1.

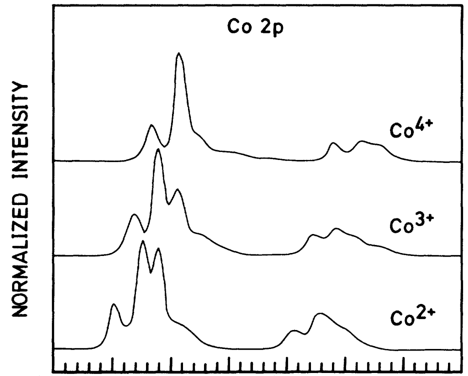

FIG. 3. Atomic-multiplet simulations of the Co 2*p* x-ray-absorption spectra for Co ions with different 3*d* counts, the calculations were performed using $10Dq = 2.1$ eV in all cases. The absolute energy scale of the calculation is shifted by approximately 2 eV. The relative energy shifts are expected to be more accurate.

C. O 1*s* XAS spectra

Figure 4 shows the experimental O 1*s* XAS spectra of $LaCoO_3$ taken at different temperatures. The spectra correspond to transitions to unoccupied O *p* states mixed in bands of primary metal character. The main character of each band can be estimated from the parent molecular-orbital level.[42] The relative order of such levels can be predicted by taking into account the relative strength of the different metal-oxygen interactions. In this way, the features around 530 eV are attributed to Co 3*d* bands, the dominant bump at 536 eV to La 5*d* bands, and the structure with two peaks above 539 eV to Co 4*sp* bands. These assignments are in agreement with previous work in related compounds[37] and are consistent with band-structure calculations for $LaTiO_3$.[43]

Aside from the general assignments made above, the O 1*s* spectra taken at different temperatures present several noticeable changes. First, the phonon broadening increases with temperature over the entire spectra; this effect is more evident in the higher-energy regions. Second, the peaks in the Co 4*sp* region of the 550 and 630 K spectra move to lower energies and increase their separation as indicated by the dashed line in Fig. 4; this effect is related to crystallographic changes which occur in the mixed-spin phase; see below. Finally, there are significant changes in the Co 3*d* bands which are related to the spin-state transition.

Figure 5 shows the Co 3*d* bands region of the O 1*s* XAS spectra in an expanded energy scale. The bands are mounted on a rising background coming from the overlap with the adjacent La 5*d* region. The spectral shapes

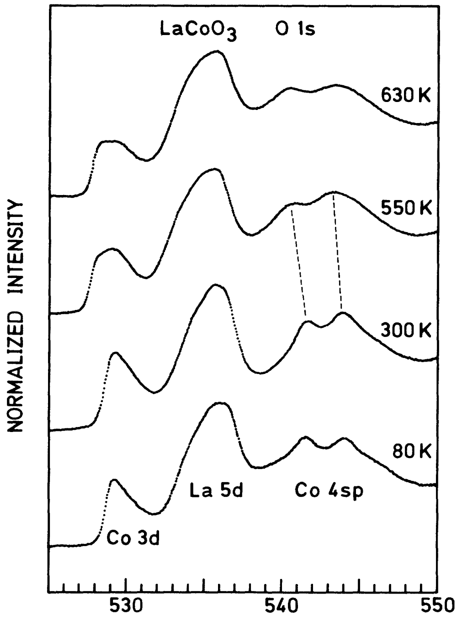

FIG. 4. O 1*s* x-ray-absorption spectra of $LaCoO_3$ taken at different temperatures. The spectra taken above 300 K present important changes in the Co 3*d* bands region, around 530 eV. Changes in the Co 4*sp* region are indicated by the dashed line.

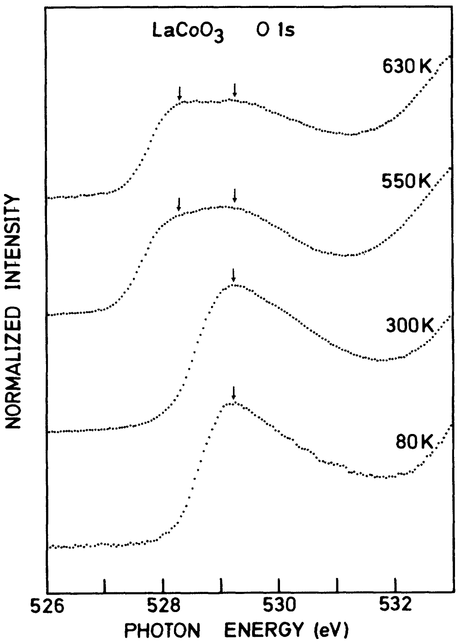

FIG. 5. Co 3*d* bands region of the O 1*s* x-ray-absorption spectra shown in Fig. 4 in an expanded energy scale. The spectra taken at 80 and 300 K present a single contribution at 529.2 eV; this contribution is due to the unoccupied e_g subband. By contrast, a second component appears at 528.2 eV in the spectra taken at 550 and 630 K; this lower-energy component is related to the unoccupied t_{2g} subband.

at 80 and 300 K are quite similar and present a single contribution at 529.2 eV; this is again consistent with a low-spin state at low temperatures. Indeed, the electronic configuration of low-spin Co^{3+} is t_{2g}^6 and only the e_g subband can be expected to contribute to the spectra. By contrast, a second component appears at 528.2 eV in the spectra taken at higher temperatures (550 and 630 K), see Fig. 5. This splitting within the Co 3*d* bands is due to crystal-field effects and signals a mixed-spin state. In particular, the low-energy component is attributed to the contribution of the t_{2g} subband coming from high-spin Co^{3+} ions with a $t_{2g}^4e_g^2$ configuration. The lowest unoccupied state in low-spin $LaCoO_3$ cannot be reached by a one-electron process; this might help to explain the higher onset of the O 1*s* XAS spectra at low temperatures.

The reported onset of metallic behavior at approximately 570 K (Ref. 12) coincides with the appearance of the t_{2g} related states. This indicates that the increase in the conductivity is due to indirect Co-3*d*–O-2*p*–Co-3*d* interactions in delocalized bands of primary Co t_{2g} character.[44] The photoemission spectra below show that the Fermi level at low temperatures is pinned at, or very close to, the top of the valence band. The Fermi level in the O 1*s* XAS spectra can be determined from the spectrum at 550 K. The comparison with the spectrum at 300 K gives an estimate of the gap of about 0.9±0.3 eV.

The changes in the Co 4*sp* region above 550 K, see Fig. 4, are attributed to crystallographic changes associated to the mixed-spin state. The high-spin Co^{3+} ion is larger than the low-spin ion because the high-spin configuration $t_{2g}^4e_g^2$ populates two antibonding e_g orbitals, whereas the low-spin configuration t_{2g}^6 contains only relatively nonbonding t_{2g} electrons. This implies, in turn, that the Co-4*sp*–O-2*p* interactions are weaker for high-spin Co^{3+} because they decrease with Co-O distance. Accordingly, as the high-spin Co^{3+} ions are populated in the mixed-spin state, the center of gravity of the Co 4*sp* region is expected to shift towards lower energies. We note, however, that these changes in the O 1*s* spectra reflect *local distortions,* because of the local character of XAS. Whether these distortions order in a cooperative way to give long-range order, as proposed by Raccah and Goodenough,[6,7] still remains controversial.[10]

D. Photoemission spectra

Figure 6 shows the valence-band XPS spectra of $LaCoO_3$ taken at different temperatures. The spectrum taken at room temperature agrees well with previous data.[45,46] In a first approximation, the experimental spectra can be related to the one-particle removal spectral function by the appropriate weighting factors. The spectra are dominated by features related to Co 3*d* electrons because at this energy, 1486.6 eV, the photoionization cross section for this subshell $(0.4\times10^{-2}$ Mb) is larger than for O 2*p* states $(0.6\times10^{-3}$ Mb).[47]

The spectra present several features in the first 8 eV below the Fermi level; this structure is caused by strong multiplet effects in the final state. The most relevant contribution to the spectra in the case of low-spin Co^{3+} ions is a single line corresponding to the photoionization of the $3d^6$ part of the ground state, i.e., the

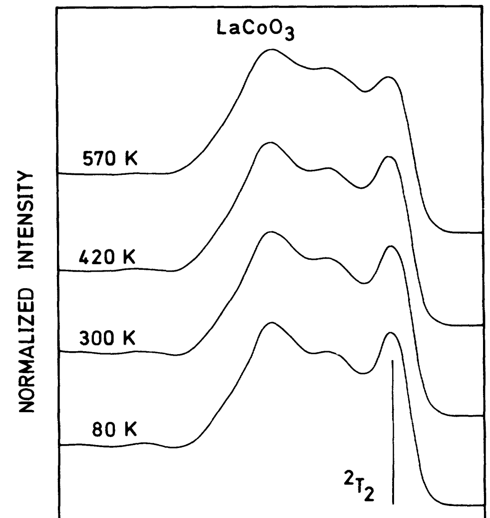

FIG. 6. Valence-band x-ray photoelectron spectra of $LaCoO_3$ taken at different temperatures. The $^2T_2$ line at 1.3 eV, which corresponds to the $t_{2g}^6(^1A_1)+h\nu\rightarrow t_{2g}^5(^2T_2)+e$ photoemission channel, gives an idea of the amount of low-spin Co^{3+} ions. The intensity of the $^2T_2$ line decreases in the spectrum taken at 570 K as the low-spin state population is depleted.

$t_{2g}^6(^1A_1)+h\nu\rightarrow t_{2g}^5(^2T_2)+e$ channel. This contribution is particularly strong because all the spectral weight is concentrated in only one line peaking at 1.3 eV, as illustrated in Fig. 6. This assignment is derived from cluster-model calculations and is consistent with previous work.[45,46] By contrast, the contribution to the spectra corresponding to the photoionization of the $3d^7\underline{L}$ part of the low-spin state consists of a complex multiplet spread over the entire 0–8 eV range. Similarly, both the $3d^6$ and the $3d^7\underline{L}$ parts of the ground state of high-spin Co^{3+} ions give rise to a widely spread multiplet. This means that the intensity of the $^2T_2$ line is related to the amount of low-spin Co^{3+} ions as a function of temperature (unfortunately it is not directly proportional because of covalency effects).

This relationship between the intensity of the $^2T_2$ line and the amount of low-spin Co^{3+} ions can be used to get additional information on the spin-state transition of $LaCoO_3$. The spectra taken at 80 and 300 K are rather similar and present no significative change. These spectra are characteristic of the low-spin state; this can be concluded from preliminary cluster-model calculations and is also in agreement with previous work.[45,46] The same arguments apply to the 420 K spectrum because there are no relevant changes and the intensity of the $^2T_2$ line remains the same. By contrast, the intensity of the $^2T_2$ line decreases significantly in the spectrum taken at 570 K due to the expected depletion of the low-spin population. These results indicate that the low-spin state dominates up to 420 K approximately; this conclusion is in disagreement with a high-spin component at low temperatures reported in previous work.

E. Spin transition

A successful model of the spin-state transition in $LaCoO_3$ should explain the following experimental facts: (i) a low-spin state up to approximately 420 K; (ii) an increase of the high-spin component in the interval 420–650 K; and (iii) a possible ordering of high-spin and low-spin ions at 650 K. It is clear that a simple two-level thermal population analysis cannot reproduce these characteristics. This model predicts a smooth temperature dependence without any onset as well as a dominant high-spin population at higher temperatures because of the much larger degeneracy of the high-spin state.

The first improvement with respect to this situation was the inclusion of spin-lattice interactions suggested by Chesnut.[15] The crystallographic changes at 650 K were later rationalized within the framework of the two-sublattice model proposed by Bari and Sivardière.[16] At low temperatures, 0–420 K, the high-spin state of $LaCoO_3$ lies approximately 0.08 eV above the low-spin state.[6,7] At higher temperatures, particularly at 650 K, a cooperative distortion with alternating order of high-spin and low-spin ions lowers the electronic energy at both ion sites at the expense of minimum elastic energy losses. A decrease of the Co-O distance stabilizes even more the low-spin ion sites because an increase of the Co-$3d$–O-$2p$ interactions results in a larger $10Dq$. The opposite is true at the high-spin ion sites, an increase of the Co-O distance results in weaker Co-$3d$–O-$2p$ interactions and in a more stable high-spin state. This kind of ordering presents striking similarities with the well-known cooperative Jahn-Teller effect.[48]

However, this model still cannot explain the peculiar temperature onset of the spin-state transition. It is then worthwhile to note the possible influence of an effect which was not taken into account in previous analyses. This effect is the change in the relative energy of the low-spin and high-spin states caused by the thermal expansion of the lattice, due just to anharmonic terms in the elastic energy, and the ensuing decrease of the crystal-field interactions. This effect could be playing a role here because the increase in the Co-O distance in the temperature interval 80–650 K, approximately 0.03 Å as determined by neutron diffraction,[10] is of the order of the difference between the tabulated ionic radii of high-spin and low-spin Co^{3+} ions, 0.06 Å.[49] It is then plausible that the gradual spin transition in $LaCoO_3$ could be driven by a thermal population of the high-spin state aided by a simultaneous collapse of the energy difference respect to the low-spin state. This effect could help to explain the unexpected temperature onset of the spin-state transition.

IV. SUMMARY AND CONCLUSIONS

In summary, we measured the Co $2p$ and O $1s$ XAS spectra of $LaCoO_3$ at different temperatures in the range 80–630 K. Complementary XPS spectra of the valence band were also measured in the range 80–570 K. The Co $2p$ XAS spectra provide information on the symmetry and spin of the ground state. The O $1s$ spectra reflect unoccupied bands of primary metal character. The changes in the spectra taken at different temperatures give information on the spin-state transition in $LaCoO_3$. The nature of the ground state was analyzed in terms of a configuration-interaction approach.

$LaCoO_3$ is in a highly covalent low-spin state at low temperatures; this includes the range 80–300 K and extends, possibly, up to 420 K approximately. The main contribution to the ground state in this case is given by $t_{2g}^6(^1A_1)$ with an occupancy of 0.56. The results indicate a transition to a mixed-spin state at higher temperatures (550 and 630 K). The main contribution to the high-spin part of the mixture is given by $t_{2g}^4e_g^2(^5T_2)$ with an occupancy of 0.71. There is no evidence of charge disproportionation in the temperature range 80–630 K. The O $1s$ XAS spectra reflect important changes in the unoccupied Co $3d$ bands: in the low-spin state (80 and 300 K) only the e_g subband contributes to the spectra, whereas in the mixed-spin state (550 and 630 K) both the t_{2g} and e_g subbands can be observed. Other changes in the O $1s$ XAS spectra are attributed to *local distortions* in the mixed-spin state caused by the different size of the high-spin and low-spin Co^{3+} ions.

This example illustrates clearly the potential of XAS in the study of the electronic structure changes across phase transitions. We note, however, that this fascinating compound is significantly more complex than originally expected and its electronic properties are far from being completely understood. In particular, more work will have to be done to elucidate the microscopic origin of the driven force behind the spin-state transition.

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