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# Photoelectron-spectroscopy investigation of the spin-state transition in $LaCoO_3$

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We report the valence-band and Co $2p$ photoemission spectra of $LaCoO_3$ obtained at different temperatures (100, 300, and 573 K). Analysis of the core-level spectrum in terms of a configuration interaction model suggests that both low- and high-spin states coexist at the low temperature (100 K). It also indicates that there is a decrease in the low-spin contribution at 573 K related to local structural changes. Photoemission spectra of the valence-band region further support this interpretation.

## I. INTRODUCTION

Lanthanum cobalt oxide ($LaCoO_3$) is a ground-state insulator with a rhombohedrally distorted perovskite structure. $LaCoO_3$ is known to undergo a spin state transition as a function of temperature.[1–4] The exchange interaction and the crystal-field-splitting strengths in this compound are believed to be comparable, resulting in the low-spin $Co^{3+}$ ($t_{2g}^6 e_g^0$) state and the high-spin ($t_{2g}^4 e_g^2$) state with very similar energies, the low-spin state being more stable by approximately 0.08 eV.[1] Jonker[4] proposed the presence of a thermally populated high-spin state in the temperature range 50–350 K. Raccah and Goodenough[1] also reached similar conclusions based on x-ray-diffraction, magnetic-susceptibility, and conductivity studies. While some doubts have been expressed[5] about the validity of the older magnetic-susceptibility studies due to the possible presence of impurities, recent polarized and unpolarized neutron-scattering measurements[6] clearly established the presence of temperature-induced magnetic moment in $LaCoO_3$ even at 50 K. The magnetic moment was found to increase with temperature up to about 100 K quite rapidly, indicating the existence of thermally populated high-spin states and then much more slowly beyond 100 K up to room temperature. Resistivity as a function of temperature for $LaCoO_3$ suggests a broad metal-insulator transition between 520 and 750 K,[7] with the possibility of a further increase in the high-spin state. X-ray-diffraction studies[1] indicated a structural transition from $R\bar{3}c$ to $R\bar{3}$ symmetry at 648 K. In a later neutron diffraction study[8] over a temperature range of 4.2–1248 K, the evidence for the $R\bar{3}$ symmetry was found only at 668 K, while at other temperatures the symmetry was $R\bar{3}c$. However, recent extended x-ray absorption fine structure (EXAFS) measurements[9] clearly indicate the presence of two different Co-O distances as in the $R\bar{3}$ symmetry for temperatures above 523 K. This suggests that locally two types of Co ions, characterized by two different sized $CoO_6$ octahedra, exist at temperatures above 523 K, though the structural ordering of these two types of octahedra exists only in the vicinity of 668 K in accordance with neutron diffraction measurements.[8]

Electron spectroscopic techniques[10–14] have been used in the past to elucidate the spin-state transition in $LaCoO_3$. Veal and Lam[10] studied the x-ray photoelectron (XP) valence-band spectra of $LaCoO_3$ at room temperature and 573 K. The comparison of the experimental spectra with the multiplet structure arising in the low- and high-spin states indicated the presence of the high-spin state at room temperature and an increased occupation of the high-spin state at the higher temperature. The presence of multiplets corresponding to the high-spin state was also observed[11] in the He II spectra of $LaCoO_3$ at 77 K. The temperature dependence of the He II spectra[12] of $LaCoO_3$ could be explained in terms of the decreasing population of the low-spin state at higher temperatures. A recent report[13] of the electron emission spectrum resulting from the thermal collisions of He* atoms with $LaCoO_3$ suggests that the Co $3d$ character is spread out over several spectral features spanning about 4 eV below $E_F$, indicating the existence of the high-spin state along with the low-spin state at room temperature. In contrast to these reports, however, Abbate *et al.*[14] have recently concluded that $LaCoO_3$ is in the low-spin state up to ~420 K and it is only at higher temperature that the high-spin component exists, based on a Co $2p$ and O $1s$ x-ray absorption spectroscopy (XAS). The results of Abbate *et al.*[14] are also in disagreement with the neutron measurements.[6] This is somewhat surprising, since magnetic-susceptibility and inelastic neutron-scattering measurements should be the most suitable techniques for probing the existence of a magnetic moment and thus the existence of the high-spin state. Thus it was felt necessary to reinvestigate the spin-state transition in $LaCoO_3$ with a related spectroscopic technique. It is to be noted here that the earlier spectral analysis of the valence band in Ref. 10 and of the Co $2p$ XAS in Ref. 14 have been performed within essentially ionic models, neglecting configuration interactions arising from substantial Co $3d$–O $2p$ transfer integrals. The valence-band analysis presented in Ref. 14, on the other hand, does not account for the finite strength of the intra-atomic Coulomb interaction. Here we report the photoemission Co $2p$ core-level spectra recorded at different temperatures and analyzed within the configuration interaction model.[15] We point out that the present results are consistent with the results of neutron measurements. We also report the temperature-dependent valence-band spectra of $LaCoO_3$ using He I, He II, and Mg

$K\alpha$ radiations and relate the thermally induced changes in the spectral features to the structural transition. Use of different photon sources allows us to understand the origin of various features appearing in the valence-band spectra.

## II. EXPERIMENT

Polycrystalline $LaCoO_3$ samples were prepared by heating predried $La_2O_3$ and $CoC_2O_4$, $2H_2O$ in required proportions at 1673 K. Powder x-ray-diffraction (XRD) and resistivity measurements were carried out to characterize the samples. The XRD pattern did not show the presence of any impurity phase. The oxygen content, determined by using electrochemical titrations, confirmed the oxygen stoichiometry in the samples. The electron spectroscopic experiments were carried out in a commercial spectrometer from VSW Scientific Limited, U.K. A clean and reproducible sample surface was obtained by scraping the sample with an alumina file in a vacuum of $5\times10^{-10}$ mbar till the various core levels did not show any further change. The cleanliness of the surface was further monitored by recording C 1*s* and O 1*s* spectral regions. While O 1*s* exhibited a single peak spectrum, the intensity of C 1*s* was negligible. Moreover, the similarity of the valence-band spectrum of the present polycrystalline sample to that obtained from a single crystal[14] indicates that the sample surface studied in the present work is free from contaminations. The experiments were carried out at about 100 K, 300 K, and 573 K. However, the sample surface temperature is expected to be somewhat different as the thermocouple was in contact with the cold finger on which the sample is mounted. Thus we expect the temperatures at the surface to be about 120±10, 295±5, and 553±10 K, respectively.

## III. RESULTS AND DISCUSSION

Figure 1 shows the valence-band spectra of $LaCoO_3$ at two temperatures, 100 K and 573 K obtained with He I (21.2 eV) and He II (40.8 eV) and Mg $K\alpha$ (1253.6 eV) radiations. All the spectra show three features at about 1.0, 3.0, and 5.0 eV binding energies. The relative intensities of the features at 3 and 5 eV binding energies are found to increase with decreasing photon energy, suggesting a dominant origin from the O 2*p* states. On the contrary, the lowest binding energy peak loses intensity rapidly with decreasing photon energy indicating that it primarily originates from Co 3*d* photoionization. This spectral feature has been assigned[10,14] to the transition $|t_{2g}^6 : {}^1A_1\rangle \longrightarrow |t_{2g}^5 : {}^2T_2\rangle$ arising from a low-spin $Co^{3+}$ state. An analysis of the valence-band XP spectrum of $LaCoO_3$ in terms of crystal field final states did also find[10] evidence for the existence of the high-spin state at room temperature. Furthermore, a recent analysis[13] of the He I valence-band spectrum of $LaCoO_3$ found evidence for substantial admixture of Co 3*d* character at about 3 eV binding energy, beyond the low-spin signature at 1 eV, suggesting the existence of a high-spin $Co^{3+}$ state at room temperature. Interestingly, the spectral features do not change noticeably between 100 K (Fig. 1) and 300 K (not shown). Such an invariance of the spectral features with temperature (up to 420 K) has also been reported in Ref. 14 in the case of the XP spectrum. In that work,[14] it has been suggested on the basis of this observation that there is negligible population of the high-spin $Co^{3+}$ state and the Co ions exist only as a low-spin ion up to about 420 K. We, on the contrary, interpret this relatively unaffected spectral shape with temperature between 100 K and 420 K as an evidence that the proportion of high-spin $Co^{3+}$ contribution, though substantial, is relatively constant over this temperature range. This interpretation is further supported by the analysis of the Co 2*p* core-level spectral shape presented below and is in agreement with other electron spectroscopic data[10,11,13] as well as neutron measurements.[6]

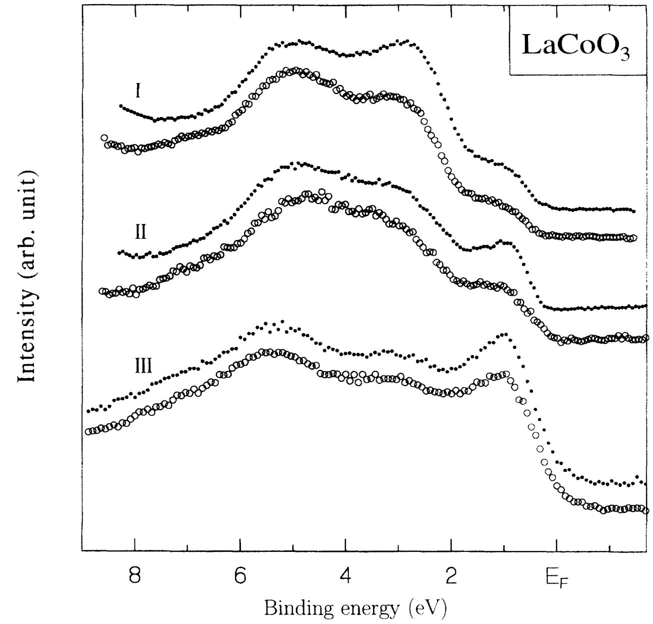

FIG. 1. The valence-band photoemission spectra of $LaCoO_3$ recorded with 21.2 eV (I), 40.8 eV (II), and 1253.6 eV (III) photon energies at 100 K (dots) and 573 K (open circles).

Co $2p_{3/2}$ core-level spectra obtained at two different temperatures, 100 K and 573 K, are shown in Fig. 2. The spectrum recorded at 300 K was indistinguishable from the spectrum at 100 K. Both the spectra exhibit a prominent main peak at 780.1±0.2 eV. Moreover a weaker satellite feature can also be seen in the spectra near 789.5 eV accompanying the main peak. It is now a routine procedure to extract the initial state information by analyzing such spectra in terms of the configuration interaction model.[15] Thus we have tried to synthesize the 100 K spectra allowing for both low- and high-spin contributions. We calculate the core-level spectra for these two spin configurations separately within the cluster approximation including configuration interactions for $(CoO_6)^{9-}$ clusters. The intra-atomic Coulomb interaction, $U_{dd}$, was kept equal to the experimental estimate[15] of 3.4 eV and the core 2*p* hole–valence 3*d* hole interaction, $U_{dc}$, was set equal to $1.1\times U_{dd}$, as is usually done.[15] The hopping matrix elements $t_\pi$ between the Co $t_{2g}$ and O $2p_\pi$ were assumed to be half of the hopping matrix element between the Co $e_g$ and O $2p_\sigma$ orbitals, $t_\sigma = \sqrt{3}t_{pd\sigma}$, with $t_{pd\sigma}$ being the Slater-Coster integral $(pd\sigma)$.[16] Furthermore, the satellite structure for the high-spin configuration was given an extra broadening in order to simulate the extensive multiplet structure present in the high-spin case compared to the low-spin case.[17] The low temperature spectrum could be simulated very well assuming 70±10% and 30±10% contributions from the low- and the high-spin configurations, respectively [Fig. 2(a)], with the charge transfer energy $\Delta$ and $t_{pd\sigma}$ equal to 4.0 eV and 2.0 eV, respectively. While the spectral shape is described well by the calculation, there is an obvious mismatch near 783±2 eV. This discrepancy may arise from our neglect of multiplet interaction in the core ionized states as well as from various multi-impurity effects not included in the present model, including a single transition metal ion. It turns out that the fit in the satellite region [inset, Fig. 2(a)] is not quite satisfactory if we assume only one spin configuration and the satellite shape thus indicates the simultaneous presence of both low- and high-spin states. The present calculation suggests that the Co $2p_{3/2}$ main peak at 780.1 eV corresponds to the final state with approximately 28% $d^6$, 50% $d^7\underline{L}^1$, and 22% $d^8\underline{L}^2$ configurations while the satellite at 789.5 eV has 49% $d^6$, 4% $d^7\underline{L}^1$, 33% $d^8\underline{L}^2$, and 14% $d^9\underline{L}^3$ character. We find that the low-spin initial state at 100 K corresponds to having 43% $d^6$, 45% $d^7\underline{L}^1$, and 12% $d^8\underline{L}^2$ configurations, while the high-spin state at the same temperature has 60% $d^6$, 35% $d^7\underline{L}^1$, and 5% $d^8\underline{L}^2$ configurations. Thus the presence of substantial hopping matrix elements $t_{pd\sigma}$ in comparison to $\Delta$ and $U_{dd}$ leads to strongly mixed characters for both the spin states and thus these states cannot be even approximately associated with any single ionic configuration either for the low-spin or the high-spin state. The contributions of the $d^6$ configuration for both low- and high-spin states turns out to be somewhat smaller than the estimate in Ref. 14. We believe that this difference arises primarily from the neglect of the $d^8\underline{L}^2$ configuration in the earlier work.

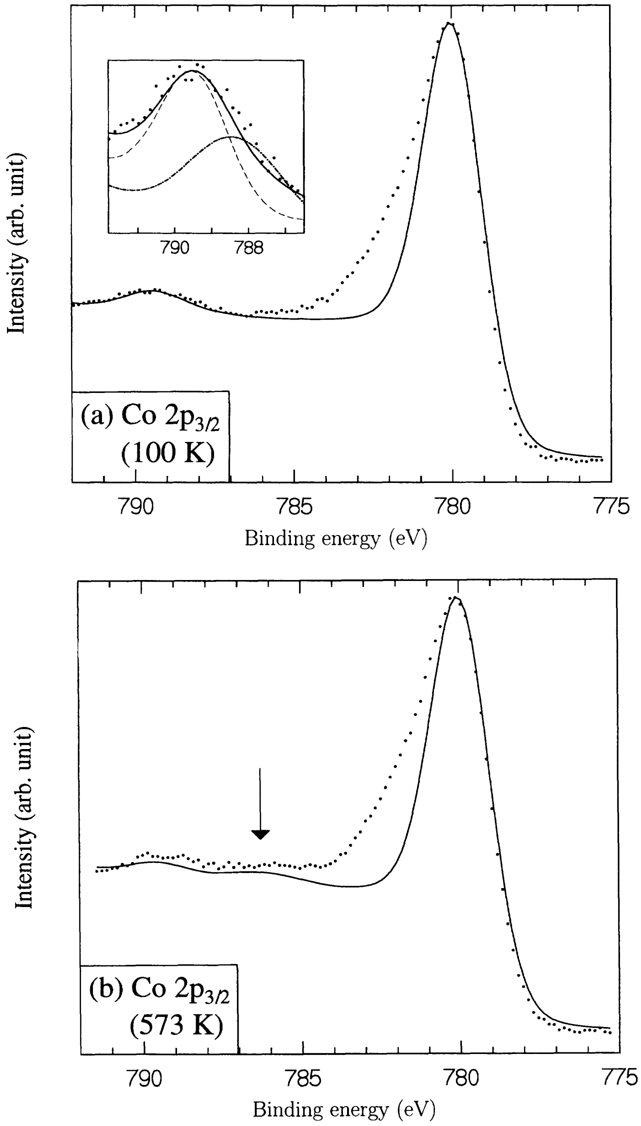

FIG. 2. The experimental (dots) and calculated (solid line) Co $2p_{3/2}$ spectra of $LaCoO_3$ at (a) 100 K and (b) 573 K. The inset in (a) shows the fit to the satellite region of the $2p_{3/2}$ spectra at 100 K using 70% low- and 30% high-spin (solid line), only low-spin (dashed line) and only high-spin (dot-dashed line) states.

On increasing the temperature to 573 K, the most noticeable change in the Co $2p_{3/2}$ spectrum is near the satellite with the emergence of a feature at about 786 eV binding energy, marked with an arrow in Fig. 2(b). In order to interpret the Co 2$p$ spectrum at 573 K with the help of similar configuration interaction calculations, we first note that at higher temperatures ($T$ > 523 K) there are two Co-O distances present in this compound.[9] The larger of the two Co-O distances has been attributed to the high-spin states present at these temperatures. Thus the structural data suggest that the hopping matrix element relevant for the high-spin state at the higher temperature will be smaller than that at the lower temperature. Accordingly, for the simulation of the 573 K spectrum we have used a $t_{pd\sigma} = 1.4$ eV for the high-spin state, while keeping every other parameter the same as in the case of the low temperature (100 K) spectrum. The resulting calculated spectrum synthesized by the admixture of 50±10% low-spin and 50±10% high-spin configurations provides a reasonable description for the experimental spectrum [see Fig. 2(b)]. The present calculation clearly shows that the satellite feature at 786 eV is due to the $Co^{3+}$ high-spin state, while that at 789.5 eV is due to the low-spin state. The satellite features are well separated in energy at this higher temperature in contrast to the low temperature spectrum [Fig. 2(a)]. This is primarily because of the decrease in $t_{pd\sigma}$ for the high-spin state arising from an increased Co-O distance. Thus the core-level spectrum provides an indirect, but unambiguous, evidence of local changes in the bond lengths. The calculated main peak at 573 K [Fig. 2(b)] corresponds to the combination of approximately 35% $d^6$, 48% $d^7\underline{L}^1$, and 17% $d^8\underline{L}^2$ configurations. The satellite feature at 786 eV corresponding to the high-spin state is characterized by approximately 49% $d^6$, 21% $d^7\underline{L}^1$, and 30% $d^8\underline{L}^2$ configurations, while the satellite feature at 789.5 eV at the same temperature related to the low-spin state is an admixture of 50% $d^6$, 33% $d^8\underline{L}^2$, and 17% $d^9\underline{L}^3$ configurations.

In conclusion, an analysis of the Co $2p$ spectra in terms of a configuration interaction model suggests the presence of the high-spin state (~30%) even at a low temperature (100 K). We interpret the insensitivity of the spectral features on temperature below 420 K as a consequence of the relatively constant proportion of the high-spin state between 100 K and 420 K, in agreement with the inelastic neutron measurements.[6] It will be interesting to carry out the electron spectroscopic investigations at substantially lower temperatures than has been done till now as the core and the valence level spectra are expected to change considerably at lower temperatures due to a rapid decrease of the high-spin $Co^{3+}$ component. At higher temperatures (573 K), the state of $LaCoO_3$ is characterized by a partial transformation of the low-spin $Co^{3+}$ to the high-spin configuration, the high-spin component being approximately 50%. This higher temperature transition appears to be driven by changes in the local Co-O bond lengths. The initial state of $LaCoO_3$ has been characterized as a highly mixed valent state with substantial $d^6$ and $d^7\underline{L}^1$ configurations.

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