

Direct Measurement of the Low-Temperature Spin-State Transition in LaCoO_3

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LaCoO_3 exhibits an anomaly in its magnetic susceptibility around 80 K associated with a thermally excited transition of the Co^{3+} -ion spin. We show that electron energy-loss spectroscopy is sensitive to this Co^{3+} -ion spin-state transition, and that the O K edge prepeak provides a direct measure of the Co^{3+} spin state in LaCoO_3 as a function of temperature. Our experimental results are confirmed by first-principles calculations, and we conclude that the thermally excited spin-state transition occurs from a low to an intermediate spin state, which can be distinguished from the high-spin state.

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The perovskite-oxide LaCoO_3 has been studied intensely over the last 40 years due to its unique magnetic behavior and its related nonmetal-metal transitions [1–13]. Specifically, two broad transitions in the magnetic susceptibility of LaCoO_3 are of interest, the first one occurring at 50–90 K when LaCoO_3 undergoes a gradual transition from a nonmagnetic to a paramagnetic semiconductor, followed by a second transition at 500–600 K that coincides with a semiconductor-to-metal transition. While these two transitions have been attributed to spin-state transitions of the Co^{3+} -ion spins [1,3,9,14], the underlying electronic structure and spin states have not yet been fully understood. Goodenough [3,15,16] first interpreted these magnetic transitions as spin-state transitions of the Co^{3+} ions from a low spin-state (LS) to a high-spin state (HS) due to the close values of the intra-atomic exchange energy (J_H) and the crystal field splitting ($10Dq$) at the Co^{3+} sites. Thus, depending on the relative values of the J_H and $10Dq$, either the LS with $t_{2g}^6 e_g^0$ resulting in $S = 0$, or the HS with $t_{2g}^4 e_g^2$ resulting in $S = 2$ were suggested to be more stable. While this model can explain the high-temperature transition in LaCoO_3 , several different models for the Co^{3+} spin state in the temperature regime between 80 and 500 K, and the associated transition at 80 K have been proposed in the past [6,9,15].

One popular model is the mixed spin state of the Co^{3+} -ions, where the population of the HS state is increased with increasing temperature, resulting in a stable LS-HS spin-state array (ratio between LS and HS of 1:1). Many spectroscopic studies, including photoemission spectroscopy (XPS) [8], and x-ray absorption spectroscopy (XAS) [13,14,17] have been reported, investigating these spin-state models in LaCoO_3 . Abbate *et al.* [14], using

XAS on LaCoO_3 single crystals, measured the changes in the Co L edge and O K edge, showing clear differences in both the Co $2p$ as well as in the O $1s$ spectra between 300 and 630 K. In particular, the O K edge prepeak exhibited an additional peak at $T > 550$ K, which was attributed to the presence of a HS state in addition to the LS state at this temperature. However, at low temperatures ($80 \text{ K} < T < 300 \text{ K}$), neither the Co L edge nor the O K edge showed any changes in the XAS, which lead to the conclusion that the LS state is preserved at temperatures up to 420 K [14].

Subsequent LDA + U calculations of the total energy for different spin-states in LaCoO_3 raised questions about the existence of a mixed LS-HS state, and, moreover, predicted the occurrence of an intermediate spin state (IS, $S = 1$) with $t_{2g}^5 e_g^1$ of the Co^{3+} ion. Korotin and co-workers [9] have shown that this IS-state is energetically comparable to the LS state, and much more stable than the HS state, due to the larger O $2p$ Co $3d$ hybridization, as well as orbital ordering effects. The calculated density of states for the HS state explains the previously reported appearance of a second peak in the O K edge prepeak, as an effect of the increasing density of unoccupied states in the e_g^1 band. These calculations also predict changes in the total DOS between the LS and the IS states, due to the increased filling of the eg band and the splitting of the spin-up and spin-down spin projection [18].

In this Letter we will demonstrate that a combination of analytical TEM and electron energy-loss spectroscopy (EELS) [19] with *in situ* cooling capabilities, and *ab initio* density-functional theory (DFT) calculations can be used to measure the changes in the electronic structure resulting from the Co^{3+} spin-state transition at ~ 80 K. While pre-

vious studies have primarily used XAS to study the near-edge fine-structure of either the O K edge or the Co L edge in LaCoO_3 as a function of temperature, due to the excellent energy resolution of XAS [14,20], these studies were not able to study individual grains, or defects within the LaCoO_3 crystal structure due to the inherent lack of spatial resolution of XAS. On the other hand, EELS can achieve atomic-column spatial resolution, but its energy-resolution in conventional TEMs cannot compete with that in XAS (i.e., 1.0 eV vs 0.12 eV at 500 eV energy loss). However, we will show that it is sufficient to distinguish the different Co^{3+} spin-states by EELS. The results shown in this Letter can further be used to not only determine the spin-state of the Co^{3+} ions in LaCoO_3 , but also provide an atomic-resolution probe of the spin state in other, more complex Co-oxide materials, furthering our understanding of the fundamental structure-property relationships in this class of magneto-resistive materials.

First-principles GGA and LDA + U calculations [21–23] are used to simulate the near-edge fine-structure of the O K edge and total energy of LaCoO_3 for three different spin states. We have calculated the projected density of unoccupied states for LaCoO_3 in the LS state that can be found at low temperatures ($T < 80$ K), for an IS state and for a HS state. The EELS spectra were calculated using the TELNES.2 package included in the WIEN2K code [24], a full-potential linear augmented plane-wave plus local-orbitals method within DFT. In order to simulate the spectra for the different spin states (e.g., $S = 0, 1$, and 2) of LaCoO_3 , the fixed-spin-moment calculation were used to constrain the total spin magnetic moment. In our calculations, we have further considered the lattice parameter determined by powder neutron diffraction as a function of temperature [25]. As shown in the earlier LDA + U calculations, we find that over the entire temperature range considered here ($80 \text{ K} < T < 500 \text{ K}$), the IS state is energetically more favorable than the HS state [9]. To study the effect of the on-site Coulomb interaction on the total energy of LaCoO_3 for different Co^{3+} spin states, our LDA + U calculations were performed using several different values for U , including 2, 4, 6, 7.8, 8, and 10 eV. In addition, we calculated the total energy using the generalized gradient approximation (GGA) and find that the total energy of LaCoO_3 as a function of the Co^{3+} spin-state does neither depend on U nor on approximation used in our calculations. Moreover, all of our calculations also show that for an increasing lattice constant ($a > 5.36 \text{ \AA}$), the IS becomes lower in energy than the LS state [9].

In all three simulated spectra (Fig. 1), three peaks can be seen in the O K edge. While the peaks labeled b and c are very similar for all three spin-states, our calculations show a clear difference in the intensity and energy position of the O K edge prepeak (a) for $S = 1$ and $S = 2$. The O K edge prepeak energy is shifted towards lower energies by 1.2 eV from the LS to the HS state, while the prepeak in the IS spectrum shows only a small shift in energy and a decrease

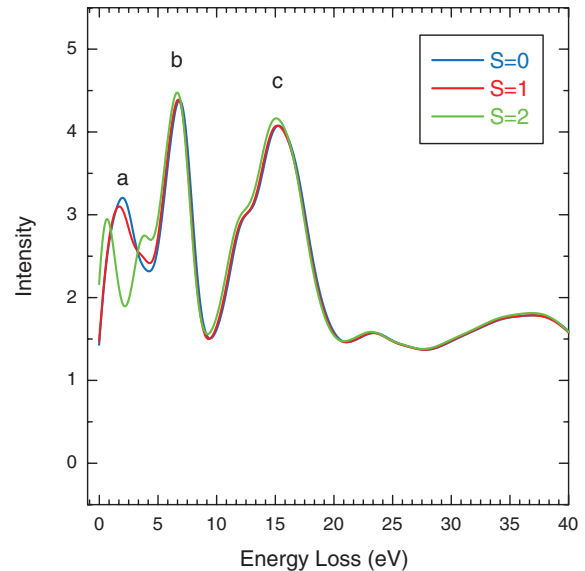


FIG. 1 (color). Calculated EELS spectrum of the O K edge broadened by 1.0 eV for the low, intermediate, and high-spin-state using the GGA.

in the prepeak intensity compared to the LS spectrum. Simply changing the lattice parameter of LaCoO_3 , but not the spin of the Co^{3+} ions results in only minor changes in the O K edge fine structure that would not have been detectable in the experimental spectra.

Thus, our DFT calculations not only confirm the splitting of the O K edge prepeak for LaCoO_3 in the HS state as previously measured by XAS [14], but further predict that the low-temperature spin-state transition from a LS into an IS state should be resolved by core-loss EELS of the O K edge.

The LaCoO_3 powder samples were fabricated by the conventional solid-state reaction of La_2O_3 and Co_3O_4 powders at 1000°C for one week (for more details see [12]). Susceptibility and resistivity measurements as a function of temperature in a magnetic field of $H = 50 \text{ kOe}$ and $H = 0$, respectively, show a clear anomaly in the magnetic as well as in the electronic behavior at 80 K [12].

High-resolution TEM images (Fig. 2) and diffraction patterns (Fig. 2(b)) were obtained using the BNL JEOL3000F [26] and a Gatan 363LHe-holder. They show that no significant structural transition occurs that could explain the observed changes in the susceptibility and resistivity. The space group for LaCoO_3 remains $R\bar{3}c$ over the entire temperature range measured here and only a small decrease in the lattice parameter from 300 to 10.4 K can be seen, consistent with earlier neutron powder diffraction data [25].

EELS spectra (Fig. 3) of the O K edge at 300, 86, and 10 K were taken from the grain shown in Fig. 2 and exhibit three main peaks as previously predicted by our DFT calculations. The O K edge prepeak (peak a in Fig. 3) decreases notably above 86 K, while the peaks labeled b

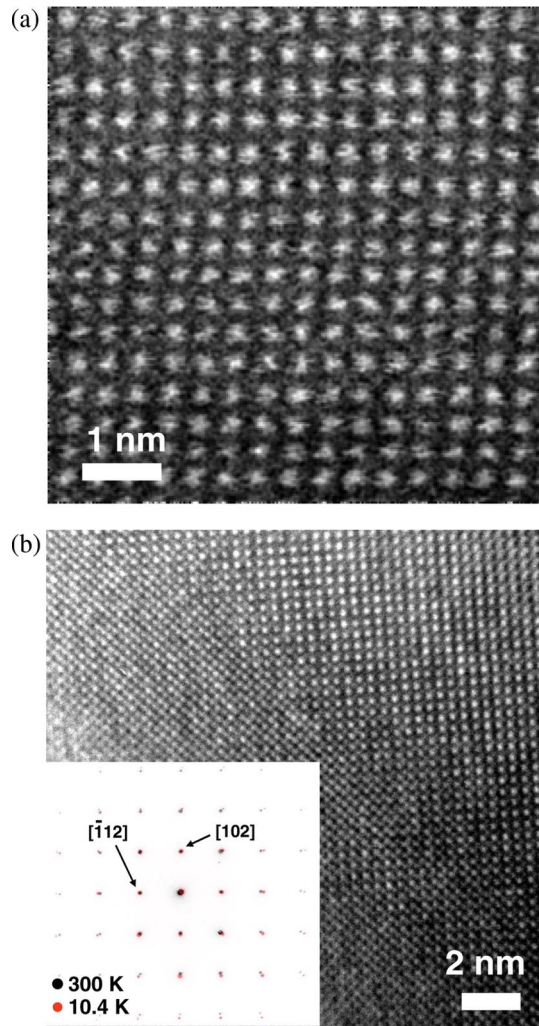


FIG. 2 (color). (a) Z-contrast image of LaCoO_3 $[2\bar{2}1]$ at 85 K showing the square lattice of La atoms; (b) High resolution TEM image of LaCoO_3 $[2\bar{2}1]$ at 10 K. Inset: Diffraction pattern at 300 and 10 K superimposed.

and peak *c* remain unchanged. The Co L_3 and L_2 edges (Fig. 3) do not exhibit any change in either the white line intensity ratio or the edge onset. Finally, the integrated intensity ratio of the Co L edge and the O K edge (not shown here) remains constant within the margin of error as a function of temperature, indicating that the stoichiometry of LaCoO_3 grain does not change during the cooling experiment.

In order to fully understand why the Co L edge remains unchanged and the O K edge prepeak decreases during the Co^{3+} -ion spin-state transition, we have to take a closer look at the origin of the different peaks in both the Co L edge and the O K edge. Several studies have shown the correlation between the Co L edge energy onset (and intensity ratio) and the local Co valence [14,27–30]. Since neither the Co L edge fine-structure nor energy changes in the temperature range studied here, we conclude that the Co L edges, measured with an energy resolution of 1.0 eV, are not sensitive to the Co^{3+} spin-state. Recent XAS mea-

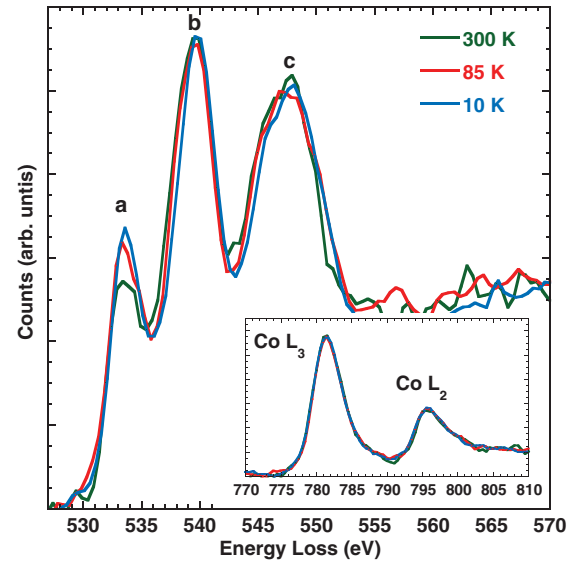


FIG. 3 (color). EELS spectrum of the O K edge at 300, 85, and 10 K. The Co L edge at these temperature is shown in the inset.

surements [20] showed small changes in the Co L edge fine structure, related to the Co^{3+} spin-state transition. However, these changes could not be detected by EELS.

Focusing now on the O K edge, it was previously shown that the preedge feature is related to the filling of the hybridized O $2p$ and Co $3d$ states [14,31]. Further, the peak at 540 eV (peak *b*) is commonly attributed to the La $5d$ band, while the peak at 548 eV stems from the Co $4sp$ bands [14]. Therefore, the O K edge features reveal that the bonding between the O $2p$ with the La $5d$ and the Co $4sp$ bands remains unchanged during the *in situ* cooling experiment. However, the electronic structure of the hybridized Co $3d$ O $2p$ bands changes with the onset of the spin-state transition of the Co^{3+} ions. The change in the O K edge prepeak intensity can best be understood by considering the different filling of the Co $3d$ states for the different Co^{3+} spin-states. When the Co^{3+} is in the LS state, the $3d t_{2g}$ -levels are completely filled and the e_g -levels are vacant [32]. This allows the electrons from the filled O $2p$ levels to be shared with the Co e_g orbital, creating O $2p$ holes. Thus, the hybridization of the Co $3d$ with the O $2p$ states allows electron transitions between the O $1s$ and the unfilled O $2p$ states, which are apparent as a preedge feature of the O K edge. In the higher spin states of Co^{3+} (i.e., $S > 0$), the e_g orbitals are starting to be populated, thus preventing the charge transfer from occurring. Therefore, the O K edge prepeak intensity can be used as a direct measure of the spin-state in LaCoO_3 , assuming that the stoichiometry of LaCoO_3 remains unchanged.

The experimental EELS spectra (Fig. 3) clearly show that the O K edge prepeak changes as a function of temperature, and comparing the experimental spectra with the DFT calculations, it is obvious that the changes in the O K edge prepeak for $S = 2$ are not observed in the temperature range between 10 and 300 K. Moreover, the

observed decrease in the O *K* edge prepeak intensity without any measurable chemical shift shows that spin-state transition at 80 K in LaCoO₃ occurs from a LS to a IS state of the Co³⁺-ions. A mixed LS-HS state can be excluded since no chemical shift or significant broadening of the prepeak was measured. It should be noted that the spectra of the O *K* edge (Fig. 3) show a small peak at 529.5 eV at both 10 and 300 K that might indicate the existence of a HS state even at 10 K. However, this peak remains within the noise level and its position might be purely coincidental. While our study does not report atomic-resolution EELS of LaCoO₃, the methods and results reported here, in particular, the changes in the O *K* edge prepeak intensity with increasing Co³⁺ spin, can in the future be directly used to perform column-by-column EELS. Thus, EELS in combination with Z-contrast imaging provides a unique tool directly measuring the Co³⁺-spin state with atomic resolution, which cannot be achieved by any other technique, including XAS.

In summary, we have shown that the thermally excited spin-state transition in LaCoO₃ occurs from the LS to the IS state, and can be directly quantified using the EELS near-edge fine-structure of the O *K* edge. Thus, we have shown that the O *K* edge prepeak provides an ideal fingerprint for identifying the different spin state of the Co³⁺ ions in LaCoO₃ and related compounds. Our results present the first demonstration of spin-state sensitive EELS in the TEM.

Finally, it had been previously suggested that oxygen vacancies or additional electrons (holes) bound to the Co³⁺-sites in LaCoO₃ locally induce LS to HS transitions at low temperature, while leaving the remaining Co³⁺ ions in the LS state [33]. This magnetic exciton has been predicted as a precursor to the magneto-electronic phase separation at high hole/vacancy concentration [34]. The existence of such magnetic excitons, and potential interfacial ferromagnetism can now be directly measured using the fingerprinting EELS methods described in this Letter.

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