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Structural Changes Accompanying the Spin-State Transition in $LaCoO_3$: A Variable Temperature Co-*K*-EXAFS Study

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Variable-temperature Co-*K*-EXAFS measurements establish the occurrence of two cobalt sites, probably associated with the two spin states, above 400 K. The population of the two Co sites becomes equal around 670 K, at which temperature the change in space group occurs. © 1993 Academic Press, Inc.

Amongst the transition metal oxides, $LaCoO_3$ occupies a special place since it shows fascinating changes in the electron states of cobalt with change in temperature, culminating in a transition from localized to collective-electron behavior at high temperatures (*1–3*). Furthermore, $LaCoO_3$ is one of the few oxides showing a spin-state transition (*4*). Raccah and Goodenough (*1*), in their seminal paper, employed X-ray diffraction to investigate the structural changes in this perovskite and proposed that the space group changes from $R\bar{3}c$ to $R\bar{3}$ around 650 K. In the room-temperature $R\bar{3}c$ structure, there is only one Co-site, but in the $R\bar{3}$ structure, there are two distinguishable octahedral cobalt positions, Co_I and Co_{II}, characterized by widely differing Co–O distances (~0.5 Å), occupied by low- and high-spin cobalt ions, respectively. Raccah and Goodenough suggested that there was long-range ordering of the two spin states in the high-temperature structure with nearly equal populations of the two species. The essential features of this model have been verified by Mössbauer spectroscopy and related techniques (*3*). More recently, based on neutron diffraction studies, Thornton *et al.* (*5*) have reported that the $R\bar{3}$ symmetry becomes evident only at 668 K and that the $R\bar{3}c$ symmetry is retained at all other temperatures. Their 668-K neutron data, however, yielded a difference of only ~0.02 Å between the two Co–O distances in the $R\bar{3}$ structure. Thornton *et al.* therefore concluded that there was only marginal evidence for spin-state ordering at high temperatures. Since the structural changes involving two Co sites associated with the high- and low-spin states of trivalent cobalt is of vital significance in understanding the properties of $LaCoO_3$, we considered it important to investigate this oxide by an atom-specific probe such as extended X-ray absorption fine structure (EXAFS) which would directly provide information on the primary coordination of the cobalt ions. For this purpose, we have carried out a Co-*K*-EXAFS investigation on $LaCoO_3$ from 300 to 773 K.

$LaCoO_3$ was prepared by the decomposition of lanthanum cobalticyanide at 1273 K. The sample was cooled slowly to room temperature at a rate of 1 K/min in order to avoid quenching of the high temperature phase. The sample was characterized by X-ray diffraction using a JEOL diffractometer.

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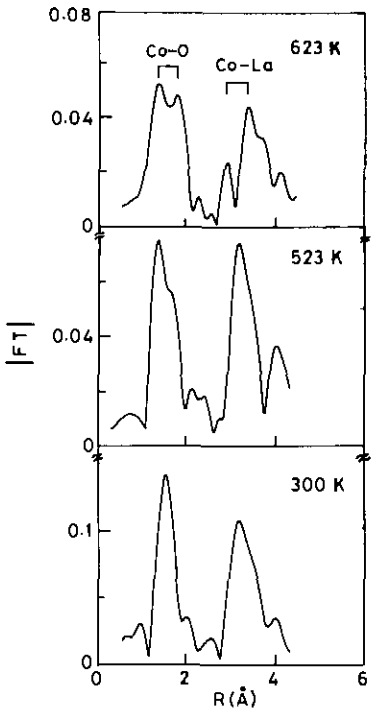

FIG. 1. Fourier transforms of Co *K*-EXAFS of $LaCoO_3$ at 300, 523, and 623 K.

For EXAFS measurements, the sample was pressed in the form of a self-supporting wafer after mixing with boron nitride and was mounted in an indigenously developed high-temperature cell which allowed spectra to be recorded upto 800 K. Co-*K*-EXAFS spectra were recorded at 300, 400, 523, 623, 723, and 773 K using a Rigaku spectrometer attached to a rotating anode X-ray generator (Rigaku-Ru 200B, Japan). A Ge(220) crystal was used as the monochromator with a 0.1-mm slit for X-rays from the Mo target. Fourier transforms (FTs) of the EXAFS data were obtained with $k_{min} \sim 2.8$ and $k_{max} \sim 11.8$ $Å^{-1}$ after weighting the data by k^3. Curve-fitting analysis was carried out using the multiphasic model involving the additive relationship of EXAFS function.

In Fig. 1 we show the Fourier transforms (FTs) of the Co-*K*-EXAFS of $LaCoO_3$ at 300, 523, and 623 K. The room temperature FT shows a prominent peak at 1.54 Å which, on curve-fitting with Co–O parameters from $CoAl_2O_4$, yielded a coordination number of 6 and a Co–O distance of 1.92 Å. The FT remains nearly the same at 400 K. Interestingly, with increase in temperature to 523 K, the peak due to Co–O coordination shifts to 1.36 Å and we see a prominent shoulder around 1.8 Å. Curve-fitting of the inverse transformed data employing a wide *R*-window (1.1–2.0 Å) gave Co–O coordinations of 3 and 2.2 at 1.72 and 2.2 Å. The shoulder around 1.66 Å emerges as a distinct peak at higher temperatures, with a simultaneous decrease in the intensity of the feature at 1.36 Å (see the FT at 623 K in Fig. 1). Curve-fitting analysis (*R*-window 1–2 Å) led to Co-O coordinations of ~3 around 1.66 and 2.2 Å.

In Fig. 2 we show the variation of the Co-O distance with temperature. At 300 and 400 K, there is only one Co–O distance (~1.92 Å) corresponding to a single octahedral Co site, while at higher temperatures (> 523 K), we clearly see two Co–O distances around 1.66 and 2.2 Å arising from two distinguishable Co sites. These distances correspond exactly to those reported by Raccah and Goodenough (*1*) for octahedral Co_I and Co_{II} sites. We have estimated the relative populations of the two Co sites

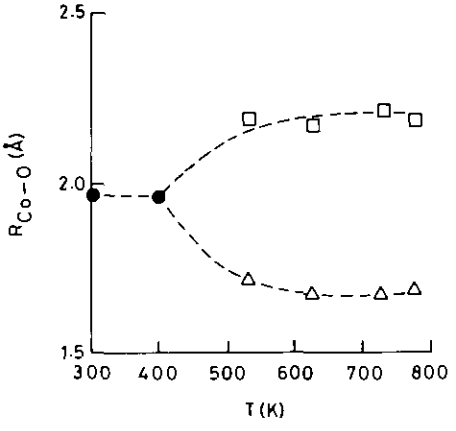

FIG. 2. Variation of Co–O distances with temperature: closed circles, indistinguishable Co sites; triangles, Co_I site; and squares, Co_{II} site.

based on the coordination numbers obtained from the curve-fitting analysis. We find that only one type of Co site exists below 400 K and the population of the two sites becomes nearly equal between 650 and 700 K. This suggests there could be ordering of the two spin-states of Co around this temperature. What is noteworthy is that Thornton *et al.* (*4*) also found a change in symmetry in this temperature region.

The features due to Co–La and Co–Co coordinations can be seen from the FTs in Fig. 1 in the higher *r*-region. Accordingly, the peak at 3.12 Å (at 300 K) corresponds to Co–La coordination, while the shoulder around 3.4 Å arises due to Co–Co coordination. It is interesting that two Co–La peaks emerge at higher temperatures coinciding with the occurrence of two Co–O distances.

The present results establish that two types of Co–O distances manifest themselves in $LaCoO_3$, probably associated with the two spin states of trivalent cobalt. The populations of these two spin states become nearly equal around 670 K. Interestingly, it is in this temperature region that Raccah and Goodenough proposed the occurrence of spin-state ordering and a change in the space group from $R\bar{3}c$ to $R\bar{3}$.

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