

# Evidence for Orbital Ordering in $\text{LaCoO}_3$

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## Introduction

The study of  $\text{LaCoO}_3$  is of considerable interest because of its unusual magnetic and transport properties, caused by the puzzling nature of the two transitions in this compound. At low temperatures, its magnetic susceptibility increases exponentially with the temperature, showing a maximum near 100K followed by a second anomaly at 500K that is accompanied by an insulator-to-metal transition. By using LDA+U calculations, M.A. Korotin et al. [1] proposed that the stabilization of the intermediate spin (IS) state is a result of the large hybridization between the Co- $e_g$  and O-2p levels as well as the orbital ordering effect. Recent magnetic susceptibility and thermal expansion measurements [2] indicate that the maximum at 100K is not associated with a phase transition in the thermodynamic sense. These data are interpreted with a thermal population of the  $\text{Co}^{3+}$  ions from the low spin (LS) ground state to the Jahn-Teller (JT) active IS state. However, all structural studies based on powder x-ray and neutron diffraction experiments are consistently interpreted in rhombohedral  $R\bar{3}c$  symmetry, and no structural transitions are reported in the temperature interval of 4.2 to 1248K. A cooperative JT distortion is incompatible with this space group. This triggered our study to detect a coherent JT distortion and to investigate why recent high-quality structural studies failed to observe such a state.

## Methods and Materials

The symmetry of the structure was carefully analyzed by using high-resolution x-ray diffraction experiments on both powder and single crystals. The measurements were performed on the triple-axis high-energy diffractometer with a photon energy of 115 keV at BESSRC beamline station 11-ID-C at the APS.  $\omega$ - $\chi$  scans were collected on a single crystal approximately 1 mm in size.

## Results and Discussion

In the powder diffraction experiment, we measured the temperature dependence of the profile of the (4 0 0) reflection (the Miller indices are referred to the double cubic unit cell). The correspondent lattice spacing (1.91 Å) of this reflection matches the lattice spacing of the analyzer crystal such that the maximum resolution is

gained. The peak width is constant ( $0.0025^\circ$ ) up to 65K and starts to broaden gradually as the temperature is increased, reaching  $0.0036^\circ$  at 145K. The broadening of the reflection cannot be attributed to Debye-Waller factors. A likely explanation is the lifting of the degeneracy (splitting) of this reflection due to the lowering of the rhombohedral symmetry. We therefore associate the gradual broadening of the Bragg reflection with a gradual distortion of the structure. We think that the observed broadening is compatible with the convolution of the (4 0 0) and (0 4 0) reflections in the monoclinic  $I2/a$  symmetry. Moreover, the associated splitting indicates that the differences between  $a$  and  $b$  lattice parameters of the pseudo-cubic subcell are evidence for different Co-O distances in the  $ab$  plane. Thus the broadening of this reflection is attributed to a gradual increase of the cooperative JT distortion with increasing temperature.

In order to investigate the possibility of the symmetry being lower, single-crystal x-ray diffraction

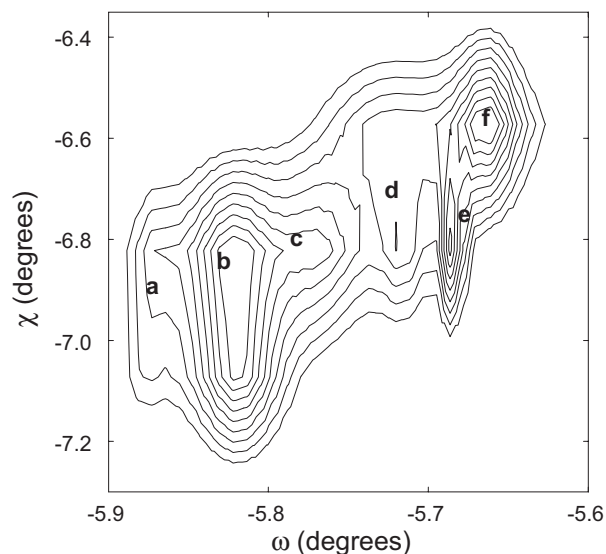


FIG. 1. The profile of a (10 2 8) (the Miller indices are referred to the double cubic unit cell) reflection in a  $\omega$ - $\chi$  scan at 60K. The two rhombohedral fractions positioned at  $\omega_1$  of  $\approx 5.82^\circ$  and  $\omega_2$  of  $\approx 5.69^\circ$  split further into three peaks that represent the monoclinic twins and are labelled a, b, c and d, e, f, respectively

experiments were also carried out by using synchrotron radiation and high angular resolution ( $0.01^\circ$  step). The presence of the twinning was verified by performing  $\omega$ - $\chi$  scans. We observed a large splitting that we attribute to the twinning caused by the decrease in symmetry from cubic to rhombohedral in the cooling process during the crystal growth. However, we also observed a smaller splitting that we attribute to the twinning caused by the decrease in symmetry from rhombohedral to monoclinic (Fig. 1). The observed splitting indicates that the monoclinic symmetry is maintained in the temperature interval of 20 to 300K. Thus, the small monoclinic distortion gives rise to pseudo-merohedral twinning, which we were able to detect in  $\omega$ - $\chi$  scans.

For the structure determination, full data sets were measured at different temperatures (90, 120, 140, 160, 200, 250, and 295K) on the Bruker APEX diffractometer by using Mo-K $\alpha$  radiation. The intensities of the reflections were obtained from the largest rhombohedral twin fraction, which includes the integrated intensity of the monoclinic twin fractions

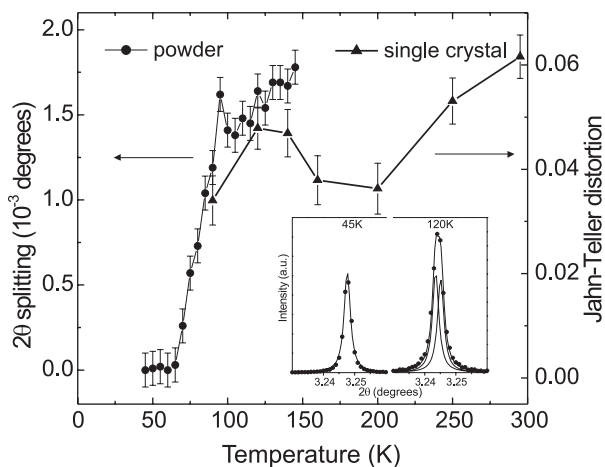


FIG. 2. Left: Temperature dependence of the splitting of  $(4\ 0\ 0)$  reflection in  $\theta$ - $2\theta$  geometry (below 65K, the line width is resolution-limited). Right: The JT distortion parameter versus temperature as determined from the single-crystal refinements. The lines are guides for the eye. Inset: Profile of  $(4\ 0\ 0)$  reflection at 45K and 120K. The profile at 120K can be accurately fitted by two Lorentzians with the line width of the 45K data.

together. The precise positions of the atoms were obtained by making use of the monoclinic twin relation in the refinements. We derived three unequal Co-O bond lengths over the studied temperature range: one short, one long, and one medium. The long and short Co-O distances correspond with the bonds in the  $ab$  plane, while the medium Co-O distances are the out-of-plane bonds. These results indicate a clear, coherent JT effect associated with a Q2 type of distortion. The right side of Fig. 2 shows the temperature dependence of the JT parameter, defined as the difference between the long and short bond lengths normalized by their average. The left side of Fig. 2 shows the temperature dependence of the splitting in  $2\theta$  of the  $(4\ 0\ 0)$  reflection derived from the powder x-ray diffraction experiments.

The distortion of the octahedra lifts the degeneracy of the  $e_g$  orbitals. The  $z^2$ -like orbitals have an antiferrodistortive ordering along all three directions, which suggests a ferromagnetic coupling between magnetic sites [1]. Our measurements are in agreement with the recent magnetic and x-ray absorption spectroscopy (XAS) measurements [2], which were interpreted with a thermal activation of the IS spin state.

We conclude that LaCoO<sub>3</sub> exhibits a monoclinic distorted structure in the temperature interval of 20 to 300K. The monoclinic distortion state is brought about by a cooperative JT effect, which triggers the long-range orbital ordering of the  $e_g$  orbitals. The gradual increase of the JT distortion with temperature suggests the thermal population of the IS state of the Co<sup>3+</sup> ions.

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## References

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