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# Constraints on the possible long-range orbital ordering in LaCoO<sub>3</sub>



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## ABSTRACT

A neutron powder diffraction measurement was performed to distinguish between the proposed monoclinic (I2/a) structure of LaCoO<sub>3</sub>, which is consistent with orbital ordering, and the rhombohedral  $(R\overline{3}c)$  structure, which is inconsistent with orbital ordering. These two structures were differentiated through a measurement of a superlattice reflection with a d-spacing of approximately 4.43 Å which is only generated by I2/a. This reflection was not observed, and instead a restrictive upper bound was placed on its structure factor. The data is inconsistent with the monoclinic structure and suggests that there may be no long-range Jahn–Teller distortion in LaCoO<sub>3</sub>.

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## 1. Introduction

LaCoO<sub>3</sub> is a perovskite compound for which Co<sup>3+</sup> ions undergo a spin-state transition upon increasing temperature [1], which is quite controversial and has generated a surprisingly large number of investigations [2-8]. The ground state of the compound is nonmagnetic, accounted for by the S = 0 ( $t_{2g}^6 e_g^0$ ) configuration of the Co 3d electrons in an octahedral crystal field. An increase in temperature populates non-zero spin-states so that magnetic moments are introduced and the system becomes paramagnetic, with a maximum in the magnetic susceptibility occurring around 100 K [1]. The greatest source of controversy resides in whether the excited moments have S = 1 ( $t_{2g}^5 e_g^1$ ) or S = 2 ( $t_{2g}^4 e_g^2$ ).

One of the arguments pertinent to S = 1 versus  $\overline{S} = 2$  regards the existence or not of a Jahn–Teller lattice distortion, which might be expected in the presence of lone, singly occupied  $e_g$  orbitals. The experimental data regarding the structure of LaCoO<sub>3</sub> is, itself, not uncontroversial. Several powder neutron diffraction studies have reported the structure to be rhombohedral ( $R\overline{3}c$ ), which does not allow a Jahn–Teller distortion since all nearest-neighbor Co–O bondlengths are identical [9,10], as illustrated in Fig. 1. Subsequent to this work, a high-resolution X-ray diffraction study of the twinning of LaCoO<sub>3</sub> combined with Rietveld refinement of powder diffraction data suggested a monoclinic space group I2/a, which allows a Jahn–Teller distortion [11]. As shown in Fig. 1, the I2/aspace group allows for three different Co–O bondlengths in each

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octahedron, which leads to the possibility of an orbital ordering with the occupied  $e_g$  orbital pointing in the direction of the longest Co–O bondlength. This monoclinic model was supported in a subsequent X-ray refinement [12]. A very recent Letter [8] argues that the agreement of Rietveld refinement of neutron powder diffraction data is not substantially improved by lowering the symmetry from  $R\overline{3}c$  to I2/a, and moreover, that the model of I2/a does not agree well with the pair-distribution function obtained by Fourier transforming the diffraction data into real space. Thus, at present, the correct symmetry of LaCoO<sub>3</sub> is unclear, though ultimately this is an important property that should affect theoretical and experimental interpretations of the magnetic properties of LaCoO<sub>3</sub>. In particular, knowing the correct symmetry is essential for distinguishing between the S = 1 and S = 2 states of Co<sup>3+</sup>.

Distinguishing between pseudosymmetric structures using Rietveld refinement of powder data is not a task that necessarily yields a correct or unambiguous answer because the agreement factors can turn out to be quite similar. This is well-known for other perovskite materials, such as  $PbZr_{1-x}Ti_xO_3$  [13,14]. Moreover, assignment from single crystal diffraction can be extremely difficult because of the twinning that often occurs [11]. The point of the present work is to highlight a straightforward method of diffraction that distinguishes between I2/a and  $R\overline{3}c$  space groups for LaCoO<sub>3</sub> and depends neither on Rietveld refinement nor on resolving tiny peak splittings. In particular, these two space groups can be distinguished by the fact that the I2/a space group generates an additional (weak) Bragg reflection with a d-spacing of approximately 4.43 Å. In the present neutron diffraction measurements, this peak is not observed. Instead, a tight constraint is placed upon its maximum value. Calculations indicate a substantial

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**Fig. 1.** The Co–O octahedra for the l2/a and  $R\overline{3}c$  space groups. The l2/a structure has 3 unique Co–O bond-lengths in each octahedron, whereas the  $R\overline{3}c$  structure has only one unique Co–O bond-length. The bond-lengths shown are from the structures reported in Ref. [11] for l2/a at 200 K and Ref. [10] for  $R\overline{3}c$  at 200 K. The Co atoms at the center of each octahedron are shown in blue, and the oxygen atoms are shown in red. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

shift in atomic positions would have to occur for the peak to lie within this constraint.

#### 2. Materials and methods

A powder sample of LaCoO<sub>3</sub> was synthesized by solid state reaction at 1200 °C (two 50 h firings in air) from initial starting materials of La<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>, and the perovskite phase was confirmed by powder X-ray diffraction. Neutron diffraction measurements were performed on the SPINS cold neutron triple-axis spectrometer at the NIST Center for Neutron Research using a wavelength of 4.054 Å. The measurements were performed using a PG 002 monochromator and analyzer (3 flat blades) and with horizontal beam collimations of Guide(39')-80'-80'-Open. Two cooled Be filters were used (one in-pile and one after the sample) to suppress harmonic contamination. The sample had a mass of 16.8 g and was measured in a sealed vanadium can. The measurement was performed only at 200 K in a closed cycle He refrigerator. This temperature was chosen because it is the temperature for which the atomic positions are listed in Ref. [11] for I2/a. A second sample, synthesized using the same reaction conditions, was magnetically characterized using a vibrating sample magnetometer.

The following notation is adopted. A subscript of pc refers to indexing with respect to a pseudocubic unit cell that contains only one formula unit ( $a_{pc} \approx 3.8$  Å), while a subscript of *h* refers to indexing with respect to space group  $R\overline{3}c$  with a hexagonal unit cell [10]. Finally, a subscript *m* refers to indexing with a monoclinic cell of space group I2/a [11].

### 3. Results and discussion

Fig. 2 shows the zero-field-cooled (ZFC) and field-cooled (FC) mass magnetization ( $\sigma$ ) of the LaCoO<sub>3</sub> powder sample as a function of temperature in (a)  $\mu_0H=0.1$  T and (b)  $\mu_0H=9$  T. The data taken in  $\mu_0H=9$  T demonstrates the spin-state transition as expected (see, e.g. Ref. [15]), with the magnetization increasing as the temperature increases above ~27 K, reaching a maximum at  $T\sim112$  K. Below ~27 K, a low temperature increase in the magnetization is observed as the temperature is lowered. This low temperature increase has been consistently documented in LaCoO<sub>3</sub> samples [16,15]. In a smaller field of  $\mu_0H=0.1$  T, an additional contribution is apparent, where the magnetization increases with decreasing temperature below ~93 K. The FC and ZFC magnetization then bifurcate below ~75 K. Yan et al. previously demonstrated this feature in polycrystalline samples, showing that it was a ferromagnetic component related to a surface effect through



**Fig. 2.** Mass magnetization ( $\sigma$ ) versus temperature for the powder sample of LaCoO<sub>3</sub> in (a)  $\mu_0H$ =0.1 T and (b)  $\mu_0H$ =9.0 T. Zero-field-cooled (ZFC) and field-cooled (FC) data are displayed in both panels (they overlap for  $\mu_0H$ =9.0 T.).



**Fig. 3.** Mass magnetization versus applied magnetic field at 10 K, 60 K, and 120 K. The data was collected after cooling in  $\mu_0 H$ =9.0 T. The inset shows the same data over a more narrow range in order to show the opening of the 10 K loop and the slight opening of the 60 K loop.

a comparison of single crystals to pulverized single crystals [16]. This has been further shown through studies of magnetization versus particle radius [17]. In high fields, the thermally excited spin-state transition dominates over the smaller ferromagnetic contribution. Fig. 3 shows magnetization versus magnetic field loops at 10 K, 60 K, and 120 K. The loop is linear at 120 K, as expected for paramagnetic spins. However, at 60 K, the loop slightly opens, and at 10 K the loop significantly opens, confirming the presence of a ferromagnetic component in the present sample.

The Bragg reflection of highest d-spacing generated for the model with I2/a is  $011_m$ , with a multiplicity (m) of 4 and which can also be indexed as  $\frac{1}{2} \frac{1}{2} \frac{1}{2pc}$ . This is forbidden for  $R\overline{3}c$ , for which the reflection of highest d-spacing is  $012_h$  (m = 6), corresponding to  $100_{pc}$ . As a means of evaluating the intensity of a scan measured through  $\frac{1}{2} \frac{1}{2} \frac{1}{2pc}$ , the intensity must be compared to that of another Bragg reflection. For this purpose, the  $110_{pc}$  multiplet was chosen, which is a doublet for  $R\overline{3}c$  consisting of  $120_h$  (m = 6) and  $104_h$  (m = 6), and a quadruplet for I2/a consisting of  $020_m$  (m = 2),  $\overline{1}12_m$  (m = 4),  $112_m$  (m = 4), and  $200_m$  (m = 2). Because of the expected very small monoclinic distortion of the I2/a, only 2 peaks would be expected to be resolved. Fig. 4(a) shows a measurement of the  $110_{pc}$  multiplet. The data was fit by a model of two Gaussians, for which the integrated intensity of a Bragg peak for a powder is given by [18]

$$I = \frac{Am_{hkl}\lambda^3 |F_N(hkl)|^2}{\nu_0^2 \sin \theta \sin (2\theta)}$$
(1)

where *A* is a normalization constant,  $\lambda$  is the wavelength,  $\nu_0$  is the unit cell volume,  $2\theta$  is the scattering angle,  $m_{hkl}$  is the multiplicity, and  $F_N(hkl)$  is the nuclear structure factor, which is given by [18]

$$F_N(hkl) = \sum_j b_j e^{i\overrightarrow{Q} \cdot \overrightarrow{d_j}} e^{-W_j}$$
<sup>(2)</sup>

where the sum is taken over all atoms in the unit cell,  $\vec{Q}$  is the wave-vector transfer of the Bragg reflection, and  $b_i$ ,  $\vec{d}_i$ , and  $W_i$ 



**Fig. 4.** (a) The  $110_{pc}$  multiplet. (b) Measurement through the expected  $001_m$  peak position. The dashed line shows the expected peak shape based on the I2/a model [11]. Error bars represent the  $1\sigma$  uncertainties of the intensities.

refer to the neutron scattering length, position, and Debye–Waller factor for the *j*th atom, respectively. Using these two equations, the  $011_m$  intensity can be directly compared to that of the  $110_c$  multiplet. However, given that we are using cold neutrons and the sample is large and contains a reasonably large neutron absorber/incoherent scatterer (Co), the relative angular dependent attenuation for the  $011_m$  reflection compared to the  $110_c$  multiplet should be considered. A calculation was performed using the Lobanov and alte da Veiga function as described in [19], where it was found that attenuation has a 7% reduction of the relative intensities  $011_m$ :110<sub>c</sub>. This has been considered in the subsequent analysis.

Fig. 4(b) shows a measurement through the expected position of the  $011_m$  peak. The measurement was performed over a very long time (at least 115 min per point) in order to resolve the smallest possible peak from the background, which is high because of the relatively large incoherent scattering cross-section of Co. It is important to note that  $011_m$  is a singlet, which means that, since it occurs at a large d-spacing, and assuming that the monoclinic structure is long-range ordered, its measured width should correspond to the instrumental resolution. Taking the I2/astructure reported in Ref. [11], and taking into account the instrumental resolution, the dashed line shown in Fig. 4 (b) shows the expected pattern based on the integrated intensity measured for  $110_{pc}$  while using Eqs. (1) and (2). Clearly any possible peak is much smaller than that predicted by this model. In order to quantify this, the following data fitting procedure was carried out. The data in Fig. 4(b) was iteratively fit with a Gaussian peak plus a background, with the integrated intensity of the Gaussian and peak width fixed (the peak position was allowed to move over a limited range). This was carried out for a large number of values of integrated intensity, and then the resultant  $\chi^2$ values were plotted as a function of integrated intensity. In this way, the change in  $\chi^2$  can define a confidence limit for the integrated intensity of the peak [20]. The 99% confidence level indicates that the maximum integrated intensity of 011<sub>m</sub> compared to the 110pc multiplet is 0.066% (the 99.73% confidence level limit is 0.072%), about an order of magnitude smaller than that predicted (0.77%). It is notable that it is impossible to rule out a peak at  $011_m$ ; in fact, the best fit has a non-zero integrated intensity of about 0.035%, and an integrated intensity of 0.0 lies outside the 99% confidence level; however, the potential of a weak harmonic beam contamination and a visual inspection of the raw data suggest that this peak is not convincingly real.

Given the upper bound placed on  $011_m$ , it is useful to then consider how  $|F_N(011_m)|^2$  is changed by the atomic positions of the I2/a structure. As provided, in Ref. [11, Table 2], the atom positions are: La at (0.25, 0.25019, 0), Co at (0.75 0.25 0.25), O1 at (0.25, -0.3068, 0), and O2 at (0.0241, 0.0332, 0.2293). In fact, there are only four refinable atomic position parameters that affect this structure factor: La y, O1 y, O2 y and O2 z. Fig. 5 shows how the ratio of the integrated intensity of  $011_m$  to the  $110_{pc}$  multiplet depends on the displacement of each of these parameters away from the reported position. For the ratio to fall below the upperbound, an atomic displacement of roughly a magnitude of 0.04 Å in either the La y or O2 z parameters is required, and even larger for the O1 y position. As a means of comparison, the uncertainties in the positions of the La y, O2 y, and O2 z atoms are all less than 0.006 Å in the refinements [11]. This leads to the conclusion that the present data is not consistent with this I2/a structure.

Note that above the shifts of single atoms alone, rather than the simultaneous shifts of atoms together, have been considered due to the multiple degrees of freedom. Therefore, it is also useful to consider how  $|F_N(011_m)|^2$  changes as atoms are displaced away from their equilibrium positions in the  $R\overline{3}c$  structure. To do this, the atom positions of the  $R\overline{3}c$  structure of Ref. [10] were



**Fig. 5.** Relative integrated intensity (in percent) of the  $011_m$  peak compared to the  $110_{pc}$  multiplet assuming l2/a symmetry. The curve shown in black represents the displacements from the mean values reported in Ref. [11, Table 2]. The curve shown in blue represents the displacements from the rhombohedral structure reported in [10] which has been transformed into an l2/a space group as described in the text. The dashed lines (red) show the upper bound from the present measurement. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

transformed into a description in the I2/a space group (the thermal parameters were kept the same as in the calculation above, except that the two oxygen atoms are given the same thermal parameter here while the O1 and O2 atoms have different thermal parameters above.) The transformed atom positions are La at (0.25, 0.25, 0), Co at (0.75 0.25 0.25), O1 at (0.25, -0.3013, 0), and O2 at (0.02565, 0.02565, 0.22435). The ratio of the integrated intensity of  $O11_m$  to the  $110_{pc}$  multiplet as a function of the displacement from these positions is also shown in Fig. 5. The calculation provides an indication of the atomic displacements away from the undistorted  $R\overline{3}c$  structure that would be necessary to resolve a peak in the experiment if the true space group is I2/a. Again, it is found that this ratio is strongly dependent on the La y, O1 y, and O2 z parameters, but is very insensitive to the O2 x and O2 y parameters.

## 4. Conclusion

The detailed structure of the twins shown in Ref. [11] is likely an important subtle clue about the structure of the LaCoO<sub>3</sub> single crystal that was measured. Indeed, it could be that the single crystal that was measured has a monoclinic structure. However, the present data suggests that the I2/a model with its orbital ordering is inconsistent with the structure of a powder sample. Since the

majority of Co<sup>3+</sup> ions also undergo the spin-state transition in powder samples, as demonstrated by their high-field magnetization, the present measurements suggest that the long-range orbital ordering model that has been proposed in the I2/a structure is not intrinsic to the physics of the spin-state transition in LaCoO<sub>3</sub>. This conclusion is strengthened by the recent pair distribution function analysis of neutron diffraction data [8], which also does not favor the monoclinic structure. Recently, superlattice reflections were observed by transmission electron microscopy which show a tripling of the lattice along the  $[100]_{pc}$  direction [21], and a different monoclinic structure of space group  $P2_1/m$  was suggested. Since tripling is not reported in X-ray or neutron diffraction studies of bulk materials, it is unknown if this is a bulk property. Another aspect of the structural problem of LaCoO<sub>3</sub> regards the possibility of local, rather than long-range, Jahn-Teller distortions, but unfortunately the appearance or not of the  $011_m$  Bragg peak cannot resolve the contoversy [8,22] surrounding the local structure. In summary, the present neutron scattering measurements place a constraint on the maximum amplitude of the structure factor of a superlattice reflection that should be generated by the I2/a space group, which suggests that a long-range Jahn-Teller distortion is not associated with the Co<sup>3+</sup> spin-state transition. This has important implications upon the interpretation of the spin-state transition, as it is inconsistent with an eg orbital ordering that has been anticipated for the  $t_{2g}^5 e_g^1$  (S = 1) configuration.

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