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Constraints on the possible long-range orbital ordering in $LaCoO_3$

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ABSTRACT

A neutron powder diffraction measurement was performed to distinguish between the proposed monoclinic ($I2/a$) structure of $LaCoO_3$, 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 $LaCoO_3$.

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1. Introduction

$LaCoO_3$ is a perovskite compound for which Co^{3+} 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 non-magnetic, accounted for by the $S=0$ ($t_{2g}^6e_g^0$) 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 $S=1$ ($t_{2g}^5e_g^1$) or $S=2$ ($t_{2g}^4e_g^2$).

One of the arguments pertinent to $S=1$ versus $S=2$ 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 $LaCoO_3$ 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 $LaCoO_3$ 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 $I2/a$ space group allows for three different Co–O bondlengths in each 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 $LaCoO_3$ is unclear, though ultimately this is an important property that should affect theoretical and experimental interpretations of the magnetic properties of $LaCoO_3$. In particular, knowing the correct symmetry is essential for distinguishing between the $S=1$ and $S=2$ states of Co^{3+}.

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 $LaCoO_3$ 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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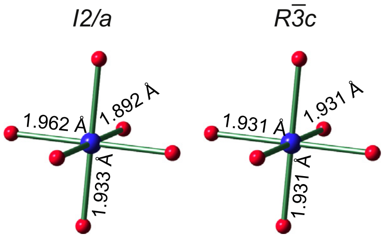

Fig. 1. The Co–O octahedra for the $I2/a$ and $R\bar{3}c$ space groups. The $I2/a$ structure has 3 unique Co–O bond-lengths in each octahedron, whereas the $R\bar{3}c$ structure has only one unique Co–O bond-length. The bond-lengths shown are from the structures reported in Ref. [11] for $I2/a$ at 200 K and Ref. [10] for $R\bar{3}c$ 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 $LaCoO_3$ was synthesized by solid state reaction at 1200 °C (two 50 h firings in air) from initial starting materials of La_2O_3 and Co_3O_4, 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 $R\bar{3}c$ 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 (σ) of the $LaCoO_3$ 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 $T \sim 112$ 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 $LaCoO_3$ 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 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.

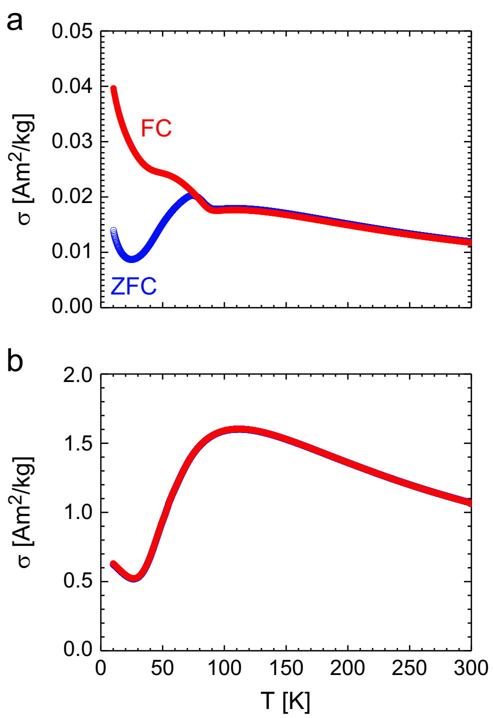

Fig. 2. Mass magnetization (σ) versus temperature for the powder sample of $LaCoO_3$ in (a) $\mu_0H = 0.1$ T and (b) $\mu_0H = 9.0$ T. Zero-field-cooled (ZFC) and field-cooled (FC) data are displayed in both panels (they overlap for $\mu_0H = 9.0$ T.).

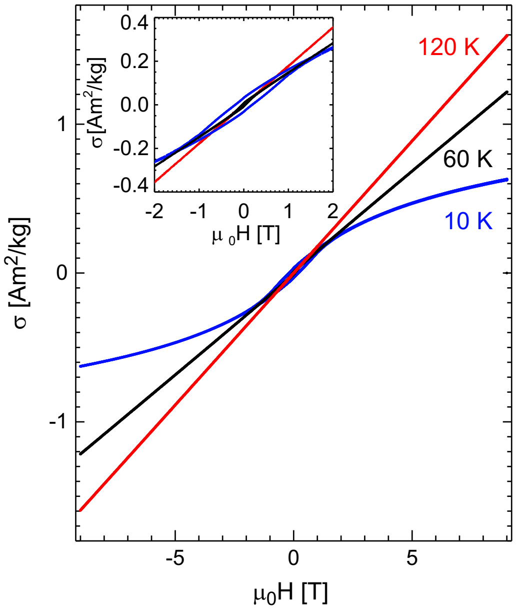

Fig. 3. Mass magnetization versus applied magnetic field at 10 K, 60 K, and 120 K. The data was collected after cooling in $\mu_0H = 9.0$ T. The inset shows the same data over a more narrow range in order to show the opening of the 10 K loop and the slight opening of the 60 K loop.