Experimental report

09/11/2023

Proposal: 7-01-586 **Council:** 4/2023

Title: Anomalous dispersion of Co-O breathing modes in LaCoO3

Research area: Physics

This proposal is a new proposal

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Samples: LaCoO3

Instrument	Requested days	Allocated days	From	To
ORIENTEXPRESS	1	1		
IN8	8	8	19/09/2023	27/09/2023

Abstract:

LaCoO3 exhibits a rhombohedrally distorted perovskite-structured lattice, where the cobalt ions are surrounded by six oxygen atoms. It shows two crossovers at 100 K and 500 K: the first crossover is a result of the thermally activated spin-state crossover of the Co ions, and the second crossover is associated with the metal-insulator crossover. Both crossovers are connected to the spin state evolution of the Co ions from a low spin (LS) to a high spin (HS) configuration. It was proposed that the two different spin states form a 3D checkerboard-type dynamic short-range order near the room temperature. Here we propose to investigate the Co-O breathing mode, whose atomic displacement pattern perfectly mimics the proposed order.

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Motivation

We proposed to investigate the lanthanum cobaltite single crystal $LaCoO_3$, which exhibits a rhombohedrally distorted perovskite-structured lattice, where the cobalt ions are surrounded by six oxygen atoms. It shows two crossovers at 100 K and 500 K: the first crossover is a result of the thermally activated spin-state crossover of the Co ions, and the second crossover is associated with the metal-insulator crossover. Both crossovers are connected to the spin state evolution of the Co ions. It was proposed that the two different spin states form a 3D checkerboard type dynamic short-range order near the room temperature. Here we proposed to investigate the Co-O breathing mode, whose atomic displacement pattern perfectly mimics the proposed order.

Technical Details

To obtain a reasonably good resolution at the high energy transfers, 60 meV $\leq$ E $\leq$ 90 meV, we used double-focusing cooper (Cu 200) monochromator and Cu200 analyzer with the final energy at the analyzer fixed to 14.7 meV. The measurements were performed in the range 10 – 500 K. To achieve the wanted temperature range, we used orange cryofurnace (1.8 - 550 K). The reactor power was reduced to 42 MW.

Experimental details

We performed measurements of the phonon modes at finite wave vectors $\boldsymbol{Q}$ = (2.5, 2.5, 2.5), $\boldsymbol{Q}$ = (2.5, 2.5, -2.5), $\boldsymbol{Q}$ = (1.5, 1.5, 1.5), $\boldsymbol{Q}$ = (1.5, 1.5, -1.5), and we measured the Co-O breathing mode dispersing around 70 meV in the wave vector range from $\boldsymbol{Q}$ = (2, 2, 2) to $\boldsymbol{Q}$ = (2.5, 2.5, 2.5). The measurements were performed at several temperatures: 10, 100, 200, 300, 400 and 500 K.

Problems during the Experiment

During the beamtime we had to deal with several issues. Starting with the reactor operation time, which was postponed, however, our beamtime was also prolonged, respectively to the initial beamtime duration. Due to previously planned trips, we had to finish the beamtime remotely. There was a leakage problem, which was fixed by heating and changing the sample stick. Another problem was the A6 (analyser angle) movement deviated from its position by about 0.1 degree, which is not a big deviation, however, may need addition check.

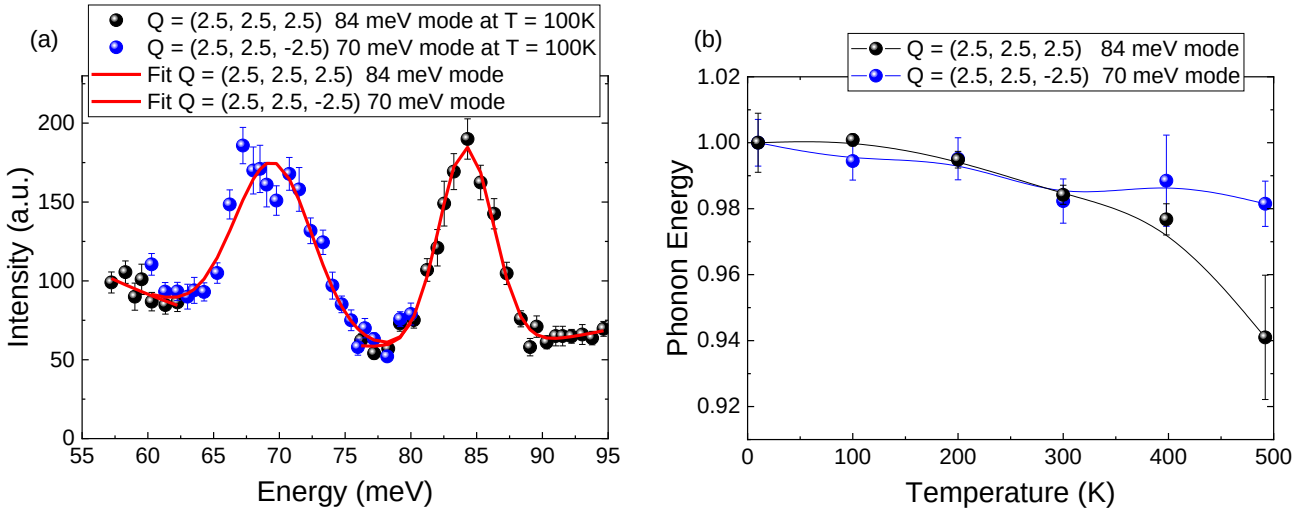

Figure 1. (a) Experimental data taken at 100 K: black and blue circles measured at ***Q*** = (2.5, 2.5, 2.5) and ***Q*** = (2.5, 2.5, -2.5). The red lines are the Gaussian fits; (b) Temperature dependence of the phonon energy of the 70 and 84 meV phonon modes for ***Q*** = (2.5, 2.5, -2.5) and ***Q*** = (2.5, 2.5, 2.5), respectively. The solid line are guides to the eye.

Observed results

Two high energy phonon modes at 68 meV and 84 meV were observed at ***Q*** = (2.5, 2.5, -2.5) and ***Q*** = (2.5, 2.5, 2.5), respectively. Figure 1 (a) shows the raw data at 100 K. The phonon energies are supported by calculations with two maxima at 67.96 meV and 79.05 meV. Following the phonon energies, we extracted the temperature dependence of two phonon modes (Fig. 1b). We observe the softening of both phonon modes. However, there is a slight difference between 68 and 84 meV phonon modes: the high energy phonon softens stronger. Continuous softening with increasing temperature is in accordance with the quasi-harmonic calculations based on the experimental lattice constants.

Also, we measured the Co-O breathing mode dispersing around 70 meV in the wave vector range from ***Q*** = (2, 2, 2) to ***Q*** = (2.5, 2.5, 2.5) to look for the signatures of the dynamic checkerboard patterns at several temperatures across the crossovers, at 100 K, 200 K, 300 K, 400 K and 500 K. Additional analysis is required. Observed phonon dispersions will be compared to ab-initio lattice dynamical calculations.