Lack of a Jahn-Teller Distortion in $La_{1-x}Sr_xCoO_3$ Determined by EXAFS and Neutron PDF Studies

The transition metal oxides exhibit a wide range of interesting properties, of which superconductivity in the copper oxides and colossal magnetoresistance in the manganese oxides are perhaps the best known. However, the strange magnetic behavior of several cobalt oxides is another example of these unusual properties, although not yet as intensively studied. The cobaltite system $La_{1-x}Sr_xCoO_3$ (LSCO) has a rich temperature-concentration phase diagram with anti-ferromagnetism and insulating behavior at low Sr concentrations, and ferromagnetism and metallic behavior at higher concentrations. The magnetism for the end compound $LaCoO_3$ (LCO) is particularly unusual; it has no Co spin magnetic moment at low T (and is diamagnetic). As T increases from 4K, the magnetic susceptibility increases dramatically up to roughly 100K, and then decreases as T is increased to 300K. This behavior has been attributed to Co^{+3} having several different spin configurations. Initially only two were considered, a low spin state (LS, S=0) that is not magnetic and a high spin state (HS, S=2) that is strongly magnetic. In the '90s a third, intermediate spin configuration (IS, S=1) was proposed by Potze, et al. and Korotin, et al; this configuration should result in a distortion of the CoO_6 octahedra (called a Jahn-Teller (JT) distortion). In the late '90s, Louca et al. reported neutron PDF results indicating a distorted Co-O environment, comparable to the Mn-O distortions observed in the similar manganite systems $La_{1-y}Ca_yMnO_3$ (LCMO) and $La_{1-z}Sr_zMnO_3$ (LSMO). However, to date, these neutron PDF data for the cobaltites are the only structural results that support a JT distortion. While some recent experimental results are argued to be consistent with a large Co-O JT distortion and its associated IS state, many others appear to be inconsistent with such an interpretation. Our group at UC Santa Cruz, therefore took a closer look at the possibility of a JT distortion of the CoO_6 octahedra, using a combination of the EXAFS and neutron PDF techniques; here we focus on the Co K-edge EXAFS results, for data collected at SSRL.

Before discussing Co, we first discuss three important energies that determine the ordering of the energy levels, and hence the spin configuration. For the free atom the 3d spatial states form a 5-fold degenerate multiplet, but in a cubic crystal field, these states are split into 2-fold degenerate e_g and 3-fold degenerate t_{2g} multiplets, with a splitting energy called 10Dq. The second important energy is called the exchange energy, E_{ex}, which is roughly the energy to add a spin-down electron to a state that is occupied by a spin-up electron. The third energy comes from the Jahn-Teller (JT) interaction when there is only one e_g electron present. Then a local distortions about the Co ion, such as two long Co-O bonds and four short Co-O bonds, will split the e_g states (one state decreases in energy and the other increases), and the electron can go to the lower energy state if this distortion takes place – See Fig 1. Note that the total energy is not lowered if two e_g electrons are present. The distortion does cost a small strain energy, but for e_g states the net energy is lowered and the crystal locally spontaneously distorts. When the energies 10Dq and E_{ex} are comparable, a tiny change in energy could change the system from high spin to low spin (See Fig. 1) – and for one possible set of energy levels (10Dq $\sim E_{ex}$), including a JT distortion can lead to the intermediate spin state.

For LCO, with six 3d electrons on Co, the filled energy states for the three localized spin state models are: 1) LS - $t_{2g}^6 e_g^0$, with no e_g electrons and all six t_{2g} spins paired (observed at low T); 2) HS - $t_{2g}^4 e_g^2$, expected at high T, note that with two e_g electrons it is not JT

active; and 3) IS - $t_{2g}^5 e_g^1$, - with one e_g electron it should be JT active, creating Co-O bonds of different lengths in the lattice. Thus a significant JT distortion is a *signature* for the IS state; if such a distortion is observed, then the IS state must be included in modeling the magnetism; however, if no JT distortion is present, no localized states containing one e_g electron exist and the IS state should not be important.
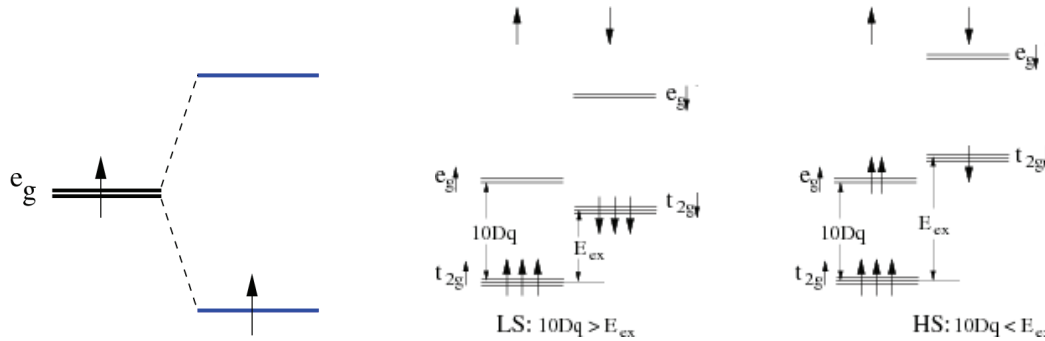

Fig. 1. (Left) Diagram for Jahn-Teller splitting. The e_g states are doubly degenerate in a cubic environment (left, black); if the environment is locally distorted the two energy levels are split (blue). When there is a single electron in the e_g states for a cubic crystal, the energy can be lowered via a distortion, and the crystal spontaneously distorts. (Right) Filling of the spin states for low spin (LS) and high spin (HS) states – it depends on the relative values of 10Dq and E_{ex}.

Temperature dependent (4 - 330K) EXAFS transmission Co K-edge data were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) for powdered LSCO samples over a range of Sr concentrations, x = 0.0-0.3. A standard data reduction (RSXAP) package was used to extract the EXAFS spectra which were fit in r-space to theoretical EXAFS functions generated by FEFF 8.20. Our primary interest here is σ, the width of the Co-O pair distribution function, which parameterizes the amount of variation present in the lengths of the Co-O bonds; the results are generally plotted as σ^2 vs T. There are several contributions to $\sigma^2(T)$ for the Co-O bond, thermal vibrations (or phonons), possibly some small static disorder from doping, and a JT distortion if it is present. Note that different contributions to σ^2 add up in quadrature if their mechanisms are uncorrelated; i.e. $\boldsymbol{\sigma^2 = \sigma^2_{static} + \sigma^2_{phonons} + \sigma^2_{Jahn\text{-}Teller}}$. If no JT distortions are present, the $\sigma^2(T)$ data can be fit to the correlated Debye model plus a static offset; this model is usually a good approximation for all phonon modes including acoustic and optical phonons. The thermal phonon contributions were determined from a fit of σ^2 vs. T, for 4 ≤ T ≤ 330 K.

Figure 2 shows $\sigma^2(T)$ (Co-O peak) for x = 0.0 and 0.3; there is no evidence for a step in $\sigma^2(T)$, or any significant excess static distortion at low T that would indicate any JT effect. The inset shows a fit of the Co-O peak. In Fig. 3, we plot similar $\sigma^2(T)$ data and the correlated Debye fits for two different $La_{0.8}Sr_{0.2}CoO_3$ samples (designated MZ and NS). We also plot, for comparison, corresponding results for a 22% Ca-doped LCMO sample which has a metal-insulator transition around 190 K associated with a significant Jahn-Teller distortion of the MnO_6 octahedra. Between 100 and 200 K, a JT splitting develops, with two longer Mn-O bonds and four relatively shorter bonds for some sites (at low T, the Mn-O octahedron has six bonds of nearly equal length). The proposed JT distortion of the Co-O bonds in LSCO is of comparable magnitude to that observed in LCMO. However, the lack of any significant step for LSCO in Figs. 2 and 3 and the rather small static distortion at 4K (≤ 0.0006 Å²) means that there is very little JT distortion of the Co-O PDF peak between 4 and

300 K for the 20% Sr doped LSCO samples. One cannot, of course, rule out the possibility of a few percent of sites having a JT distortion. Together these results show no evidence for a significant fraction of the Co having a JT distortion and hence strongly question the presence of the proposed intermediate spin state. Our neutron PDF data also show no evidence for a JT distortion in LCO or LSCO, in complete agreement with the EXAFS results described above.
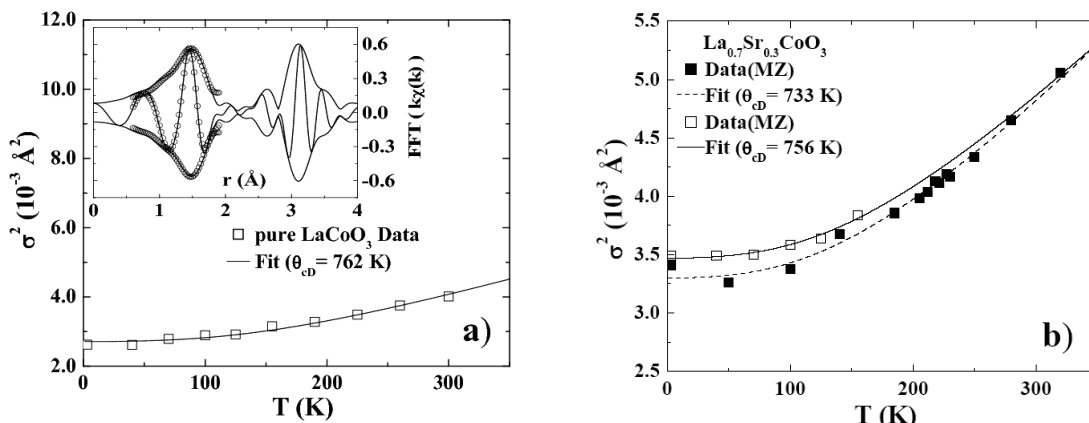

Fig. 2 a) $\sigma^2(T)$ for $LaCoO_3$ and the correlated Debye fit (line). Inset is an example of 4 K r-space data (solid line) and a fit to the Co-O first peak (open circles), Fourier Transform (FT) range is 3.3 - 12.0 $Å^{-1}$ with a Gaussian broadening of width 0.3 $Å^{-1}$, and the r-space fit range is 1.1 to 1.7 Å - note that we are fitting to the fast oscillating real and imaginary (not shown) parts of the FT. A good fit is obtained from 0.7 - 1.8 Å. **b)** $\sigma^2(T)$ for the $La_{0.7}Sr_{0.3}CoO_3$ MZ samples, the solid squares represent the data from the first measurement, and open squares represent the data from the second measurement showing consistency between measurements taken a year apart; the dashed line is the correlated Debye fit for the first experiment data, while the solid line is the fit for the second experiment data.
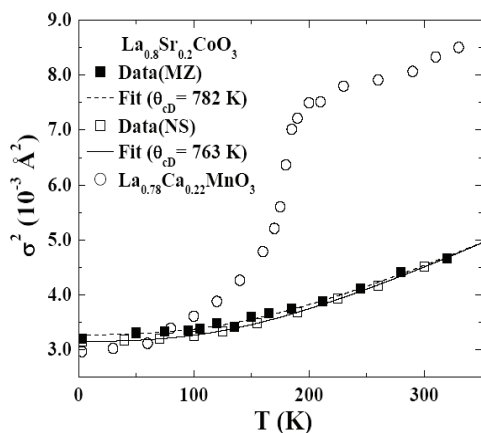

Fig. 3: $\sigma^2(T)$ for $La_{0.8}Sr_{0.2}CoO_3$ samples from two sample makers [MZ (solid squares) and NS (open squares)], as well as the correlated Debye fits (dashed line for MZ and solid line for NS samples). The data overlap very well within the errors. The corresponding data for a $La_{0.78}Ca_{0.22}MnO_3$ sample (Mn-O bond), using the same technique, are replotted here with open circles; this sample has a large JT distortion that develops between 100 and 200 K.

Primary Citation

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