XANES study of the role of Sr doping in LaCoO₃

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Abstract: With the comparisons of experimental XAFS data of Sr doped LaCoO₃ samples taken at room temperature and LDA+U (with U = 0.4eV and 8eV, respectively) model calculations of LaCoO₃, it is found that the experimental XAFS data of Sr doped samples can be well reconstructed if the samples are phase separated. When U takes 4eV or 8eV, the ground state of LaCoO₃ is Mott insulator and the curve shape of calculated XAFS data is even the same as that of the experimental data; when U=0 the HOMO-LUMO band gap vanishes and the calculated XAFS data gets an extra peak. The curve can be well fitted with experimental data of Sr doped LaCoO₃ sample. It shows that the doped LaCoO₃ sample is not traditional Mott insulator but with some properties of charge transfer type, that is, when Sr ions are doped in LaCoO₃, the trivalent Co ions become tetravalent and leave an extra hole in each Co e_g orbital. The charge carriers can hop back and forth between trivalent Co ions and tetravalent ones in which way close the band gap.

1. Introduction:

There is a long argument about the spin state of Co ions (1) and the corresponding local structure of CoO₆ octahedral (2) in LaCoO₃, i.e., it is thought that intermediate spin state of Co ions is Jahn-Teller active while high-spin state or low-spin state of Co ions is not. These issues are determined by the local electronic structure of the materials, e.g., the competition of Hund energy and crystal field energy of CoO₆ octahedron can dominate the electron occupancy of sub-orbitals of Co 3d orbital (3). Near edge X-ray absorption fine structure (NEXAFS) is very sensitive to local structure and can be properly used in the determination of local electronic structure of CoO₆ octahedron in LaCoO₃.

Previous experiments with extended X-ray absorption fine structure (EXAFS) have obtained many interesting results, like in reference (2) the authors have obtained that few Jahn-Teller active Co ions exist in La₀.₇Sr₀.₃CoO₃ for x < 0.35. It has been interpreted that this is mainly because the charge carriers hop in these samples much faster than the phonon time scale, and the wave function of the conducting charges may spread over several sites to form metallic clusters. In reference (4) the authors have found that there was no evidences of the variations of edge positions of Co K edge in LaCoO₃ although different amount of Sr ions were doped. It is further argued that the holes are in fact doped on O sites rather than on Co sites. For transition metal oxides, pure ionic bonding is rare but with some degree of covalent bonding, thus the doped holes, even if on O sites, would lead to some variation on Co sites, especially the outer shells of Co ions, i.e., e_g orbits (considering the octahedral crystal field). An important parameter is the electron correlation strength U that we consider in this report.

Previous ab-initio calculations considering nonzero U values have already got many important results, i.e., in reference (5), spin-orbit coupling has been considered to take an important role in determining the electronic structure of Co ions in this series of materials. There have been also some disagreements between model calculations (1, 5) and experimental results (6).
The properties of doped LaCoO$_3$ are different from those of pure LaCoO$_3$, i.e., when a certain amount of charge carriers are introduced by doping Sr ions at La sites, the samples will become ferromagnetically metallic (7). It is also thought that the doped LaCoO$_3$ is phase separated (8), but what is the role of Sr ions in La$_{1-x}$Sr$_x$CoO$_3$ is still unclear. In the present work, with the combination of NEXAFS experiment and ab-initio calculation, we would like to give a localized picture of the influences of Sr doping on LaCoO$_3$.

2. Experiments and Calculations:

La$_{1-x}$Sr$_x$CoO$_3$ ($x=0.0, 0.1, 0.2$ and $0.3$) samples were synthesized by traditional solid-state reaction method. Moderate amount of La$_2$O$_3$, SrCO$_3$, and Co$_2$O$_3$ were properly mixed and ground, followed by calcining for several days between $1000^\circ$C $\sim 1100^\circ$C, then the mixture was pressed into pellets and annealed at $1200^\circ$C. The crystal structure of the samples was characterized by x-ray diffraction measurements. The local structure was measured by x-ray absorption fine structure measurement (XAFS) at Co K edge at National Synchrotron Radiation Laboratory (NSRL), University of Science and Technology of China.

The ab-initio calculations were carried out with the QUANTUM ESPRESSO (9) software packages. As there were arguments about the crystal structure of LaCoO$_3$ series which was firmly relative to the spin state ground state of Co ions, the I2/a spacegroup was chosen since there are un-equivalent Co-O bond lengths in this structure model (10). In fact, we also carried out the calculations with the R-3C space-group (which has equivalent Co-O bond length) to cross-check the results, and the R-3C spacegroup structure model did not give out obvious difference from the I2/a model calculations.

3. Results and Discussions:

![Image of calculated band structure](image1)

Figure 1. The calculated band structure of LaCO$_3$ in I2/a structure with U=0 shows that the ground state is metallic.

Fig. 1 shows the calculated results of the state density of O 2p orbitals in LaCoO$_3$ with U=0. As shown in the figure, the O (we simply show the ones with the Co-O bond length of 0.1922 nm, the results from the O ions with Co-O bond length of 0.198 nm is even the same as the results from 0.1922 nm-long Co-O bonds) $p_x$ and $p_y$ orbitals have some intensities around the Fermi level. At the same time, there is a prominent amount of intensity around Fermi level of LaCoO$_3$ that comes from Co t$_{2g}$ ($d_{xy}$, $d_{yz}$, $d_{zx}$) orbitals. When $U$ takes 4 eV or 8 eV, as shown in Fig. 2, the e$_g$ orbitals lie above the Fermi level, and the t$_{2g}$ orbitals lie below the Fermi level. The band gap is open and there is little intensity around the Fermi level, thus the ground state of the samples is insulator. The NEXAFS of the samples have also been calculated with the xspectra program as shown in the upper panel of Fig. 3. The curves’ shape of the U=4 eV and U=8 eV are even the same. The calculated NEXAFS data of the U=0 model has an extra peak compared with the nonzero-U model calculations.

The experimental NEXAFS data of both doped and un-doped samples is shown in the lower panel of Fig. 3. The undoped samples have only a broad peak at the absorption edge. When Sr concentration increases, another peak appears at energy lower than the absorption edge of undoped LaCoO$_3$. The intensity of this new peak increases with the increase of Sr concentration. The experimental XANES curves of the samples can be well fitted with the calculated ones as shown in Fig. 4. The main peak of the experimental data of the undoped samples is corresponding to the calculated edges with $U$=4 eV or 8 eV.
The experimental data of the doped samples can be well fitted with the combination of calculated curves with $U=0$ and the nonzero-$U$ models.

**Figure 2.** The opening of the band gap when $U$ takes 4 eV or 8 eV.

**Figure 3.** The comparison of calculated XAFS with experimental data.

Previous works about the Sr ions doping in LaCoO$_3$ have the results that when the Sr concentration of La$_{1-x}$Sr$_x$CoO$_3$ reaches a considerable value, the ground state of the samples become metallic. The possible explanation is that the doped Sr ions will introduce some charge carriers (holes) around Co ions, the charge carriers can hop back and forth to make the samples metallic. With the comparison of experimental NEXAFS data of Sr doped LaCoO$_3$ samples taken at room temperature and LDA+U (with $U=0$, 4 eV and 8 eV, respectively) model calculations of LaCoO$_3$, it is found that the experimental NEXAFS data of Sr doped samples can be well reconstructed if the samples are phase separated (11), i.e.,
at the Co sites around the Sr ions, the experimental NEXAFS data of Co K edge can be well fitted with the calculated curves of $U=0$. While at sites far from Sr ions, the experimental curves are most like the calculated curves with nonzero $U$ model. That is also the reason why the relative intensity of peak A (the absorption peak located at energy lower than the one of un-doped LaCoO$_3$, see Fig.3) in the experimental NEXAFS data of doped LaCoO$_3$ increases with the increase of Sr concentration.

When $U$ is zero the HOMO-LUMO band gap vanishes and the Co $t_{2g}$ orbits and O $p_x$, $p_y$ will form the “\(\pi\)” bonds. When $U$ takes 4 eV or 8 eV, the bands split into two parts as shown in Fig. 2. The energy split of the $U=8$ eV case is larger than the $U=4$ eV case, thus there is little density of state around the Fermi level. Comparing with the experimental data, the differences between the undoped LaCoO$_3$ and Sr doped LaCoO$_3$ are mainly that when Sr ions are doped, the electrons of the outer shells ($e_g$ orbitals) of Co$^{3+}$ ions which are very near to Sr$^{2+}$ ions get lost, thus the interaction between $t_{2g}$ electrons and $e_g$ electrons vanishes, then the screening effect disappears, leading to the bonding of Co $t_{2g}$ electrons with O $p$ orbits. As the electrons can hop between O ions and Co ions, metallic clusters will form.

4. Conclusions:

From these results, we conclude that the doped samples are not traditional Mott insulator but with some properties of charge transfer type, that is, when Sr ions are doped in LaCoO$_3$, the nearby trivalent Co ion becomes tetravalent and leaves an extra hole in $e_g$ orbital. The charge carriers can hop back and forth between trivalent Co ions and tetravalent ones through the O ions bridge, in which way the band gap is closed (12).

References:

1. A. Podlesnyak et al., Spin-State Transition in LaCoO$_3$: Direct Neutron Spectroscopic Evidence of Excited Magnetic States. Phys. Rev. Lett. 97, 247208 (2006).

2. N. Sundaram et al., Local Structure of La$_{1-x}$Sr$_x$CoO$_3$ Determined from EXAFS and Neutron Pair Distribution Function Studies. Phys. Rev. Lett. 102, 026401 (2009).
3. L. Siurakshina, B. Paulus, V. Yushankhai, E. Sivachenko, Quantum chemical study of Co$^{3+}$ spin states in LaCoO$_3$. *Eur. Phys. J. B* **74**, 53 (2010).

4. Y. Jiang *et al.*, Study of the local distortions of the perovskite system La$_{1-x}$Sr$_x$CoO$_3$ (0 <= x <= 0.35) using the extended x-ray absorption fine structure technique. *Phys. Rev. B* **80**, 144423 (2009).

5. S. K. Pandey *et al.*, Investigation of the spin state of Co in LaCoO$_3$ at room temperature: Ab initio calculations and high-resolution photoemission spectroscopy of single crystals. *Phys. Rev. B* **77**, 045123 (2008).

6. R. F. Klie *et al.*, Direct Measurement of the Low-Temperature Spin-State Transition in LaCoO$_3$. *Phys. Rev. Lett.* **99**, 047203 (2007).

7. D. Louca, J. L. Sarrao, Dynamical Disorder of Spin-Induced Jahn-Teller Orbitals with the Insulator-Metal Transition in Cobaltites. *Phys. Rev. Lett.* **91**, 155501 (2003).

8. J. Wu, C. Leighton, Glassy ferromagnetism and magnetic phase separation in La$_{1-x}$Sr$_x$CoO$_3$. *Phys. Rev. B* **67**, 174408 (2003).

9. G. Paolo *et al.*, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys.: Condens. Matter* **21**, 395502 (2009).

10. N. Sundaram *et al.*, Local Structure of La$_{1-x}$Sr$_x$CoO$_3$ Determined from EXAFS and Neutron Pair Distribution Function Studies. *Phys. Rev. Lett.* **102**, 026401 (2009).

11. B. Raveau, The crucial role of mixed valence in the magnetoresistance properties of manganites and cobaltites. *Phil. Trans. R. Soc. A* **366**, 83 (January 13, 2008, 2008).

12. Y. Tokura *et al.*, Thermally induced insulator-metal transition in LaCoO$_3$: A view based on the Mott transition. *Phys. Rev. B* **58**, R1699 (1998).