Oxygen stoichiometry, crystal structure, and magnetism in La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$

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Abstract. We have prepared a series of polycrystalline samples La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ with $0 < \delta \leq 0.21$ and characterized their oxygen content, crystal structure, and magnetic properties. While the fully oxygenated samples are good ferromagnets, samples with larger $\delta$ values display increasingly broad magnetic transitions. The saturation magnetization at 5 K falls rapidly as $\delta$ increases. First principles electronic structure calculations provide insights into the magnetic behavior of the fully oxygenated compound, and the manner in which ferromagnetic ordering is affected by increasing oxygen non-stoichiometry.

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1. Introduction

LaCoO$_3$ has a rich history\cite{1,2} and yet remains the focus of a number of studies. For example, temperature dependence of the structure of LaCoO$_3$ has been carefully re-examined by neutron\cite{3} and single-crystal X-ray diffraction,\cite{4} with the latter providing evidence for orbital ordering at intermediate temperatures, as electrons are thermally activated from low- to intermediate-spin states.

The substituted, mixed-valent phases La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ have also attracted a great deal of interest due to their finding use as cathodes in solid-oxide fuel cells,\cite{5,6,7} because they display colossal magnetoresistance,\cite{8,9} and because they provide non-fatigue epitaxial electrodes for ferroelectrics.\cite{10} In these compounds, it is well known that crystal structure, as well as electrical transport and magnetic properties depend sensitively on the oxygen non-stoichiometry.\cite{11,12,13,14}

In this contribution, we have examined the effect of the oxygen non-stoichiometry $\delta$ on the properties of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$. To our knowledge, this is the first systematic study describing how changes in $\delta$ influence structure and magnetic properties of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$. A similar study of La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ with $x = 0.0$ and $x = 0.3$ has been performed by Mineshige et al.\cite{15} Sunstrom et al.\cite{12} have considered the effects of chemical oxidation of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$. We have also considered the detailed electronic structure, from first principles density functional calculations, of a plausible model for La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ with $\delta = 0$; tetragonal LaSrCo$_2$O$_6$. Our calculations indicate that La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ is a good ferromagnet, albeit with significant mixing of majority and minority states at the Fermi energy. It is such mixing that gives rise to a magnetic moment which is greatly reduced from the expected high-spin value.

2. Experimental

La$_2$O$_3$ was dehydrated prior to use by firing at 900°C for 24 h. SrCO$_3$, La$_2$O$_3$, and Co$_3$O$_4$ taken in appropriate stoichiometric amounts (0.01 mole basis) were ground together in an agate mortar and pestle, and heated in air at 850°C for 24 h in a dense alumina crucible. The resulting powder was then reground, pelletized, and heated in air at 1100°C for 24 hours. A final reheating for 24 h, when required, was performed at 800°C in different atmospheres.

For determining oxygen content, redox titrations were performed by dissolving a weighed quantity (typically about 100 mg) of sample in 20 cm$^3$ of an acidified, 0.1 N Fe(II) sulfate solution. The ferrous ions reduce all cobalt to the Co(II) state. Left-over Fe(II) was determined by titration against a 0.1 N K$_2$Cr$_2$O$_7$ solution, with the end-point being determined electrochemically using a redox electrode. Between 3 and 5 titrations were performed for every sample. Precise analysis of the titration data require an accurate estimate of the mole numbers of the sample used. This in turn requires a knowledge of the oxygen content. A Mathematica$^\text{TM}$ Notebook was developed and used to perform this analysis in a self-consistent manner.
Table 1. List of the different annealing atmospheres (800°C for 24 h) and the corresponding values of the oxygen non-stoichiometry δ in La$_{0.5}$Sr$_{0.5}$CoO$_{3-δ}$ obtained from redox titration.

| Atmosphere          | δ    | error |
|---------------------|------|-------|
| O$_2$, slow cooling*| 0.01 | 0.029 |
| O$_2$               | 0.04 | 0.009 |
| Air, as-prepared**  | 0.09 | 0.009 |
| N$_2$               | 0.17 | 0.013 |
| UHP Ar              | 0.21 | 0.022 |

* Cooled from 800°C to 200°C at 2°C min$^{-1}$.
** This sample was not subject to the final re-heating.

X-ray diffraction data was collected on a Scintag X-2 diffractometer operated in the Bragg-Brentano geometry and using CuKα radiation. Data was collected in the 2θ range of 10 to 120° with a step-size of 0.015° and a step time of 5 seconds. Rietveld refinement of the x-ray diffraction profiles made use of the XND Rietveld code.[15] Magnetization data as a function of temperature and field was collected using a Quantum Design MPMS 5XL magnetometer, operated between 5 K and 350 K.

3. Computational methods

First principles electronic structure calculations on La$_{0.5}$Sr$_{0.5}$CoO$_3$ were performed using the linear muffin tin orbital (LMTO) method within the atomic sphere approximation as implemented in the Stuttgart TB-LMTO-ASA program.[16] 396 $k$ points in the irreducible wedge of the Brillouin zone were used for the calculation. The Perdew-Wang [17] formulation of the gradient-corrected exchange correlation potential within the spin-density approximation was employed.

4. Results and discussion

Redox titrations indicate that the final heating atmospheres and/or protocols strongly control the oxygen non-stoichiometry δ in La$_{0.5}$Sr$_{0.5}$CoO$_{3-δ}$, and δ can be tuned between 0.01 and 0.21. Table 1 lists the different atmospheres which allow these concentrations to be obtained. We henceforth refer to samples by their oxygen non-stoichiometry, δ. For the air-heated sample we obtain δ = 0.09(1), which is close to the value of δ = 0.06(1) reported by Señarís-Rodríguez and Goodenough.[11] Sunstrom et al.[12] obtain fully oxygenated La$_{0.5}$Sr$_{0.5}$CoO$_3$ in air, but from a slightly different heat treatment.

X-ray diffraction profiles (displayed for three samples in Fig. 1) of the different samples of La$_{0.5}$Sr$_{0.5}$CoO$_{3-δ}$ are well-fitted using the rhombohedral perovskite structure
Table 2. Rhombohedral and cubic crystal structures obtained from the Rietveld refinements of the different La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ samples.

| $\delta$ | Rhombohedral* SG = $R\overline{3}cH$ | Cubic** SG = $Pm\overline{3}m$ |
|---|---|---|
| $a$ (Å) | $c$ (Å) | $x$(O) | $a_p$ (Å) |
| 0.01 | 5.4274(2) | 13.2317(6) | 0.459(1) | 3.8329(1) |
| 0.04 | 5.4292(2) | 13.2345(6) | 0.459(1) | 3.8337(2) |
| 0.09 | 5.4256(3) | 13.240(1) | 0.456(2) | 3.8324(2) |
| 0.17 | 5.4284(4) | 13.29(2) | 0.455(2) | 3.8378(2) |
| 0.21 | 5.4416(7) | 13.308(4) | 0.459(3) | 3.8458(2) |

* (La/Sr) at (0,0,1/4); Co at (0,0,0) and O at ($x$,0,1/4).
** (La/Sr) at ($1/2$,1/2,1/2); Co at (0,0,0) and O at ($1/2$,0,0).

In a hexagonal setting ($R\overline{3}cH$). As $\delta$ increases, the widths of the Bragg peaks broaden and counts decrease indicating that microscopic inhomogeneities are created around the oxygen vacancies.[7] In keeping with the increased peak-broadening and decreased counts, $R_{\text{Bragg}}$ values systematically decrease from 9% for $\delta = 0.01$ to 7% for $\delta = 0.21$; broader profiles being easier to fit. When we used the cubic perovskite structure, the $R_{\text{Bragg}}$ values were slightly higher for samples with small $\delta$. As $\delta$ increases, peak-broadening makes the rhombohedral distortion difficult to observe, and refinements in the cubic perovskite structure are equally satisfactory. Rhombohedral and cubic structures obtained from the refinements for different $\delta$ values are summarized in Table 2.

Figure 2 displays the variation of the hexagonal cell parameters $a$ and $c$ with $\delta$. The initial increase in $\delta$ does not greatly influence the cell parameters. It is only when $\delta$ exceeds 0.1 that the cell parameters increase. This increase suggests why annealing experiments are limited in the range of $\delta$ which can be obtained, unlike strained thin films (tensile strain on SrTiO$_3$ which has $a = 3.905$ Å) where much lower oxygen concentrations (larger $\delta$ values) have been reported.[7]

To examine the effect of oxygen non-stoichiometry on the magnetic properties of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$, we have recorded the temperature dependence of magnetization of the different samples on warming in a 1000 Oe field, after cooling under zero field (ZFC) and on warming in a 1000 Oe field after cooling under a 1000 Oe field (FC). Data are displayed in Fig. 3(a). For $\delta$ smaller than 0.1, the samples show relatively sharp ferromagnetic transitions. The domain behavior for this $\delta$ regime is typical of a hard ferromagnet. The $\delta = 0.17$ sample has a rather broad transition. The $\delta = 0.21$ sample shows almost no ZFC magnetization at low temperatures. On warming, the magnetization displays a hump after a slow initial rise. To further understand the origins of the unusual temperature dependence of magnetization, we have carried out AC measurements under a 50 Oe field at frequencies of 10 Hz, 100 Hz, and 1000 Hz. We find no dispersion in the magnetization, or in the transition, ruling out the presence of glassy magnetic phases. The variation in the Curie temperature with $\delta$ is displayed in
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Figure 1. X-ray diffraction profiles (points), Rietveld fits, and difference profiles for La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ with $\delta = 0.01$, 0.09 and 0.21. The data and fits have been slightly offset from the difference profile for clarity.

Figure 2. (a) Variation of the hexagonal $a$ and $c$ lattice parameters with $\delta$. (b) Variation of the pseudocubic cell parameter calculated from the volume $[(V/6)^{1/3}]$ of the hexagonal cell with $\delta$, compared with the $\delta$-dependence of the cubic perovskite cell parameter $a_P$ obtained from Rietveld refinements using the cubic perovskite structure.
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Figure 3. (a) ZFC (dashed) and FC (solid) magnetization of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ under a 1000 Oe field. (b) Variation of $T_C$ with $\delta$ for La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$.

Fig. 3(b). It is interesting that in a manner which parallels the cell-parameter variation, there is hardly any change in $T_C$ in the region $0 \leq \delta \leq 0.1$, but when $\delta \geq 0.1$, $T_C$ drops rapidly. $T_C$ for the oxygenated samples (near 250 K) is in agreement with earlier reports.[12, 14]

Hysteresis loops of the 5 K magnetization of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ as a function of magnetic field are shown in Fig. 4(a). As $\delta$ increases the saturation magnetization is decreased. All the samples are hard magnets at 5 K. The coercive field increases with $\delta$ and then decreases, with a maximum corresponding to $\delta = 0.09$. The increased coercive field perhaps corresponds to structural imperfections which pin the magnetization. The sample with $\delta = 0.21$ shows unusual hysteretic behaviour. The initial rise from zero of the magnetization is rather slow, and is not retraced during the second field ramp. Once magnetized, the sample behaves like a soft ferromagnet.

Figure 4(b) displays the variation of the 5 K saturation magnetization with $\delta$. For $\delta = 0.01$, $M_{\text{sat.}} = 1.82 \mu_B$ per Co. As $\delta$ increases, the saturation magnetization falls rapidly, following no simple trend. For example, if the decrease in Co oxidation state with increasing $\delta$ were translated into a simple reduction of the number of spins, the magnetization would be expected to fall according to $2 \times \delta$, indicated as a dashed line, as discussed further in the section regarding the electronic structure. The actual fall is much larger than $2 \times \delta$. In Fig. 4(b), we have also displayed as a filled square, the
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*Figure 4.* (a) Magnetization of \(\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3\)−\(\delta\) with field at 5 K. The different labels (i-v) are the same as in the previous figure. The different loops have been shifted on along the field axis for clarity. (b) Variation of \(M_{\text{sat.}}(5\ \text{K, 2 T})\) with \(\delta\) in \(\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3\)−\(\delta\). The straight dashed line is the expected spin-only reduction of the saturation magnetization. The square is the magnetic moment from LMTO calculations.

For density functional calculations, a model tetragonal \((P4/mmm)\) structure was constructed by stacking a cubic perovskite \((a_P = 3.8329\ \text{Å}\), directly obtained from Rietveld refinement in the cubic structure\) cell of \(\text{LaCoO}_3\) on top of a similar cubic perovskite cell of \(\text{SrCoO}_3\). The effect of the artificial ordering of La and Sr has not been investigated; this is not expected to be significant because of the similarity in size. Of all \(\text{Ln}_{0.5}\text{A}_{0.5}\text{CoO}_3\) phases, \(\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3\) has the highest Curie temperature, in keeping with cation-size disorder being the least.[14] The pseudocubic perovskite of this composition is closely related in structure to the actual rhombohedral phase; indeed for the nearly fully-oxygenated \(\delta = 0.01\) sample, Rietveld refinement in the rhombohedral \(R\overline{3}cH\) space-group \((R_{\text{Bragg}} = 9.0\%)\) was only a slight improvement over the cubic \(Pm\overline{3}m\) space group \((R_{\text{Bragg}} = 11.6\%)\). Taken together, we believe these validate the model compound used for the calculation.

The calculations show how the saturation magnetization of \(\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3\)−\(\delta\) is significantly reduced from the high-spin value, as a result of having both majority and calculated (LMTO) magnetic moment for a sample that is effectively “\(\delta = 0.00\)”.
minority spin states at the Fermi energy. The calculated magnetic moment of 1.56 \( \mu_B \) per Co atom, compared with experiment in Fig. 4(b), is slightly reduced from the experimental value of \( M_{\text{sat.}} = 1.82 \mu_B \) per Co obtained on the \( \delta = 0.01 \) sample. It is in-between the spin only values for low (LS) and high (HS) octahedral \( \text{Co}^{3.5+} \) in \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \), which are respectively, 0.5 \( \mu_B \) and 4.5 \( \mu_B \) per Co. LMTO densities of state for tetragonal \( \text{LaSrCo}_2\text{O}_6 \) are displayed in Fig. 5 in the two spin directions. The origin of the energy axis is the Fermi energy. In the majority (\( \uparrow \)) spin direction, the Fermi energy lies in a broad band just above a sharper, narrow band centered at around -1 eV and about 1.5 eV wide. In the minority (\( \downarrow \)) spin direction, the same sharply peaked states are now centered at the Fermi energy. The exchange splitting is therefore the difference, which is 1 eV. It must be noted that such narrow, sharply peaked states at the Fermi energy would normally be suggestive of electron correlation, and an instability towards a Mott-Hubbard ground state. It is interesting that \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \) avoids such a ground state and remains a ferromagnetic metal, as known from transport measurements, [11] because of broader states which cross \( E_F \) in the majority spin direction.

A clearer understanding of the electronic structure is obtained from an examination of the band structures displayed in Fig.6(a-d). A feature of the LMTO program is the ability to decorate bands with a width – so-called fatbands – corresponding to specific orbital contributions to the different eigenvectors. [18] If at some \( k \) point, the contribution from a specific orbital is 100\%, then the width of the fatband at that point is 2.5\% of the total energy scale, or in the present case, 0.3 eV.

The \( t_{2g} \) fatbands displayed in Fig.6(a) and (b) in the two spin directions are not very disperse. In the \( \uparrow \) band structure \( t_{2g} \) states are centered at -1 eV. In the minority band structure [Fig.6(b)], the poorly disperse \( t_{2g} \) states are centered around \( E_F \) with a width that is less than 2 eV. In Fig.6(c), we observe the partially filled \( e_g(\uparrow) \) band is very disperse, extending in the \( \Gamma - M - X \) region of the Brillouin zone from approximately
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Figure 6. (a,c) LMTO energy bands in the $\uparrow$ or majority spin direction and (b,d) in the $\downarrow$ or minority spin direction. Bands deriving from Co $t_{2g}$ and $e_g$ states have been decorated as explained in the text.

-1 eV to 3 eV. It is this band that gives rise to the disperse states which cross $E_F$ in the majority spin direction, seen in Fig.5. In the $\downarrow$ spin direction, [Fig.6(d)] it is seen that $e_g$ states are empty, but similarly disperse. It is well known in AMO$_3$ perovskites that corner-sharing of MO$_6$ octahedra results in those $d$ states which point towards the ligand $p$ orbitals, namely $e_g$ states, to be disperse because of M-O-M covalency, while $t_{2g}$ are narrow because $d$ orbital lobes point away from ligand $p$. This is precisely what is observed in the electronic structure of La$_{0.5}$Sr$_{0.5}$CoO$_3$, which has bandwidths of approximately 1.5 eV and 4 eV for $t_{2g}$ and $e_g$ respectively.

The electronic structure of La$_{0.5}$Sr$_{0.5}$CoO$_3$ summarized in Fig.5 and Fig.6 emphasizes the danger in assigning spin states in extended solids. The $e_g$ band is so much more disperse than $t_{2g}$ that there is effectively no crystal field gap; This despite the centroids of the $t_{2g}$ and $e_g$ manifolds being separated by at least 3 eV. An exchange splitting of 1 eV in conjunction with a crystal field splitting of 3 eV would normally correspond to a low spin configuration.

The electronic structure of LaSrCo$_2$O$_6$ allows us to speculate on the effect of creating oxygen vacancies. These would reduce the effective oxidation state of Co, resulting in
a spin state which is close to low-spin, non-magnetic Co$^{3+}$ with a $t^6_{2g}$ configuration. Increasing $\delta$ therefore concurrently reduces both the number of unpaired spins as well as decreases the extent of spin-polarization, accounting for the rapid fall in the saturation magnetization with $\delta$ observed in Fig. 4(b).

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