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Spin state and magnetic ordering of half-doped $Nd_{0.5}Sr_{0.5}CoO_3$ cobaltite

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ABSTRACT

Cobaltites show intriguing magnetic and transport properties, when compared with manganites for instance, as they exhibit an additional degree of freedom: the spin state of the Co ions. For $Nd_{0.5}Sr_{0.5}CoO_3$ this spin configuration is not well-established, as well as the magnetic ordering below the Curie temperature. Thus, in the present effort, magnetization measurements and a mean-field theoretical model were developed in order to understand in detail these aspects of the half-doped $Nd_{0.5}Sr_{0.5}CoO_3$ cobaltite. These results show that the Co and Nd magnetic sub-lattices couple antiferromagnetically below Curie temperature $T_c=215$ K down to very low temperature. These findings clarify the presence of the plateau observed at 80 K on $M(T)$ curve, which is erroneously attributed, in the literature, to the onset of an antiferromagnetic ordering. Magnetization data also clearly shows that Co^{3+} and Co^{4+} are in an intermediate spin state. In addition, experimental and theoretical magnetic entropy changes were determined and a comparative analysis among these two leads to ratify the results above claimed. Finally, from all those results, a magnetic phase diagram for $Nd_{0.5}Sr_{0.5}CoO_3$. could be drawn.

1. Introduction

Perovskite cobaltites exhibit general formula of type $Ln_{1-x}A_xCoO_3$ (Ln: lanthanides, A: alkaline-earth metals) and are very interesting materials due to the their remarkable magnetic and electrical properties that lead to effects such as the giant magnetoresistance [1], giant anisotropic magnetostricition [2], huge values of Hall coefficient [3] and magnetocaloric effect [4,5], just to name a few. The interest on these materials has been revived in recent years due to the possibility of applications on solid oxide fuel cells [6], chemical reactors, gas separation membranes [7] and other applications [8].

Physical properties of cobaltites, as well as manganites, depend on the interplay between charge, spin, orbital and lattices degrees of freedom; however, cobaltites have an additional degree of freedom as Co^{3+} and Co^{4+} can occur in three different spin configurations [9]: low-spin LS ($t_{2g}^6e_g^0$ for Co^{3+} and $t_{2g}^5e_g^0$ for Co^{4+}), intermediate-spin IS ($t_{2g}^5e_g^1$ for Co^{3+} and $t_{2g}^4e_g^1$ for Co^{4+}) and high-spin HS ($t_{2g}^4e_g^2$ for Co^{3+} and $t_{2g}^3e_g^2$ for Co^{4+}). This unusual flexibility arises from the comparable energies between Hund's coupling and the crystal-field splitting [9].

Those intriguing magnetic and transport properties are mainly ruled by the doping level x, which induces lattice distortions and changes the valence of the Co ions. Compounds with $x=0$ contain only Co^{3+} ($3d^6$), while those with $x=1$ have only Co^{4+} ($3d^5$); and, obviously, intermediate values of x lead to mixed valence compounds. Rao et al. [10] investigated $Ln_{1-x}A_xCoO_3$ (with Ln=Eu, Nd, Pr, Sm and Gd and A=Sr, Ca and Ba) and show that, in general, lower values of x lead to a very high electrical resistivity with no magnetic ordering; and above a critical value of x, a ferromagnetic ordering occurs. The Curie temperature, for this heavy doped region of the phase diagram, decreases with decreasing the size of the rare-earth ion. $La_{1-x}Sr_xCoO_3$ [8,1,2] and $Pr_{1-x}Sr_xCoO_3$ [11,12,4] series are the most studied cobaltites, and the latter are more interesting due to the non-zero magnetic moment of Pr. Some compounds of $Pr_{1-x}Sr_xMnO_3$ series, for example, exhibit a broad peak in the susceptibility data around 90 K, whose origin is an open question in the literature [4]; with some authors claiming that it is due to a state spin transition from the intermediate to low-spin state [13], while other researchers argue that it is only changing in the ferromagnetic state associated with orbital ordering [11].

$Nd_{1-x}Sr_xCoO_3$ compounds have also been intensely investigated. Fondado and co-workers [14], for example, studied the compounds in the composition range of $0 \le x \le 0.4$. The authors found that, for $x > 0.2$, the system is ferromagnetic; but for $x = 0$ ($NdCoO_3$), the material is paramagnetic due to the zero

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paramagnetic effective magnetic moment of Co ions, which indicates that these are in low spin configuration. However, for $T > 250$ K a deviation from linearity appears on $\chi^{-1}(T)$, that indicates an onset of a spin transition of Co ions. This behavior is in fact observed for those samples with $x \le 0.1$. Transport measurements [14] show that as x increases from 0.1 to 0.4, the activation energy also increases, which would induce different spin-state of the Co ions for the $Nd_{1-x}Sr_xCoO_3$ compounds; but the authors were not able to define if the spin state transition occurs due to thermal energy or crystal distortion due to x change. However, for $x=0.33$, Paraskevopoulos et al. [9] showed that the Co^{3+} and Co^{4+} are in the IS and LS configurations, respectively, at temperatures above T_C (~173 K), which confirms the change of the spin-state of the Co ions as x increases. For samples of half-doped $Nd_{1-x}Sr_xCoO_3$, the spin-state is not yet well defined and, in addition, the broad maximum around 80 K is also an open question in the literature.

The present effort reports on the magnetic investigation of half-doped $Nd_{0.5}Sr_{0.5}CoO_3$ cobaltite. Magnetization measurements were made and a mean field theoretical model developed in order to clarify the magnetic arrangement of Co and Nd sub-lattice, as well as on the spin-state of Co ions. In addition, magnetic entropy change was also explored, and those results are also consistent with our other findings. We close this contribution with a complete magnetic phase diagram for this half-doped cobaltite.

2. Experimental details

The $Nd_{0.5}Sr_{0.5}CoO_3$ sample was prepared by sol–gel Pechini method [15]. A citric acid solution was used to dissolve neodymium(III) nitrate hexahydrate $Nd(NO_3)_3 \times 6H_2O$ (Sigma Aldrich, 99.9%) and strontium nitrate $Sr(NO_3)_2$ (Sigma Aldrich, 99.995 %). These two resulting solutions were mixed and stirred until to obtain a transparent Nd–Sr solution. The same method was used to dissolve cobalt(II) nitrate $Co(NO_3)_3 \times 6H_2O$ (Sigma Aldrich, 99.999 %), where a pink Co solution was obtained. All those solutions were mixed and stirred at 70 °C for 20 min. Once ethyldiamine is added as a polymerizing agent a pink violet gel is obtained after 2–3 h. The gel was heated in a furnace for 4 h at 350 °C in order to evaporate the water and acids and subsequently heated 8 h at 900 °C resulting in a micropowder. This powder was compact and finally heated 3 days at 1100 °C.

Room temperature synchrotron powder diffraction measurements were carried out at beamline 17-BM at the Advanced Photon Source using a 100 µm monochromated x-ray beam at a wavelength of $\lambda=0.727750$ Å. Diffraction data were collected in situ using a Perkin Elmer amorphous-Si flat panel detector centered on the x-ray beam. The sample-to-detector distance was nominally set at 300 mm, yielding an available 2θ scattering angle of 27.5°, enabling access of Bragg reflections with d spacing as low as 1.52 Å. The diffractometer geometrical parameters (such as precise sample-to-detector distance and tilt of the detector) were optimized with respect to a NIST a LaB6 (660a) standard. Diffractograms were analyzed by standard Rietveld refinement employing the FULLPROF program [16]. Magnetization measurements were carried out as a function of temperature and magnetic field using a commercial Superconducting Quantum Interference Device (SQUID) from Quantum Design®.

3. Magnetostructural relationship

Crystal structure and magnetism are strongly related; and for the present case, in which Co ions are able to assume low, intermediate and high spin configurations, the understanding of this relationship is indeed of great importance. This section discusses first the crystal structure of $Nd_{0.5}Sr_{0.5}CoO_3$ cobaltite (see Fig. 1). A discussion on the Co energy levels is also carried out and then the possible Co spin configurations are presented.

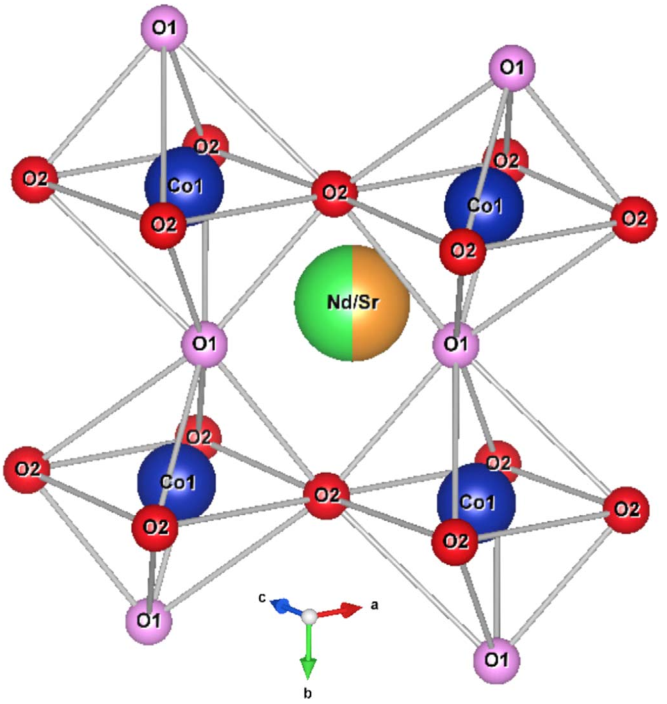

Fig. 1. Partial crystal structure of $Nd_{0.5}Sr_{0.5}CoO_3$ cobaltite, where the Co octahedral environment is highlighted.

3.1. Crystal structure

Rietveld analysis of $Nd_{0.5}Sr_{0.5}CoO_3$ diffractogram shows a single phase sample, as can be seen in Fig. 2; and indeed it crystallizes in an orthorhombic structure with space group Imma [17]. In this structure, the rare-earth metal, Sr and one of the oxygens ions (O1 –apical) occupy the Wyckoff position 4e (0,1/4,x), Co occupies the 4b site (0,0,1/2) and the other oxygen (O2 – equatorial) occupies the 8g (3/4,y,1/4) positions. The lattice parameters of our sample are presented in Table 1 and these are in very good agreement with the literature [17]. The table also shows the interatomic

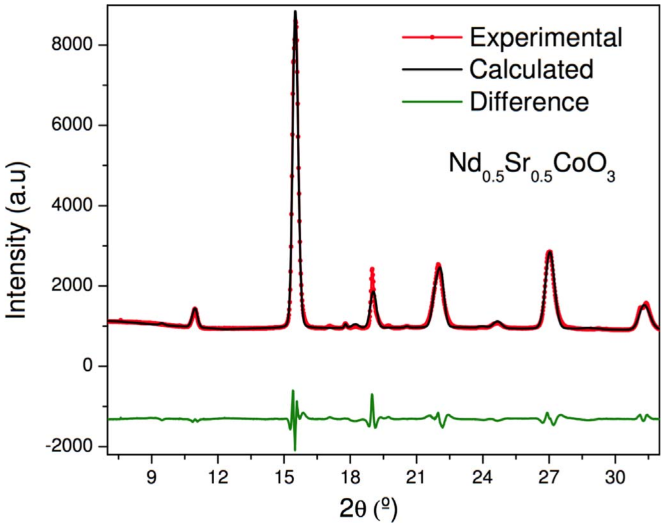

Fig. 2. X-ray diffraction pattern for $Nd_{0.5}Sr_{0.5}CoO_3$ cobaltite using synchrotron radiation with a wavelength of $\lambda=0.727750$ Å. Fitting was performed with Rietveld method.