Spin state and magnetic ordering of half-doped $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ 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 $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ 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 $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ 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 change 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 $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ could be drawn.

Keywords: Cobaltites, magnetic phase diagram, anomalous XRD, synchrotron, magnetic entropy change, magnetocaloric effect

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1. Introduction

Perovskite cobaltites exhibit general formula of type $\text{Ln}_{1-x}\text{A}_x\text{CoO}_3$ (Ln: lanthanides, A: alkaline-earth metals) and are very interesting materials due to their remarkable magnetic and electrical properties, that lead to effects such as the giant magnetoresistance[1], giant anisotropic magnetostriction[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, depends 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 the 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 $x = 0$ contains 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 $\text{Ln}_{1-x}\text{A}_x\text{CoO}_3$ (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. $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ [8, 1, 2] and $\text{Pr}_{1-x}\text{Sr}_x\text{CoO}_3$ [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 $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ series, for example, exhibit a broad peak in the susceptibility data around 90 K, whose origin is a open question on 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 a changing on the ferromagnetic state associated with orbital ordering[11].

$\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ compounds have also been intensely investigated. Fonfado and co-workers[14], for example, studied the compounds in the compo-

sition range of $0 \leq x \leq 0.4$. 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 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 $x \leq 0.1$. 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 $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ 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 $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$, the spin-state is not yet well defined and, in addition, the broad maximum around 80 K is also an open question on the literature.

The present effort reports on the magnetic investigation of half-doped $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ 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 $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ sample was prepared by sol-gel Pechini method [15]. A citric acid solution was used to dissolve neodymium(III) nitrate hexahydrate $\text{Nd}(\text{NO}_3)_3 \times 6 \text{ H}_2\text{O}$ (Sigma Aldrich, 99.9%) and strontium nitrate $\text{Sr}(\text{NO}_3)_2$ (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 $\text{Co}(\text{NO}_3)_2 \times 6 \text{ H}_2\text{O}$ (Sigma Aldrich, 99.999 %), where a pink Co solution was obtained. All those solutions were mixed and stirred at 70 °C for 20 minutes. Once ethyldiamine is added as a polymerizing agent a pink violet gel is obtained after 2-3 hours. 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 $\lambda = 0.727750 \text{ \AA}$. 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 $1.52 \text{ \AA}$. 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 $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cobaltite (see figure 1). A discussion on the Co energy levels is also carried on and then the possible Co spin configurations are presented.

3.1. Crystal structure

Rietveld analysis of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ diffractogram shows a single phase sample, as can be seen on figure 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 distances, where it is possible to see that O1 - Co distance (apical distance of octahedron) is larger than O2-Co (basal distance), which indicates that, at least at room temperature, the octahedron is on average and mostly elongated. In other words,

Figure 1: (color online) Partial crystal structure of Nd_{0.5}Sr_{0.5}CoO₃ cobaltite, where the Co octahedral environment is highlighted.

Figure 2: (color online) X-ray diffraction pattern for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cobaltite using synchrotron radiation with a wavelength of $\lambda = 0.727750 \text{ \AA}$. Fitting was performed with Rietveld method.

the equatorial oxygen (O2) are symmetrically arranged around the cobalt ion with a distance of $1.898 \text{ (\AA)}$, while the Co-O1 distance (apical oxygen) is of $1.986 \text{ (\AA)}$; and this difference is of almost 4.5 %. These values of the Co-O distances are larger than those reported before[18] for $\text{Nd}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$ compound, where the Co ions are assumed to be in a low-spin configuration. Considering that the ionic radius of high spin Co can be 10 % larger than a low spin Co[18], this is a likely signal that the Co spin state is either on intermediate or high spin configuration. This is an important point further on the discussion of the magnetic properties of this system.

4. Magnetic phase diagram

As discussed above on section 1, one open question on the literature of cobaltites regards on the Nd and Co magnetic arrangement, as well as on the Co spin state. In order to achieve a reliable phase diagram and Co state description, magnetization measurements and a simple theoretical model were performed; and to support our findings, magnetocaloric effect has been experimentally and theoretically evaluated. These whole set of data were then enough to achieve our goal to determine the Co spin state and build up a magnetic phase diagram to $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cobaltite.

Table 1: Refined crystallographic data and reliability factors for Nd_{0.5}Sr_{0.5}CoO₃.

Lattice parameters			
a (Å)	b (Å)	c (Å)	V (Å ³)
5.353(2)	7.681(1)	5.385(2)	221.4(1)
Interatomic distances			
O1-Co(Å)	O2-Co(Å)	Nd-Co(Å)	O1-O1 / O2-O2 (Å)
1.986(5)	1.898(1)	3.294(7)	3.972(6) / 3.797(2)
Interatomic distances and angles			
Nd-Nd (Å)	Co-Co(Å)	Co-O1-Co (°)	Co-O2-Co (°)
3.785(8)	3.796(8)	150.5(5)	177(1)
Reliability factors			
R_{wp} (%)	R_p (%)	R_{exp} (%)	χ^2
10	4	2	2.8

4.1. Cobalt spin state and mean field environment

Magnetization as a function of temperature was obtained under applied magnetic field of 1000 Oe, as shown on figure 3 (left axis). In that curve it is possible to see a clear transition at $T_c = 215$ K and a broad maximum peaking at $T_k = 80$ K, consistent with previous reports[5, 9].

The reciprocal magnetic susceptibility could also be obtained, and is presented on figure 3 (right axis). **Ferrimagnetic materials have a hyperbolic magnetic susceptibility [19, 20]; however, for high temperatures and the case in which the intercept temperature is positive, like the present case, the magnetic susceptibility assumes a Curie-Weiss structure[19, 20] and therefore we can write for this material:**

$$\chi(T) = \chi_0 + \frac{C}{T - \theta_p} \quad (1)$$

where $C = \frac{1}{2}(C_{Nd} + C_{Co^{3+}} + C_{Co^{4+}})$ is the molar Curie constant, since each formula unit contains $\frac{1}{2}Nd$, $\frac{1}{2}Co^{3+}$ and $\frac{1}{2}Co^{4+}$, θ_p is the paramagnetic Curie temperature (for this ferrimagnetic case it is related to the Curie constant of each sub-lattice, as well as the exchange parameters[19, 20]) and χ_0 was added to take into account any temperature independent contribution. The fitting of the above equation to the experimental data returns $\chi_0 = 6.2 \times 10^{-7}$

Figure 3: (color online) Experimental magnetization (left axis) and reciprocal susceptibility (right axis) as a function of temperature for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cobaltite. Solid line is the fitting of equation ?? to the experimental data. The output parameters of this fitting are displayed on the figure.

emu/Oe FU , $\theta_p = 215 \text{ K}$ and $p_{eff} = 4.3\mu_B/\text{FU}$. The latter was calculated considering the contribution of all magnetic atoms (Nd and Co).

The experimental molar Curie constant is depicted on figure 4, as well as the theoretical value for several Co spin configurations. Those spin configurations were determined considering that the $\text{HS-}d^6$ octahedral environment of Co^{3+} suffers a compression, while $\text{IS-}d^6$ environment elongates, due to Jahn-Teller effect (JTE), and $\text{LS-}d^6$ octahedral does not feel JTE, which produces corresponding spin and orbital (s,l) values of (2,0), (1,0) and (0,0), respectively. On the other hand, $\text{HS-}d^5$ octahedral of Co^{4+} also does not feel JTE, while $\text{IS-}d^5$ environment compresses and $\text{LS-}d^5$ octahedral elongates, producing spin and orbital (s,l) values of (5/2,0), (3/2,0) and (1/2,0), respectively. Those theoretical Curie constants on figure 4 considered the Lande factor for both Co sub-lattices $g_{\text{Co}} = 2$ and, for the Nd sub-lattice, $g_{\text{Nd}} = 8/11$ [19]; while $J_{\text{Nd}} = 9/2$ and $J_{\text{Co}} = S_{\text{Co}}$, i.e., there is no orbital contribution. Numerical values for this last quantity are summarized on table 2 and depend on the Co spin configuration. The experimental Curie constant matches the theoretical one for both Co ions (Co^{3+} and Co^{4+}) on intermediate state; and, in addition, with $g = 2$. These results are consistent with our considerations

Figure 4: (color online) Experimental (open square) and theoretical (solid lines) Curie constants considering the possible spin states for the Co^{3+} and Co^{4+} . This result clearly indicates that both, Co^{3+} and Co^{4+} are on intermediate state.

presented before: the distortions occur in such way to quench the orbital momentum, and, thus, we would expect that the Co^{3+} octahedral environment elongated and Co^{4+} octahedral environment compressed. However, no such distinction is apparent in the diffraction data directly, most likely because it probes long range order and in this case of this family of materials there are no reports in the literature of charge (or orbital) ordering.

In addition, the Curie temperature T_c satisfactorily matches the paramagnetic Curie temperature θ_p , an indication that the system can be described within the mean-field approach. This observation was already established for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cobaltite in reference [5], in which those authors found mean-field critical exponents for magnetization as a function of temperature and magnetic field, as well as magnetic susceptibility.

To conclude this subsection, from the data above presented, we claim that both Co ions are on IS state, with no orbital contribution. Consequently, the Lande factor is $g = 2$ and due to the quench of the orbital momentum it is not possible to observe magnetic anisotropy. Finally, we also concluded that the material is suitable to follow a mean-field approach, as well as those spin momenta have a localized character.

4.2. Mean Field Model

To further understand the magnetic behavior of the material under consideration, three localized magnetic sub-lattices (Co^{3+} , Co^{4+} and Nd^{3+}) shall be considered, as well as the crystal field on the Nd site (as there is no Co local magneto-crystalline anisotropy due to the quench of its orbital momentum). A mean field model with the relevant angular parameters (see table 2) describe the system in detail. However, it is not a one-step task to build this mean-field numerical code; and therefore, since the aim of this subsection is to understand the magnetic behavior depicted on figure 3, we will considered only two magnetic sub-lattices without crystal field correction (a qualitative approach). In spite to be relatively simple in ideas, the experimental-theoretical comparison was successful and a deeper understanding on the magnetic profile of the material achieved.

Table 2: Angular values for the three magnetic sub-lattices: Nd^{3+} from reference [19] and Co contributions taking into account the spin and orbital values presented before in section 4.1.

	s	l	j	g
Nd^{3+}	$3/2$	6	$9/2$	$8/11$
Co^{3+}	1	0	1	2
Co^{4+}	$3/2$	0	$3/2$	2

Our simple model considers then two magnetic sub-lattices and a mean field approach without crystal field to the Nd environment. In this case, the total molar magnetization reads as:

$$M = M_1 + M_2 \quad (2)$$

where

$$M_i = f_i g_i j_i \mathcal{B}(x_i) \mu_B \quad (3)$$

is the magnetization of the first ($i = 1$) or second ($i = 2$) sub-lattices, that depend on the Brillouin function $\mathcal{B}(x_i)$, where

$$x_i = \frac{\mu_B g_i j_i H_i}{k_B T}. \quad (4)$$

Above, H_i is the mean-field, given by:

$$H_1 = H_0 + \alpha \lambda M_1 - \lambda M_2 \quad (5)$$

$$H_2 = H_0 - \lambda M_1 + \beta \lambda M_2 \quad (6)$$

It means that the sub-lattice ‘1’ feels the external field H_0 plus a molecular field $\alpha\lambda M_1$, created by the own sub-lattice ‘1’, and other molecular field $-\lambda M_2$, created from the sub-lattice ‘2’. In other words, ions into sub-lattice ‘1’ interacts each other with strength $\alpha\lambda$ (parallel fashion), and interact with those into sub-lattice ‘2’ with strength $-\lambda$ (anti-parallel fashion). In a similar way, ions into sub-lattice ‘2’ interact each other with strength $\beta\lambda$ (parallelly) and, reciprocally, with ions into sub-lattice ‘1’ with strength $-\lambda$ (anti-parallelly). Finally, f_i is the molar fraction of each sub-lattice, g_i is the Lande factor and j_i the total angular momentum. It is important to mention that, in agreement with the magnetic interpretation described in previous reports[18], we considered Nd and Co sub-lattices aligned in an antiparallel fashion.

Here we assign the Nd sub-lattice as ‘1’ (with molar fraction $f_1 = 1/3$) and the Co sub-lattice as ‘2’ (with molar fraction $f_2 = 1 - f_1 = 2/3$). Those other needed parameters are on table 2 and we consider the sub-lattice ‘2’ with $j = s = 1$. Since that the Nd (‘1’) sub-lattice has an intra-exchange interaction weaker than the Co (‘2’) sub-lattice[18] we considered $\alpha = 1$ and $\beta = 10$. The λ parameter rules the Nd-Co interaction and can be written analytically for this simple model as[19, 22]:

$$\lambda = \frac{2T_c}{(f_1\alpha C_1 + f_2\beta C_2) + [(f_1\alpha C_1 - f_2\beta C_2)^2 + 4f_1f_2C_1C_2]^{1/2}} \quad (7)$$

where

$$C_i = \frac{g_i^2 j_i(j_i + 1)\mu_B^2}{3k_B} \quad (8)$$

is the Curie constant of each sub-lattice. Considering $T_c = 215$ K (close to those values experimentally found and depicted on figure 3), we could found $\lambda\mu_B = 18.3$ T. These are the parameters of this simple model, as close as possible to the real material.

From the model and parameters above described, the mean field magnetization could be numerically and self-consistently evaluated; and it is placed on figure 5-top. Note there are three curves: M_1 , M_2 and $M_T = M_1 + M_2$. Due to the antiparallel arrangement among ‘1’ and ‘2’ sub-lattices, M_1 is negative and M_2 is positive. Since $\beta \gg \alpha$, the ‘2’ sub-lattice rules the critical temperature, as can be seen on figure 5-top. On the other hand, sub-lattice ‘1’ increases its absolute value at low temperature, due to the low intra-lattice exchange interaction, and then becomes to be remarkable and non-negligible.

Since it occurs at a temperature in which M_2 is already saturated and therefore temperature independent, the increasing of the absolute (but negative) value of M_1 promotes a decreasing of the total magnetization $M_T = M_1 + M_2$ resulting in the peak at T_k .

Few words on the meaning of T_k are appropriated to a deeper understanding on the observed behavior. Figure 5-bottom depicts the derivative of each sub-lattice magnetization with respect to the temperature. Note those curves crosses each other at T_k ; as well as the total magnetization, which crosses zero (as expected, since T_k is the peak of the total magnetization curve). In other words, at higher temperatures (just below T_c), the temperature derivative of M_2 is remarkable, while the same derivative of M_1 is not; and, as a consequence, M_2 dominates the trend observed in magnetization. At lower temperatures we observe the inverse situation and M_1 rules the process, since M_1 is negative an overall reduction in the magnetization occurs resulting in the observed peak at T_k .

At this point we can compare the theoretical (figure 5-top) and experimental (figure 3) magnetization curve. Indeed, Nd sub-lattice has a ferromagnetic intra-lattice arrangement, as well as the Co sub-lattice. On the other hand, Nd-Co sub-lattices aligns in an antiparallel fashion each other; and therefore the overall arrangement is ferrimagnetic. It is important to note here that previous reports in the literature[18] ascribe T_k as the onset of antiferromagnetism, i.e., the Nd-Co ordering is antiparallel only below T_k . However, from the above theoretical results, it is clear that Nd-Co sub-lattices are always antiparallel, for any temperature below T_c ; and at T_k the Nd sub-lattice becomes more pronounced and starts to rule the total magnetization.

Finally, we emphasize that we developed a simple model, focusing on a qualitative understanding of the experimental data. Although we consider only two magnetic sublattices, our experimental data were satisfactorily described. A more quantitative analysis would be possible if we had considered three sublattices and the crystal field effect, however, the increased complexity of the model is not expected to lead to a change in any of the described trends and, as such, would not benefit the aim of this work, as that resides primarily in understanding the relative scale and sign of the interactions that drive the observed behaviour.

Figure 5: (color online) Top: theoretical mean field magnetization curve obtained from a simple model of two sub-lattices with ferromagnetic intra-lattice arrangement and ferromagnetic inter-lattice ordering. The aim of this evaluation is to elucidate the Nd and Co ordering by a simple comparison of this result with those experimental data on figure 3. Bottom: temperature derivative of each magnetization in order to achieve the physical meaning of T_k , the temperature in which the total magnetization peaks. In few words, T_k means the temperature below which the negative magnetization becomes to rule the total magnetization.

4.3. Deepening the understanding considering the magnetocaloric effect

The magnetocaloric effect (MCE) is characterized by the ability, due to a change of applied magnetic field, of magnetic materials to increase/decrease its temperature (considering an adiabatic process); or exchange heat with a thermal reservoir (considering an isothermal process). This effect is maximum close to the critical temperature of the material. Therefore, for applications on cooling devices, the refrigerant material should have its critical temperature well matched to the working temperature of the device. On the other hand, the MCE can also be useful to access deeper and hidden information on the magnetic behavior of materials, in particular the magnetic entropy associated with ordering phenomena. Such analysis was applied successfully previously for instance on Pr-Ca manganites[23] and MnP single crystal[24]. This is possible since the MCE is directly related to the entropy of the system.

Quantitatively speaking, the MCE can be measured by its magnetic entropy change:

$$\Delta S(T, \Delta H) = \int_0^H \left. \frac{\partial M}{\partial T} \right|_H dH \quad (9)$$

that, on its turn, depends on the magnetization map $M(T, H)$. Thus, to access this quantity, magnetization as a function of magnetic field, for several temperatures, have been measured. These curves are on figure 6(a) and for the sake of clarity, from the full set of data collected, only selected temperatures are shown on this figure. It is noteworthy that the 4 K isothermal has a negative value of magnetization at low values of magnetic field with as an upturn; both characteristic patterns of a ferrimagnetic material[19]. From the previous data, the magnetization as a function of temperature, for several applied magnetic fields, could then be acquired, as shown on figure 6(b). This data presents another important signature of a ferrimagnetic arrangement: a compensation temperature T_{comp} , in which the positive and negative sub-lattices have equal magnitude. From data, it is possible to extract the magnetic entropy change as a function of temperature, for several values applied magnetic field change, as depicted on figure 6(c). This result has some interesting signatures: (i) a peak at T_c , similarly to what is observed on ferromagnetic materials, and (ii) a crossing to positive values at T_k . The literature[18] claims that the system is ferromagnetic above T_k and antiferromagnetic below this temperature, due to the signal (either positive or negative) of the magnetic entropy change[5]. In the following section, we

will now proceed to apply the model presented to assess how well it replicates the experimental data.

4.3.1. Theoretical approach

The magnetic entropy change under discussion can also be written as:

$$\Delta S(T, \Delta H) = S(T, H) - S(T, 0) \quad (10)$$

and therefore it can be accessed from the knowledge of the entropy $S(T, H)$ of the system. For two sub-lattices, the magnetic entropy can be written as:

$$S(T, H) = R \{f_1[\ln Z_1 - x_1 \mathcal{B}(x_1)] + f_2[\ln Z_2 - x_2 \mathcal{B}(x_2)]\} \quad (11)$$

where R is the universal gas constant and

$$Z_i = \frac{\sinh(ax_i)}{\sinh(bx_i)} \quad (12)$$

is the partition function of each sub-lattice. Above, $a = 1 + b$ and $b = 1/2j_i$. Note that the magnetization, hidden inside the parameter x_i must be evaluated self-consistently, as done in the previous section.

From the above theoretical recipe we can obtain the zero field magnetic entropy and, for instance, the one at 50 kOe; as shown on figure 7-top. Note there is a crossing of these curves exactly at T_k , emphasizing that this temperature is indeed of extreme importance to the whole magnetic phenomena that occurs in this sample. The difference of these curves, i.e., the magnetic entropy change, for several values of applied magnetic field change, is on figure 7-bottom. Note this theoretical result is qualitatively the same as that obtained experimentally and presented on figure 6(c). It ratifies our claim that this material is indeed ferrimagnetic for the whole temperature range and T_k is the temperature in which the magnetic entropy curves cross; and not the one below which the Nd-Co becomes antiparallel, as claimed by the literature[5].

4.4. Phase diagram

Based on the previous results and analysis, it is possible to construct a phase diagram of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, as depicted on figure 8. This material has a paramagnetic phase above c.a. 215 K, below which the system changes to a ferrimagnetic ordering, with Nd sub-lattice in opposition to both Co sub-lattices (Co^{3+} and Co^{4+}). Due to the difference of intra-exchange interaction

Figure 6: (color online) Experimental magnetization as a function of (a) magnetic field and (b) temperature; (c) magnetic entropy change as a function of temperature, for several values of applied magnetic field change. T_k and T_{comp} represent, respectively, the temperature in which the magnetization peaks and the one in which Nd and Co sub-lattices are equal in magnitude.

Figure 7: (color online) Top: theoretical zero field and field (50 kOe) magnetic entropy as a function of temperature. Bottom: magnetic entropy change due to a magnetic field change. Comparison of this bottom theoretical figure with the experimental one, on figure 6(c), confirms our claim that the system is genuinely ferrimagnetic; and T_k is the crossing temperature of the zero and non-zero field magnetic entropies.

Figure 8: (gray scale) Experimental magnetic phase diagram for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$.

(Co-Co interaction is much stronger than Nd-Nd interaction), Co sub-lattice rules the Curie temperature; while at low temperatures, when the positive Co magnetization is almost constant, the negative Nd magnetization keeps increasing its magnitude and rules the total magnetization, resulting in the T_k temperature (also represented on the proposed phase diagram). Finally, at even lower temperatures and low field, due to the ferrimagnetic arrangement, a compensation temperature T_{comp} emerges, as evidenced on the phase diagram.

5. Conclusions

X-ray diffraction using synchrotron radiation with Rietveld refinement shows that the sample is single phase and that O1-Co (apical distance) is, on average, larger than O2-Co (equatorial distance). The Curie constant indicates that the system is on intermediate spin state for both, Co^{3+} and Co^{4+} . From magnetization data we also found no orbital contribution and, consequently, a Lande factor $g = 2$; and due to the quench of the orbital momentum it is possible to ensure no Co magnetic anisotropy. While using the Jahn-Teller theorem, the octahedral around Co^{3+} should elongate and the one around Co^{4+} compress, that is not observed in the diffraction data -

that shows and overall average elongation of the octahedra, probably due to disorder or dynamic effects, as the measurement was made at ambient temperature, where the transport is higher. Magnetization data shows a critical temperature $T_c = 215$ K and a broad maximum at $T_k = 80$ K. While previous published reports[5] associate these features to a ferromagnetic transition and the onset below which the Nd and Co sub-lattices become antiparallel. We show that those temperatures are, respectively, the ferrimagnetic transition and the onset below which Nd sub-lattice (negative) magnetization rules the total magnetization. In addition, T_k is the temperature in which (i) the temperature derivative of Nd and Co magnetizations become equal to each other and (ii) the field and zero-field magnetic entropy cross each other. The magnetic entropy change was also experimentally and theoretically calculated and these two results are consistent with our results. Finally, from all these results, the magnetic phase diagram for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cobaltite could be drawn.

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AMS and LP set up and carried out the measurements. MSR, DLR, RJC, BP and RT discussed and analyzed the experimental data. RJC synthesized and characterized the sample. MSR planned, headed the project and developed the theoretical model. All the authors contributed to write the paper. .

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