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## Ferrimagnetic behavior of $\text{Nd}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$

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The orthorhombic rare-earth cobaltate  $\text{Nd}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$  is studied by neutron powder diffraction. The Co sublattice orders ferromagnetically below  $T_c \approx 200$  K with the magnetic moments aligned along the  $c$  axis. On cooling,  $\text{Nd}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$  revealed an induced ferromagnetic order of the Nd sublattice coupled antiparallel to the Co lattice. Within a simple spin-only picture, steric considerations give evidence for a mixed-valent mixed-spin configuration of the Co ions. This is compared to an intermediate valence-state scenario that shows the necessity of detailed electronic-structure calculations.

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### INTRODUCTION AND EXPERIMENTAL DETAILS

The possibility of inducing and controlling a spin-state transition<sup>1</sup> gave rise to a recent study of the doped cobaltates  $R_{0.67}\text{Sr}_{0.33}\text{CoO}_3$  ( $R = \text{La}, \text{Pr}, \text{Pr}_{0.5}\text{Nd}_{0.5}, \text{Nd}, \text{Nd}_{0.5}\text{Sm}_{0.5}, \text{Sm}$ ) which have been investigated by magnetic, thermodynamic, and transport measurements.<sup>2,3</sup> All compounds reveal a ferromagnetic transition with increasing ordering temperature  $T_c$  for increasing average ionic radius  $\langle r_R \rangle$ . The magnetic moments as deduced from the magnetic measurements provide experimental evidence for a spin-state transition as a function of  $\langle r_R \rangle$ . An additional low-temperature magnetic transition characterized by a reduction of the magnetization takes place within the ferromagnetically ordered state, most pronounced for  $R = \text{Nd}$  (corresponding to a reduction of the magnetization by  $\approx 40\%$ ) but also observed for  $R = \text{Sm}$ .<sup>3</sup> In order to elucidate this peculiar magnetic behavior, neutron-powder-diffraction experiments on  $\text{Nd}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$  have been performed.

Polycrystalline samples of the doped cobaltates  $R_{0.67}\text{Sr}_{0.33}\text{CoO}_3$  ( $R = \text{La}, \text{Pr}, \text{Pr}_{0.5}\text{Nd}_{0.5}, \text{Nd}, \text{Nd}_{0.5}\text{Sm}_{0.5}, \text{Sm}$ ) have been synthesized by a conventional ceramic technique.<sup>3</sup> All samples were characterized by powder x-ray diffraction ( $\text{Cu } K\alpha_1$  radiation) at room temperature and revealed distorted perovskite structures without any indications of a second phase. The crystallographic structure of  $\text{Nd}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$  (as well as for  $R = \text{Pr}, \text{Pr}_{0.5}\text{Nd}_{0.5}, \text{Nd}_{0.5}\text{Sm}_{0.5}$ , and  $\text{Sm}$ ) has been found to be isotypic to pure  $R\text{CoO}_3$  ( $R = \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}$ ) with orthorhombic space group  $Pbnm$ .<sup>7-9</sup> In this structure the rare-earth metal Sr and one oxygen ion occupy the Wyckoff position  $4c$  ( $x, y, 1/4$ ), Co occupies the  $4b$  ( $1/2, 0, 0$ ), and the remaining oxygen ions occupy the  $8d$  ( $x, y, z$ ) positions, respectively. Neutron-diffraction experiments were carried out on the instrument E6 at the Hahn-Meitner-Institut, Berlin. The samples were filled in a vanadium container and mounted in a cryostat allowing for temperatures  $1.5 \text{ K} \leq T \leq 300 \text{ K}$ . The instrument uses a double-focusing graphite monochromator resulting in an incident neutron wavelength of  $\lambda = 2.45 \text{ \AA}$ . The diffraction data were analyzed by standard Rietveld refinement employing the FULLPROF program.<sup>4</sup> For the refinement

of the neutron-diffraction patterns, the nuclear scattering lengths  $b(\text{Nd}) = 7.69 \text{ fm}$ ,  $b(\text{Sr}) = 7.02 \text{ fm}$ ,  $b(\text{Co}) = 2.50 \text{ fm}$ , and  $b(\text{O}) = 5.805 \text{ fm}$  have been used.<sup>5</sup> Neutron magnetic form factors of  $\text{Co}^{3+}$  and  $\text{Nd}^{3+}$ , respectively, were taken from the *International Tables of Crystallography*.<sup>6</sup>

### RESULTS AND DISCUSSION

The neutron-diffraction data of  $\text{Nd}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$  confirmed the  $R\text{CoO}_3$ -type structure, as determined on the basis of the x-ray diffraction results. The neutron-diffraction patterns at  $T = 1.5 \text{ K}$ ,  $90 \text{ K}$ , and  $225 \text{ K}$  are shown in Fig. 1. The powder patterns collected below  $200 \text{ K}$  show additional intensities, all at positions that can be indexed using the crystallographic cell. As this cell is primitive, a propagation vector  $\mathbf{k} = 0$  is characteristic for the magnetic structure. The strongest magnetic contribution was found at the (110) reflection, indicating a ferromagnetic order of the Co and Nd ions with a moment direction parallel to the  $c$  axis. The refinement of the magnetic structure revealed that the moments of the two ferromagnetic sublattices of Nd and Co are aligned antiparallel resulting in a ferrimagnetic structure. This antiparallel alignment can be observed most clearly in the temperature dependence of the (131) reflection centered around  $2\theta \approx 55^\circ$ . The difference of the intensities  $I_{131}(T = 1.5 \text{ K}) - I_{131}(T = 225 \text{ K})$  shows a clear ferromagnetic contribution due to the ordering of the Co sublattice. However, the intensity difference  $I_{131}(T = 1.5 \text{ K}) - I_{131}(T = 90 \text{ K})$  becomes negative as a result of the antiparallel alignment of the Nd sublattice magnetization. The temperature dependence of the sublattice magnetization however is rather unusual. The total magnetization ( $\mu_{\text{Co}} + \mu_{\text{Nd}}$ ) is shown in Fig. 2 and reveals a significant decrease below  $T < 50 \text{ K}$ , in agreement with the temperature dependence of the magnetization measurements<sup>3</sup> (small open circles in Fig. 2). The temperature dependence of the sublattice moments of Nd and Co, respectively, are given separately in the inset of Fig. 2. On increasing temperature the magnetic moment of the Nd ions strongly decreases and, within experimental uncertainties, no magnetic intensity could be observed above  $\approx 60 \text{ K}$  (see Fig. 2). The Co moment vanishes at much higher temperatures when approaching  $T_c \approx 200 \text{ K}$ . In first respect this implies

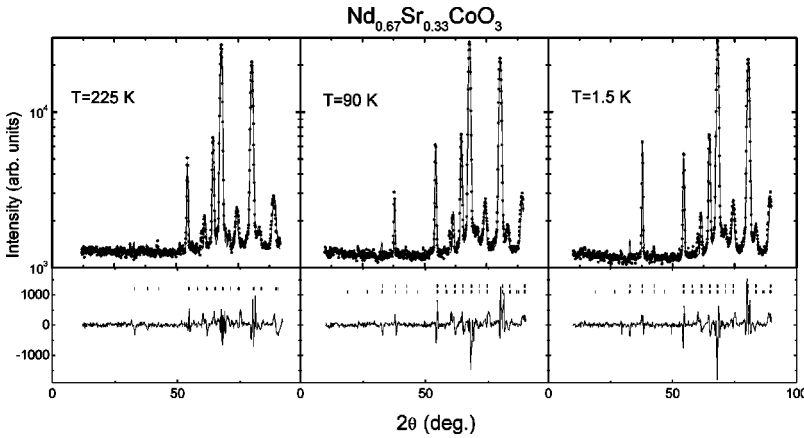


FIG. 1. Neutron-powder-diffraction patterns of  $\text{Nd}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$  at  $T=225$  K (left part), 90 K (middle), and 1.5 K (right part) on a logarithmic scale. The difference between observed and calculated intensities, as well as peak positions are shown on a linear scale in the bottom of the figure.

that the order in the Nd sublattice is predominantly induced via the Co moments. However, it is important to note that the Nd moments are aligned antiparallel to the field created by the Co moments and hence some Nd-Co coupling must be invoked. Antiferromagnetic superexchange interactions of two only weakly coupled magnetic sublattices are responsible for the induced ferromagnetism. Accordingly, induced magnetic moments of the Nd sublattice should start to develop with the onset of the ferromagnetic order of the Co lattice below  $T_c \approx 200$  K (compare with Fig. 2). Due to the weak superexchange coupling of the two sublattices, appreciable magnetic intensity is only observed for  $T \leq 60$  K. The occurrence of “induced” ferrimagnetic order on the Nd lattice at low temperatures is a remarkable result. The induced nature of the Nd sublattice magnetization is also evidenced by the absence of any appreciable anomaly in the susceptibility, magnetization, or specific heat,<sup>3</sup> as well as by the anomalous temperature dependence of the Nd sublattice magnetization. It should be noted that, in particular, compounds based on Co and Nd are known to exhibit induced magnetic order.<sup>10,11</sup> For example, in  $R_2\text{Co}_{12}\text{P}_7$  and  $R\text{Co}_2\text{P}_2$  ( $R = \text{Pr}, \text{Nd}$ ), all compounds display long-range magnetic order of the Co lattice (ferromagnetic for  $R_2\text{Co}_{12}\text{P}_7$  and antiferromagnetic for  $R\text{Co}_2\text{P}_2$ , respectively). However, in both cases the Nd-containing compounds reveal an induced mag-

netic order of the Nd lattice without a well-defined ordering temperature, whereas the Pr compounds show a sharp second-transition temperature when the Pr ions order ferromagnetically.<sup>10,11</sup> This difference of the magnetic behavior has been ascribed to a considerably stronger single-ion anisotropy of the Pr ions as compared to Nd. Remarkably,  $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$  does not show any indications of magnetic order of the Pr sublattice.<sup>3</sup>

Steric considerations of the crystallographic structure of  $\text{Nd}_{0.67}\text{Sr}_{0.33}\text{CoO}_3$  also have important implications on the magnetic properties. A basic crystallographic unit of the distorted perovskite structure are elongated  $\text{CoO}_6$  octahedra. For an octahedron with a Co ion in its center, the Rietveld refinement reveals an equatorial Co-O distance of 1.738 Å whereas the Co-O distance for the apical oxygen is 1.909 Å. Comparing these values with the Shannon ionic radii<sup>12</sup> of Co and O it is found that the equatorial Co-O distance is slightly smaller than the sum of the smallest ionic radii of Co and O. This provides evidence for strong hybridization of  $d$  electrons and  $2p_\sigma$  orbitals of oxygen. The ionic radius of Co strongly depends on the valence and spin configuration, coordination number, and crystallographic site. For a given valence state, the ionic radius of the high-spin configuration of Co is approximately 10% larger as compared with the corre-

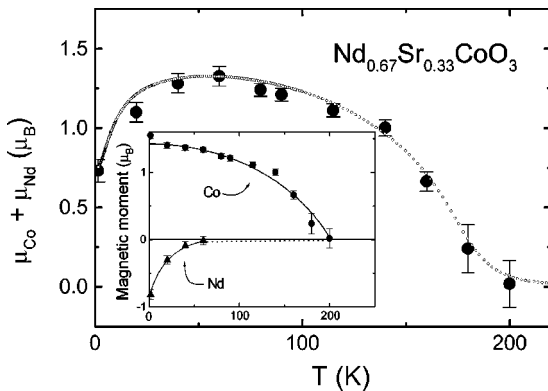


FIG. 2. Temperature dependence of the sum of the ordered magnetic moments of the Co and Nd sublattice, compared to the temperature dependence of the magnetization (small circles). The inset shows the temperature dependence of the ordered magnetic moments of the individual Co and Nd sublattice, respectively.

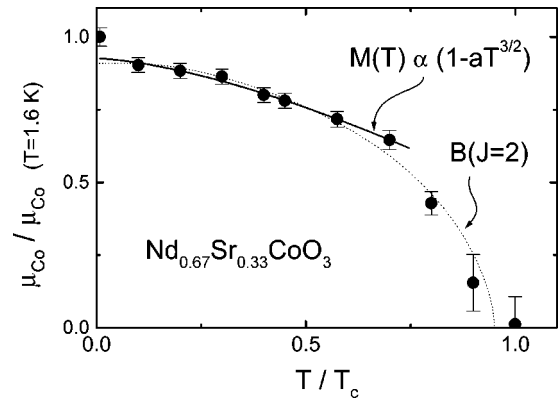


FIG. 3. Temperature dependence of the ordered magnetic moment of the Co ions, normalized to its value at  $T=20$  K. Up to  $T=140$  K, the full line corresponds to a fit assuming that the decrease of the ordered magnetic Co moments is well accounted for by magnon excitations. The dotted line is a fit with a  $S=2$  Brillouin function.

TABLE I. The nuclear and magnetic structure of Nd<sub>0.67</sub>Sr<sub>0.33</sub>CoO<sub>3</sub> as obtained by Rietveld refinements: The data were determined by neutron powder diffraction with an incident wavelength of  $\lambda = 2.45$  Å. The overall temperature factor  $B_{ov}$  of all atoms has been refined from the data at 225 K and was held constant for the refinement of the low-temperature-diffraction patterns. The Nd(Sr) and the O1 atoms are on the Wyckoff position 4c ( $x, y, 1/4$ ), while the Co and O2 atoms occupy the positions 4b ( $1/2, 0, 0$ ) and 8d ( $x, y, z$ ), respectively.  $R_N$  and  $R_M$  are the residuals of the nuclear and magnetic structure, respectively.

<i>Pbnm</i>	1.6 K	90 K	225 K
<i>a</i> (Å)	5.349(2)	5.351(2)	5.360(2)
<i>b</i> (Å)	5.389(1)	5.396(1)	5.408(1)
<i>c</i> (Å)	7.605(3)	7.618(4)	7.640(4)
<i>V</i> (Å <sup>3</sup> )	219.2	220.0	221.5
<i>x</i> (Nd, Sr)	-0.058(2)	-0.057(2)	-0.34(1)
<i>y</i> (Nd, Sr)	-0.003(1)	-0.002(2)	-0.003(2)
<i>x</i> (O1)	0.009(2)	0.007(2)	0.009(2)
<i>y</i> (O1)	0.530(2)	0.528(2)	0.526(2)
<i>x</i> (O2)	-0.273(2)	-0.272(1)	-0.271(2)
<i>y</i> (O2)	0.225(1)	0.225(1)	0.225(1)
<i>z</i> (O2)	-0.036(1)	-0.036(1)	-0.035(1)
$B_{ov}$ (Å <sup>2</sup> )	0.10	0.10	0.15(2)
$R_N$	0.041	0.044	0.043
$\mu_{exp}$ (Nd) ( $\mu_B$ )	-0.82(5)		
$\mu_{exp}$ (Co) ( $\mu_B$ )	1.55(5)	1.26(4)	
$R_M$	0.054	0.038	

sponding low-spin configuration. The small Co-O distances therefore points towards a low-spin configuration of the Co ions.

Within the distorted perovskite structure there is only one crystallographic Co site. Due to the substitution of trivalent Nd by divalent Sr a formal valence state of +3.33 of Co ions can be assigned. Either such an intermediate-valence state is physically realized in Nd<sub>0.67</sub>Sr<sub>0.33</sub>CoO<sub>3</sub> or, alternatively, a mixed-valence state of 1/3 Co<sup>4+</sup> ions and 2/3 Co<sup>3+</sup> ions is also possible. From a crystallographic point of view, the existence of a mixed-valence state implies a mixed-spin state. Since there is only one crystallographic Co site, the different ionic radii of Co<sup>3+</sup> and Co<sup>4+</sup> ions, respectively, have to be compensated by different spin states resulting in a single average ionic radius for both valence configurations of Co ions. The electronic configuration of the Co ions must be compatible with the values of the magnetic moments, namely,  $2.55\mu_B$  for the effective paramagnetic moment  $p_{eff}$  and  $1.55\mu_B$  for the ordered magnetic moment at low temperatures. Based on the small Co-O distances we assign a *LS* state to the Co<sup>4+</sup> ions corresponding to an effective  $S=1/2$  ion. Within a simple spin-only picture ( $g=2$ ) we calculate  $p_{eff}$  and  $\mu_S$  according to  $p_{eff}=g[S(S+1)]^{1/2}$  and  $\mu_S=gS$  resulting in  $p_{eff}=1.73\mu_B$  and  $\mu_S=1\mu_B$  for  $S=1/2$ . To explain the experimentally observed values of the magnetic moments, the remaining 2/3 of Co<sup>3+</sup> are necessarily in an intermediate spin state ( $S=1$ ) resulting in average magnetic moments of  $p_{eff}=2.46\mu_B$  and  $\mu_{ord}=1.66\mu_B$  in good agreement with experiments. We thus conclude that, within a

simple spin-only picture, a mixed-valence, mixed-spin state of the Co ions can account for the magnetic properties of Nd<sub>0.67</sub>Sr<sub>0.33</sub>CoO<sub>3</sub>.

We now consider an intermediate-valence state of Co<sup>+3.33</sup> ions. An intermediate valency of the Co ions leads to noninteger numbers of electrons in the *d* orbitals (Co<sup>+3.33</sup> corresponding to a  $d^{5.67}$  configuration). This is in fact not unusual for ionic transition metal compounds. A noninteger number of *d* electrons has been found for the simple oxide CoO though cobalt is in a conventional 2+ valence state.<sup>13</sup> This has also been inferred from theoretical studies.<sup>13</sup> The reason is that counting electronic charge depends sensitively on the choice of radii and is insufficient to resolve questions of ionicity.<sup>13</sup> Assigning a formal spin value of 5.67/2 to the intermediate-valence state cannot reproduce the experimentally determined values of the ordered and paramagnetic moment. However, electronic structure calculations are needed for a quantitative comparison in case of an intermediate-valence state, including hybridization with 4*s* electrons and orbital contributions. The structural data of the present neutron-diffraction study may serve as a starting point for such band-structure calculations that could explore the nature of the ferromagnetic ordering of the Co ions. In the case of the manganites the dominant Hund's coupling enables ferromagnetic ordering via the double-exchange mechanism. However, it is well established that the crystal-field energies of the cobaltates are of the same order of magnitude as the Hund's coupling, thus calling the application of the double exchange into question.

In the temperature range  $1.5 \text{ K} \leq T \leq 140 \text{ K}$ , the decrease of the ordered Co magnetic moment can be described perfectly by the excitation of ferromagnetic spin waves according to  $M(T)\alpha(1-aT^{3/2})$ , as shown in Fig. 3. For higher temperatures, the number of data points is insufficient to determine the critical behavior. A fit employing an  $S=2$  Brillouin function, as indicated by the dashed line in Fig. 3, may also account for the temperature dependence of the ordered Co magnetic moment, though such a fit is not fully convincing. The best fit was achieved when assuming a saturation moment corresponding to the  $T=20 \text{ K}$  value and a slightly reduced ordering temperature (compare with Fig. 3). Therefore mean-field theory may be considered as a rough approximation of the temperature dependence of the ordered magnetic moment of the Co sublattice. For a proper description of the critical behavior, crystalline electric field (CEF) effects will certainly have to be taken into account. The sharp increase of the ordered Co moment when cooling from 20 K to 1.5 K may be explained by the induced magnetic order of the Nd sublattice with antiferromagnetic exchange interactions.

The crystallographic and magnetic structure of Nd<sub>0.67</sub>Sr<sub>0.33</sub>CoO<sub>3</sub> as obtained by the Rietveld analysis of the neutron powder diffraction is summarized in Table I.

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