

Inhibition of Nd magnetic order in $\text{NdFe}_{1-x}\text{Co}_x\text{O}_3$ by magnetic vacancies

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The low-temperature specific heat of $\text{NdFe}_{1-x}\text{Co}_x\text{O}_3$ ($x=0, 0.03, 0.1, 0.25,$ and 0.5) has been measured to study the magnetic ordering of the Nd sublattice as a function of Co content. The results, satisfactorily explained by a mean-field model, show the inhibition of the Nd cooperative ordering for $x \geq 0.1$. © 2005 American Institute of Physics. [DOI: 10.1063/1.1848354]

NdMO_3 are model systems to investigate the magnetic interaction between Nd (or other rare-earths) and $3d$ or $4d$ metal ions (M) in oxides. In general, the magnetic exchange interactions follow the hierarchy of M - M , M -Nd, and Nd-Nd in descending strength. In the compounds with a nonmagnetic M , Nd-Nd leads to antiferromagnetic ordering at about $T \sim 1$ K.¹⁻³ This is the case in NdCoO_3 , where the Co^{3+} ions are in a low-spin diamagnetic state, and $T_N = 1.20$ K.^{4,5} When M is magnetic, the magnetic ordering temperature T_N of the M sublattice ranges from ~ 700 K for $M = \text{Fe}$ to ~ 75 K when $M = \text{Mn}$. Below T_N , the ordered M sublattice polarizes the paramagnetic Nd sublattice. The isotropic M -Nd exchange is compensated by the contributions due to antiparallel moments, but the anisotropic exchange is not cancelled and an internal field $H_{M\text{-Nd}}$ splits the Nd ground state doublet, polarizing the Nd sublattice at low temperatures and reducing the magnetic entropy available for cooperative ordering of Nd. Indeed, a competition takes place between M -Nd and Nd-Nd interactions, and Nd cooperative ordering appears in some cases, as in NdFeO_3 ,⁶ while it is inhibited in others, as in NdCrO_3 ,⁷ depending on the relative intensity of Nd- M and Nd-Nd interactions.

In $\text{NdFe}_{1-x}\text{Co}_x\text{O}_3$, the substitution of Fe by low-spin Co can be considered as the introduction of a magnetic vacancy in the Fe sublattice, as sketched in the inset of Fig. 1. Our objective was to study how the vacancies modify the $H_{\text{Fe-Nd}}$ interaction, and its influence on Nd ordering. The magnetic dilution of the Fe sublattice provokes the lowering of T_N until the quenching of magnetic ordering for $x \geq 0.65$, the percolation limit. In this article, we deal with the low Co content region ($x \leq 0.5$) and very low temperatures, thus the Fe sublattice is ordered, containing randomly distributed magnetic vacancies.

The $\text{NdFe}_{1-x}\text{Co}_x\text{O}_3$ powder samples ($x=0, 0.03, 0.1, 0.25,$ and 0.5) were obtained by mixing the appropriate proportions of the binary oxides to achieve the desired solid solutions. The mixtures were calcined in air at 1000°C for two days with intermediate grindings. The resulting powder was pressed to 5 kbar into pellets and sintered in air at 1300°C for 6 h. The quality of the samples was checked by x-ray diffraction. In $\text{NdFe}_{1-x}\text{Co}_x\text{O}_3$, the specific heat from spurious contributions below ~ 5 K (lattice, Nd excited doublets, Fe magnons) is fully negligible in comparison to the ground-doublet magnetic one.³ The data shown in Fig. 1 are

not appreciably modified by subtraction of the lattice contribution.

In Fig. 1, we show the specific heat of the $\text{NdFe}_{1-x}\text{Co}_x\text{O}_3$ series below 6 K (◐). The specific heat of NdFeO_3 , shown in the upper part of the figure, features a Schottky-like anomaly, with a maximum at $T = 2.35$ K (about 7% lower than the ideal doublet Schottky curve), as well as a small sharp peak at $T_{N2} = 1.05$ K, proving the on-set of Nd long-range order. The same features are found in $x = 0.03$, but the Nd critical temperature decreases to $T_{N2} = 0.72$ K, slightly increasing the temperature of the Schottky maximum (from $T = 2.35$ K to $T = 2.6$ K) as well as its height, which is nearer to the ideal Schottky value. With only $x = 0.1$, the small λ peak on the low-temperature side has already disappeared, and the Schottky maximum appears at $T = 2.9$ K. Thus, the dilution of Fe with diamagnetic Co destroys the cooperative ordering of Nd for Co contents as low as a few percent. This is accompanied with a slight but clear shift of the Schottky maximum to higher temperatures for increasing x , corresponding to an enhancement of the Zeeman splitting of the Nd ground doublet from ~ 6 K ($x=0$) to ~ 7 K ($x=0.1$). These provide clear evidence of the increase of the average internal field

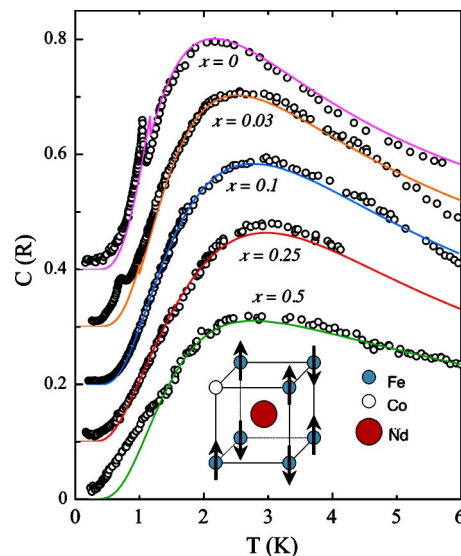


FIG. 1. (Color online) From top to bottom: experimental specific heat of $\text{NdFe}_{1-x}\text{Co}_x\text{O}_3$ with $x=0, 0.03, 0.1, 0.25,$ and 0.5 . The results of the mean-field model are shown as solid lines for $x=0$ (purple), 0.03 (orange), and 0.1 (blue). Equation (3) generates the curves for $x=0.25$ (red) and 0.5 (green) with the values given in Tables I and II.

acting on the Nd sublattice from $x=0$ to $x=0.1$.

The specific heat curves of $x=0.25$ and $x=0.5$ are similar to the $x=0.1$ one. However, the two trends observed in the range $x \leq 0.1$ are reversed on the $x \geq 0.1$: the temperature and height of the specific heat maximum decreases for increasing x and its shape is distorted with growing Co concentration, completely losing the characteristic two-level Schottky shape. This may be indicative of a broad distribution of Zeeman splittings of Nd^{3+} ions.

We have developed a simple mean-field model^{2,6,8} that describes the specific heat, ground-doublet Zeeman splitting and neutron diffracted intensities due to M -Nd polarization above and below T_{N2} in Nd orthoperovskites. $\text{NdFe}_{1-x}\text{Co}_x\text{O}_3$ system has an orthorhombically distorted perovskite structure, space group D_{16}^{2h} ($Pbnm$), with four formula units per elementary cell. The magnetic configurations are described in terms of linear combinations of spin operators⁹ for different $3d$ metal or rare-earth sites, whose Cartesian components transform as one of the eight irreps of the reduced space group D_{16}^{2h} . The Fe configuration in NdFeO_3 is $G_z F_x$, belonging to the Γ_2 irrep. The internal field $H_{\text{Fe-Nd}}$ produced by Fe must transform as Γ_2 , too, which in terms of the Nd allowed modes corresponds to $c_y f_x$.¹⁰ The ferromagnetic moments F_x and f_x have never been detected by neutron diffraction, and will be neglected in the following (the thermodynamics of the model are not essentially modified by this approximation). The effect of the $H_{\text{Fe-Nd}}$ internal field will be described by a Zeeman term with c_y configuration. The experimental $C_p(T)$ curve of NdFeO_3 evidences a true phase transition at $T_{N2}=1.05$ K, implying that the Nd-Nd interaction favors a magnetic arrangement belonging to an irrep other than Γ_2 . Therefore, the Nd-Nd exchange interaction will be described by two terms: the first one is proportional to the polarized mode, the c_y symmetry, which has as order parameter $\chi = -1/2\langle c_y \rangle$, as argued earlier, and the second one corresponds to a yet unknown \hat{n}_α cooperative mode ($\alpha \neq y$). The mean-field Hamiltonian can be written as

$$\mathcal{H} = -2\theta_c \nu \hat{n}_\alpha - (2\theta_p \chi - g_y \mu_B H_{\text{Fe-Nd}}) \hat{c}_y - 2\theta_c \nu^2 - 2\theta_p \chi^2, \quad (1)$$

where the first and second terms describe the Nd-Nd exchange in cooperative and polarized modes, with exchange constants θ_c and θ_p , respectively. The mean-field order parameters for the cooperative and polarized modes are $\nu = -\frac{1}{2}\langle \hat{n}_\alpha \rangle$ and $\chi = -\frac{1}{2}\langle \hat{c}_y \rangle$, respectively. The third term is the Nd-Fe Zeeman term created by the $H_{\text{Fe-Nd}}$ exchange field. The last two are self-energy correction terms.

Nd atoms may lose one or more magnetic nearest neighbor Fe atoms due to the introduction of magnetic vacancies as a random substitution (see Fig. 1). The net effect is a further decompensation of the internal field due to a contribution from the isotropic and anisotropic components of the Fe-Nd interaction. Therefore, the internal field due to one vacancy in a pseudocubic cell can add or subtract to the anisotropic average field $H_{\text{Fe-Nd}}$, depending on the position occupied by the magnetic vacancy.¹¹ Besides, $H_{\text{Fe-Nd}}$ will be reduced due to the loss of one compensated pair of Fe spins. Therefore, if we impose the effective field acting on the Nd

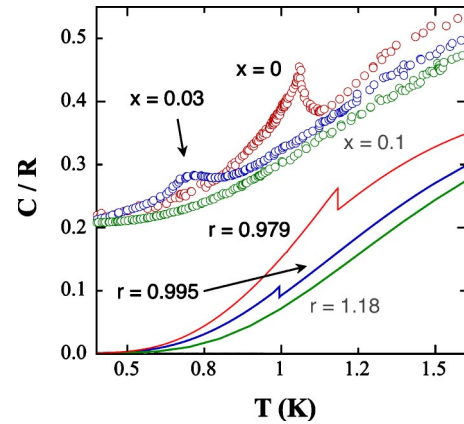


FIG. 2. (Color online) Detail of the specific heat of $x=0$ (red), 0.03 (blue), and 0.1 (green) and the mean-field model results.

moment as $H_{\text{eff}} = [(z-2)/z]H_{\text{Fe-Nd}} + \eta H_{\text{ex}}$, two values of the perturbed splitting arise when solving Hamiltonian 1, Δ^\pm , corresponding to $\eta = \pm 1$. The free energy of the system has to be modified consequently, as

$$\mathcal{F} = \frac{1}{2}(\theta_c \nu^2 + \theta_p \chi^2) + (1 - zx)T \ln \left[2 \cosh \left(\frac{\Delta}{2T} \right) \right] + \frac{1}{2} \sum_{\eta=\pm 1} (zx)T \ln \left[2 \cosh \left(\frac{\Delta^\pm}{2T} \right) \right]. \quad (2)$$

Minimizing this expression with respect to ν and χ , the order parameter evolution with temperature can be numerically computed, and the heat capacity thereafter.⁶ The net result is equivalent to having a perturbing field superposed to the average $\langle H_{\text{Fe-Nd}} \rangle$, which is the value we obtain from experiment. It is convenient to introduce the parameter $r = g_y \mu_B \langle H_{\text{Fe-Nd}} \rangle / 2(|\theta_p| - |\theta_c|)$, the ratio between Fe-Nd and Nd-Nd exchanges, since this adimensional parameter directly expresses the existence ($r < 1$) or inhibition ($r \geq 1$) of the long-range transition.

The results obtained for $x=0, 0.03$ and 0.1 are shown in Fig. 1 superimposed on the corresponding data. $x=0$ is satisfactorily fitted with the parameter values $\theta_c = 2.7$ K and $\theta_p = -0.83$ K, equivalent to an average exchange interaction of $J/k_B = -0.88$ K between Nd ions, and $r = 0.979$; that is, an average internal field of $H_{\text{Fe-Nd}} = 59$ kOe (using $\mu_{\text{Nd}} = 0.92 \mu_B$ [6]). The fit to the $x=0.03$ heat capacity curve is achieved with the same θ_c and θ_p as for the pure compound but with $r = 0.995$, or equivalently $H_{\text{Fe-Nd}} = 60$ kOe; that is, a 1.5% increase. This value of r is in the range where both the Schottky maximum and the lambda peak are still observable. However, $r = 1.18$ for $x=0.1$, beyond the limit of inhibition of Nd ordering, with $H_{\text{Fe-Nd}} = 71$ kOe. A detailed plot of the experimental and theoretical results in the temperature range around $T \sim 1$ K for $x=0, 0.03$ and 0.1 is shown in Fig. 2, where the inhibition of Nd magnetic order with increasing Co concentration can be neatly observed.

Depending on x , the fraction of Nd ions with a given number G of uncompensated spins varies (from 0 for no vacancies around the Nd to 4 for maximum uncompensation). G can be calculated as a function of x and are given in Table I. Since the Schottky heat capacity depends just on the

TABLE I. Fraction p_G of Nd^{3+} ions with a degree G of magnetic uncompensation.

G	$x=0$	$x=0.03$	$x=0.1$	$x=0.25$	$x=0.5$
0	1	0.796	0.518	0.325	0.274
1	0	0.195	0.411	0.465	0.437
2	0	0.009	0.066	0.175	0.219
3	0	~ 0	0.005	0.033	0.062
4	0	~ 0	~ 0	0.002	0.008

ground-doublet splitting, and is a single-particle contribution, it can be calculated as a weighted sum:

$$C_p = \sum_{G=0}^4 p_G \text{Sch}(\Delta_G), \quad (3)$$

where the weight p_G are given in Table I and the function $\text{Sch}(\Delta_G)$ is the Schottky specific heat for a two-level system with splitting Δ_G . The $x=0.25$ and 0.5 curves (shown in Fig. 1 with the corresponding data) have been fitted under this hypothesis to account for the broadening effect on the Schottky anomaly. The best fits for $x=0.03$ and 0.1 cannot be distinguished from the curves obtained from the mean-field model, except for the low-temperature peak on $x=0.03$. The excellent fit obtained with this simple approach validates the initial proposition of each vacancy contributing by an approximately constant amount to the internal field acting on the Nd^{3+} ion. (See Table II.)

We have shown that in the case of substitution of Fe atoms by Co, equivalent to the inclusion of magnetic vacancies at the Fe sites in NdFeO_3 , the Nd atoms are polarized by an effective field originating from the Fe sublattice, which increase in intensity of the number of vacancies increases,

TABLE II. Energy splittings Δ_G of the Nd^{3+} ground doublet as obtained from the fit of the experimental curves.

E/k_B (K)	$x=0.03$	$x=0.1$	$x=0.25$	$x=0.5$
Δ_0	5.31(1)	4.93(6)	4.05(4)	3.32(3)
Δ_1	10.4(1)	8.15(7)	7.65(5)	7.19(4)
Δ_2		12.1(5)	10.2(3)	15.6(2)
Δ_3				34.6(1.2)

overcoming the Nd-Nd interaction and inhibiting the Nd long-range-order transition.

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