Induced and cooperative order of Nd ions in $NdNiO_3$

F. Bartolomé[a)] and J. Bartolomé
I.C.M.A., C.S.I.C.-Universidad de Zaragoza, 50009 Zaragoza, Spain

R. S. Eccleston
ISIS Department-C.L.R.C. Rutherford Appleton Laboratory, United Kingdom

Low-temperature specific heat measurements on $NdNiO_3$ evidence the onset of Nd cooperative ordering at $T_{N2}=0.77$ K. Because of the particular arrangement of the Ni magnetic moments, half of the Nd ions have an antiferromagnetically compensated environment while the other half have a noncompensated one. We show that both types of Nd ions are affected by a different but non-negligible Nd–Ni exchange field, in contrast with the current model used in literature. [S0021-8979(00)70708-0]

RMO_3 are model systems to investigate the interactions between the two types of magnetic atoms (R=rare earth, M=3*d* or 4*d* metal). It has been shown in $NdMO_3$ systems[1] that when Nd–Nd interaction is in isolation, i.e., M is diamagnetic, Nd orders at $T_N \approx 1$ K. The introduction of a magnetic 3*d* transition metal leads to magnetic ordering of the M sublattice at T_{N1}, which ranges from ~700 K for $NdFeO_3$ to ~200 K for $NdCrO_3$ and $NdNiO_3$. Below T_{N1}, the M sublattice polarizes the Nd sublattice, with the same symmetry as the M magnetic order, as seen clearly by neutron diffraction. This M–Nd polarization splits the Nd ground doublet reducing the magnetic entropy available for cooperative ordering. Thus, Nd cooperative ordering appears in some cases, as in $NdFeO_3$,[2] while it is fully inhibited in others, as in $NdCrO_3$,[1] depending on the relative intensity of Nd–M and Nd–Nd interactions.

$NdNiO_3$ is a rather peculiar case. Ni moments order at $T_{N1}=200$ K, at which a metal–insulator transition takes place,[3] $T_{M-I}=T_{N1}$. An orbital superlattice has been described to set in below that temperature for the occupation of the *d* Ni states, giving rise to a very unusual antiferromagnetic structure.[4] It can be described as alternating layers perpendicular to [001] ($A^+A^+A^-A^-A^+A^+\cdots$). Ni magnetic moments are almost parallel to the *a* axes. Within an $A^{\pm}$ layer, the Ni moments forming rows parallel to the *b* axes are ferromagnetic, in such a way that a $++--++\cdots$ antiferromagnetic array is formed along the *a*-axes direction. Finally, in A^- layers all Ni spins are inverted with respect to those in A^+ ones. The magnetic unit cell is composed of four *Pbnm* cells. This alternated structure induces the existence of two Nd sites with respect to its ''magnetic environment.'' Each Nd ion is placed approximately at the center of a cube of Ni ions. Those occupying a site between A^+ and A^- planes have an antiferromagnetic environment (four parallel and four antiparallel Ni neighbors, labeled B^0 Nd layers). In contrast, those Nd ions placed between two A^+ (or two A^-) Ni planes have an uncompensated magnetic environment (six parallel and two antiparallel Ni neighbors, $B^{\pm}$ Nd layers). It has been proposed that this superstructure provokes induced magnetic order in $B^{\pm}$ Nd layers (paramagnetic planes acted by a ''strong'' Ni–Nd exchange field) and a pure paramagnetic state of Nd in B^0 planes (free moments under a negligible Ni–Nd field). The whole magnetic structure was refined with this hypothesis as a function of temperature.[4] The ordered Nd moment on $B^{\pm}$ layers follow, after Ref. 4, a Langevin function governed by an exchange field $H^{\pm}_{exc}=2.5(2)$ T, while the Nd moments on B^0 planes are fully unpolarized till $T=1.5$ K ($H^0_{exc}\approx 0$). The analysis of muon-spin-relaxation (MSR) experiments confirmed, after García Muñoz *et al.*,[5] this peculiar Nd arrangement. Independent neutron diffraction experiments have been analyzed within the same framework in the range $30<T<0.2$ K.[6] A sharp increase of the intensity due to Nd is observed at 0.2 K, which was attributed either to the onset of Nd–Nd interactions or to the hyperfine enhancement of the neutron reflections.[7]

$H^{\pm}_{exc}$ is similar to other published values for Nd–M interaction: $H^{Nd-Fe}_{exc}=0.9$ T in $NdFeO_3$ (Ref. 8) and $H^{Nd-Cr}_{exc}=11.5(3)$ T in $NdCrO_3$.[8] It has to be emphasized that in $NdFeO_3$ and $NdCrO_3$, Nd occupy *compensated* magnetic environments, and despite that, Nd–M exchange fields are similar or even quite higher than that assumed to correspond to *uncompensated* Nd ions in $NdNiO_3$. The comparison renders unlikely the $H^0_{exc}\approx 0$ value for B^0 Nd.

The temperature dependence of the Nd induced ordering obtained from the neutron diffraction analysis allows us to calculate the entropy and specific heat associated to each Nd subsystem. If B^0 Nd ions are actually unpolarized, its magnetic entropy is constant, [$(R/2)\ln(2)$], thus, not contributing to the specific heat. The entropy of $B^{\pm}$ Nd ions would be that of a paramagnet under a constant field and the corresponding specific heat is a Schottky curve.

Figure 1 shows our low-temperature specific heat measurements on $NdNiO_3$. Two different samples were measured at ICMA, Zaragoza ($0.25<T<4$ K, ''○'') and the Kamerlingh Onnes Laboratorium (KOL), Leiden ($0.07<T<2.5$ K, ''×''). Both curves agree within the experimental error, as shown in the figure.

The lattice contribution, estimated from measurements on $LaNiO_3$ and $LaGaO_3$ (Ref. 9) is orders of magnitude smaller that the magnetic contribution below $T=4$ K and will be neglected. The measured specific heat curve, *C*, pre-

[a)]Electronic mail: bartolom@posta.unizar.es

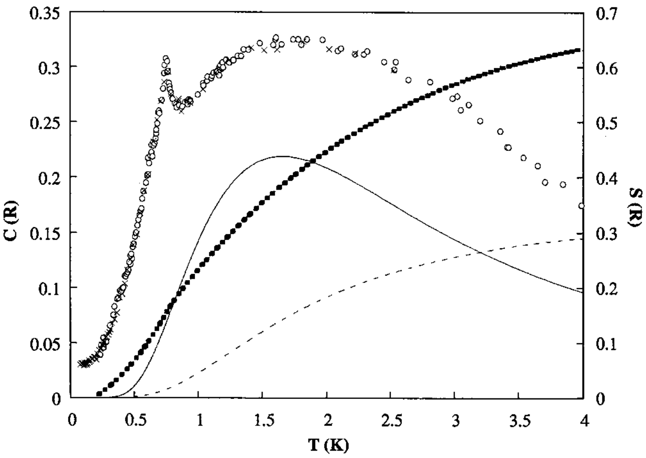

FIG. 1. Left scale: Experimental (○,×) and calculated from Ref. 4 (thin full line) specific heat of $NdNiO_3$. Right scale: Magnetic entropy of $NdNiO_3$ as calculated from our C data (thick dotted line) and from Ref. 4 (thin dashed line).

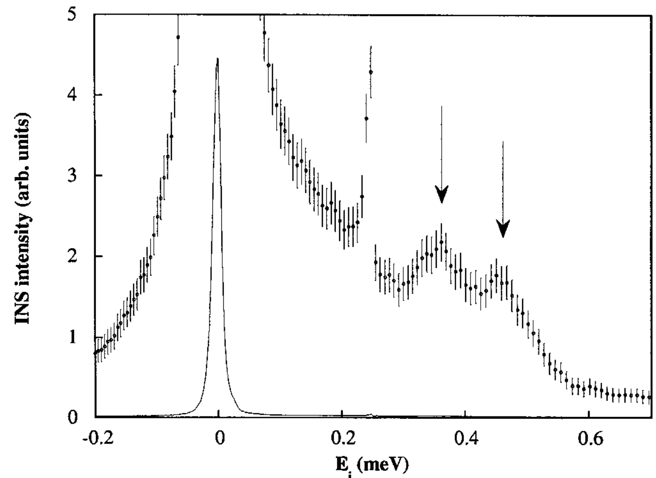

FIG. 2. High resolution INS spectrum. The Nd Zeeman excitation peaks are marked by arrows. The feature at 0.24 meV is a spurious diffraction peak from the monocromator. The full-scale spectrum is also shown.

sents a broad Schottky-like maximum, with $T_{\max}$ between 1.5 and 2 K, a small λ peak at 0.77 K, and a plateau below 0.2 K, probably related with a hypefine contribution.[1] From the experimental curve we can calculate the magnetic entropy, also shown in Fig. 1 (thick dotted curve, right scale). The specific heat (thin full line) and its corresponding entropy (thin dashed line) calculated from the results of Ref. 4 are represented in the same scales as the experimental results in Fig. 1. This figure evidences a total disagreement between the model assumed from neutron diffraction refinements[4] and the experiment. From the experimental *C(T)* curve, it is derived that $S(T=4\text{ K})=0.63(2)R$, representing 91% of the magnetic entropy of the *whole* Nd system. This indicates that *every* Nd ion is (partially) polarized below 4 K and not only one half of them. This rules out the magnetic structure labeled ''model 1'' in Ref. 4, at least in the nontrivial result that Nd ''B^0'' ordered magnetic moment would vanish. Indeed, the peak observed in $C(T)$ at $T_{N2}=0.77$ K evidences the onset of cooperative magnetic ordering of the whole Nd subsystem.

The Zeeman splitting by the Nd–Ni exchange field of the Nd ground doublet at the B^0 and $B^{\pm}$ sites can be directly probed by high-resolution inelastic neutron scattering (INS). We performed an INS experiment at the IRIS spectrometer of the ISIS facility, the British spallation neutron source. The INS spectrum recorded on 2.5 g of powdered $NdNiO_3$ at $T=2$ K is shown in Fig. 2. Two distinct excitation channels are observed, at $\Delta^0=0.35$ meV (4.1 K) and $\Delta^{\pm}=0.46$ meV (5.2 K), where the notation of Ref. 4 is maintained. It is important to note the similar INS experiments yielded single excitation peaks on $NdFeO_3$ (Ref. 10) ($\Delta^{\text{NdFe}}=5.7$ K) and $NdCrO_3$ (Ref. 11) ($\Delta^{\text{NdCr}}=27$ K). In those cases, the INS excitation energies are in excellent agreement with the splitting calculated from the Schottky curves observed in specific heat measurements.[1] Our INS experiment experimentally evidences the magnetic polarization of both Nd subsystems by Nd–Ni interaction, in accord with the entropy considerations developed earlier. Moreover, it rules out the hypothesis of an unpolarized Nd sublattice since it should have $\Delta^0=0$.

The $C(T)$ dependence of $NdNiO_3$ is similar to that of $NdFeO_3$. In a recent paper we developed a mean field model[2] including Nd–Fe and Nd–Nd interactions for equivalent Nd ions, which describe the specific heat and the neutron diffracted intensities due to Nd–Fe polarization above and below T_{N2} in $NdFeO_3$. However, the model has to be modified to quantitatively reproduce the $NdNiO_3$ C curve, by assuming that half of the Nd ions are acted by a greater Nd–Ni exchange field than the other half. One has to take into account that below T_{N1}, the *Pbnm* symmetry breaks down and the unit cell includes 16 Ni and 16 Nd ions. Then, a base of spin operators has 16 magnetic modes for Ni and 16 more for Nd. Let us denote $\hat{\mathbf{N}}_{\mathbf{x}}$ the mode in which Ni orders after García Muñoz *et al.*[4] The Ni–Nd polarization acts in the Nd ions with the same symmetry as $\hat{\mathbf{N}}_{\mathbf{x}}$, belonging to the same irep of the magnetic group. We will denote $\hat{\mathbf{n}}_{\mathbf{x}}$ the Nd mode due to Nd–Ni exchange. The experimental $C(T)$ curve evidences a true phase transition at $T_{N2}=0.77$ K. This implies that the Nd–Nd interaction favors a magnetic arrangement belonging to a different irep of the magnetic group than $\hat{\mathbf{n}}_{\mathbf{x}}$. The corresponding spin operator will be denoted $\hat{\mathbf{r}}$, whose exact form is not yet known.

The mean-field Hamiltonian for the Nd ions is

$$\mathcal{H}=-2\,\theta_c\rho\hat{\mathbf{r}}-2\,\theta_p\nu\hat{\mathbf{n}}_x-g_x\mu_BH_{\text{exc}}\hat{\mathbf{n}}_x-2\,\theta_c\rho^2-2\,\theta_p\nu^2, \tag{1}$$

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 $\rho=-\frac{1}{2}\langle\hat{\mathbf{r}}\rangle$ and $\nu=-\frac{1}{2}\langle\hat{\mathbf{n}}_x\rangle$. The third term is the Nd–Ni Zeeman term, with H_{exc} depending on the Nd site. The two later terms are mean-field self-interaction corrections.

If one imposes $H^{\pm}_{\text{exc}}>_{\neq}H^0_{\text{exc}}$, the free energy splits into two,

$$\mathcal{F}^{\alpha}=\sum_{\alpha=\pm,0}\frac{1}{2}\theta_c\rho^2+\frac{1}{2}\theta_p\nu^2-T\ln\left[2\cosh\left(\frac{\Delta^{\alpha}}{2T}\right)\right] \quad (2)$$

where $\alpha=$ ''$\pm$'' or ''0'' and

$$\Delta^{\alpha}=\sqrt{(2\theta_c\rho)^2+(g_x\mu_B H_{\mathrm{exc}}^{\alpha}+2\theta_p\nu)^2} \quad (3)$$

is the exchange splitting of the Nd^{3+} ground doublet. By minimizing $\mathcal{F}^{\alpha}$ with respect to ρ_α and ν_α, one gets the characteristic equations

$$\rho=\rho\frac{2\theta_c}{\Delta^{\alpha}}\tanh\frac{\Delta^{\alpha}}{2T}, \quad (4)$$

$$\nu=\frac{g_x\mu_B H_{\mathrm{exc}}^{\alpha}+2\theta_p\nu}{\Delta^{\alpha}}\tanh\left(\frac{\Delta^{\alpha}}{2T}\right). \quad (5)$$

Two distinct situations are possible for the Nd system from the solutions of these two equations: a paramagnetic phase, with existence of polarization but not cooperative order ($\rho=0$), and a polarized *and* cooperatively ordered phase ($\rho\neq 0$). The entropy of the Nd system can be calculated from Eq. (2), and the specific heat is easily computable from this equation by numeric integration.[2]

We dispose of four parameters to fit the specific heat: θ_c, θ_p, $H_{\mathrm{exc}}^{\pm}$, and H_{exc}^{0}. The value $\theta_c=0.8$ K has been well determined in $NdGaO_3$,[12] where Nd–Nd interaction is isolated. $\theta_p=0.2$ K was determined in $NdFeO_3$ (though the anisotropy of the Nd–Nd exchange would be quite different in $NdNiO_3$). With the exchange constants fixed to that value, the best fit for the specific heat is shown in the upper panel of Fig. 3 (thick line), together with the experimental data. The contributions from each Nd sublattice are also shown (thin lines). The model properly reproduces the experimental $C(T)$. However, this fit gives $\Delta_0=2.6$ and $\Delta^{\pm}=5.3$ K, with Δ^0 too low compared with the experimental value (4.1 K). If Δ_0 and $\Delta^{\pm}$ are optimized while the theoretical T_{N2} is relaxed during the fitting, one can obtain a compromise best fit. Indeed, ordering temperature is systematically overestimated by mean-field models, while Δ^0 and $\Delta^{\pm}$ have been experimentally obtained. This best compromise yields $\theta_c=0.88$, $\theta_p=0.82$, $\Delta^0=3.6$, and $\Delta^{\pm}=5.6$ K, with $T_{N2}=0.82$ K, properly reproducing the $C(T)$ shape in the Nd paramagnetic regime. The obtained values of Δ^0 and $\Delta^{\pm}$ are quite comparable, within experimental errors, to those yielded by INS experiments. The ordered regime is not well described, as the mean-field model does not take into account spin wave contributions.

In conclusion, this work shows that *both* Nd subsystems, B^0 and $B^{\pm}$, are strongly polarized by Nd–Ni exchange when cooling down from 20 K to $T_{N2}=0.77$ K, temperature at which cooperative ordering of the Nd ions sets on. These results are in strong contradiction with the previously proposed low-temperature behavior of Nd in $NdNiO_3$.[3–6] A reanalysis of the low-temperature neutron diffraction and MSR data is due to achieve a full understanding of the phenomenology.

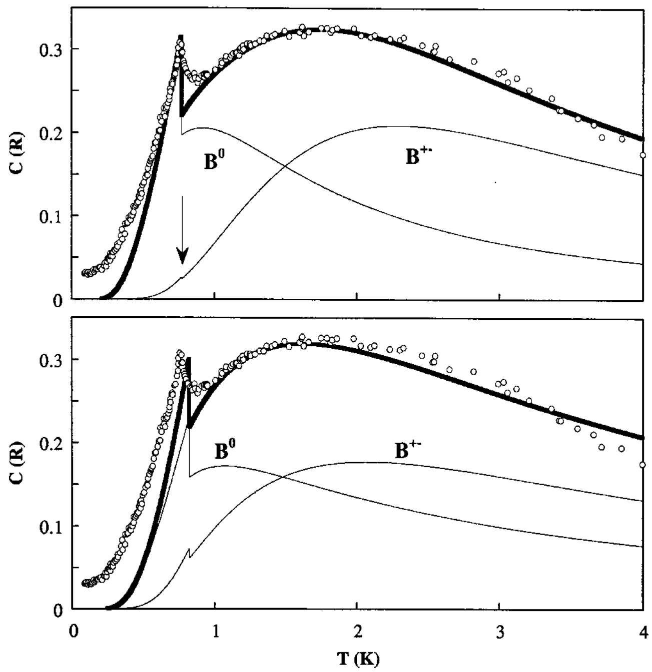

FIG. 3. Specific heat data (○) compared with the best fit obtained with the mean field model. Upper panel: Optimized fit of the calorimetric data. Lower panel: Compromise best fit including the INS $\Delta^{\pm}$ and Δ^0 data in the fitting procedure.

The authors thank Y. E. Volokitin and L. J. de Jongh from the Kamerlingh Onnes Laboratorium for assistance and helpful discussions. This work has been supported by CICYT projects MAT99-1142 and MAT97-0987, and INTAS97-10177 project.

[1] J. Bartolomé and F. Bartolomé, Phase Transit. **64**, 57 (1997).
[2] J. Bartolomé, E. Palacios, M. D. Kuz'min, F. Bartolomé, I. Sosnowska, R. Przenioslo, R. Sonntag, and M. M. Lukina, Phys. Rev. B **55**, 11432 (1997).
[3] M. L. Medarde, J. Phys.: Condens. Matter **9**, 1679 (1997).
[4] J. L. García Muñoz, J. Rodríguez-Carvajal, and P. Lacorre, Phys. Rev. B **50**, 978 (1994).
[5] J. L. García Muñoz, J. P. Lacorre, and R. Cywinski, Phys. Rev. B **51**, 15197 (1995).
[6] S. Rosenkranz, Ph.D. thesis, ETH Zürich, 11853, 1996.
[7] W. Marti, M. Medarde, S. Rosenkranz, P. Fisher, A. Furrer, and C. Klemenz, Phys. Rev. B **52**, 4275 (1995).
[8] R. M. Hornreich, Y. Komet, R. Nolan, B. M. Wanklyn, and I. Yaeger, Phys. Rev. B **12**, 5094 (1975).
[9] M. Castro, Ph.D. thesis, University of Zaragoza, 1995.
[10] M. Loewenhaupt, I. Sosnowska, and B. Frick, J. Phys. (France) **12**, C8-921 (1988).
[11] N. Shamir, M. Melamud, H. Shaked, and S. Shtrikman, Physica B **90**, 217 (1977).
[12] F. Luis, M. D. Kuz'min, F. Bartolomé, M. Artigas, J. Rubín, V. M. Orera, and J. Bartolomé, Phys. Rev. B **58**, 798 (1998).