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2009 J. Phys.: Condens. Matter 21 126003

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Direct evidence for the Nd magnetic ordering in NdMnO₃ from the hyperfine field splitting of Nd nuclear levels

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Received 11 November 2008, in final form 11 February 2009

Published 3 March 2009

Online at stacks.iop.org/JPhysCM/21/126003

Abstract

We investigated the low energy excitations in NdMnO₃ in the μeV range by a backscattering neutron spectrometer. The energy spectra on polycrystalline NdMnO₃ samples revealed inelastic peaks at $E = 2.15 \pm 0.01 \mu\text{eV}$ at $T = 2 \text{ K}$ on both energy gain and energy loss sides. The inelastic peaks move gradually towards lower energy with increasing temperature and tend to merge with the elastic peak at the electronic magnetic ordering temperature of Nd, $T_{\text{Nd}} \approx 20 \text{ K}$. However, at temperatures higher than $T_{\text{Nd}} \approx 20 \text{ K}$ the energy of the inelastic peak decreases at a much slower rate and remains finite up to $T = 55 \text{ K}$, the highest temperature investigated. We interpret the inelastic peaks to be due to the transition between the hyperfine-split nuclear level of the ¹⁴³Nd and ¹⁴⁵Nd isotopes with spin $I = 7/2$ caused by the magnetic ordering of Nd electronic moment below $T_{\text{Nd}} \approx 20 \text{ K}$. We ascribe the finite energy of the inelastic peak and its much smaller temperature dependence at $T > 20 \text{ K}$ to be due to the polarization of the Nd magnetic moment by the field of Mn moments that order below $T_{\text{N}} \approx 78 \text{ K}$.

(Some figures in this article are in colour only in the electronic version)

LaMnO₃, PrMnO₃ and NdMnO₃ are the parent compounds of the hole-doped colossal magnetoresistive materials that have been investigated quite intensively [1, 2]. These compounds crystallize with the GdFeO₃ type crystal structure with the *Pbnm* space group. The crystal structure is shown in figure 1(a). The MnO₆ octahedra are distorted due to the Jahn–Teller effect. There are three Mn–O distances called short *s*, medium *m* and long *l*. Co-operative Jahn–Teller distortion removes the degeneracy of the e_g orbitals in the t_{2g}³e_g¹ electron configuration of the Mn³⁺ ions and stabilizes d_{3x²-r²}/d_{3y²-r²} orbitals, which are ordered. The orbital order consists of the ordering of the d_{3x²-r²} and d_{3y²-r²} orbitals in an alternate staggered pattern in the *a*–*b* plane shown in figure 1(b). The orbital ordering pattern repeats itself along the *c* axis. This type of orbital order induces A-type antiferromagnetic (AF)

ordering [3, 4] below $T_{\text{N}} \approx 141 \text{ K}$. In the A-type AF phase the spins in the *a*–*b* plane are ferromagnetically ordered. The ferromagnetic planes are stacked antiferromagnetically along the *c* axis. The antiferromagnetic phase transition in LaMnO₃ has been investigated quite intensively [5, 6]. The orbital order persists in the paramagnetic phase above T_{N} . LaMnO₃ undergoes presumably a orbital order–disorder transition at the orbital ordering temperature $T_{\text{OO}} \approx 750 \text{ K}$ from the orbitally ordered orthorhombic phase to a high temperature orbitally disordered orthorhombic phase that is nearly cubic [7, 8]. The orbital order–disorder transition in LaMnO₃ and La_{1-x}Nd_xMnO₃ has also been investigated by several other workers [9–13]. A complete understanding of the mechanism stabilizing the observed order in the insulating parent compounds are a prerequisite for understanding fully the

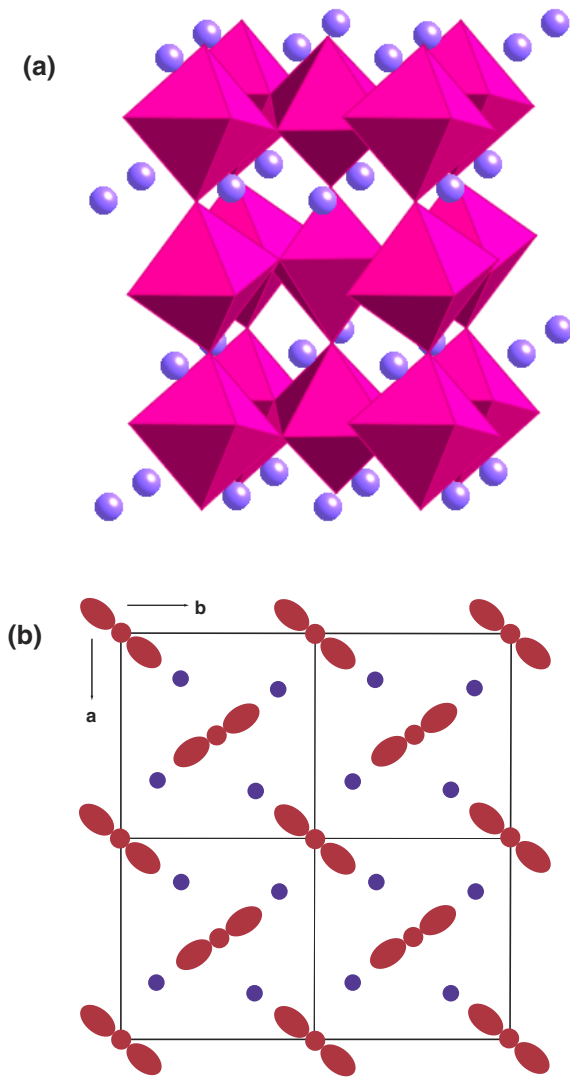


Figure 1. (a) Schematic representation of the orthorhombic crystal structure of LaMnO₃ in which only the La ions and the MnO₆ octahedra are shown. (b) The staggered ordering of the $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbitals in the a - b plane. The orbital ordering pattern is repeated along the c axis.

complex interplay among the spin, charge, orbital and lattice degrees of freedom in the doped manganites. For this reason a large number of theoretical investigations have already been undertaken, especially on stoichiometric LaMnO₃ itself [14].

Although the optimally hole-doped PrMnO₃ and NdMnO₃ show very large magnetoresistive effects these parent compounds have attracted much less theoretical as well as experimental investigations. This is certainly due to the presence of the second rare-earth magnetic sublattices that makes them more complex than LaMnO₃. The most significant effect on the crystal structure by decreasing ionic radius r_R of the rare-earth ion R is an enhancement of the co-operative rotation of the MnO₆ octahedra (the GdFeO₃ type distortion) characterized by the decrease of the Mn–O–Mn bond angle ϕ . This causes a profound effect on the orbital ordering temperature T_{OO} and also the magnetic ordering temperature T_N . The orbital ordering

temperature T_{OO} increases monotonically whereas the T_N decreases significantly. Also the A-type AF phase goes to the E-type phase through the intermediate incommensurate structure. It has now become clear that by replacing La by the magnetic rare earths the A-type antiferromagnetic structure, that is made up of ferromagnetic a - b planes, is destabilized. The resulting incommensurate phases in GdMnO₃, TbMnO₃ and DyMnO₃ allows ferroelectricity, thus making them important multiferroic materials. Kimura *et al* [15] argued that the combination of the orbital order and next-nearest-neighbour superexchange interaction brings about a nontrivial effect on the magnetic ground state of the system with the orbital degeneracy and the large GdFeO₃-type distortion. Microscopic calculation shows that the magnetism in this system is mapped onto the frustrated spin model [15] that well reproduces the magnetic phase diagram of RMnO₃. Even the lighter NdMnO₃, SmMnO₃ and EuMnO₃ can be made incommensurate and multiferroic by doping with the smaller ion Y. Thus the lighter PrMnO₃, and especially NdMnO₃ which is the parent compound of both colossal magnetoresistive and multiferroic materials, obviously deserves more experimental and theoretical investigations.

Neutron diffraction [16–18] investigations have established that NdMnO₃ undergoes an antiferromagnetic transition at $T_N \approx 78$ K. The Nd atoms in NdMnO₃ form a simple cubic sublattice. The lattice parameters of NdMnO₃ at room temperature are $a = 5.7119 \pm 0.0009$, $b = 5.4119 \pm 0.0008$ and $c = 7.5890 \pm 0.0013$ Å. The ferromagnetic (001) layers are stacked antiferromagnetically along the [001] axis. The magnetic moments in the ferromagnetic a - b planes are parallel to the b axis. At a temperature below $T = 70$ K a ferromagnetic component along the c axis develops [17]. At $T_{Nd} \approx 13$ K the Nd magnetic moments get ordered with a ferromagnetic arrangement [17] parallel to the c axis. At $T = 1.5$ K the ordered magnetic moment per Mn atom is $3.22 \pm 0.09\mu_B$ and that for the Nd atom is $1.2 \pm 0.2\mu_B$. However, the ordering of the Nd atoms has not been observed by Quezel-Ambrunaz [16] or Wu *et al* [18]. In order to resolve this controversy we investigated the possible magnetic ordering of the Nd sublattice at low temperature. We measured the hyperfine splitting of the Nd nucleus by inelastic neutron scattering on high resolution backscattering neutron spectrometers that have an energy resolution of about $0.7 \mu\text{eV}$. The experimental results show directly that the Nd magnetic moments do indeed order at low temperature.

With the advent of high resolution backscattering neutron spectrometer, Heidemann and co-workers investigated the hyperfine fields in Co- and V-based compounds [19–25]. The hyperfine splitting lies typically in the energy range of a few μeV . The inelastic spin-flip scattering of neutrons from the nuclear spins can yield this information provided the neutron spectrometer has the required resolution better than or equal to $1 \mu\text{eV}$ and also the incoherent scattering of the nucleus is strong enough. It was established that the hyperfine field produced at the nucleus is roughly, but not exactly, proportional to the electronic magnetic moment of the 3d shell. Heidemann [19] worked out the double differential cross section of this scattering process. The process can be

summarized as follows: if neutrons with spin \mathbf{s} are scattered from nuclei with spins \mathbf{I} , the probability that their spins will be flipped is $2/3$. The nucleus at which the neutron is scattered with a spin-flip changes its magnetic quantum number M to $M \pm 1$ due to the conservation of the angular momentum. If the nuclear ground state is split up into different energy levels E_M due to the hyperfine magnetic field or an electric quadrupole interaction, then the neutron spin-flip produces a change of the ground state energy $\Delta E = E_M - E_{M\pm 1}$. This energy change is transferred to the scattered neutron. The double differential scattering cross section [19] is given by the following expressions:

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{\text{inc}}^0 = \overline{(\bar{\alpha}^2 - \bar{\alpha}'^2 + \frac{1}{3}\alpha'^2 I(I+1))} e^{-2W(k)} \delta(\hbar\omega), \quad (1)$$

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{\text{inc}}^{\pm} = \frac{1}{3}\overline{\alpha'^2 I(I+1)} \sqrt{1 \pm \frac{\Delta E}{E_0}} e^{-2W(k)} \delta(\hbar\omega \mp \delta E) \quad (2)$$

where α and α' are coherent and spin-incoherent scattering lengths, $W(k)$ is the Debye–Waller factor, E_0 is the incident neutron energy and δ is the Dirac delta function. If the sample contains one type of isotope then $\bar{\alpha}^2 - \bar{\alpha}'^2$ is zero. Also $\sqrt{1 \pm \frac{\Delta E}{E_0}} \approx 1$ because ΔE is usually much less than the incident neutron energy E_0 . In this case $2/3$ of incoherent scattering will be spin-flip scattering. One therefore expects a central elastic peak and two inelastic peaks of approximately equal intensities. Obviously the measured spectrum will be a convolution of the cross section given in (1) and (2) with the resolution function of the spectrometer.

Nd has the natural abundances of 12.18% and 8.29% of ^{143}Nd and ^{145}Nd isotopes, respectively. Both of these isotopes have nuclear spins of $I = 7/2$ and their incoherent scattering cross sections [26] are 55 ± 7 and 5 ± 5 b for ^{143}Nd and ^{145}Nd , respectively. Therefore Nd-based compounds are very much suitable for such studies. We investigated low energy nuclear spin excitations on Nd metal and several Nd-based compounds [27–30] by inelastic neutron scattering and found that the energy of the excitations in these compounds are approximately proportional to the ordered 4f electronic magnetic moment that is usually much reduced from the free ion value of $3.27\mu_B$ due to the crystal-field effects. Recently Przenioslo *et al* [31] investigated nuclear ordering and excitations in NdFeO_3 and found similar results.

We performed inelastic neutron scattering experiments on polycrystalline NdMnO_3 at low temperatures by using the high resolution backscattering neutron spectrometer SPHERES of the Jülich Centre for Neutron Science located at the FRMII reactor in Munich. Additional measurements were done on the high resolution backscattering spectrometer IN16 of the Institut Laue-Langevin in Grenoble. The wavelength of the incident neutrons was $\lambda = 6.271 \text{ \AA}$ in both experiments. The NdMnO_3 samples were prepared by using the solution chemistry technique described by Bhattacharya *et al* [13]. We did x-ray and neutron powder diffraction measurements on the sample and the Rietveld refinement of the crystal structure showed that the sample was single phase and

stoichiometric within our experimental resolution. About 5 g of polycrystalline samples of NdMnO_3 was placed in a flat aluminium sample holder and was fixed to the cold tip of a cryostat. We observed inelastic signals in NdMnO_3 at energy $E = 2.15 \pm 0.02 \mu\text{eV}$ on both energy gain and loss sides at $T = 2 \text{ K}$ in our experiment on SPHERES. In our experiment on IN16 we observed a lower energy of $E = 2.06 \pm 0.02 \mu\text{eV}$. We attribute this difference in energies determined in two independent experiments to be due to the different instrumental calibration. The inelastic signals observed cannot be due to splitting of the Kramers doublet due to the Nd–Mn exchange because Hemberger [32] determined this splitting to be about 20 K or 1.7 meV from their specific heat investigations. Jandl *et al* [33] also found this splitting from their infrared study to be about 14 cm^{-1} or 1.7 meV. Thus this electronic excitations in NdMnO_3 lie far outside the window of the backscattering spectrometer that, in our case, was $\pm 4 \mu\text{eV}$ only. So we can safely ascribe the inelastic excitations to be due to the hyperfine splitting of the Nd nuclear levels. However the observation of low energy inelastic signals at low temperature in NdMnO_3 is direct evidence of the ordering of Nd magnetic moments and clearly resolves the controversy in favour of the ordering of Nd magnetic moments at below about $T_{\text{Nd}} \approx 20 \text{ K}$. Figure 2 shows typical energy spectra of NdMnO_3 measured at the backscattering spectrometer IN16 of the Institut Laue-Langevin at several temperatures. For comparison we also show a typical spectrum of NdMnO_3 measured at the backscattering spectrometer SPHERES in figure 3. The spectra is the result of summing the counts of the individual detectors placed at different scattering angles. In order to extract the energies of the inelastic peaks we fitted three Gaussian functions to the spectra. At low temperatures the inelastic peaks are well separated from the elastic peak and we could fit the three Gaussian functions without any constraints. However, at higher temperatures the inelastic signals are too close to the central elastic peak and we had to constrain the fitting parameters. Figure 4 shows the temperature dependence of the energy of the inelastic peak. The energy of the inelastic peak decreases continuously but, instead of becoming zero, decreases at a much lower rate from about $T = 20 \text{ K}$. The spontaneous ordering of Nd moments takes place at about $T_{\text{Nd}} \approx 20 \text{ K}$ which can be obtained approximately by extrapolating the temperature dependence of energy by taking only the low temperature data. However, the temperature dependence of energy of the inelastic peak changes its slope above $T_{\text{Nd}} \approx 20 \text{ K}$ and decreases at a much slower rate. We attribute this to the polarization of the Nd moments caused by the field of the Mn moments that order below $T_N \approx 78 \text{ K}$. There are two ^{143}Nd and ^{145}Nd isotopes with nuclear spin $I = 7/2$ in NdMnO_3 . So one might expect two inelastic lines corresponding to these two isotopes. But experimentally only one resolution-limited inelastic line is observed. This is also the case in Nd_2CuO_4 [27], NdCu_2 [29] and NdGaO_3 [30]. Two inelastic lines were seen in Nd metal [28] which we interpreted as due to the two different crystallographic hexagonal and cubic sites of the dhcp structure of Nd and are not due to two different Nd isotopes. The reason for only one inelastic signal in Nd_2CuO_4 , NdCu_2 and

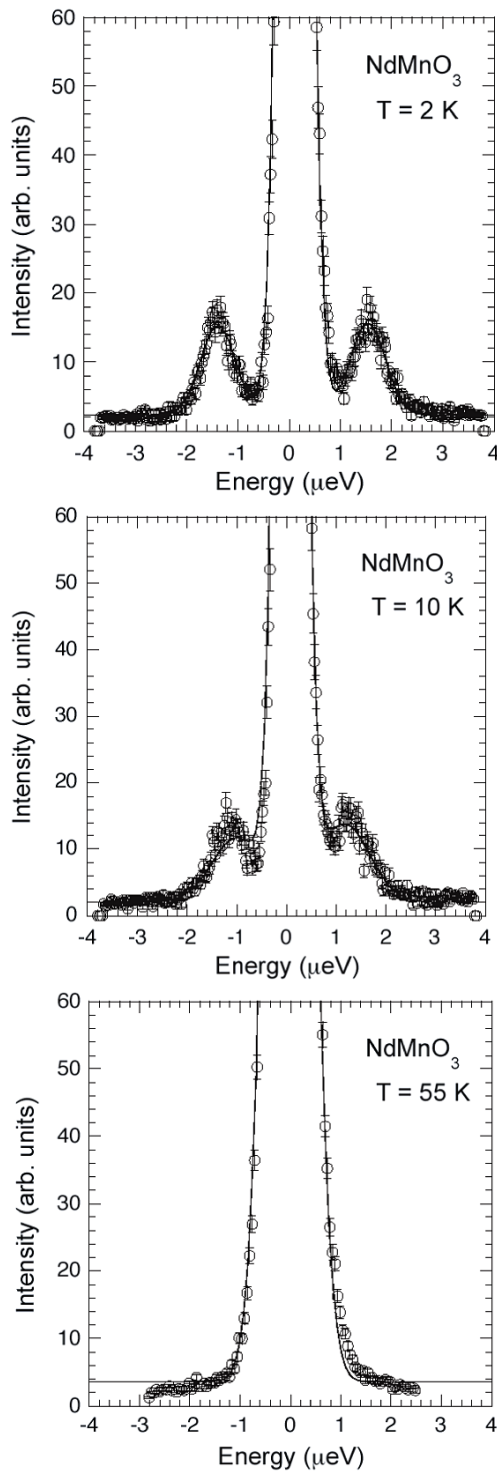


Figure 2. Typical energy spectra of NdMnO₃ measured at the backscattering spectrometer IN16 of the Institut Laue-Langevin at several temperatures. The inelastic peaks are seen on both energy loss and energy gain sides along with the central elastic peak. The inelastic peaks move towards the central elastic peak with increasing temperature and finally merges with it. The fit of the data at $T = 55$ K by a Gaussian function is not very good due to the fact that the resolution function cannot be described by this function.

NdGaO₃ is probably that the ¹⁴⁵Nd isotope contributes little to the scattering due to the small incoherent scattering cross section of ¹⁴⁵Nd (5 ± 5 b). The data that we collected

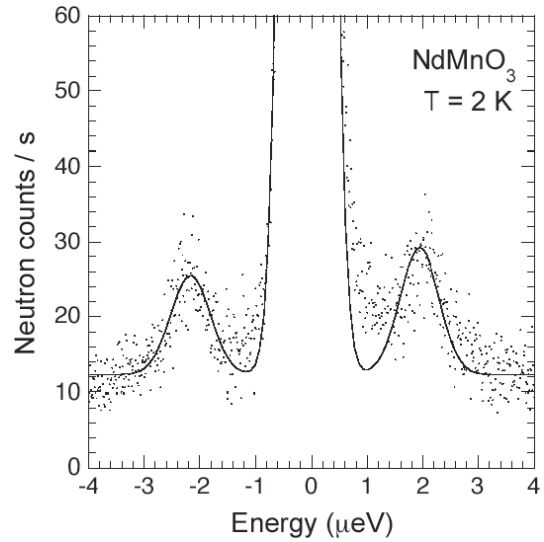


Figure 3. Typical energy spectra of NdMnO₃ measured at $T = 2$ K at the backscattering spectrometer SPHERES of the Jülich Centre for Neutron Science located at the FRMII reactor in Munich.

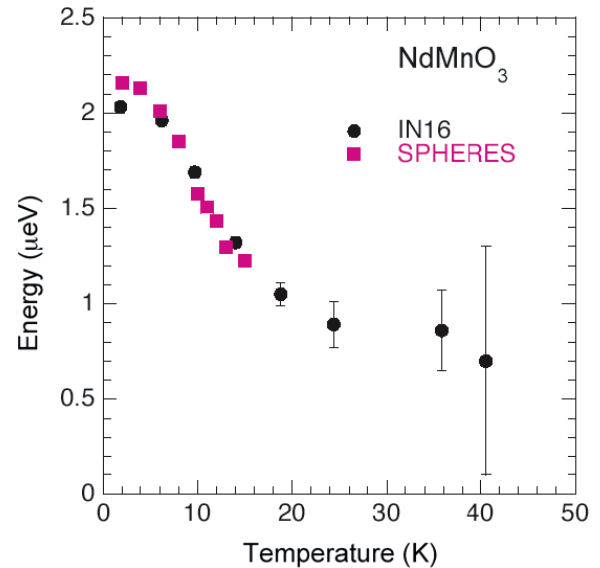


Figure 4. Temperature variation of the energy of the inelastic peak of NdMnO₃. The filled circles and squares represent data points measured on the backscattering neutron spectrometer IN16 of the Institut Laue-Langevin and on the backscattering neutron spectrometer SPHERES of the Jülich Centre for Neutron Science located at the FRMII reactor in Munich, respectively. For the visibility of the fitted curve the error bars from the data points have been removed. However, the scattering of the data clearly indicates large error bars.

suggest that the ordering temperature of the Nd sublattice is higher than $T_{Nd} \approx 13$ K determined by Munoz *et al* [17] and is about $T_{Nd} \approx 20$ K. Also there is significant polarization of the Nd moment at higher temperatures due to the magnetic field of the Mn moments that order below $T_N \approx 78$ K.

The magnetic hyperfine field at the nucleus of the Nd³⁺ ion in the ordered state in an Nd-based compound is caused

by the open 4f shell, core polarization and, if the sample is metallic, by conduction electron polarization. The dominant contribution from the 4f shell can be written as [34, 35]

$$H_{4f} = 2\mu_B \langle J || N || J \rangle \langle r^{-3} \rangle_{\text{eff}} \langle J_z \rangle. \quad (3)$$

For the $^4I_{9/2}$ ground state of Nd^{3+} the reduced matrix element $\langle J || N || J \rangle$ is 1.31 [34, 35]. We take a mean value of $\langle r^{-3} \rangle_{\text{eff}} = 5.78$ a. u. for Nd^{3+} . $\langle J_z \rangle$ is given by $\mu_z = g_L \mu_B \langle J_z \rangle$ and with $g_L = 8/11$ one calculates $H_{4f} = 129.3\mu_z$, where μ_z is the Nd^{3+} ionic moment. The contribution of core polarization is approximately given by $H_c = -90(g_L - 1)J$ which is 12.5 T for Nd^{3+} in the $^4I_{9/2}$ state. We assume that the contribution of the conduction electron polarization is negligible. So one expects a hyperfine magnetic field of $H = H_{4f} + H_c = 116.8\mu_z$ T at the Nd nucleus. Neglecting the quadrupolar term the hyperfine magnetic field at the Nd nucleus produces the splitting ΔE of $I = 7/2$ into eight equally spaced levels given by

$$H = \frac{I \Delta E}{\mu \mu_N} \quad (4)$$

where μ_N is the nuclear magneton and μ is the number of nuclear magnetons the nucleus possesses. From equations (3) and (4) one expects the energy ΔE of the inelastic line to be proportional to the ordered Nd ionic magnetic moment. From equation (4) one can calculate the hyperfine field at the nucleus from the experimental value of ΔE determined by inelastic neutron scattering provided one knows the ionic magnetic moment of the nucleus. The magnetic moments of ^{143}Nd and ^{145}Nd nuclei are tabulated by Bleaney [35] to be -1.063 ± 0.005 and $-0.654 \pm 0.004\mu_N$, respectively. We believe that in inelastic neutron scattering we mainly see the signal from ^{143}Nd . Therefore to calculate the hyperfine field from the experimental value of the splitting ΔE we use the magnetic moment of -1.063 ± 0.005 nuclear magnetons in equation (4). The hyperfine field at the ^{143}Nd nucleus is calculated to be 160.9 T for NdMnO_3 by using the experimental value $\Delta E = 1.54 \pm 0.01 \mu\text{eV}$ at 2 K. The magnetic moments of ^{143}Nd and ^{145}Nd nuclei are given in [36] to be -1.208 and -0.744 nuclear magnetons, respectively. Using these values we recalculate the hyperfine field at the ^{143}Nd nucleus from the measured ΔE to be 141.6 T for NdMnO_3 .

Figure 5 shows a plot of energy of inelastic peaks in NdCuO_4 [27], Nd metal [28], NdCu_2 [29], NdGaO_3 [30], NdMg_3 [37], NdCo_2 [37], NdAl_2 [38], NdFeO_3 [31] and NdMnO_3 versus the corresponding ionic magnetic moment of Nd in these compounds determined by the refinement of the magnetic structure using magnetic neutron diffraction intensities. The data lie approximately on a straight line, showing that the hyperfine field at the nucleus is approximately proportional to the Nd ionic magnetic moment. It is to be noted that the data for the hyperfine splitting is rather accurate whereas the ionic magnetic moment determined by neutron diffraction has a large standard deviation and is dependent on the magnetic structure model. The magnetic structure is often not determined unambiguously. Hence the ionic magnetic moment obtained by the neutron diffraction is relatively uncertain. In such cases the investigation of

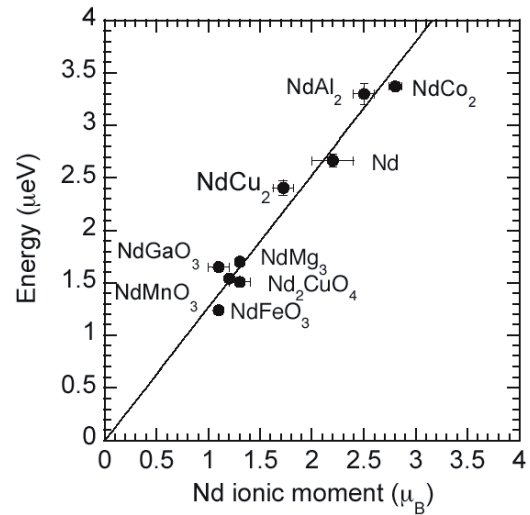


Figure 5. Plot of the energy of the inelastic signals in several Nd-based compounds versus the corresponding saturated ionic magnetic moment of Nd in these compounds at low temperatures.

the low energy excitations from the Nd magnetic sublattice described here can be of additional help. This is especially useful for the complex magnetic structures with two magnetic sublattices, such as the present compounds of high- T_c cuprate and Fe-pnictide, colossal magnetoresistive manganites and some multiferroic materials. However, this technique is useful only for a few elements due to their favourable large spin-dependent scattering cross sections. So far such low energy excitations have been observed only in compounds containing Nd, V and Co. We are, however, exploring such possibilities with other elements. The present technique is good for detecting magnetic ordering in a similar fashion as the other local probes but cannot say anything about the detailed spin configurations. For that, one has to rely on powder or single-crystal neutron diffraction techniques.

In conclusion we have investigated the low energy excitations in NdMnO_3 by the backscattering neutron spectrometer. We have resolved an old controversy and have established that Nd sublattice does order at low temperatures. The present results together with our previous results on several Nd-based compounds also show that the ordered ionic magnetic moment of the Nd ion is linearly proportional to the energy of excitations or the hyperfine splitting. In the case of complex magnetic structures with two magnetic sublattices, the present technique can give additional information about the ordered ionic magnetic moment or the ordered parameter.

Acknowledgments

We wish to thank Mr H Schneider and Dr M Prager for their help during the experiment.

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