Low-energy nuclear spin excitations in NdAl$_2$

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We investigated the low energy excitations in NdAl$_2$ in the μeV range by a backscattering neutron spectrometer. The energy scans on a NdAl$_2$ single crystal revealed inelastic peaks at $E=3.3\pm0.1$ μeV at $T=3$ K on both energy gain and energy loss sides. The inelastic peaks move gradually toward lower energy with increasing temperature and finally merge with the elastic peak at the electronic magnetic ordering temperature $T_N \approx 79$ K. We interpret the inelastic peaks to be due to the transition between hyperfine-split nuclear level of the ^{143}Nd and ^{145}Nd isotopes with spin $I=7/2$.

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Heidemann *et al.*[1–7] investigated the hyperfine fields in Co and V based compounds by using high resolution back-scattering neutron spectrometers. 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 of about 1 μeV or less 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—an expected result. Heidemann[1] worked out the double differential cross section of this scattering process. The process can be summarized as follows: if neutrons with spin **s** are scattered from nuclei with spins **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 $M\pm1$ 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 in the ground state energy $\Delta E=E_M-E_{M\pm1}$. This energy change is transferred to the scattered neutron. The double differential scattering cross section[1] is given by the following expressions:

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

(1)

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

(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 $\overline{\alpha^2}-\overline{\alpha}^2$ is zero. Also $\sqrt{1\pm\frac{\Delta E}{E_0}}\approx1$ 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. Also one expects a central elastic peak and two inelastic peaks of approximately equal

intensities. The ^{59}Co is such a case. However most of the elements have more than one isotope and therefore in general we expect both isotope and spin-incoherent scattering, and therefore the equality of the intensity of central elastic peak and two inelastic peaks is not valid. Obviously the measured spectrum will be a convolution of the cross section given in Eqs. (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 spin of $I=7/2$ and their incoherent scattering cross sections[8] are relatively large, 55 ± 7 and 5 ± 5 b for ^{143}Nd and ^{145}Nd, respectively. Taking into account the natural abundance of these isotopes the total spin-incoherent scattering of the natural Nd is $\sigma_i(\text{spin})=7.1$ b. From the bound coherent scattering lengths tabulated by Sears[8] one can calculate isotope incoherent cross section of natural Nd to be $\sigma_i(\text{isotope})=1.94$ b. The total incoherent scattering cross section of natural Nd is then $\sigma_i=\sigma_i(\text{spin})+\sigma_i(\text{isotope})$ $=9.1\pm0.8$ b. Because of relatively large spin-incoherent cross section of natural Nd, the Nd-based compounds are very much suitable for the studies of nuclear spin excitations. We did such studies on Nd metal and several Nd-based compounds[9–14] by inelastic neutron scattering and found that the energy of the excitations in these compounds is approximately proportional to the ordered $4f$ electronic magnetic

TABLE I. Ordered electronic moment of Nd and the energy of Nd nuclear spin excitations.

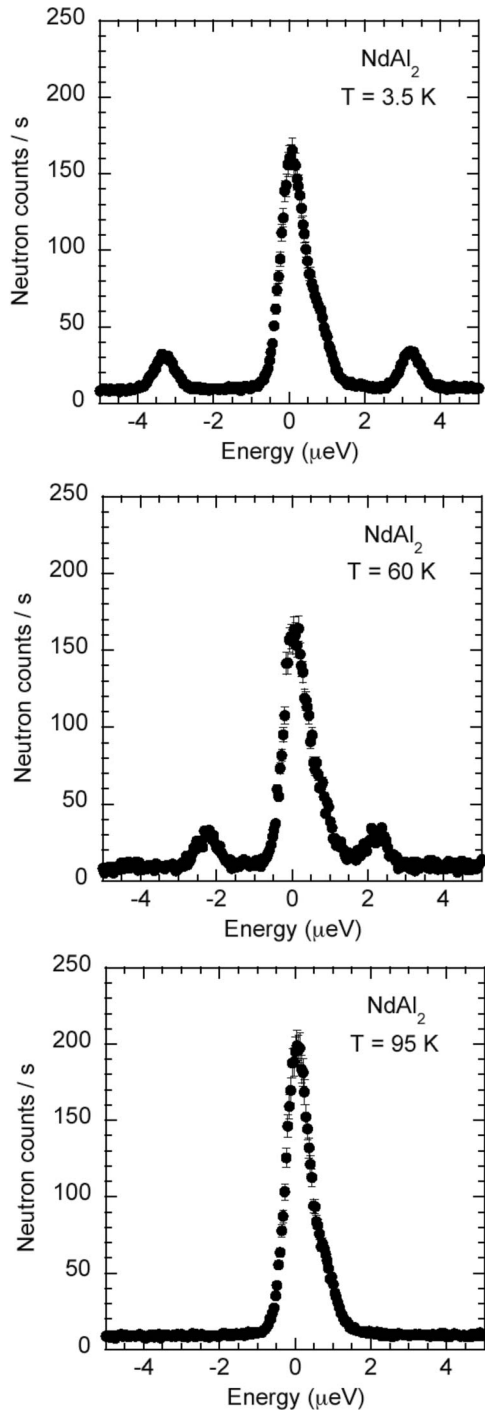| Compound	Moment (μ_B)	ΔE (μeV)	Ref.
Nd$_2$CuO$_4$	1.3(1)	1.51(5)	9
Nd	2.2(2)	2.67(6)	10
NdCu$_2$	1.72(10)	2.41(7)	11
NdGaO$_3$	1.1(1)	1.650(4)	12
NdMg$_3$	1.30(4)	1.70(1)	13
NdCo$_2$	2.80(6)	3.37(1)	13
NdMnO$_3$	1.20(2)	1.54(1)	14
NdAl$_2$	2.5(1)	3.3(1)	Present work
NdFeO$_3$	1.100(7)	1.24(1)	15

FIG. 1. Typical energy spectra of NdAl$_2$ at several temperatures.

moment that is usually much reduced from the free ion value of $3.27\mu_B$ due to the crystal-field effects. Przenioslo *et al.*[15] investigated nuclear ordering and excitations in NdFeO$_3$ and found similar results. Table I shows the results of these investigations.

In order to check the validity of the linear relationship between the ordered electronic magnetic moment and the energy of excitations or the hyperfine splitting we investigated low energy excitations in several Nd compounds that order with antiferromagnetic structures at low temperatures.

Here we have investigated the intermetallic Nd compound NdAl$_2$ that orders with a ferromagnetic structure at low temperatures. NdAl$_2$ belongs to the family of RAl$_2$ compounds that crystallizes with the fcc Laves phase crystal structure with the $Fd3m$ space group. The lattice constant of NdAl$_2$ at room temperature is 7.987 Å. Neutron diffraction investigations[16,17] have established that NdAl$_2$ undergoes a ferromagnetic transition at $T_C \approx 79$ K. The ordered electronic moment of NdAl$_2$ at low temperature has been determined by neutron diffraction[16] to be $(2.5 \pm 0.1)\mu_B$.

We performed inelastic neutron scattering experiments on a NdAl$_2$ single crystal by using the high resolution backscattering neutron spectrometer SPHERES (Ref. 18) of the Jülich Centre for Neutron Science located at the FRMII reactor in Munich. The wavelength of the incident neutrons was $\lambda = 6.271$ Å. The instrumental resolution of the SPHERES spectrometer was about 0.7 μeV. A large NdAl$_2$ single crystal of cylindrical shape with a diameter of about 8 mm and length of about 25 mm was fixed on the cold tip of a Displex refrigerator with its [110] crystallographic direction vertical. We observed inelastic signals in NdAl$_2$ at energies $E = 3.3 \pm 0.1$ μeV on both energy gain and loss sides at $T = 2$ K. The energy of the inelastic signal decreases continuously as the temperature is increased and finally merges with central elastic peak at $T_C \approx 79$ K. Figure 1 shows typical energy spectra of NdAl$_2$ at several temperatures. The spectra are the result of averaging the counts of the individual detectors placed at different scattering angles. The inelastic signals have resolution-limited widths at least at low temperatures. At higher temperatures where the inelastic peaks are very close to the central elastic peak it was difficult to determine the widths by the fitting procedure and had to be constrained. The shape of the elastic peak at $E = 0$ at low temperature is essentially determined by the resolution function of the backscattering spectrometer. The resolution function was found to be asymmetric with a shoulder on the positive energy side. We attribute the asymmetric shape to the deviation from the perfect backscattering geometrical situation. The asymmetric line shape hindered us to get a good determination of the position, intensity, and width of the inelastic peaks especially the one at the positive energy side close to the ferromagnetic ordering temperature at which the inelastic peak is very close to the central elastic peak. There are two ^{143}Nd and ^{145}Nd isotopes with nuclear spin $I = 7/2$ in NdAl$_2$. 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$_2$CuO$_4$,[9] NdCu$_2$,[11] NdGaO$_3$,[12] NdMg$_3$,[13] NdCo$_2$,[13] NdMnO$_3$,[14] and NdFeO$_3$.[15] Two inelastic lines were seen in Nd metal[10] 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$_2$CuO$_4$,[9] NdCu$_2$,[11] NdGaO$_3$,[12] NdMg$_3$,[13] NdCo$_2$,[13] NdMnO$_3$,[14] and NdFeO$_3$ (Ref. 15) is probably that the ^{145}Nd isotope contributes little to the scattering due to its smaller incoherent scattering cross section and also due to its smaller natural abundance. The other possibility is that the hyperfine fields generated by the electronic moment of the Nd ion to the ^{143}Nd and ^{145}Nd with the same nuclear spin $I = 7/2$ are almost identical and therefore the corresponding
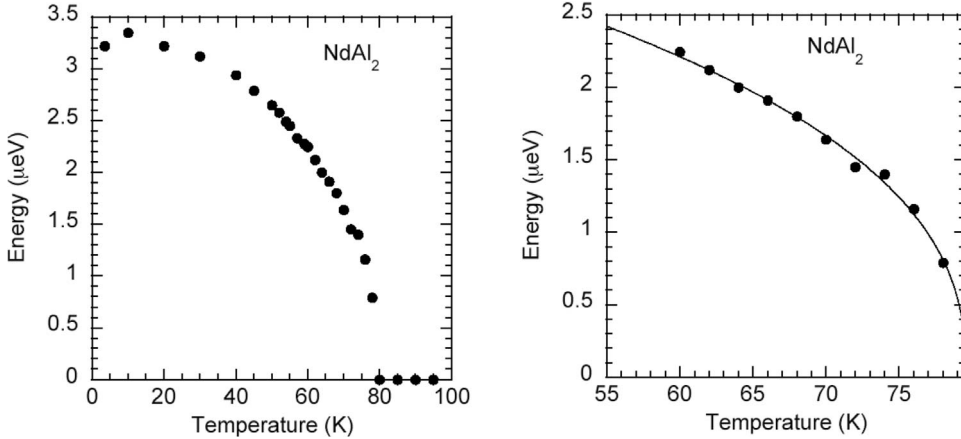
FIG. 2. (Left panel) Temperature variation of the energy of the inelastic peak of NdAl$_2$. (Right panel) Power law fit of the of the data close to T_C.

inelastic peaks appear at the same position. However the hyperfine fields at ^{143}Nd and ^{145}Nd deduced from electron spin resonance measurements[19] on Nd salts are very much different. We therefore consider that the inelastic intensity is mainly due to the scattering from the ^{143}Nd isotope.

Figure 2(a) shows the temperature dependence of the energy of the inelastic peak. The energy of the inelastic peak decreases continuously and becomes zero at $T_N \approx 79$ K. The energy of the inelastic peak can be considered to be the order parameter of the phase transition. Although there are not enough data close to the ferromagnetic transition temperature, we still attempted to extract the critical exponent from the power law fit of the data close to T_C using the equation

$$E = A[(T_C - T)/T_C]^{\beta}. \tag{3}$$

Figure 2(b) shows the result of the fit least-squares fit that gave $T_C = 79.5 \pm 0.5$ and the critical exponent $\beta = 0.39 \pm 0.03$ which is equal within experimental accuracy to the expected three-dimensional Heisenberg value[20] $\beta = 0.367$.

It is to be noted that the intensity of the inelastic peak at $T = 2$ K is about one sixth of that of the elastic peak. We already discussed that the elastic peak has additional intensity due to the isotope incoherent scattering σ_i(isotope) $= 1.9$ b of the natural Nd containing seven isotopes. The NdAl$_2$ sample and also Al sample holder give additional scattering due to the incoherent scattering cross section $\sigma_i = 0.0092 \pm 0.0007$ b of Al. Also the coherent Bragg peaks from the sample contribute to the intensity of the incoherent elastic peak. These are the possible origin of the extra intensity in the elastic peak. Heidemann *et al.*[2,3,6] observed similar excess of intensity at the elastic peak in several experiments on vanadium oxides.

The magnetic hyperfine field at the nucleus of Nd^{3+} ion in the ordered state in a Nd-based compound is caused by the open $4f$ shell, by core polarization, and if the sample is metallic, by conduction electron polarization.[19,21] The hyperfine magnetic field at the Nd nucleus produces the splitting ΔE of $I = 7/2$ into eight equally spaced levels neglecting quadrupolar term given by

$$H = \frac{I \Delta E}{\mu \mu_N}, \tag{4}$$

where μ_N is the nuclear magneton and μ is the number of nuclear magnetons the nucleus possesses. From the Eq. (4)

one expects the energy ΔE of the inelastic line to be proportional to the ordered Nd electronic magnetic moment. From Eq. (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 magnetic moment of the nucleus. The magnetic moments of ^{143}Nd and ^{145}Nd nuclei are tabulated by Bleaney[19] to be -1.063 ± 0.005 and -0.654 ± 0.004 nuclear magnetons, respectively. Different values of magnetic moments of ^{143}Nd and ^{145}Nd nuclei are given in Ref. 22 to be -1.208 and -0.744 nuclear magnetons, respectively. We argued before that the inelastic signals observed are entirely due to the ^{143}Nd. Therefore to calculate the hyperfine field from the experimental value of the splitting ΔE we use the magnetic moments of -1.063 (Ref. 19) or -1.208 (Ref. 22) nuclear magnetons in Eq. (4). Table II gives the calculated values of hyperfine fields at the ^{143}Nd for the two values of the magnetic moments.

Figure 3 shows a plot of energy of inelastic peaks in Nd$_2$CuO$_4$,[9] Nd metal,[10] NdCu$_2$,[11] NdGaO$_3$,[12] NdFeO$_3$,[15] NdMg$_3$,[13] NdCo$_2$,[13] NdMnO$_3$,[14] and NdAl$_2$ vs the corresponding electronic magnetic moment of Nd in these compounds determined by the refinement of the magnetic structure using magnetic neutron diffraction intensities. The data

FIG. 3. Plot of energy of the inelastic signals in Nd$_2$CuO$_4$ (Ref. 9), Nd metal (Ref. 10), NdCu$_2$ (Ref. 11), NdGaO$_3$ (Ref. 12), NdFeO$_3$ (Ref. 15), NdMg$_3$ (Ref. 13), NdCo$_2$ (Ref. 13), NdMnO$_3$ (Ref. 14), and NdAl$_2$ vs the corresponding electronic magnetic moment of Nd in these compounds determined by the refinement of the magnetic structure using magnetic neutron diffraction intensities.
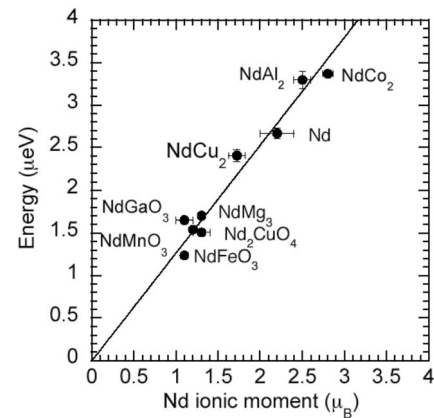
TABLE II. Hyperfine fields at the ^{143}Nd nucleus.

Compound	ΔE (μeV)	H(T) $\mu=-1.063$	H(T) $\mu=-1.208$	Ref.
Nd$_2$CuO$_4$	1.51(5)	157.7	138.8	9
Nd	2.67(6)	278.9	245.4	10
NdCu$_2$	2.41(7)	251.7	221.5	11
NdGaO$_3$	1.650(4)	172.3	151.7	12
NdMg$_3$	1.70(1)	177.6	156.2	13
NdCo$_2$	3.37(1)	352.0	309.8	13
NdMnO$_3$	1.54(1)	160.9	141.6	14
NdAl$_2$	3.3(1)	344.7	303.3	Present work
NdFeO$_3$	1.24(1)	129.5	114.0	15

lie approximately on a straight line showing that the hyperfine field at the nucleus is approximately proportional to the electronic magnetic moment. The slope of the linear fit of the data gives a value of 1.27 ± 0.03 μeV/μ_B. It is to be noted that the data for the hyperfine splitting are rather accurate whereas the magnetic moments determined by neutron diffraction have large standard deviations and are dependent on the magnetic structure models. The magnetic structures are seldom determined unambiguously and the magnetic moment determined from the refinement of a magnetic structure model is relatively uncertain. In such cases the investigation of the low energy excitations described here can be of additional help.[14] This is specially true for the complex magnetic structures with two magnetic sublattices of which one sublattice contains Nd. Such complex magnetic structures, such as the parent compounds of newly discovered Fe-based superconductors, colossal magnetoresistive manganites, and some multiferroic materials, are currently under intense study.

We interpret the inelastic signal observed in NdAl$_2$ due to the excitations of the Nd nuclear spins $I=\frac{7}{2}$ of the ^{143}Nd and also ^{145}Nd isotopes. In a first approximation one can consider these inelastic peaks to arise due to the transitions between the hyperfine-field-split nuclear levels. This is the single-nucleus effect. However the nuclear spins are coupled through Suhl-Nakamura interaction.[23,24] So one expects nuclear spin wave excitations (cooperative lattice effect) discussed by de Gennes *et al.*[25] according to which the nuclear spin waves should have dispersions at a very small q. Word *et al.*[26] discussed the possibility of measuring nuclear spin waves by inelastic neutron scattering. Also they have developed the differential scattering cross section and scattered state polarization for the scattering of neutrons from systems described by Suhl-Nakamura Hamiltonian in the formalism of van Hove correlation function. In our experiment, due to the insufficient Q resolution of the backscattering spectrometer, we could not measure the expected dispersion of the nuclear spin waves. The dispersion of the nuclear spin waves can perhaps be measured on single crystals at very low temperatures by a neutron spin echo (NSE) spectrometer.

In conclusion we have investigated the low energy excitations in NdAl$_2$ by the backscattering neutron spectrometer. The present results together with our previous results on several Nd-based compounds have shown that the ordered electronic magnetic moment of Nd ion is linearly proportional to the energy of excitations or the hyperfine splitting. In case of complex magnetic structures with two magnetic sublattices, the present technique can give additional information[14] about the ordered electronic magnetic moment or the order parameter.

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