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Nuclear magnetic resonance studies of ^{143}Nd and ^{145}Nd in Nd-Co compounds

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The nuclear magnetic resonances of ^{143}Nd and ^{145}Nd have been studied at 4.2°K in the compounds Nd_2Co_{17}, $NdCo_5$, and $NdCo_3$. The Nd hyperfine fields and quadrupole interaction parameters have been obtained. The magnetic moments derived from the hyperfine fields are found to be appreciably reduced from the free-ion value. For $NdCo_3$ a crystal-field model is used to calculate the moment reduction at the two Nd sites and the calculated moments agree well with the experimental ones. The experimental quadrupole interaction parameters are compared with calculated ones which take into account $4f$ and lattice contributions to the electric field gradient.

I. INTRODUCTION

The rare-earth cobalt intermetallic compounds have recently attracted considerable attention as permanent magnet materials because of their large magnetic anisotropies, large magnetic moments, and high Curie temperatures. From the basic hexagonal RCo_5 structure, where R denotes a rare-earth metal or yttrium, one can form a variety of related structures like R_2Co_{17} and RCo_3. The R_2Co_{17} structure is formed by the ordered replacement of certain R atoms with pairs of Co atoms, while the RCo_3 structure is formed by replacing certain Co atoms with R atoms.[1]

The magnetic anisotropy of these compounds is determined to a large extent by the single-ion anisotropy of the rare earths, as has been discussed by Greedan and Rao[2] for the RCo_5 and R_2Co_{17} compounds, and by Yakinthos and Rossat-Mignod[3] for the RCo_3 compounds. It is of considerable interest, therefore, to study in detail the way in which the crystal fields acting on the rare-earth ions affect the rare-earth magnetic moments and the magnetic anisotropy. Nuclear magnetic resonance (NMR) or Mössbauer studies of the rare-earth ions are of particular interest because the magnetic hyperfine fields are expected in general to be at least approximately proportional to the magnetic moments, while the quadrupole splittings can give information concerning the crystal fields at the rare-earth site.

In a previous paper,[4] a brief discussion of the ^{143}Nd and ^{145}Nd NMR in three compounds Nd_2Co_{17}, $NdCo_5$, and $NdCo_3$ was reported. The purpose of the present paper is to present a more detailed discussion of both the theory and experiment than was possible in the earlier paper.

A brief preliminary discussion of the magnetic structure and hyperfine interactions is given in Sec. II. Experimental techniques and results of the spectral NMR studies are given in Sec. III. In Sec. IV, the results are discussed and the hyperfine fields at various sites are compared with magnetic moments. In Sec. V, a crystal-field model is used to make a detailed calculation of the magnetic moments and magnetic anisotropy in the Nd-Co compounds. In Sec. VI, a detailed discussion of the various contributions to the nuclear quadrupole splitting is given.

II. PRELIMINARY DISCUSSION

A. Magnetic and crystallographic properties of the Nd-Co alloys

As already mentioned, both the R_2Co_{17} and RCo_3 structures can be related to the hexagonal RCo_5 structure.[5] Both $NdCo_5$ and Nd_2Co_{17} (which has a rhombohedral structure[6]) have only one type of site available to the rare-earth ion. $NdCo_3$, whose structure is isotypic with that of $PuNi_3$, has two types of rare-earth sites.[1,3] Magnetic and neutron diffraction studies have shown that in all three compounds, the total Nd and Co moments are aligned ferromagnetically corresponding to an antiferromagnetic coupling of the ionic spins.[1] Magnetic studies[7,8] indicate that for $NdCo_5$ and Nd_2Co_{17}, the easy direction of magnetization at low temperatures is in the basal plane perpendicular to the hexagonal c axis. As discussed in Ref. 2, this is in agreement with what one would expect from the sign of the crystal field acting on the rare-earth ions. In $NdCo_3$, the sign of the crystal field is different at the two types of rare-earth sites. As discussed in Ref. 3, the local anisotropy of type I ions (at $3a$ positions) would favor a magnetization perpendicular to the c axis, while that of type II ions (at $6c$ positions) would favor a magnetization along the c axis. Experimentally the magnetization at 4.2°K is found[9] to be perpendicular to the c axis like that of $NdCo_5$ and $NdCo_{17}$ indicating the greater importance of type I ions in determining the anisotropy.

B. Hyperfine interaction

If we take the nuclear quantization direction to be along the z axis, which coincides with the direction of the electronic magnetization, then the diagonal part of the nuclear Hamiltonian has the usual form

$$\mathcal{H}=a_0 I_z+P[I_z^2-\tfrac{1}{3}I(I+1)]\,. \tag{1}$$

Evaluating the above for the case of ^{143}Nd or ^{145}Nd, both of which have $I=\frac{7}{2}$, gives seven nuclear transitions. The frequency of the central $\frac{1}{2}\leftrightarrow\frac{1}{2}$ transition is just a_0/h, while the separation between adjacent transitions is just $2P/h$. The effective hyperfine field at the nucleus H_N can be obtained directly from the frequency of the central transition, while the effective electric-field gradient at the nucleus V_{zz} can be related to P through the relation

$$P=3eQV_{zz}/4I(2I-1)\,, \tag{2}$$

where Q is the quadrupole moment.

III. EXPERIMENTAL

A. Equipment and measuring technique

The ^{59}Co NMR in the Nd-Co alloys investigated occurs in the frequency range from 20 MHz to about 230 MHz, while the ^{143}Nd and ^{145}Nd NMR occurs in the frequency range from about 400 to 1000 MHz. The spin-echo equipment employed high-power pulsed oscillators, receivers, and calibration oscillators to cover the required frequency ranges. The resonant element was a tuned coil at the lower frequencies and a cylindrical quarter-wave coaxial cavity in the 400–1000-MHz range, which was tuned by varying the length of the reentrant stub. Double stub tuners were used in both input and output lines of the cavity.

The samples were prepared by melting the appropriate amounts of Nd and Co metals. The ingots were then crushed or filed into approximately 50-μm powders. X-ray studies carried out on the powders established to an accuracy of about 5% that only the major phase was present.

All measurements were carried out at 4.2 °K with an exposed-tip Dewar vessel, the tip of which fitted into the coil or cavity.

The NMR spectra were obtained by the usual technique of plotting spin-echo intensity as a function of frequency.

Although the majority of the studies were made with no external dc field, in some cases an external dc field of several kG was applied to the sample in order to help clarify the interpretation.

B. Results

Since the ^{59}Co NMR spectra were shown in detail and discussed previously, only the ^{143}Nd and ^{145}Nd results will be considered here. The ^{143}Nd NMR spectra at 4.2 °K for the three compounds which were investigated are shown in Fig. 1. We see that, in general, the resonance is split into 7 lines by the quadrupolar interaction but that in some cases the splitting is not resolved. Corresponding ^{145}Nd spectra were obtained in the range around 500 MHz. Due to the smaller quadrupole moment,[10] the ^{145}Nd quadrupole splittings were generally not resolved.

In these materials, the magnetization should be confined to the basal plane by the strong planar anisotropy which these compounds possess at low temperatures. Consequently, the NMR can be assumed to arise from nuclei associated with magnetic moments which lie in the basal plane. If we neglect any anisotropy within this plane, each crystallographic site should exhibit a unique magnetic hyperfine field and quadrupole splitting. This is seen to be the case for Nd_2Co_{17} and also for $NdCo_5$, if we neglect the lower frequency tail which extends from the main line.

$NdCo_3$ having two crystallographic sites should exhibit two hyperfine fields. If we consider the $NdCo_3$ spectra of Fig. 1, we see that in addition to the set of lines centered at around 818 MHz, a

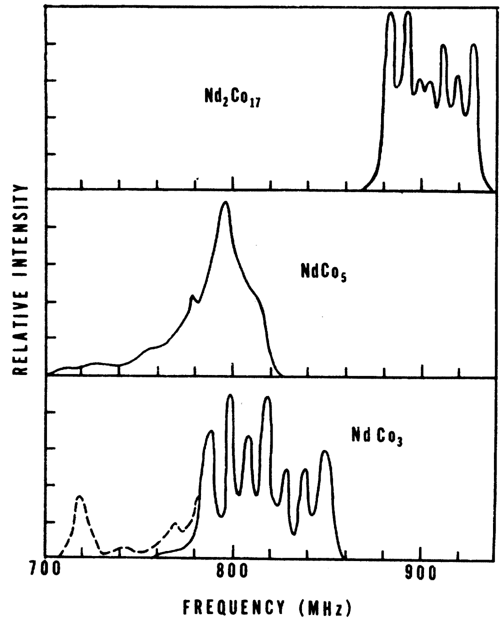

FIG. 1. The ^{143}Nd NMR spectra at 4.2 °K for the three compounds investigated. The lower frequency spectrum of $NdCo_3$ is dashed since the echo was observed with more closely-spaced exciting pulses.

second distribution of resonances appears from about 710 to 780 MHz. The transverse relaxation time T_2 for the group of lines around 818 MHz was about 50 μsec compared with a T_2 of about 3 μsec for the lower frequency set. After a correction was made for the different relaxation times, the relative intensities of the two groups of lines was found to be comparable. The unusual shape of the lower frequency spectrum may be due to relaxation effects. The fact that both sets of resonances were reduced by only a small factor when an external field of 5 kG was applied suggests that *both* sets of resonances arise from nuclei in domains (as opposed to domain walls), and that they correspond to the two types of Nd sites in $NdCo_3$. On the basis of a crystal-field calculation discussed in Sec. V, we have identified the set of resonances corresponding to the higher hyperfine field with Nd ions at the type I sites of $NdCo_3$. Center frequencies and quadrupole interaction parameters P (in frequency units) associated with sites in the different compounds are summarized in Table I. Also included for comparison is corresponding data for Nd in Gd metal obtained from NMR studies.[11] Note that the NMR studies do not allow a determination of the sign of P.

IV. DISCUSSION OF MAGNETIC HYPERFINE FIELDS

The most important contribution to the magnetic hyperfine field H_N at the rare earth arises from the $4f$ electrons of the parent ion (the "free ion" contribution). For a given rare-earth ion this contribution can be shown to be proportional to $\langle J_z \rangle$. In addition to the free-ion term, one must consider the contributions coming from conduction electrons polarized by the rare-earth spin and the spins of neighboring ions. Bleaney[12] has calculated the free-ion hyperfine field (including the contribution from core polarization) to be about 4.30×10^6 G for Nd. Since the conduction electron contributions to H_N are only of the order of $(0.1-0.2) \times 10^6$ G, we expect the proportionality between H_N and $\langle J_z \rangle$ to be fairly good. Since the rare-earth magnetic moment μ is also proportional to $\langle J_z \rangle$ we expect a fairly good proportionality between H_N and μ.

TABLE I. NMR center frequencies and quadrupole interaction parameters for various Nd compounds.

Compound	$\nu(^{143}Nd)$ (MHz)	$\nu(^{145}Nd)$ (MHz)	$P(^{143}Nd)$ (MHz)
Nd_2Co_{17}	905	563	±3.5
$NdCo_5$	795	494	±3 (or less)
$NdCo_3$ (site I)	818	507	±5
$NdCo_3$ (site II)	743	461	±4
Nd in Gd[a]	834	519	±2.3

[a]Reference 11.

TABLE II. Hyperfine fields and derived magnetic moments in various Nd compounds.

Compound	$H_N(MG)$	$\mu(\mu_B)$ calculated from H_N	$\mu(\mu_B)$ neutron diffraction
(Free ion)	4.30	3.27	
Nd_2Co_{17}	3.91	3.0	
Nd in Gd	3.60	2.7	
$NdCo_5$	3.44	2.6	2.45 ±0.30[a]
$NdCo_3$ (site I)	3.53	2.7	
$NdCo_3$ (site II)	3.21	2.4	2.4 ±0.4[b]

[a]Reference 1.

[b]Reference 3.

In Table II, we have listed the values of H_N calculated from the NMR frequencies. The nuclear moment of ^{143}Nd was taken[10] to be $-1.063\mu_N$, while the ratio $\mu_N(^{143}Nd)/\mu_N(^{145}Nd)$ was taken[13] to be 1.608. Taking for the free-ion hyperfine field a value[12] of 4.30×10^6 G, and taking the free-ion moment to be $3.27\mu_B$, we have derived magnetic moments from the H_N values by assuming a proportionality between H_N and μ. The derived values of μ are listed in Table II along with values of μ obtained from neutron diffraction studies. In those cases where a comparison is possible, the agreement is quite good.

V. MAGNETIC-GROUND-STATE CALCULATION

In the RCo_3 compounds and to some extent in the RCo_5 and R_2Co_{17} compounds, the crystal fields acting on the rare earth can become important in comparison with the exchange fields and the relatively large moment reduction from the free-ion value indicated in Table II is probably a consequence of crystal-field effects. In this section, we carry out a detailed calculation of the magnetic moments expected at the two types of rare-earth sites of $NdCo_3$.

The Hamiltonian describing the perturbations on the Nd $J=\frac{9}{2}$ level can be written as the sum of an exchange-field term and a crystal-field term[2,3]

$$\mathcal{H}=\mathcal{H}_{ex}+\mathcal{H}_c . \tag{3}$$

If we choose the quantization direction to coincide with the direction of electronic magnetization, then for the case when the magnetization is parallel to the c axis, the Hamiltonian becomes just

$$\mathcal{H}=g\mu_B J_z H_M+\alpha_J V_2^0[3J_z^2-J(J+1)] . \tag{4}$$

In the above expression, H_M is the effective exchange field acting on J, and α_J is the Stevens factor. V_2^0 is defined by the relation

$$V_2^0 = A_2^0 \langle r^2 \rangle (1 - \sigma_2) , \qquad (5)$$

where the factor $(1 - \sigma_2)$ accounts for the screening of the crystal field. Following Greedan and Rao,[2] we have neglected all terms in the crystal-field Hamiltonian except V_2^0. Other terms are found to be smaller.[14]

When the magnetization is perpendicular to the c axis, the exchange term remains the same but the effective crystal field becomes[15]

$$\mathcal{H}_c = \alpha_J \tilde{V}_2^0 [3J_z^2 - J(J+1)] + \tfrac{1}{2} \alpha_J \tilde{V}_2^2 [J_+^2 + J_-^2] , \qquad (6)$$

where

$$\tilde{V}_2^0 = -\tfrac{1}{2} V_2^0 \text{ and } \tilde{V}_2^2 = -\tfrac{3}{2} V_2^0 .$$

Values of the exchange-field and crystal-field parameters B_2^0 for the different sites in the Nd-Co compounds are listed in Table III where the notation $B_2^0 = \alpha_J V_2^0$ is used.

The crystal-field parameters B_2^0 in Table III for Nd_2Co_{17} and $NdCo_5$ were taken from Ref. 2, while those for $NdCo_3$ were taken from Ref. 3. In both cases, the B_2^0 values were obtained from point-charge calculations considering the charge on the Nd ions to be +3 and the charge on the Co ions to be zero. The value of σ_2 was taken to be about 0.6. Values of A_2^0 obtained by working back from the B_2^0 values are also listed.

For $NdCo_5$, the Nd exchange field was taken from Ref. 2 where it was determined from an analysis of the rare-earth sublattice magnetization.[16] The exchange field for Nd should be about the same in $NdCo_5$ and Nd_2Co_{17}, since the Co moments have roughly the same value in the two compounds (about $1.65\mu_B$ in Nd_2Co_{17} and $1.5\mu_B$ in $NdCo_5$), and since the rare-earth environment is similar. Yakinthos[14] has recently obtained the exchange fields for Dy in $DyCo_3$ from an analysis of the magnetic moment reduction at the two sites. We can obtain the corresponding exchange fields for Nd in $NdCo_3$ from those in $DyCo_3$ by using the relation[17]

$$H_M \sim [g - 1/g] A M_{Co} \qquad (7)$$

In Eq. (7), A should be approximately constant for a given site, M_{Co} is the Co magnetization, and g is the rare-earth "g value." Using (7) with an average cobalt moment of 1.0 in $NdCo_3$ and 0.8 in $DyCo_3$, gives the values of exchange-field parameters listed in Table III. The site II exchange field is about what one would calculate by considering the reduced moment and reduced number of Co neighbors relative to the $NdCo_5$ site. The site I exchange field seems rather small in comparison with the $NdCo_5$ value however.

Using the exchange and crystal-field parameters listed in Table III, we have calculated the eigenfunctions and eigenvalues of Eq. (3) for $NdCo_3$, for the cases of the magnetization $\vec{M}$ parallel to the c axis, and in the basal plane. The ground-state energy of the Nd ion and the magnetic moments calculated from the eigenfunctions are given in Table IV.

Note that when $\vec{M}$ is parallel to the c axis, the crystal field for site II ions is of the same sign as the exchange field for $J_z = -\frac{9}{2}$, and the result is to lower the energy of this level and stabilize this ground state. For site I ions, however, the crystal field is of opposite sign, and the ground state corresponds to $J_z = -\frac{1}{2}$. The resulting moment along the c axis is small. For $\vec{M}$ lying in the basal plane, the ground state is a mixture of different J_z levels. The moment is larger for site I ions, since now the effective diagonal crystal-field term is of opposite sign. The situation is quite analogous to that discussed for $DyCo_3$ by Yakinthos[14] where a similar moment reduction is found for $\vec{M}$ perpendicular to the c axis.

For $\vec{M}$ perpendicular to the c axis, which is the case at 4.2 °K, the calculated Nd moments 2.9 and 2.3 μ_B are in fairly good agreement with those derived from the hyperfine fields (Table II).

Taking into account the relative numbers of type I and type II sites, the average energy per Nd ion turns out to be −275 °K for $\vec{M}$ parallel to the c axis and −201 °K for $\vec{M}$ perpendicular. This is in disagreement with the fact that experimentally, $\vec{M}$ is found to be in the basal plane. The discrepancy between the crystal-field calculation and experiment may not be entirely unexpected considering that B_2^0 values based on point-charge calculations

TABLE III. Exchange-field and crystal-field parameters in Nd-Co compounds.

Compound	B_2^0/k_B (°K)	$g\mu_B H_M/k_B$ (°K)	A_2^0 (ergs/cm^2)
Nd_2Co_{17}	+0.40	115	−700
$NdCo_5$	+1.3	115	−2 500
$NdCo_3$ (site I)	+7.5	18.4	−14 500
$NdCo_3$ (site II)	−3.1	45.9	+6 060

TABLE IV. Ground-state energies of Nd ion and magnetic moments for the two sites of $NdCo_3$.

Orientation of M	Site	E/k_B (°K)	μ (μ_B)
Along c axis	Site I	−189	0.36
	Site II	−318	3.27
In basal plane	Site I	−246	2.94
	Site II	−179	2.26

were used. In fact, magnetic studies[18] and inelastic neutron scattering studies[19] of rare-earth alloys have shown large differences between point-charge crystal-field parameters and experimental ones. The discrepancy could also arise from inaccurate values of the exchange fields or from the neglect of anisotropy in the Nd-Co exchange interaction.

VI. NUCLEAR QUADRUPOLE INTERACTION

In estimating the electric field gradient at the nucleus, one must consider (i) the contribution from the $4f$ electrons of the parent ion, (ii) the contribution from the lattice charges, and (iii) the contribution from the conduction electrons. The $4f$ contribution can be written in the following form

$$eV_{zz}(4f) = -e^2\langle r^{-3}\rangle(1-R)\alpha_J\langle 3J_z^2 - J(J+1)\rangle\,. \qquad (8)$$

In the above expression, $(1-R)$ is a shielding factor and α_J is the Stevens factor that appeared in Eq. (4) and which (for Nd) is equal to -0.643×10^{-2}. For the fully polarized "free ion," where $|J_z| = J = \frac{9}{2}$, Bleaney[12] has calculated the $4f$ contribution P_{4f} to be -5.3 MHz for ^{143}Nd.

In general, J_z will be less than $\frac{9}{2}$ because of the crystal-field effects discussed in the previous section. In this case, P can be calculated directly from the wave functions obtained in the previous section, or alternatively by noting that $\langle J_z^2\rangle \approx \langle J_z\rangle^2$ and that $\langle J_z\rangle \propto \mu$. Using the latter method, we have estimated P_{4f} for ^{143}Nd for the various sites from the experimental magnetic moments. The values are listed in Table V. Note that the P_{4f} values depart significantly from the free-ion value.

The lattice contribution to the electric field gradient can be written

$$eV_{zz}(\text{lat}) = -4A_2^0(1-\gamma_\infty)\tfrac{1}{2}(3\cos^2\theta - 1)\,. \qquad (9)$$

In the above, $-4A_2^0$ is the point-charge value of $eV_{zz}(\text{lat})$, while $(1-\gamma_\infty)$ is the Sternheimer antishielding factor. Here, θ is the angle between the c axis and the magnetization direction, and the angular factor becomes just $-\frac{1}{2}$ when the magnetization is in the basal plane.

TABLE V. Contributions to the quadrupolar interaction parameter P (in MHz) for ^{143}Nd. The lattice contribution assumes an angular factor of $-\frac{1}{2}$.

Compound	P_{4f}	P_{lat}	$P_{4f+\text{lat}}$	P_{exp}
Nd_2Co_{17}	-3.9	$+0.3$	-3.6	±3.5
$NdCo_5$	-2.0	$+1.0$	-1.0	±3 (or less)
$NdCo_3$ (I)	-2.5	$+5.8$	$+3.3$	±5
$NdCo_3$ (II)	-1.2	-2.4	-3.6	±4
Nd in Gd	-2.5	$+0.5$	-2.0	±2.3

Values of P_{lat} were calculated from Eqs. (2) and (9) taking $1-\gamma_\infty = 80$ and Q (for ^{143}Nd) $= -0.484$ b. Values of P_{lat} and $P_{4f+\text{lat}}$ are listed for the different sites in Table V. The calculated $P_{4f+\text{lat}}$ values are in fairly good agreement with the experimental values from Table I. The differences between experimental and calculated values may be due to the conduction electron contribution to P.

VII. CONCLUSION

The rare-earth NMR spectra of three Nd-Co compounds have been studied and hyperfine fields and quadrupole splitting parameters have been obtained. For the case of $NdCo_3$ it appears that we are observing spectra from both types of Nd sites. The magnetic moments calculated from the hyperfine fields agree fairly well with those obtained from neutron diffraction studies. The moment reduction observed in $NdCo_3$ seems to be due in large part to crystal-field effects. The lattice contributions to the quadrupole splittings are found to be comparable with (and in some cases even larger than) the $4f$ contributions. The total calculated quadrupole splittings are found to be in fair agreement with the experimental ones.

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