

## Low-temperature spin reorientation and Co hyperfine fields in $\text{Nd}_2\text{Co}_{14}\text{B}$ studied by NMR

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A  $^{59}\text{Co}$  NMR study has been performed in  $\text{Nd}_2\text{Co}_{14}\text{B}$  for temperatures around spin reorientation (2–77 K). The onset of spin rotation was found to take place at 32 K. Taking into account the effect of the rotation on the NMR spectra the following site assignment of Co hyperfine fields has been obtained: 196(*c*), 182(*j*<sub>1</sub>), 166(*k*<sub>2</sub>), 131(*k*<sub>1</sub>), 126(*j*<sub>2</sub>), and 55(*e*) kOe. A significant hyperfine field anisotropy in the canted state was observed for the sites *c*, *k*<sub>2</sub>, and *k*<sub>1</sub>.

The discovery in 1983 of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  as an outstanding material for permanent magnets has initiated an enormous research interest in the whole family of  $R_2T_{14}\text{B}$ .<sup>1</sup> Their complex crystal structure belongs to the space group  $P4_2/mnm$  ( $D_{4h}^2$ ) (Ref. 2) and transition-metal (TM) atoms occupy six nonequivalent sites denoted as  $16k_1$ ,  $16k_2$ ,  $8j_1$ ,  $8j_2$ ,  $4c$ , and  $4e$  where the first index is the site population. Rare-earth (*R*) atoms occupy  $4f$  and  $4g$  positions and boron is on  $4g$  sites. The magnetic properties of  $R_2T_{14}\text{B}$  are determined by the exchange and crystal-field interactions. The relative importance of these interactions varies with temperature leading to a variety of spin arrangements. In particular, in  $\text{Nd}_2\text{Co}_{14}\text{B}$  a tilting of the easy magnetization direction up to  $12^\circ$  from the tetragonal *c* axis towards the  $\langle 110 \rangle$  direction has been reported below 37 K from the bulk magnetization study of a single crystal.<sup>3</sup>

In this Rapid Communication we report on the first microscopic study of this spin rotation in  $\text{Nd}_2\text{Co}_{14}\text{B}$  by recording the  $^{59}\text{Co}$  NMR spectra from 1.6 up to 77 K. This experiment shed new light on the origin of the NMR lines in this material and shows that the earlier reports on NMR in  $\text{Nd}_2\text{Co}_{14}\text{B}$  require reinterpretation. In particular, a revised site assignment of the lines and corresponding hyperfine fields should be considered in future analysis of microscopic magnetic properties.

Zero-field NMR experiments have been performed using a broadband coherent pulsed spectrometer. The  $^{59}\text{Co}$  NMR spectrum at 4.2 K is presented in Fig. 1. The higher-frequency part of our spectrum agrees in most details with spectra reported earlier,<sup>4</sup> although there are some discrepancies in the interpretation. The main difference is that we positively identify the weak signal be-

tween 191 and 204 MHz as an essential part of the Co NMR from  $\text{Nd}_2\text{Co}_{14}\text{B}$ . In addition to that, based on differences in the NMR enhancement factors and temperature dependences, we regard the signal at 217 MHz as belonging to fcc Co precipitates which are often observed in these materials. However, the most important controversy is connected with the low-frequency part of the spectrum as we interpret the structure around 55 MHz as Co NMR. A very different structure in this frequency range has been reported in Ref. 5 and interpreted as  $^{11}\text{B}$  NMR. However, a closer inspection of this spectrum leads to the conclusion that the line reported in Ref. 5 is an artifact due to a superposition of the true 55-MHz signal and a

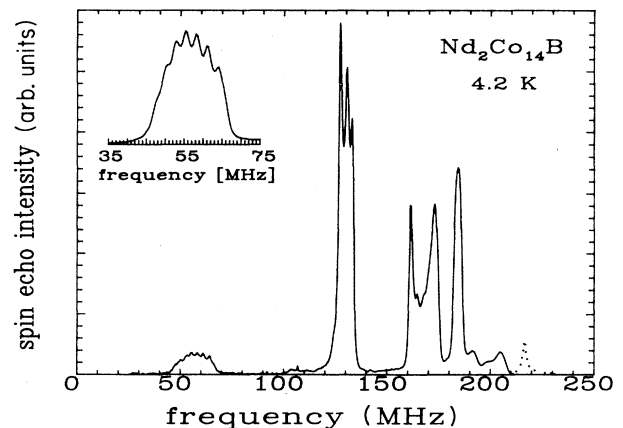


FIG. 1.  $^{59}\text{Co}$  NMR spectrum in  $\text{Nd}_2\text{Co}_{14}\text{B}$  recorded at 4.2 K. Inset: Detailed quadrupole structure around 55 MHz.

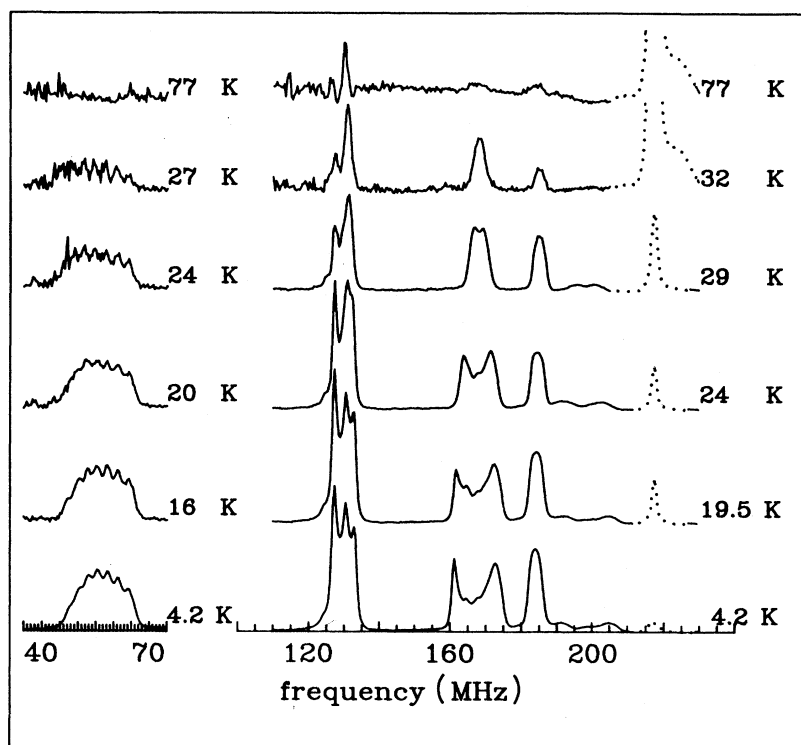


FIG. 2.  $^{59}\text{Co}$  NMR spectra in  $\text{Nd}_2\text{Co}_{14}\text{B}$  in the temperature range of spin reorientation. The frequency scale is the same for both parts of the spectrum. Intensities were scaled so as to show the most details for the two parts. Dotted lines are from fcc Co.

much stronger third subharmonic image of the 127–204-MHz resonances. The true shape of this line (shown in the inset) with seven quadrupolar peaks shows that it belongs to  $^{59}\text{Co}$  ( $I = \frac{7}{2}$ ). Moreover, extrapolating the  $^{11}\text{B}$  frequencies measured in the easy plane  $\text{R}_2\text{Co}_{14}\text{B}$  (Ref. 6) to the case of  $\text{Nd}_2\text{Co}_{14}\text{B}$  the  $^{11}\text{B}$  line is expected at much lower frequency in the latter. An unlikely possibility that the line at 55 MHz arises from Co in precipitations of other phases is ruled out by the relative line intensities and the temperature dependence of the signal, of which a detailed discussion is given below.

NMR spectra recorded at various temperatures as the sample was undergoing the transition from the canted to the uniaxial state are presented in Fig. 2. For the sake of resolution the data were taken separately for the 55-MHz structure and the high-frequency part of the spectrum. The dotted line in Fig. 2 represents the signal from fcc Co which can serve as a reference for the signal intensity. With increasing temperature the intensity of the lines belonging to  $\text{Nd}_2\text{Co}_{14}\text{B}$  drops drastically with respect to fcc Co particularly above 30 K. In the uniaxial state the signal falls below the detectable level and could be recovered at 77 K only through very long accumulation (500 scans). The same rapid drop of intensity is observed above 30 K for the 55-MHz line confirming that it belongs to  $\text{Nd}_2\text{Co}_{14}\text{B}$ .

While the position of the lines does not change significantly between 32 and 77 K the effect of canting below 32 K is very pronounced on the evolution of the spectrum shape. Indeed as the magnetization rotates away from the

$c$  axis its in-plane component introduces magnetically nonequivalent sites for each crystallographic position. This is reflected in the development of a doubletlike structure in some of the lines. Hyperfine field values corresponding to singularities on the spectrum (maxima and shoulders) are presented in Fig. 3(a) as a function of temperature. Obviously the lines are not equally affected by the in-plane component of the magnetization: The largest splitting is observed for the lines at 198, 168, and 131 MHz whereas the lines at 55, 127, and 184 MHz do not exhibit significant changes. Since the splitting is a measure of the in-plane anisotropy on each Co site, it is clear that the anisotropic properties differ strongly from site to site. Figure 3(b) shows the thermal variation of the doublet separation for the two most split lines normalized to its 1.6-K value. It reflects the thermal variation of the in-plane magnetization responsible for the splitting and hence that of the tilt angle (for small angles). A similar temperature dependence of the tilt angle has been reported for  $\text{Nd}_2\text{Fe}_{14}\text{B}$ .<sup>7</sup> The continuous character of the changes suggests a second-order transition and the extrapolated temperature for the collapse of the doublets is 32 K in agreement with the bulk magnetization studies.<sup>3</sup>

The analysis of the spectrum shape and of its temperature dependence clearly shows that the spectrum consists of six lines—some with a doublet structure—which agrees with the number of crystallographic Co sites. The integral intensities of all the lines (singlets or doublets) have been calculated in the whole investigated temperature range and their relative contribution to the overall spec-

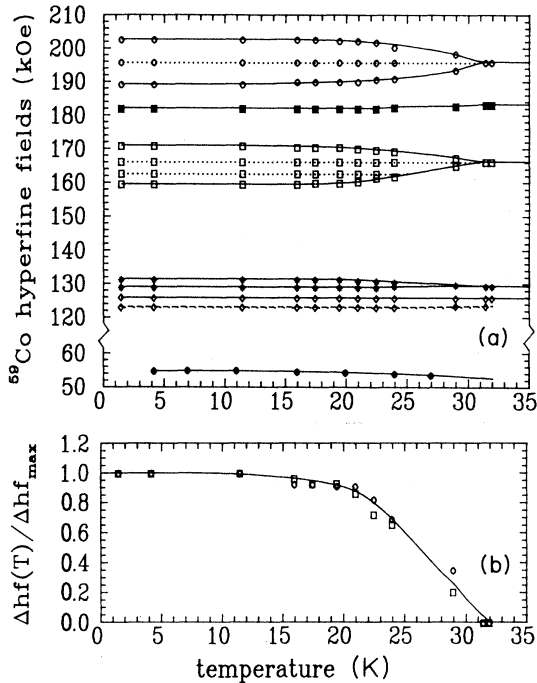


FIG. 3. (a) Hyperfine field corresponding to singularities in the spectra (solid lines: maxima; dotted lines: shoulders) as a function of temperature. The hyperfine field for the 55-MHz quadrupole structure is given by its central peak. (b) Temperature dependence of the hyperfine field splitting normalized to its value at 1.6 K:  $\square$ ,  $16k_2$  line (168 MHz);  $\circ$ ,  $4c$  line (198 MHz).

trum intensity is plotted in Fig. 4. In spite of some scatter they clearly concentrate around three values (28.6%, 14.3%, and 7.1%) which represent the correct population ratios of 16:16:8:8:4:4 atoms per unit cell. This result provides a well-founded experimental basis for grouping the respective NMR lines into the following couples of equally populated sites:  $k$  type, 131 and 168 MHz;  $j$  type, 127 and 184 MHz,  $e$  and  $c$  types, 55 and 198 MHz. A further distinction between the  $k$  sites can be made based on our NMR data in  $\text{Nd}_2(\text{Co}_{1-x}\text{Fe}_x)_{14}\text{B}$ .<sup>8,9</sup> The  $k_2$  line originating from the site which is preferentially occupied by Co and clearly visible in samples with high Fe content can be traced in the whole range of compositions; this allows us, in the limit of  $x=0$ , to locate the  $K_2$  line at 168 MHz and consequently the other intense line at 131 MHz is assigned to the  $k_1$  site. This assignment agrees with the results of neutron-diffraction studies which yield a much stronger value of the magnetic moment on the  $k_2$  site than

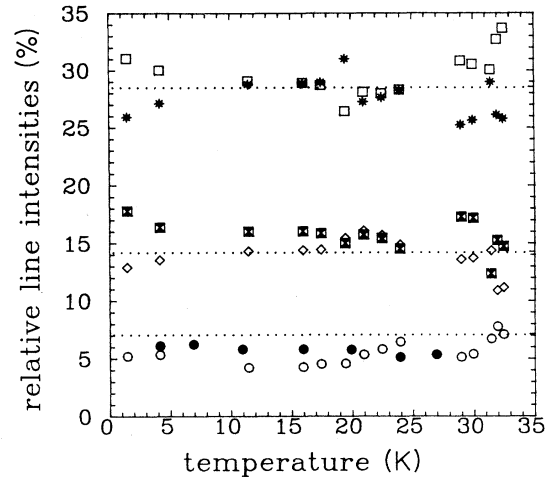


FIG. 4. Relative contribution of particular lines to the overall NMR spectrum intensity:  $*$ ,  $16k_1$  line (131 MHz);  $\square$ ,  $16k_2$  (168 MHz);  $\blacksquare$ ,  $8j_1$  (184 MHz);  $\diamond$ ,  $8j_2$  (127 MHz);  $\circ$ ,  $4c$  (198 MHz);  $\bullet$ ,  $4e$  (55 MHz).

on the  $k_1$  site.<sup>10</sup> Considering the preferential  $j_2$  site occupancy by Fe<sup>10,11</sup> and the relative intensity loss in the low-frequency part of the Co spectra in  $\text{Nd}_2(\text{Co}_{1-x}\text{Fe}_x)_{14}\text{B}$  (Ref. 9) for  $x > 0.5$ , a similar argument leads us to suggest that the 127-MHz line originates from the  $j_2$  site and the 184-MHz line from  $j_1$ . However, because of the low resolution of the NMR spectra in this concentration range this particular distinction has to be treated tentatively and needs to be verified. The neutron-diffraction data cannot help in this case since they yield equal values for the moments on both  $j$  sites. As to the lowest occupancy sites  $e$  and  $c$ , our data yield for these sites the lowest and highest values of hyperfine fields. A striking feature of the 55-MHz line is a very strong quadrupolar splitting ( $\nu_Q=3$  MHz), revealing a considerable electric field gradient at this site. Considering the asymmetry of local atomic arrangement around the  $e$  site one can predict a strong electric field gradient (EFG) at this position, leading us to assign the 55-MHz line to the  $e$  site. An equally strong EFG on the  $e$  site has also been observed for Fe in the latest Mössbauer experiments<sup>12</sup> which supports our conclusion. Consequently, the line at 198 MHz is attributed to the  $c$  site. This assignment is also supported by the neutron-diffraction data<sup>10</sup> which find the highest magnetic moment on the  $c$  site and a distinctly low moment on the  $e$  site.

The hyperfine field values resulting from our site assign-

TABLE I. Hyperfine field, hyperfine field splittings, and magnetic moments in  $\text{Nd}_2\text{Co}_{14}\text{B}$  at 4.2 K.

Site	$c$	$j_1$	$k_2$	$k_1$	$j_2$	$e$
Hyperfine field (kOe)	196.0	182.1	166.3	129.5	125.7	54.8
Hyperfine field splitting	13.1	0.0	10.9	2.4	0.0	0.0
Magnetic moment <sup>a</sup> ( $\mu_B$ )	1.8	1.5	1.7	1.2	1.5	0.9
Hyperfine coupling (kOe/ $\mu_B$ )	109	121	98	108	84	61

<sup>a</sup> Neutron diffraction data (Ref. 10).

ment, the low-temperature splitting of hyperfine fields on particular Co sites (reflecting the in-plane anisotropy), and the magnetic moments from Ref. 10 are presented in Table I. The strong correlation between the hyperfine fields given by NMR and the magnetic moments given by neutron diffraction confirms the proposed line identification. Differences between the field/moment ratios (hyperfine coupling) on the six sites (particularly for the  $e$  site) are attributed to small differences in the orbital contribution to the moment.

In conclusion, by monitoring the evolution of NMR spectra during the spin reorientation, their complex struc-

ture could be understood. Based on this and additional criteria such as line intensities, preferential substitution, and symmetry of the atomic arrangement, Co hyperfine fields have been determined for all six crystallographic positions. The proposed site assignment is self-consistent and supported by other experiments. As such it provides the basis for further analysis of the role played by Co in the  $R_2T_{14}B$  systems.

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