PHYSICAL REVIEW B
CONDENSED MATTER

THIRD SERIES, VOLUME 36, NUMBER 16 1 DECEMBER 1987

NMR study of Fe hyperfine field assignments in $Nd_{15}Fe_{77}B_8$ and Co site preference in $Nd_{15}Fe_{77-x}Co_xB_8$

Y. D. Zhang,* J. I. Budnick, and M. Wojcik†
Department of Physics and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268

E. Potenziani II
U.S. Army Electronics Technology and Devices Laboratory (LABCOM), Fort Monmouth, New Jersey 07703-5000

A. T. Pedziwiatr and W. E. Wallace
MEMS Department and Magnetic Technology Center, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

(Received 22 June 1987)

The ^{10}B, ^{11}B, and ^{57}Fe hyperfine field distributions for ^{10}B-enriched $Nd_{15}Fe_{77}B_8$ and $Nd_{15}Fe_{77-x}Co_xB_8$ ($x<12$) were measured by spin-echo NMR at 1.3 and 4.2 K for frequencies from 10 to 70 MHz. Using 98% ^{10}B enrichment makes the ^{57}Fe resonances more pronounced, which enabled us to precisely determine the hyperfine field values. As suggested by the spin-echo amplitudes and the frequency shifts caused by Co substitution, the assignment of the measured hyperfine fields of $Nd_{15}Fe_{77}B_8$ to the six Fe sites is tentatively the following: $378(j_2)$, $352(k_2)$, $334(j_1)$, $325(k_1)$, $320(c)$, and $302(e)$ kOe. The substitution of Co for Fe decreases the hyperfine fields at the Fe nuclei at the j_2, k_2, j_1, k_1, and c sites, while no obvious change in the hyperfine field at the e-site Fe nuclei nor at the B nuclei has been found. The spin-echo amplitude corresponding to the $Fe(k_2)$ site line decreases drastically with Co content. These results demonstrate that Co atoms have a strong preference to substitute for the $Fe(k_2)$ atoms.

I. INTRODUCTION

There has been considerable attention given in the last few years to Nd-Fe-B alloys for basic research and applications since the first discovery of the $Nd_{15}Fe_{77}B_8$ permanent magnet.[1,2] Hyperfine interaction experiments, including Mössbauer and NMR, have proven to be valuable in investigating the details of the structure, magnetic-moment distribution, and relative properties of the alloys on a very local scale.[3–9] In the study of the hyperfine field (HF) in Nd-Fe-B alloys the first and, perhaps, the most fundamental task is to determine the HF values at the six Fe sites ($16k_1$, $16k_2$, $8j_1$, $8j_2$, $4c$, and $4e$), the two Nd sites ($4f$ and $4g$), and the single B ($4g$) site in $Nd_2Fe_{14}B$ which is the main phase of $Nd_{15}Fe_{77}B_8$. There is, however, a significant variation in site assignments for the Fe HF values reported from Mössbauer studies due probably to the complexity of analysis for the six superposed sextet spectra of this system. Therefore, the final HF assignment to individual Fe sites is still somewhat unresolved in detail.

It is well known that the substitution of Co for Fe significantly improves the Curie temperature of this material.[10–12] In order to understand the change in magnetic properties caused by such substitution, it is important to determine whether Co substitutes for Fe randomly or selectively. The Mössbauer experiment on an Fe-doped $Nd_2Fe_{14}B$ showed a strong preference for Co atoms occupying the k_2 site,[13] while neutron diffraction seemed to support e-site preference.[14]

The NMR technique generally provides more precision than Mössbauer experiments in determining individual HF values. With increasing Co content, the Fe atomic moments may decrease as the number of their nearest Fe neighbors is decreased. For different sites, the amount of variation may be different, depending on the local site configuration and the site selection by Co atoms. Thus an NMR study of the variation in the HF of the Nd-Fe-Co-B system can provide insight concerning both the assignment of the Fe HF and the site preference of Co atoms.

II. SAMPLES AND EXPERIMENTS

In the present work all samples were made by arc melting. Two samples with the same composition

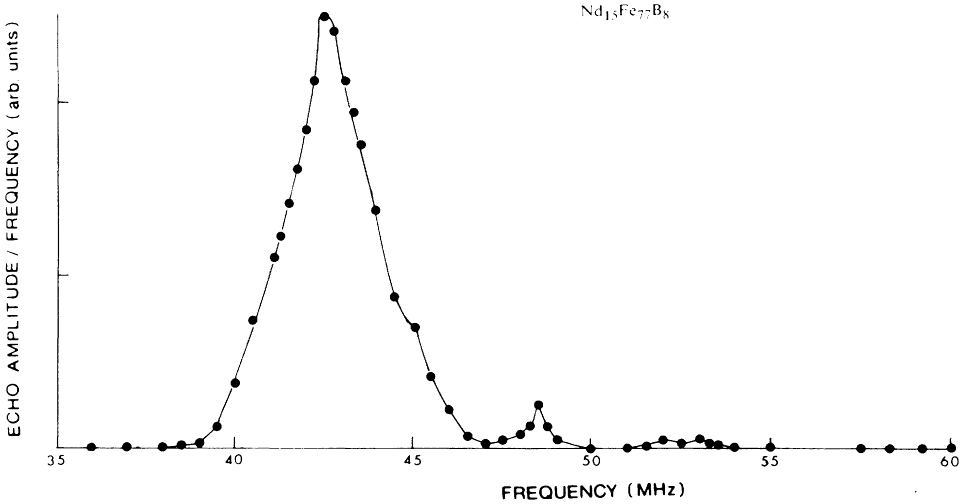

FIG. 1. Spin-echo amplitude divided by frequency in arbitrary units vs frequency in MHz at 4.2 K for naturally abundant $Nd_{15}Fe_{77}B_8$.

$Nd_{15}Fe_{77}B_8$ were made using naturally abundant and 98% ^{10}B-enriched boron, respectively; all other samples, namely $Nd_{15}Fe_{77-x}Co_xB_8$ with $x=3.9$, 7.0, and 12.0 were made using 98% or 94% ^{10}B-enriched boron. The ingots were then ground to a fine powder for x-ray and NMR experiments.

The samples were first checked by Cu $K\alpha_1$ x-ray diffraction using a Norelco diffractometer. The diffraction patterns obtained from these samples fit the tetragonal $Nd_2Fe_{14}B$ phase very well. The lattice parameters for $Nd_{15}Fe_{77}B_8$ computed by least-squares analysis are $a=8.805$ Å and $c=12.189$ Å, which are very close to the previously reported values.[1] As the Co content is increased, both a and c decrease monotonically, similar to the result shown in Ref. 15.

The ^{57}Fe, ^{10}B, and ^{11}B spin-echo NMR measurements of the HF distributions and the relaxation time T_2 were carried out at 1.3 and 4.2 K with zero magnetic field and for frequencies ranging from 10.0 to 70.0 MHz. It was found that as the spin-echo amplitude is very sensitive to

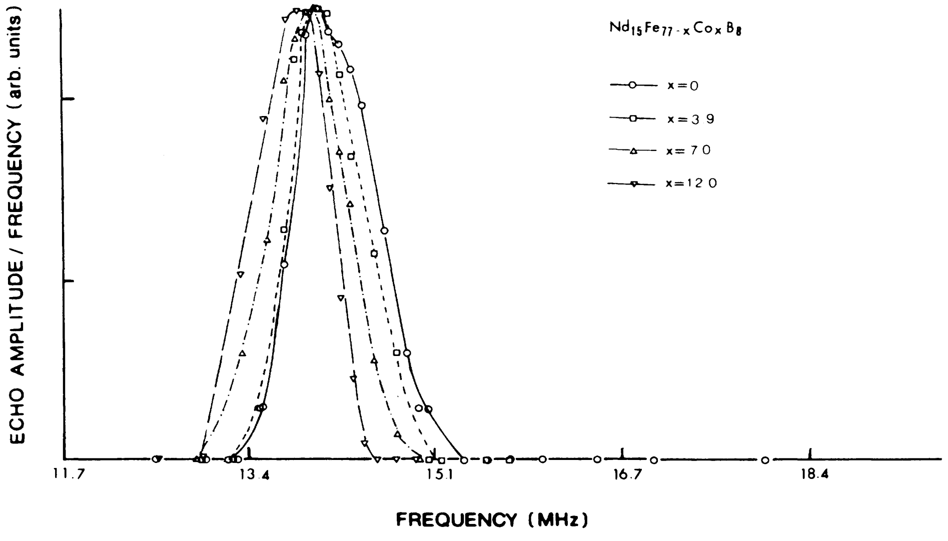

FIG. 2. The ^{10}B spin-echo amplitude divided by frequency in arbitrary units vs frequency in MHz at 1.3 K for $Nd_{15}Fe_{77-x}Co_xB_8$.

excitation power, the equipment was adjusted to get the optimum spin-echo shape and the maximum intensity at each peak for low-power excitation.

III. RESULTS AND ANALYSIS

$Nd_{15}Fe_{77}B_8$ without boron enrichment was used for a preliminary study. The resultant NMR spectrum of this sample at 4.2 K is shown in Fig. 1. The resonances centered at 52.5 and 48.5 MHz are in good agreement with a previously reported result on a $Nd_2Fe_{14}B$ sample.[4] The peak at 42.3 MHz originates from ^{11}B, which is definitely identified by a ^{10}B NMR measurement ranging from 13.0 to 15.0 MHz. The ^{11}B resonance is so strong that it almost overlaps all Fe peaks between 40 and 47 MHz and it is hard to separate the ^{57}Fe signal from the ^{11}B resonance by using the ^{10}B NMR spectrum. This is the reason that we use ^{10}B-enriched samples.

Figure 2 shows the ^{10}B NMR spectra of the ^{10}B-enriched $Nd_{15}Fe_{77-x}Co_xB_8$ samples for the compositions $x=0$, 3.9, 7.0, and 12.0. It is worthwhile mentioning that the ^{10}B spectrum of ^{10}B-enriched $Nd_{15}Fe_{77}B_8$ is identical to that of the naturally abundant sample implying that the use of ^{10}B does not cause any change in the structure of the specimens. Figure 2 shows that the addition of Co has a small effect on the HF at B nuclei. From $x=0$ to $x=12$ only an 0.18 MHz, or 1.3%, shift toward low frequency was observed.

Figure 3 shows the ^{57}Fe NMR spectrum obtained at 1.3 K for the various compositions of $Nd_{15}Fe_{77-x}Co_xB_8$

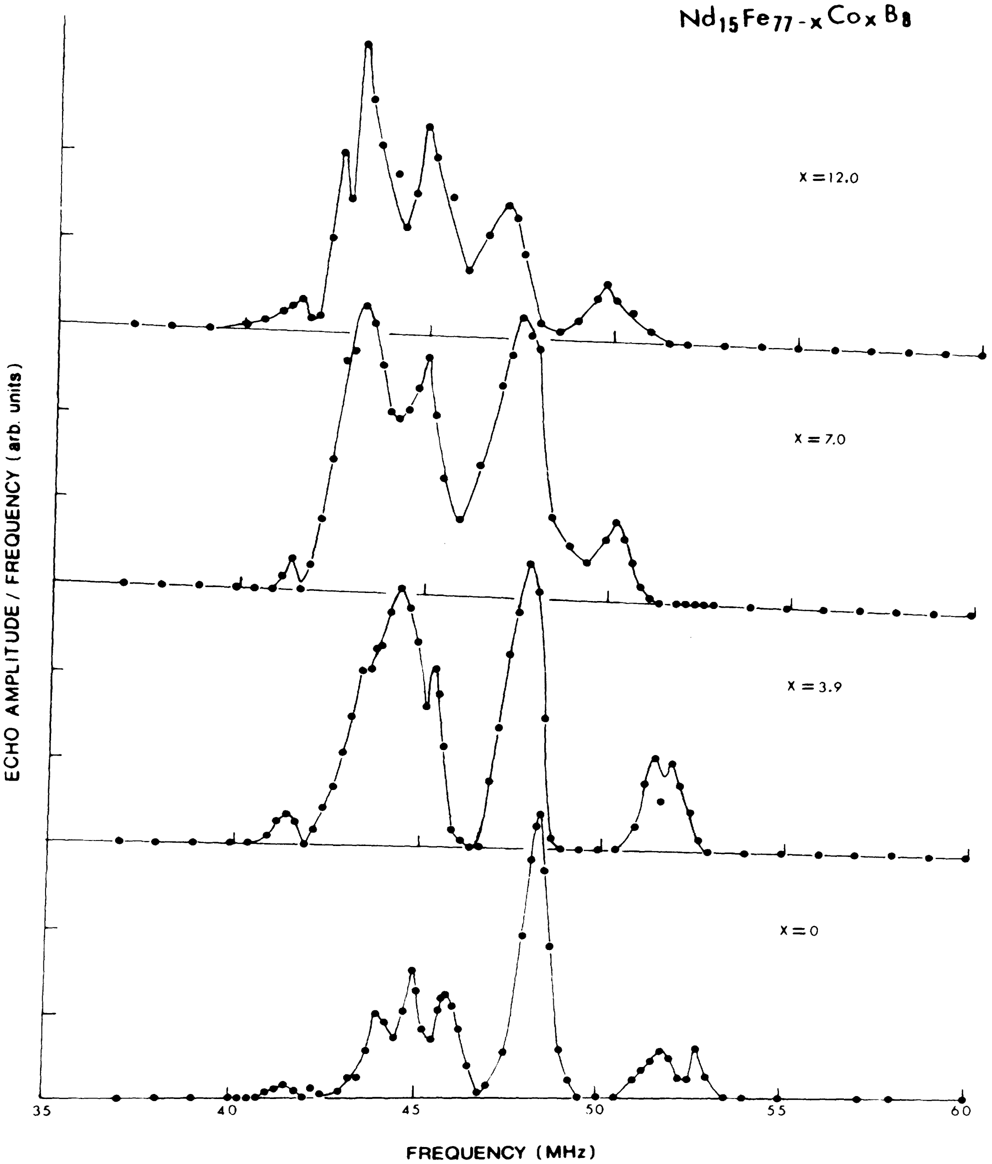

FIG. 3. The ^{57}Fe spin-echo amplitude divided by frequency in arbitrary units vs frequency in MHz at 1.3 K for $Nd_{15}Fe_{77-x}Co_xB_8$.

TABLE I. NMR and Mössbauer data on the tetragonal $Nd_2Fe_{14}B$ phase.

NMR						
f (MHz)	52.5	48.5	46.0	44.7	44.0	41.5
HF (kOe)	378	352	334	325	320	302
Mössbauer (Refs. 3–7)						
HF (kOe)	370–400	350–366	325–342	324–335	320–322	254–320
Assignments	j_2,c	c,e,k_2	j_1,k_1,k_2	j_1,k_1,e	j_1,j_2,k_1,c	e,c,j_1

alloys, from which distinct resonance lines are very well illustrated. For $x=0$, the peak frequencies and corresponding HF values obtained in the present work are listed in Table I together with the values and the assignments from Mössbauer experiments.[3–7] The two peaks at 52.0 and 53.0 MHz could be understood on the basis of a large dipolar splitting at the j_2 site, concluded from recent Mössbauer results.[6] For reference, a ^{10}B-enriched $Nd_2Fe_{14}B$ compound was also measured, and the resultant NMR spectrum of $Nd_2Fe_{14}B$ was found to be the same as for $Nd_{15}Fe_{77}B_8$. This means that the phase that NMR sees in $Nd_{15}Fe_{77}B_8$ is tetragonal $Nd_2Fe_{14}B$ despite the existence of other phases in this material. Figure 3 shows that as the Co content is increased, a majority of the peaks shift toward low frequency. The highest resonance line, 52.5 MHz for $x=0$, experienced the largest change to 49.7 MHz for $x=12$, while the 41.5 MHz resonance does not have any obvious shift. Another effect of Co substitution shown in Fig. 3 is on the spin-echo intensity. Throughout the entire composition range the relative amplitude for 52.5 MHz resonance does not change, while the peak of the 48.5 MHz resonance decreases drastically; the peak amplitude ratio of the 48.5 MHz line to the 52.5 MHz line varies from 6.5 for $x=0$ to 2.1 for $x=12$. Table II summarizes the variations in NMR frequencies and the relative intensity ratio by both the peak amplitude and the integrated intensity.

IV. DISCUSSION

As mentioned above, the spin-echo signals of these samples come from the ^{10}B, ^{11}B, and ^{57}Fe located within the tetragonal $Nd_2Fe_{14}B$ phase, in which the HF at each site is dependent on the local atomic environment. Table III lists the site population, the total Fe and B coordination, and the individual Fe coordination at each Fe site, according to Ref. 16. In the Mössbauer studies in this system, the assignment of the six HF values to the six Fe sites was based on their site population, namely, the six subspectra were constrained in intensity ratio 4:4:2:2:1:1. It turns out from Table I that the divergence of the six HF values obtained from different Mössbauer experiments[3–7] is not too much; the assignments, however, were rather different. As pointed out by Buschow, this situation implies that the intensity alone may be not sufficient for the assignment.[9] Similarly, in the consideration of site assignment using NMR spectra, the first fact we can use is to relate the spin-echo intensity to the site population. From this point of view the strongest peaks at 44.7 and 48.5 MHz may originate from the Fe nuclei at k-type sites while the smallest peaks originate from the Fe nuclei at e and c sites. However, as shown in Fig. 2, the spin-echo intensities do not exactly follow the site population. For instance, the 48.5-MHz resonance is about twice as large as the 44.7-MHz line. It makes a final and complete assignment at this time by using the NMR intensity alone questionable. On the other hand, unless Co substitutes for Fe randomly, the frequency shifts for each site must be consistent with their local environments as described in Table III. This provides another criterion to help in the assignment.

In the tetragonal $Nd_2Fe_{14}B$ the B atom is located at the center of the trigonal prism formed by two Fe(e) and four Fe(k_1) atoms. Three Nd atoms are bonded to the B atom through the rectangular prism faces with rather large distance.[17] It has been found from the ^{11}B NMR measurements of $R_2Fe_{14}B$ compounds with $R=$Nd, Y, La, and Ce that the main contribution to the transferred hyperfine field (THF) at B nuclei comes from Fe atoms.[4,18,19] Neglecting the contribution of Nd, the THF at ^{11}B can be written as

$$H(B)=[2\mu_{Fe}(e)+4\mu_{Fe}(k_1)]a\ ,$$

TABLE II. NMR data of $Nd_{15}Fe_{77-x}Co_xB_8$.

x	NMR frequency (MHz)						$I(k_2)/I(j_2)$ Peak amplitude	$I(k_2)/I(j_2)$ Integrated intensity
	j_2	k_2	j_1	k_1	c	e		
0	52.5	48.5	46.0	44.7	44.0	41.5	6.5	4.0
3.9	51.5	48.0	45.5	44.3	43.3	41.5	3.5	3.2
7.0	50.5	47.5	45.0	43.5	42.5	41.5	3.3	3.2
12.0	49.8	47.0	44.8	43.0	42.2	41.0	2.1	2.3
	(2.7)	(1.5)	(1.2)	(1.7)	(1.8)	(0.5)		

TABLE III. Fe and B coordination of each Fe site in $Nd_2Fe_{14}B$.

Site	j_2	k_2	j_1	k_1	c	e
Population	8	16	8	16	4	4
B	0	0	0	1	0	2
Total Fe	12	10	9	9	8	9
Fe(k_2)	4	3	2	3	4	0
Fe(k_1)	4	3	2	1	4	4
Fe(e)	1	0	1	1	0	1
Fe(c)	0	1	0	1	0	0
Fe(j_1)	3	1	1	1	0	2
Fe(j_2)	0	2	3	2	0	2

where $\mu_{Fe}(e)$ and $\mu_{Fe}(k_1)$ are the magnetic moments at the e- and k_1-site iron atoms, respectively, and a is the THF coupling constant which we roughly treat to be the same for e and k_1 site iron atoms. Taking $\mu_{Fe}(e)=2.10\mu_B$ and $\mu_{Fe}(k_1)=2.60\mu_B$ as obtained by neutron diffraction,[20] we get $a=2.12$ kOe/μ_B. If Co substituted for Fe randomly, then for the composition $x=12$, nearly one Fe atom among these six nearest Fe neighbors would have been replaced on average, and hence an estimated THF change as large as 2.1 kOe or 0.98 MHz for the ^{10}B resonance frequency shift should have been observed when taking $\mu_{Co}=1.4\mu_B$.[21] If, on the other hand, Co substituted preferentially for Fe at the e site, then for the composition $x=7.0$, the Fe atoms at this site would have been completely replaced and it would have produced a 1.4-MHz shift of the ^{10}B resonance frequency. However, only an 0.18-MHz shift was observed up to $x=12$, as shown in Fig. 2. This result means that the replacement of Co for Fe is selective, but neither for the e- nor for the k_1-site Fe atoms.

The peaks centered at 48.5 and 44.7 MHz are much stronger than the other lines, and they probably come from the k_1- and k_2-site Fe atoms. As the Co content is increased, the spin-echo intensity of the 48.5-MHz line drops drastically. The ratio of the spin-echo amplitudes between the 48.5- and 52.5-MHz lines decreases from 6.5 for $x=0$ to 2.1 for $x=12$. This clearly shows that Co preferentially occupies this site. Since Co atoms do not preferentially occupy the k_1 site, the 48.5-MHz resonance is therefore thought to originate from Fe(k_2) atoms and the 44.7-MHz resonance from Fe(k_1) atoms. The substitution of Co for the Fe(k_2) can be used to identify the site occupation of other lines in that the more Fe(k_2) surrounding a given Fe site, the larger the frequency shift for this site will be.

As demonstrated by neutron diffraction, the Fe atom at the j_2 site has the largest moment,[20] so we tentatively assign the 52.5-MHz resonance line to the j_2 site. Other evidence for assigning this line to j_2 is its large frequency shift, which occurs when replacing Fe by Co, being consistent with the largest number of Fe(k_2) near neighbors to the j_2 site (Table III). The fact that the spin-echo intensity of this peak does not vary with Co content is also compatible with the preference of Fe atoms for the j_2 site.[13,14,22] The 46.0-MHz resonance is then attributed as originating from the ^{57}Fe at the j_1 site based on both its intensity and the frequency shift of this line. Again, the frequency shifts can be used to distinguish between resonances of Fe atoms belonging to the c and e sites. The Fe atom at the c site has four nearest Fe(k_2) neighbors while the Fe atom at the e site has no Fe(k_2) in its nearest-neighbor shell (Table III). Based on this, the 44.0-MHz resonance is thought to originate from Fe(c), as a large frequency shift (1.8 MHz) was found with increasing Co concentration up to 12 at. %, while the 41.5-MHz line originates from Fe(e) since there was only a 0.5-MHz shift for this line. Thus, the overall NMR behavior supports the present assignment and the preference of Co atoms for the k_2 site. If Fe(k_1), rather than Fe(k_2), atoms were responsible for the 48.5-MHz resonance, the Co substitution would not produce a large frequency shift for the 44.7-MHz resonance since the k_1 site has only one Fe(k_1) atom in its nearest-neighbor shell. Even though the present NMR relative intensity ratios are not completely understood at this time, we conclude that a clear resolution of individual Fe sites is achievable from the NMR results. These NMR results should be considered in reevaluating the

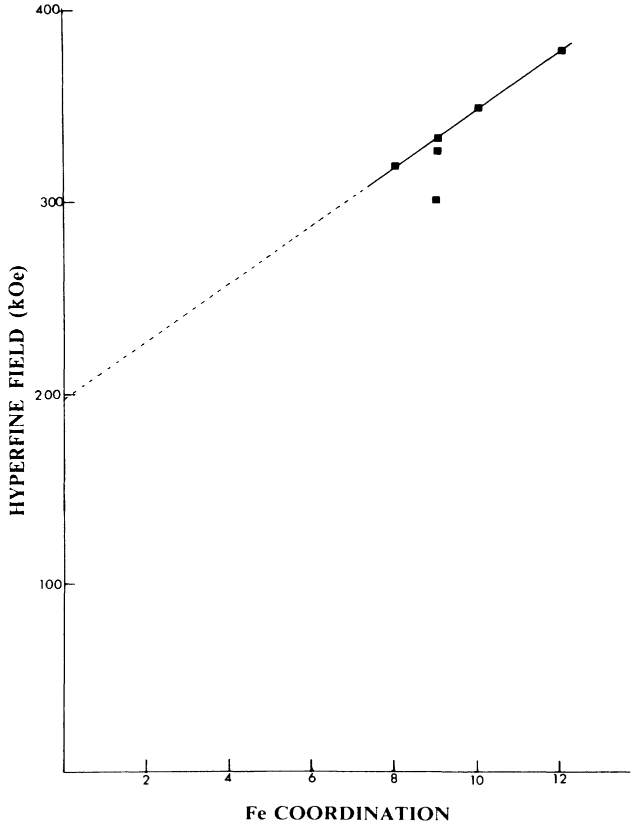

FIG. 4. The hyperfine field at the various Fe sites in $Nd_2Fe_{14}B$ at 1.3 K as a function of the Fe coordination.

present conclusions about individual site hyperfine fields deduced solely from Mössbauer data.

In general, or at least within identical crystal structures, the HF at the Fe nucleus increases with the number of nearest Fe neighbors because the THF increases and, in some cases, the core polarization contribution increases as well. Boron atoms behave as donors of electrons and tend to reduce the moment of their near Fe neighbors and hence decrease their HF. In a study on the rare-earth–iron compounds $R_x\mathrm{Fe}_y$ with different crystal structure, Gubbens *et al.* found that there is an approximately linear relationship between the hyperfine fields at the various Fe sites and the relative number of nearest Fe neighbor atoms of these sites.[23] Figure 4 illustrates the HF at the various sites as a function of the Fe coordination of the corresponding site for $\mathrm{Nd_2Fe_{14}B}$ according to the present assignment. It shows that the HF at j_2, k_2, j_1, and c sites follow a linear relationship very well. The deviation from linearity for k_1 and e sites is because of the existence of B atoms in their nearest-neighbor shell. Extrapolating the straight line to zero Fe coordination, we obtained a value for the on-site HF of 198 KOe, which is very close to the calculated value by Stearns[24] for pure α-Fe due to the on-site core-polarization field and 4*s* electron-polarization field by 3*d* electrons.

V. CONCLUSIONS

Based on the present NMR experiments, we conclude that: (1) reasonable assignments for the HF values at the corresponding Fe sites are 378 (j_2), 352 (k_2), 334 (j_1), 325 (k_1), 320 (c), and 302 (e) kOe; (2) Co atoms substitute preferentially for the Fe atoms at the k_2 site; (3) the addition of Co decreases the Fe HF at all Fe sites except the e site. Further studies to understand our observed intensity ratios are in progress. Similar discrepancies in NMR intensity ratios in other systems have been reported by several authors.[25,26]

ACKNOWLEDGMENT

The authors are grateful to W. A. Hines, D. P. Yang, and F. H. Sanchez for numerous helpful discussions.

---

*Permanent address: Department of Physics, Lanzhou University, Gansu, The People's Republic of China.

†Permanent address: Institute of Physics, Polish Academy of Science, 02668 Warsaw, Poland.

[1] M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, and Y. Matsuura, J. Appl. Phys. **55**, 2083 (1984).

[2] J. J. Croat, J. F. Herbst, R. W. Lee, and F. E. Pinkerton, J. Appl. Phys. **55**, 2078 (1984).

[3] H. Onodera, Y. Yamaguchi, H. Yamamoto, M. Sagawa, Y. Matsuura, and H. Yamamoto, J. Magn. Magn. Mater. **46**, 151 (1984).

[4] M. Rosenberg, P. Deppe, M. Wojcik, and H. Stadelmeier, J. Appl. Phys. **57**, 4124 (1985).

[5] H. M. Van Noort, D. B. de Mooij, and K. H. J. Buschow, J. Appl. Phys. **57**, 5414 (1985).

[6] R. Kamal and Y. Andersson, Phys. Rev. B **32**, 1756 (1985).

[7] R. Fruchart, P. L'Heritier, P. Dalmas de Reotier, D. Fruchart, P. Wolfers, J. M. D. Coey, L. P. Ferreira, R. Guillen, P. Vulliet, and A. Yaouanc, J. Phys. F **17**, 483 (1987).

[8] F. E. Pinkerton, and W. R. Dunhan, J. Appl. Phys. **57**, 4121 (1985).

[9] K. H. J. Buschow, Mater. Sci. Rep. **1**, 1 (1987).

[10] M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, and Y. Matsuura, J. Appl. Phys. **55**, 2083 (1984).

[11] Y. Matsuura, S. Hirosawa, H. Yamamoto, S. Fujimura, and M. Sagawa, Appl. Phys. Lett. **46**, 308 (1985).

[12] Ying-Chang Yang, Wen-Wang Ho, Hai-Ging Chen, Jin Wang, and Jian Lan, J. Appl. Phys. **57**, 4118 (1985).

[13] H. M. Van Noort and K. H. J. Buschow, J. Less-Common Met. **113**, L9 (1985).

[14] J. F. Herbst and W. B. Yelon, J. Appl. Phys. **60**, 4224 (1986).

[15] M. Q. Huang, E. B. Boltich, W. E. Wallace, and E. Oswald, J. Magn. Magn. Mater. **60**, 270 (1986).

[16] D. Givord, H. S. Li, and J. M. Moreau, Solid State Commun. **50**, 497 (1984).

[17] J. F. Herbst, J. J. Croat, F. E. Pinkerton, and W. B. Yelon, Phys. Rev. B **29**, 4176 (1984).

[18] K. Erdmann, P. Deppe, M. Rosenberg, and K. H. J. Buschow, J. Appl. Phys. **61**, 4340 (1987).

[19] M. Rosenberg, P. Deppe, K. Erdmann, M. Sostarich, and H. Stadelmaier, J. Magn. Magn. Mater. **54-57**, 599 (1986).

[20] D. Givord, H. S. Li, and F. Tasset, J. Appl. Phys. **57**, 4100 (1985).

[21] K. H. J. Buschow, D. B. de Mooij, S. Sinnema, R. J. Radwanski, and J. J. M. Franse, J. Magn. Magn. Mater. **51**, 211 (1985).

[22] P. Deppe, M. Rosenberg, S. Hirosawa, and M. Sagawa, J. Appl. Phys. **61**, 4337 (1987).

[23] P. C. M. Gubbens, A. M. Van der Kraan, and K. H. J. Buschow, Solid State Commun. **26**, 107 (1978).

[24] M. B. Stearns, Phys. Rev. B **4**, 4069 (1971); **4**, 4081 (1971).

[25] K. Inomata, Jpn. Appl. Phys. **15**, 821 (1976).

[26] E. Potenziani and D. I. Paul, Phys. Rev. B **25**, 47 (1982).