

## Direct determination of cobalt site preferences in $\text{Nd}_2\text{Fe}_{14}\text{B}$ at infinite dilution

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Using a Mössbauer source technique we have been able to make the first direct determination of the distribution of Co in  $\text{Nd}_2\text{Fe}_{14}\text{B}$  at very low concentration. Co avoids the  $j_2$  site, but occupies the remaining five at random.

Adding small amounts of cobalt to the hard magnetic material  $\text{Nd}_2\text{Fe}_{14}\text{B}$  increases both the Curie temperature and the magnetization of the alloy,<sup>1</sup> though these improvements are offset by a reduction in both the anisotropy field and coercivity,<sup>2</sup> and when more than 20% of the iron is replaced, the magnetization falls.

In order to understand the influence of cobalt on the magnetic structure of  $\text{Nd}_2(\text{Co}_x\text{Fe}_{1-x})_{14}\text{B}$  it is necessary to know how the cobalt atoms are distributed among the six crystallographically inequivalent transition-metal sites.<sup>3</sup> Attempts to detect preferential cobalt site occupation using neutron scattering,<sup>4</sup> Mössbauer spectroscopy,<sup>5,6</sup> and most recently NMR,<sup>7</sup> have led to conflicting results. A tendency for cobalt to prefer the  $e$  site and avoid the  $j_2$  site was reported from neutron measurements,<sup>4</sup> whereas recent NMR measurements<sup>7</sup> suggested that cobalt did not occupy either the  $e$  or the  $k_1$  sites and that it preferred the  $k_2$  site, their results being "also compatible with the preference of iron atoms for the  $j_2$  site." Finally, Mössbauer investigations have found that for  $x \geq 0.6$  cobalt did avoid the  $j_2$  site but there was a preference for the  $k_2$  site.<sup>5,6</sup>

All of these measurements suffer from serious defects. The identification of cobalt sites is *indirect*. It is the absence of iron which is measured, the cobalt locations being deduced by comparison with a reference  $\text{Nd}_2\text{Fe}_{14}\text{B}$  sample. As a result, in order to obtain a significant signal, relatively high concentrations of cobalt have to be employed (typically 10% or more) which lead to significant modifications to both the magnetic properties and the lattice parameters, and hence a reduction in the reliability of the analysis. Furthermore, a substantial increase in Mössbauer linewidths has been reported on cobalt substitution.<sup>6</sup> This is due to statistical variations in local iron environments and further complicates interpretation. Cobalt-cobalt interactions, unavoidable at such concentrations, may also influence the site occupancies.

Here we report the first *direct* measurement of cobalt site occupation in  $\text{Nd}_2(\text{Co}_x\text{Fe}_{1-x})_{14}\text{B}$  at an extremely low cobalt content:  $x \sim 10^{-7}$ . The method used was a Mössbauer source technique. The radioisotope  $^{57}\text{Co}$  was incorporated into a sample of  $\text{Nd}_2\text{Fe}_{14}\text{B}$ .  $^{57}\text{Co}$  decays by electron capture with a half-life of 270 days to an excited state of  $^{57}\text{Fe}$  which subsequently passes to its ground state emitting a 14.4-keV  $\gamma$  ray that may be analyzed in a standard transmission Mössbauer experiment. The signal comes from  $^{57}\text{Fe}$  nuclei in an almost pure  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy, therefore the observed subspectra are *identical* to those of

a standard sample, but the emitting iron atoms are in sites occupied before the electron-capture event and thus, are those chosen by cobalt atoms. The characteristic iron subspectra are obtained, weighted by the proportion of cobalt in each site. It must be stressed that *only* sites occupied by cobalt atoms contribute.

40 MBq of  $^{57}\text{CoCl}_2$  in 1M HCl (Ref. 8) was neutralized with  $\text{NH}_4\text{OH}$ , mixed with 1g of  $^{56}\text{Fe}$  as  $\text{Fe}_2\text{O}_3$ ,<sup>9</sup> and dried.  $^{56}\text{Fe}$  was used in order to avoid line broadening due to resonant self-absorption by  $^{57}\text{Fe}$  in natural iron. The mixture was annealed in hydrogen for 2 h at 900 °C to reduce the oxide, then rf-melted under Ti-gettered argon on a water-cooled copper boat, with appropriate amounts of Nd and B. The alloy was remelted several times to ensure homogeneity. Half of the ingot was then annealed in high-purity argon at 900 °C for 168 h followed by quenching in water both to produce a more homogeneous alloy and to investigate the effect of heat treatment on site occupations. A second sample was prepared in the same way using only natural iron to serve as a reference material.

Cu  $K\alpha$  x-ray diffraction measurements showed that all three samples were mainly tetragonal  $\text{Nd}_2\text{Fe}_{14}\text{B}$  as expected. The *as-made* source material contained some Fe and  $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$  along with traces of  $\text{Nd}_2\text{Fe}_{17}$ , annealing reduced the levels of all of these contaminants to  $\sim 1\%$ . Traces of the Nd-rich fcc phase were detected. The reference sample contained only traces of  $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ .

All Mössbauer spectra were obtained at room temperature on a conventional constant-acceleration spectrometer in transmission geometry. Sources were prepared from finely ground powder spread into a thin layer ( $\sim 20 \mu\text{m}$ , about one absorption depth of 14-keV photons in iron<sup>10</sup>) and held in place by a sheet of Kapton. A single-line absorber of 310 stainless steel 25  $\mu\text{m}$  thick was used to obtain the spectra of the sources. The reference sample was measured in the more usual absorption geometry with a 1-GBq  $^{57}\text{CoPd}$  source. This spectrum has a baseline of  $3.56 \times 10^6$  counts.

Before site occupancies of cobalt can be obtained, a reliable fit for  $\text{Nd}_2\text{Fe}_{14}\text{B}$  must be found. Starting values for the six subspectra parameters were taken from a number of published sources<sup>11-15</sup> and refined using a nonlinear least-squares fitting program. A total of 21 free parameters were used: baseline, linewidth, and total absorption plus isomer shift, quadrupole splitting, and hyperfine field for each of the six subspectra. Intensity ratios were constrained to 4:4:2:2:1:1 as required by the crystal structure.

The final parameters in Table I were found to reproduce the data most closely, and gave a  $\chi^2$  of 10.9 with a half width at half maximum of  $0.148(2)$  mms $^{-1}$ . The fit is shown in Fig. 1. The parameters are close to those found by other workers, and the ordering of hyperfine fields is consistent with iron moments determined by both the single-crystal neutron measurements of Givord, Li, and Tasset<sup>16</sup> and the band-structure calculations of Gu and Ching.<sup>17</sup>

Figure 1 also shows the spectrum of the annealed source with the velocity scale inverted so as to give the conventional ordering of the lines and to facilitate comparison with the reference sample.

Two observations may be made immediately, without recourse to fitting. (i) The characteristic line at +6 mm/s due to the  $j_2$  site is almost entirely absent from both source spectra, therefore, cobalt avoids this site. (ii) The source spectra are otherwise remarkably similar to the reference, therefore, the cobalt distribution must be close to random among the five remaining transition-metal sites. Since iron carries the largest moment in the  $j_2$  site, it is fortunate from a technological standpoint that cobalt avoids substituting for it, reducing the loss of magnetization associated with adding a low-moment transition metal.

Computer fitting was used to obtain more quantitative information. The best-fit parameters from the reference spectrum were used, with only the intensities of the six subspectra variable. The baseline and linewidth were also adjusted and contributions from  $\alpha$ -Fe and  $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$  were allowed, giving a total of ten free parameters.

Although x-ray diffraction showed only a few percent of contaminant phases,  $\alpha$ -Fe and  $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$  they accounted for 20% of the signal from the as-made source, suggesting a disproportionate substitution of cobalt in these phases. Annealing reduced the concentration of these contaminants and except for the  $k_2$  site, no change within error was observed in the cobalt site occupations in the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  primary phase. Neither  $\alpha$ -Fe nor  $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$  interfere significantly with the fitting of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  sites and their presence does not contribute to the uncertainty in the site intensities.

The results of the fits are summarized in Fig. 2. Both of the observations outlined above are confirmed. The annealed sample shows the expected occupation of all sites except the  $j_2$  which is reduced by a factor of 4. A 30%

TABLE I. Summary of fitted parameters of the six iron sites in  $\text{Nd}_2\text{Fe}_{14}\text{B}$  at room temperature. Isomer shift is relative to  $\alpha$ -Fe. Estimated errors are given in parentheses.

Site	Occupation	$\delta$ (mm/s)	$\Delta$ (mm/s)	$B_{\text{hf}}$ (T)
$k_1$	4	-0.01(1)	0.26(1)	28.8(1)
$k_2$	4	-0.09	0.17	30.6
$j_1$	2	-0.04	0.29	27.9
$j_2$	2	0.10	0.65	34.3
$c$	1	0.01	-0.78	28.8
$e$	1	-0.07	0.07	25.6

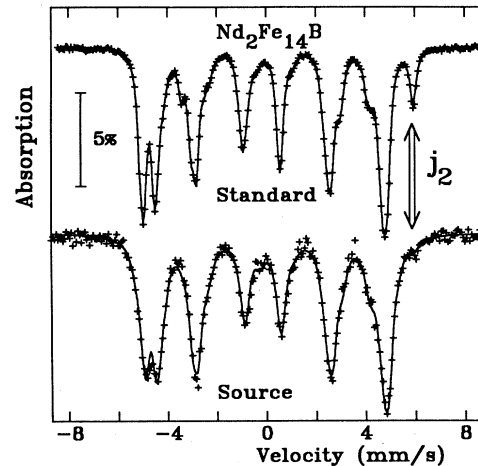


FIG. 1. Room-temperature Mössbauer spectra of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  and the annealed source. Arrow indicates the position of the  $j_2$  peak at +6 mm/s, absent from the source spectrum.

enhancement of the  $k_2$  intensity is seen in the as-made sample; this is reduced on annealing while all other site intensities remain unchanged.

Our results are consistent with previous Mössbauer studies<sup>5,6</sup> in that we observe a strong tendency for cobalt to avoid the  $j_2$  site. It is interesting to note that this preference has been seen at all cobalt concentrations from  $x=10^{-7}$  to  $x=0.98$ . The preferential occupation of the  $k_2$  site<sup>5,6</sup> is only seen in the as-made sample, annealing reduces the intensity of the  $k_2$  contribution to the level expected for random occupation. Since the  $k_2$  preference has only been observed in annealed samples at high concentrations ( $x > 0.6$ ) it is possible that it develops as a result of cobalt-cobalt interactions.

We do not find any evidence either for the selective cobalt substitution on the  $e$ -site reported from neutron diffraction measurements<sup>4</sup> or for cobalt avoiding both the  $e$  and  $k_1$  sites observed by NMR.<sup>7</sup>

It remains now only to explain the  $j_2$ - $k_2$  occupation asymmetry. The simplest argument is that site

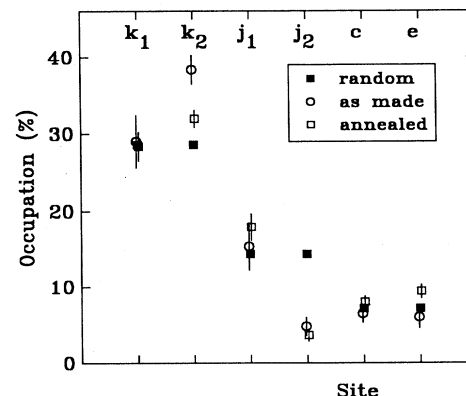


FIG. 2. Summary of fitted site intensities for the two sources compared with values expected for random occupation.

volume/atomic size plays a dominant role, i.e., the larger atom (Fe) occupies the site with the greatest volume ( $j_2$ ) and the smallest site ( $k_2$ ) is then preferred by cobalt. This was used to explain Mn site preferences in  $\text{Nd}_2(\text{Fe,Mn})_{14}\text{B}$  (Ref. 18) where the atomic size difference is quite large ( $\sim 10\%$ ). Here the atomic sizes differ by only  $\sim 1\%$  while the site volumes vary by  $\sim 10\%$ . We see no correlation between occupation and site volume other than cobalt avoiding the largest  $j_2$  site. Furthermore, the size argument fails completely when data on nickel substitution is considered.<sup>19</sup> Even though Ni is smaller than Co, it preferentially occupies both the  $k_2$  and  $j_2$  sites, the smallest and largest, respectively. The alternative explanation in terms of an expected greater affinity between cobalt and neodymium<sup>5</sup> would lead one to expect a strong tendency for cobalt to occupy the  $j_1$  and  $c$  sites as well as avoiding the  $j_2$ . We see no evidence of this.

It seems more likely in this case, where atomic volumes vary so little, that the site preferences are determined by

the symmetries of the atomic wave function and the electron distributions at each site. Detailed band structures would be needed to confirm the hypothesis.

In conclusion, our direct measurement of cobalt site occupancies in  $\text{Nd}_2(\text{Co}_x\text{Fe}_{1-x})_{14}\text{B}$  with  $x=10^{-7}$  shows that cobalt avoids the  $j_2$  site but is distributed almost randomly among the remaining five crystallographically inequivalent transition metal sites. No other site preferences are seen except for a small excess of cobalt in the  $k_2$  site in the as-made sample. The preferences are clearly driven by more subtle effects other than simply available volume or number of rare earth neighbors.

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- <sup>1</sup>Y. Matsuura, S. Hirose, H. Yamamoto, S. Fujimura, and M. Sagawa, *Appl. Phys. Lett.* **46**, 308 (1985); M. Q. Huang, E. B. Boltich, W. E. Wallace, and E. Oswald, *J. Magn. Magn. Mater.* **60**, 270 (1986).
- <sup>2</sup>R. Grössinger, R. Krewenka, X. K. Sun, R. Eibler, H. R. Kirchmayr, and K. H. J. Buschow, *J. Less Common Met.* **124**, 165 (1986).
- <sup>3</sup>J. F. Herbst, J. J. Croat, F. E. Pinkerton, and W. B. Yelon, *Phys. Rev. B* **29**, 4176 (1984); D. Givord, H. S. Li, and J. M. Moreau, *Solid State Commun.* **50**, 497 (1984).
- <sup>4</sup>J. F. Herbst and W. B. Yelon, *J. Appl. Phys.* **60**, 4224 (1986).
- <sup>5</sup>H. M. van Noort and K. H. J. Buschow, *J. Less Common Met.* **113**, L9 (1985).
- <sup>6</sup>P. Deppe, M. Rosenberg, S. Hirose, and M. Sagawa, *J. Appl. Phys.* **61**, 4337 (1987).
- <sup>7</sup>Y. D. Zhang, J. I. Budnick, W. Wojcik, E. Potenziani, A. T. Pedziwiatr, and W. E. Wallace, *Phys. Rev. B* **36**, 8213 (1987).
- <sup>8</sup>Supplied carrier free by New England Nuclear Medical Products, Boston, Massachusetts.
- <sup>9</sup>99.87%-pure <sup>56</sup>Fe supplied by Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- <sup>10</sup>*International Tables for X-ray Crystallography, Vol. III* (Kynoch, Birmingham, 1962), Table 3.2.2E.
- <sup>11</sup>H. M. van Noort, D. B. De Mooij, and K. H. J. Buschow, *J. Less Common Met.* **115**, 155 (1986).
- <sup>12</sup>Q. Ling, J. M. Cadogan, and J. M. D. Coey, *Hyper. Interact.* **28**, 655 (1986).
- <sup>13</sup>R. Fruchart, P. L'Heritier, P. Dalmas de Réotier, D. Fruchart, P. Wolfers, J. M. D. Coey, L. P. Ferreira, R. Guillen, P. Vulliet, and A. Yaouanc, *J. Phys. F* **17**, 483 (1987).
- <sup>14</sup>H. Onodera, A. Fujita, H. Yamamoto, M. Sagawa, and S. Hirose, *J. Magn. Magn. Mater.* **68**, 6 (1987).
- <sup>15</sup>F. Grandjean, D. E. Tharp, O. A. Pringle, and W. J. James, *J. Phys. (Paris), Colloq.* (to be published).
- <sup>16</sup>D. Givord, H. S. Li, and F. Tasset, *J. Appl. Phys.* **57**, 4100 (1985).
- <sup>17</sup>Z. Q. Gu and W. Y. Ching, *Phys. Rev. B* **36**, 8530 (1987).
- <sup>18</sup>C. D. Fuerst, G. P. Meisner, F. E. Pinkerton, and W. B. Yelon, *J. Appl. Phys.* **63**, 3119 (1988).
- <sup>19</sup>S. Dai, A. H. Morrish, X. Z. Zhou, B. P. Hu, and S. G. Zhang, *J. Appl. Phys.* **63**, 3722 (1988).