Direct determination of cobalt site preferences at infinite dilution in iron-based intermetallic compounds (invited)

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Extremely low doping levels (~ 1 ppm) and unambiguous interpretation combine to make the Mössbauer-source technique an ideal method for determining cobalt site preferences in intermetallic compounds. Data on Gd_2Fe_{17} and $Nd_2Fe_{14}B$ are presented and compared with earlier work using Mössbauer spectroscopy, NMR, and neutron diffraction.

I. INTRODUCTION

A standard approach to improving the performance of iron-based permanent magnet materials is to add small amounts of cobalt. Examples include the search for cheaper alternatives to the $SmCo_5$ materials among $RE_2(Fe,Co)_{17}$ alloys[1] (RE denotes rare earth) and the current attempts to improve the high-temperature performance of $Nd_2Fe_{14}B$ magnets.[2] The key to understanding or predicting the effects of cobalt additions (beyond the simple observation that a little cobalt generally helps) is knowing precisely where the cobalt substitutes on the lattice. Differences in chemistry and size will generally prevent the cobalt from occupying the rare-earth sites in the structure, but all magnet materials of either potential or realized technical significance have several crystallographically distinct transition-metal (i.e., iron) sites in their structure. It is not obvious that the cobalt should substitute at random among the possible sites.

Calculations which assume random substitution give results in fair agreement with magnetization and anisotropy measurements in $Sm_2(Co,M)_{17}$ ($M = Fe,Mn,Cr$).[3] However, anisotropic changes in lattice parameters upon adding Co to Nd_2Fe_{17},[4] the effect of replacing small amounts of iron ($\mu_{av} \sim 2.26\mu_B$) with cobalt($\mu_{av} \sim 1.40\mu_B$) on the average magnetization of the $Nd_2Fe_{14}B$,[5] and changes in the easy-magnetization-direction axis in $Y_2(Fe,Co)_{17}$ (Ref. 6) all suggest some degree of preferential cobalt substitution.

Techniques used to determine site preferences in cobalt-substituted iron-based alloys must satisfy two criteria: (i) structural sensitivity—it must be possible to distinguish crystallographic sites within the structure; (ii) chemical specificity—having distinguished the site, it must be possible to determine whether it is occupied by Fe or Co atoms, and in what proportion. Diffraction measurements (x-ray and neutron) provide excellent structural sensitivity, and with extensive computer analysis can yield a rich variety of structural and magnetic information. Both, however, fail criterion (ii) since there is limited contrast between Fe and Co scattering lengths. NMR and Mössbauer spectroscopy give extreme selectivity, being sensitive to a single isotope of the particular element being measured, but at the expense of structural information. Data analysis generally requires additional information from structural and magnetic measurements in order to identify observed contributions with particular sites in the structure.

In all cases the experimental procedures are the same: A reference (cobalt-free) sample is measured to establish a baseline and to fix as many structural parameters as possible, then a series of cobalt-substituted alloys ($Fe_{1-x}Co_x$) with $0.1 \leqslant x \leqslant 1.0$ are measured, and site preferences determined by comparison with the reference and by following trends within the series. The lowest concentration, $x \sim 0.1$, is dictated by the limited contrast in the diffraction measurements, and the fact that Mössbauer spectroscopy is only sensitive to the iron atoms, cobalt occupations being inferred from the reduction in iron signal. NMR results are complicated by the absence of any simple relationship between signal strength and site occupancy, preferential cobalt substitutions being observed indirectly through changes induced at neighboring sites. Analysis is further complicated by relatively high cobalt concentrations ($\geqslant 10\%$), which can cause samples to be significantly different from the reference material. Furthermore, at high concentrations the chemical disorder due to partial substitution can lead to severe broadening of the signal, further degrading the fit and cobalt-cobalt interactions become potentially significant and could influence the observed site preferences. None of the standard techniques actually measure cobalt site preferences directly by determining where the cobalt is; rather they infer cobalt positions

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either from the loss of, or changes in, the iron signal in the case of nuclear techniques, or a change in the average scattering length at each site in the case of diffraction techniques.

The Mössbauer-source technique eliminates these problems. It allows direct measurement of cobalt locations, and uses alloys with $x \sim 10^{-6}$ or less, which are therefore virtually indistinguishable from the reference material. In a standard Mössbauer experiment a source is prepared by incorporating the parent radioisotope (^{57}Co in the case of ^{57}Fe) into a matrix that yields a single, sharp, transition (typically Rh or Pd). The γ rays are then shone through a sample (absorber) and a spectrum is obtained by plotting the transmitted intensity versus the Doppler velocity applied to the source. Each crystallographically distinct site provides a different iron environment and so yields an independent subspectrum. The relative intensities of these subspectra correspond to the distribution of sites in the material. For a source experiment, the radioactive material is incorporated directly into the sample, and the complex emission pattern is analyzed using a single-line absorber.

^{57}Co decays by electron capture to an excited state of ^{57}Fe which subsequently passes to its ground state emitting the 14.4-keV γ-ray used in the Mössbauer experiment. The signal comes from ^{57}Fe nuclei in an almost pure alloy; therefore the observed subspectra are *identical* to those of a reference sample, but the emitting iron atoms are in sites occupied *before* the electron-capture event and thus 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.

Data on two samples are presented here. (i) $Nd_2Fe_{14}B$, chosen both for its technological importance as a permanent-magnet material and because of the large body of conflicting data on cobalt site preferences in this alloy. (ii) Gd_2Fe_{17}, selected as a representative binary rare-earth iron alloy because it has a site with a similar symmetry to one in $Nd_2Fe_{14}B$ (the c and j_2, respectively). The gadolinium compound was used because its high T_c maximizes the resolution between the subspectra at room temperature, although the fitting is complicated by magnetic subsplitting of the contributions from the f and h sites.[7] RE_2Fe_{17} alloys exist in two closely related modifications, hexagonal ($P6_3/mmc$) and rhombohedral ($R\bar{3}m$), with identical coordinations for the corresponding iron sites. In order to facilitate comparisons with other work on this system, we have used the labeling appropriate to the rhombohedral form throughout. However, the site labels for the hexagonal form, with corresponding rhombohedral labels in parentheses, are f (c), g (d), j (f), and k (h).

II. EXPERIMENTAL METHODS

Reference samples were obtained by rf-induction melting appropriate amounts of 99.95% pure elements on a water-cooled copper boat under Ti-gettered argon. Room-temperature Mössbauer spectra were obtained with a 1-GBq ^{57}Co*Rh* source on a constant-acceleration spectrometer. They were fitted using a standard nonlinear least-squares minimization routine with subspectra intensities constrained to match crystallographic probabilities. Fitted spectra with residuals are shown in Fig. 1.

^{57}Co, supplied as $CoCl_2$ in 0.5M HCl, was neutralized and evaporated to dryness with $\sim$150 mg of $^{56}Fe_2O_3$. This mixture was reduced to the metallic state by annealing at 900 °C under flowing H_2 for 2 h. ^{56}Fe is essential to prevent loss of signal from resonant self-absorption by the 2.17 at. % ^{56}Fe present in natural iron. The radioactive iron was then alloyed, as before, with the other elements. The limited range of the 14.4-keV γ ray requires the use of thin sources and restricts the total sample mass to $\sim$50 mg. Spectra were obtained with a thin layer of the material in a holder on the Mössbauer drive, and an 8-μm foil of 310 stainless steel as a single-line absorber.

All of the materials were checked for impurity phases by x-ray diffraction and thermogravimetric analysis (TGA) in a small-field gradient. Principal impurities present were α-Fe and, in the case of $Nd_2Fe_{14}B$, $Nd_{1.1}Fe_4B_4$, none of which significantly affect the data analysis.

The source spectra were fitted by taking the parameters obtained from the reference materials and allowing only the off-resonance baseline and the intensities of the individual subspectra to vary. Requiring the subspectrum parameters obtained by fitting the reference sample to fit the source material with changes only in the intensities further constrains the fit and provides a consistency check on the parameters used. Additional contributions from α-Fe and $Nd_{1.1}Fe_4B_4$ were also allowed where appropriate, but again only the intensities of these components were allowed to vary.

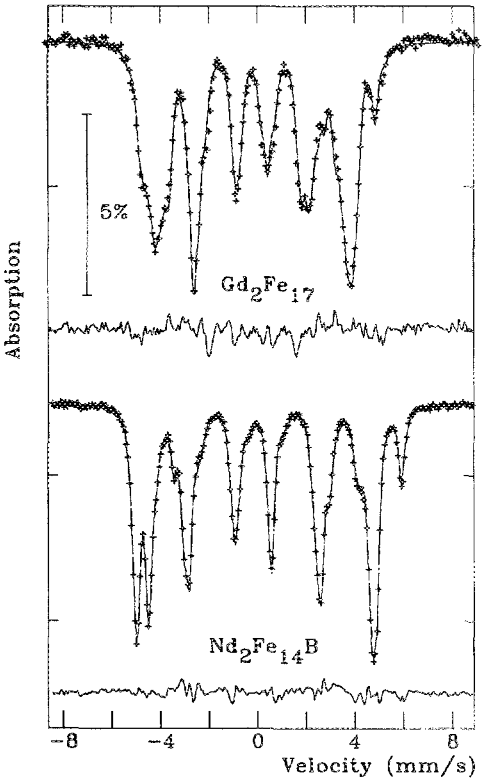

FIG. 1. Reference room-temperature Mössbauer spectra of $Nd_2Fe_{14}B$ and Gd_2Fe_{17} with fits through the data and the residuals plotted below.

TABLE I. Summary of isomer shift (δ), quadrupole splitting (Δ), and hyperfine field (B_{hf}) for the four iron sites in hexagonal Gd_2Fe_{17} at room temperature. Wyckhoff symbols for the four iron sites are indicated for the rhombohedral structure with those for the hexagonal form in parentheses. Isomer shifts are given relative to α-Fe at room temperature.

Site	Occupation	δ (mm/s)	Δ (mm/s)	B_{hf} (T)
h (k)	6	−0.15	0.30	23.9
			−0.16	23.5
			0.48	22.9
f (j)	6	−0.09	−0.43	26.5
			0.07	26.7
			−0.04	21.2
d (g)	3	−0.10	0.09	25.6
c (f)	2	0.06	0.05	30.2

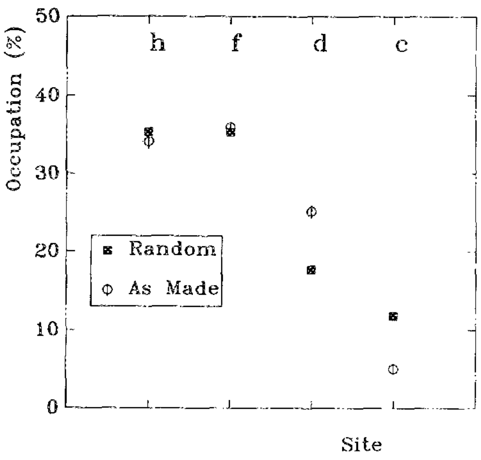

FIG. 3. Summary of fitted site intensities for the as-made and annealed Gd_2Fe_{17} sources with values expected for random occupation.

III. Gd_2Fe_{17} RESULTS

X-ray-diffraction measurements confirmed that both the reference and source materials used in this work had the hexagonal $Ni_{17}Th_2$ structure ($P6_3/mmc$). TGA showed that T_c was 486 K. The Mössbauer spectrum of the reference sample (Fig. 1) was fitted with four subspectra in the ratio 6:6:3:2 corresponding to the occupations of the h, f, d, and c sites, respectively. We included a further magnetic subsplitting of the h and f contributions into three equal-intensity components each, to take account of the magnetic easy direction being in the ab plane.[7] Parameters obtained are given in Table I. The room-temperature Mössbauer spectrum obtained from our cobalt-doped sample is shown in Fig. 2. Lines visible at ± 5.3 mm/s are due to a 6% α-Fe contamination. Annealing this material at 1050 °C for 300 h caused the precipitation of more iron but no change in the site distributions. Figure 3 summarizes the occupations of the four crystallographically distinct sites by cobalt compared to that expected from a random distribution. The most strongly affected sites are the c, which has less than 50% of its expected intensity, and the d, which shows a 40% excess. Both the h and f sites appear to be randomly occupied. Only the cobalt avoidance of the c site is in agreement with earlier work on this system.

A number of neutron-diffraction[4,8,9] and conventional Mössbauer-spectroscopy determinations[10-12] of cobalt site preferences in rhombohedral RE_2Fe_{17} alloys exist, and all agree on a definite tendency for cobalt to avoid the c site. Only two comment on distributions among the other three sites; both are neutron-diffraction measurements, but they arrive at diametrically opposed conclusions. The older work[8] finds a cobalt preference for the f site, with occupations of h and d random, while the more recent report[9] finds excess cobalt on h and d, with f random. It is unlikely that differences between the rare earth used (Y and Nd, respectively) can be responsible for this contradiction, and these differences serve to emphasize the problems in using indirect methods to determine site preferences, even at high concentrations.

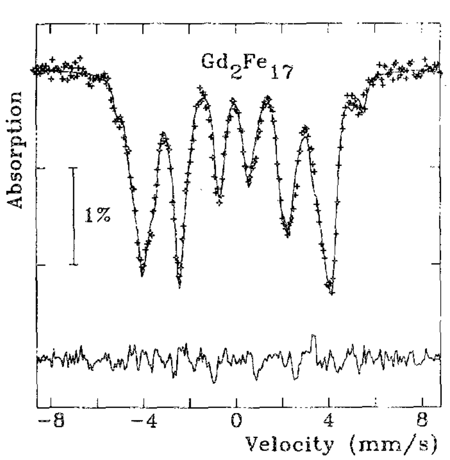

FIG. 2. Room-temperature Mössbauer spectrum of Gd_2Fe_{17} source with fit through the data and the residuals plotted below.

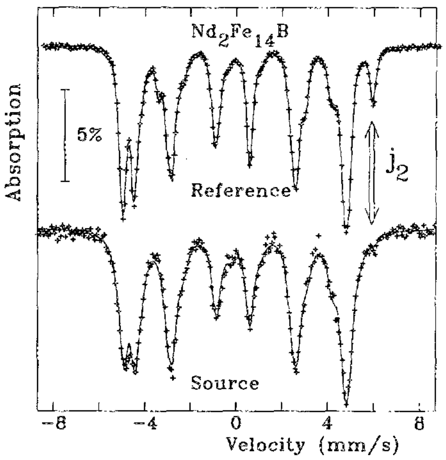

FIG. 4. Room-temperature Mössbauer spectrum of the reference $Nd_2Fe_{14}B$ sample and the annealed source. Arrows indicate the position of the j_2 peak at + 6 mm/s, absent from the source spectrum.

IV. $Nd_2Fe_{14}B$ RESULTS

X-ray diffraction and TGA confirmed that the reference sample consisted of tetragonal $P4_2/mnm$-phase $Nd_2Fe_{14}B$ with 2% $Nd_{1.1}Fe_4B_4$. The room-temperature Mössbauer spectrum in Fig. 1 was fitted with six subspectra in the ratio 4:4:2:2:1:1 corresponding to the occupations of the k_1, k_2, j_1, j_2, c, and e sites, respectively. More details of the fitting are given in Ref. 13. Figure 4 shows a comparison between the spectrum of the reference sample and that obtained from the ^{57}Co-doped source after annealing at 900 °C for 168 h. Two conclusions may be reached simply from a visual inspection: (i) the j_2 contribution is almost entirely absent from the source, indicating strong avoidance of this site by cobalt; (ii) the rest of the spectrum is largely unchanged, suggesting a close to random distribution of cobalt among the remaining five sites. The results of computer fitting with nine parameters [six intensities, baseline, α-Fe intensity (11%), and $Nd_{1.1}Fe_4B_4$ intensity (7%)] are shown in Fig. 5, and confirm the conclusions reached above. There is some evidence for excess k_2 occupation in the as-made sample, which is substantially reduced upon annealing, but the rest of the sites appear to be occupied at random.

A considerable amount of data on cobalt site preferences in $Nd_2Fe_{14}B$ has been obtained using Mössbauer spectroscopy,[14,15] neutron diffraction,[16] and, most recently, NMR.[17] As with RE_2Fe_{17}, some agreement exists, but substantial conflict remains. Both Mössbauer results are in complete agreement, finding some excess cobalt in the k_2 site, strong avoidance of the j_2, and an essentially random distribution among the rest. While neutron-diffraction data also indicate a strong tendency for cobalt to avoid the j_2 site, no evidence for preferential occupation of the k_2 was found; instead they report a small excess in the e site, with the other sites randomly populated. By contrast, the NMR results find only a preference of cobalt for the k_2, and while this is at least partially consistent with earlier Mössbauer work, they fail to observe the avoidance of the j_2, which is seen both by Mössbauer spectroscopy and neutron diffraction and is the clearest result of the present work.

Apart from the strong avoidance of the j_2, we find only a weak cobalt preference for the k_2, greatly reduced upon annealing, in contrast with other Mössbauer work. This discrepancy could possibly be due to cobalt-cobalt interactions present at high ($\geqslant 10\%$) concentrations, but this would not explain the neutron data. There is some evidence for the slight cobalt excess in the e site seen in neutron-diffraction measurements,[16] but this is a weak effect in a low-intensity site, and may not be significant.

V. DISCUSSION

The clearest results obtained in this work are strong cobalt avoidances of the c site (Gd_2Fe_{17}) and j_2 site ($Nd_2Fe_{14}B$) and a preference for the d site (Gd_2Fe_{17}). However, the origin of these preferences remains to be explained. Figure 6 shows the observed site preferences in the two alloys plotted against site volume and transition-metal/rare-earth coordination. A volume argument would appear to work quite well for Gd_2Fe_{17}, with a strong correlation between preferential occupation and site volume, it fails to account for the site preferences in $Nd_2Fe_{14}B$ even though the range of site volumes are similar in both alloys. While it may be reasonable to use site volumes to explain Mn site preferences in $Nd_2(Fe,Mn)_{14}B$, where the atomic size difference is large ($\sim 10\%$),[18] it is unlikely that the 1% size difference between Co and Fe plays a dominant role in selecting among sites whose volume varies by more than 10%. For example, although cobalt appears to strongly avoid the largest site (j_2), it shows no extra tendency to enter the smallest (k_2). The argument fails entirely for $Nd_2(Fe,Ni)_{14}B$, where Ni has been shown to substitute preferentially on *both* the j_2 and the k_2.[19] An alternative argument which appeals to a greater affinity between cobalt and rare earths[14] would lead us to expect strong cobalt preferences for sites with high rare-earth coordination (j_1 and c in $Nd_2Fe_{14}B$ and h in Gd_2Fe_{17}), whereas no such trends are observed (Fig. 6).

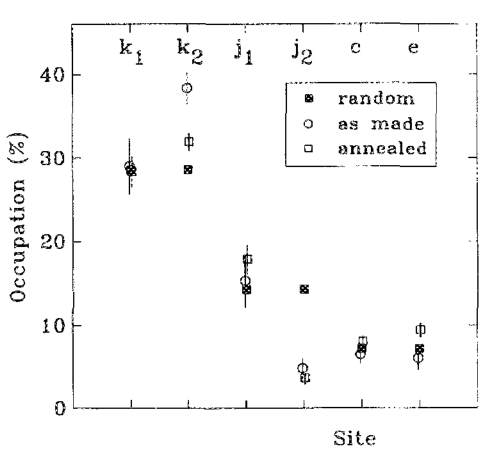

FIG. 5. Summary of fitted site intensities for the as-made and annealed $Nd_2Fe_{14}B$ sources with values expected for random occupation.

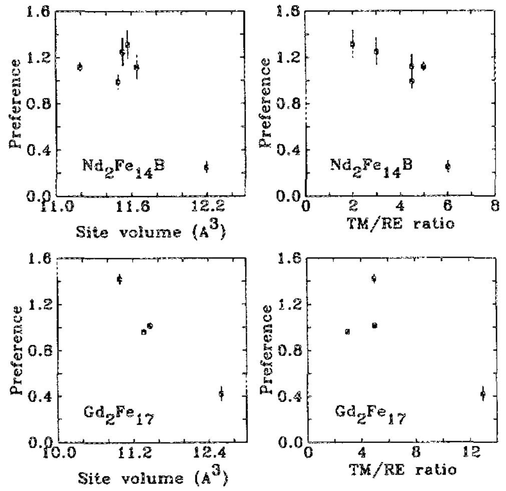

FIG. 6. Plots of site preference (ratio of observed to statistical intensities) vs site volumes and coordination (number of transition-metal neighbors/number of rare-earth neighbors) for $Nd_2Fe_{14}B$ and Gd_2Fe_{17}.

It seems far likelier that preferences in these systems are controlled by symmetry. There are two sites in the Gd_2Fe_{17} structure that resemble the j_2 in $Nd_2Fe_{14}B$, namely the c and d. All possess axial symmetry, and consist of two iron rings, one above and the other below the central atom, with a capping atom at the top and bottom. In the j_2 and d both of the caps are rare earths; in the c, one is iron. The rings are five membered in the d and six membered in the other two cases. However, the hole occupied by the central atom in the d site is prolate, stretched along its axis, whereas the other two are oblate. The d is preferred, and the c and j_2 avoided. With only three such sites with simple symmetries to draw on, further speculation would be premature. Moreover, with only two alloy systems to draw on, the possibility of chance correlations—for example, between rare-earth coordination and site volume—prevents general conclusions. The current work is being extended to the other $RE_m Fe_n$ binary alloys in order to obtain a more systematic data set.

VI. CONCLUSIONS

We have shown that the Mössbauer-source technique offers a direct and unambiguous way to determine cobalt site preferences in iron-based intermetallic compounds at extremely low doping levels. Samples of Gd_2Fe_{17} and $Nd_2Fe_{14}B$ have been investigated and a strong tendency for cobalt to avoid the c site in the former and the j_2 in the latter has been observed. A significant preference for the d site in Gd_2Fe_{17} and much weaker preferences for the k_2 and e sites in $Nd_2Fe_{14}B$ were also seen. It is remarkable that cobalt should exhibit such strong tendencies to avoid certain sites without showing equally strong preferences to occupy other sites.

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