Mössbauer determination of cobalt substitution in iron-based intermetallics

L. X. Liao, D. H. Ryan, and Z. Altounian
Centre for the Physics of Materials and Department of Physics, McGill University, 3600 University St., Montréal, Québec, Canada H3A 2T8

A Mössbauer source technique has been used in studies of cobalt site preferences in the intermetallic compounds Er_6Fe_{23} and Nd_2Fe_{17}. Data quality has been improved by the construction of a resonant conversion electron detector. This detector provides a tenfold increase in signal and allows measurements to be made with the source at reduced temperatures. Results for Er_6Fe_{23} show a strong tendency for cobalt to occupy the f_2 site and to avoid the f_1 site. For Nd_2Fe_{17}, our results reveal that cobalt while it occupies preferentially the h and d sites, is almost completely absent from the c site, and it tends to avoid the f site.

I. INTRODUCTION

Since cobalt is often added to iron-based magnetic materials in order to enhance their magnetic properties, it is of interest to know precisely where it replaces Fe in the structure so as to predict and understand the effects. Techniques used to determine site preferences in cobalt-substituted iron-based alloys include neutron scattering, Mössbauer spectroscopy, and nuclear magnetic resonance. However, only the Mössbauer source technique used here allows direct determination of cobalt locations with extremely low doping levels (~ 1 ppm).[1] Data on two samples are presented here: (i) Er_6Fe_{23}, for which no previous results on cobalt substitutions are available, and (ii) Nd_2Fe_{17} with rhombhedral structure, chosen because the results can directly be compared to neutron diffraction data[2] and our earlier work on the mixed rhombohedral/hexagonal Gd_2Fe_{17}.[3]

II. EXPERIMENTAL METHODS

Reference samples were prepared by radio-frequency (rf)-induction melting appropriate amounts of 99.9% pure elements on a water-cooled copper boat under Ti-gettered Ar. Samples of Nd_2Fe_{17} were annealed for three weeks at 1173 K under vacuum in order to obtain single phase material. Transmission Mössbauer spectra were obtained with a 1 GBq ^{57}CoRh 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.

Preparation of source samples using ^{56}Fe to eliminate self absorption in the source and incorporating about 30 MBq of ^{57}Co is described in Ref. 3. All of the samples were examined by x-ray diffraction and thermogravimetric analysis (TGA) in a small field gradient to confirm phase purity. We have constructed a resonant conversion electron detector utilising 80% ^{57}Fe enriched stainless steel foil which yields tenfold enhancement in signal-to-noise ratio over the standard method employing a single line absorber used in transmission mode.[4] Its light weight (<30 g) allows it to be mounted on the Mössbauer drive rather than the source so that the source sample may be fixed in a cryostat, making it possible to carry out source experiments at low temperatures. Spectra were obtained using the new detector mounted on the Mössbauer drive while the source sample was fixed either on a sample mount or in a cryostat.

The source spectra shown in Figs. 1 and 3 have been inverted in order to facilitate comparison with the reference spectra. They were fitted using the parameters obtained from the reference samples and allowing only the off-resonance base line and the intensities of the individual subspectra to vary. Requiring the subspectrum parameters obtained by fitting the reference sample to also fit the source material with changes only in the intensities severely constrains the fit, and provides a consistency check on the parameters used.

III. RESULTS AND DISCUSSION

A. Er_6Fe_{23}

X-ray diffraction and TGA showed that both reference and source materials used in these studies had the face-centered-cubic Th_6Mn_{23} structure ($Fm3m$). The Curie temperature of both samples was 493 K. The Mössbauer spectrum of the reference sample (Fig. 1) was fitted with

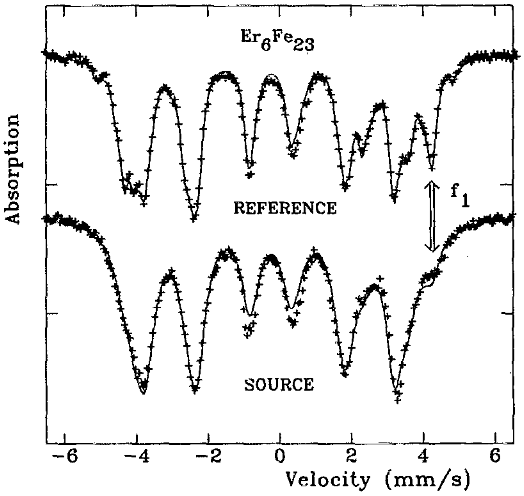

FIG. 1. Room-temperature Mössbauer spectrum of the reference and source samples for Er_6Fe_{23}. Arrows indicate that the intensity of the f_1 peak at ~4.2 mm/s is greatly reduced in the source spectrum.

0021-8979/91/106143-03$03.00

TABLE I. Summary of isomer shift (δ), quadrupole splitting (Δ) and hyperfine field (B_{hf}) for the four iron sites in Er_6Fe_{23} at room temperature. Isomer shifts are given relative to α-Fe at room temperature.

Site	Occupation	δ (mm/s)	Δ (mm/s)	B_{hf} (T)
f_1	6	0.01	0.13	26.6
	2	0.01	−0.34	26.5
f_2	6	−0.15	−0.04	21.6
	2	−0.18	0.13	20.8
d	4	−0.13	0.03	23.8
	2	−0.15	0.00	22.9
b	1	−0.03	0.03	30.8

four subspectra in the ratio 1:6:8:8 corresponding to the occupations of the b, d, f_1, and f_2 sites, respectively. A further 6:2 magnetic subsplitting was included for the f_1 and f_2 sites and a 4:2 for the d site to take account of the magnetic easy direction being along the [111] direction.[5] Fitted parameters are given in Table I. It is clear from a visual inspection of the source spectrum, shown in Fig. 1, that the line at ~4.2 mm/s (indicated by an arrow) is greatly reduced in intensity and therefore cobalt tends to avoid this site (f_1). However the broadening of the lines due to the geometry used in this measurement means that computer fitting is needed to extract more details. The observed cobalt occupations of the four crystallographically inequivalent transition metal sites is compared to that expected from a random distribution in Fig. 2. It can be seen that Co atoms preferentially occupy the f_2 site and avoid the f_1 and b sites while occupying d site essentially at random. No previous work has been done on cobalt site preferences in Er_6Fe_{23}, however a similar behavior of Mn atoms was obtained in the $Y_6(Fe_{1-x}Mn_x)_{23}$ system using neutron diffraction.[6] In this system the Mn atoms prefer to occupy the f_2 site and Fe atoms the f_1 site.

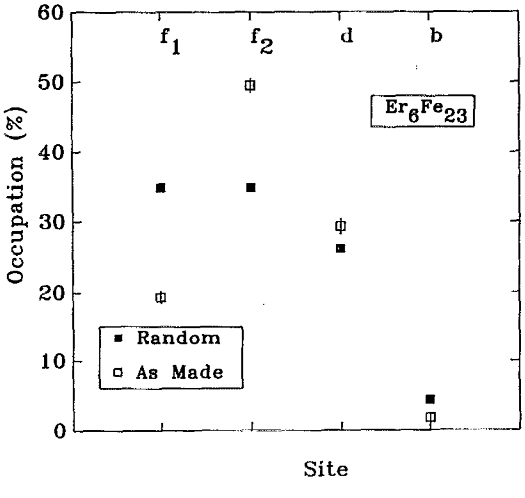

FIG. 2. Summary of fitted site intensities for the Co doped Er_6Fe_{23} sample with values expected from random occupation.

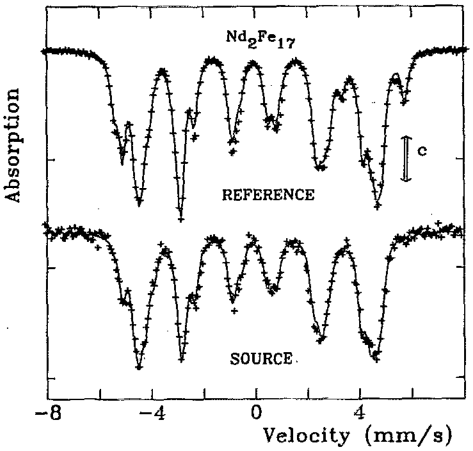

FIG. 3. Mössbauer spectrum of the reference and source samples for Nd_2Fe_{17} at 90 K. Arrows indicate the line of the c site at ~5.8 mm/s, absent from the source spectrum.

B. Nd_2Fe_{17}

Both reference and cobalt doped samples were confirmed to have the rhombohedral $R\bar{3}m$ (Th_2Zn_{17}) structure by x-ray diffraction. TGA showed the Curie temperature to be 343 K in both cases. This low ordering temperature leads to insufficient resolution of the subspectra at room temperature so all measurements were made at 90 K. The reference spectrum shown in Fig. 3 is clear and individual sites may be distinguished. It 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. Since the easy direction of the magnetization lies along the a axis,[5] we have included a further 4:2 magnetic subsplitting of the h and f contributions. Table II summarizes the parameters of the fit. As with the previous sample, the occupation of one site may be deduced immediately: the line at ~5.8 mm/s (indicated by an arrow) is absent from the doped sample, indicating almost total avoidance of this site (c) by cobalt. The complete computer fit of the source

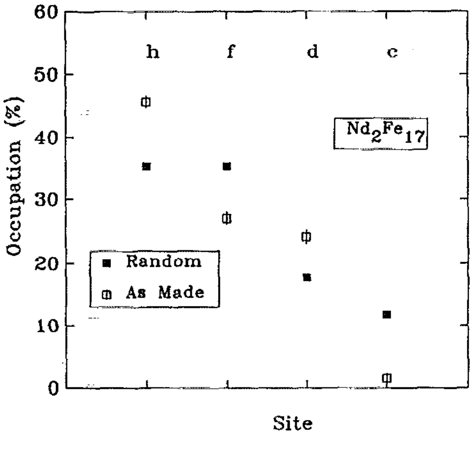

FIG. 4. Summary of fitted site intensities for the Co doped Nd_2Fe_{17} sample with values expected from random occupation.

TABLE II. Summary of isomer shift (δ), quadrupole splitting (Δ) and hyperfine field (B_{hf}) for the four iron sites in rhombohedral Nd_2Fe_{17} at 90 K. Isomer shifts are given relative to α-Fe at room temperature.

Site	Occupation	δ (mm/s)	Δ (mm/s)	B_{hf} (T)
h	4	0.06	−0.29	26.6
	2	0.05	0.42	27.8
f	4	0.00	−0.07	31.0
	2	−0.01	0.58	27.2
d	3	−0.08	0.12	28.2
c	2	0.22	0.05	34.7

spectrum confirms that cobalt is almost entirely absent from the *c* site and further shows that it tends to avoid the *f* site while preferentially occupying the *h* and *d* sites (see Fig. 4). These results agree very well with that obtained by neutron diffraction in the same compound except for the *f* site where almost random occupation of Co atoms was previously observed. The preferences observed in the weaker (*d* and *c*) sites are identical to those previously seen in Gd_2Fe_{17},[3] however the *h* and *f* sites exhibit marked preferences here in the Nd alloy rather than being occupied randomly as was observed in the Gd alloy.

IV. CONCLUSIONS

We have studied the cobalt site preferences in Er_6Fe_{23} and Nd_2Fe_{17} compounds using a Mössbauer source technique with a resonant conversion electron detector. The most striking results obtained here are strong cobalt avoidances of the f_1 site (Er_6Fe_{23}) and *c* site (Nd_2Fe_{17}) and preferences for the f_2 site (Er_6Fe_{23}) and *h*, *d* sites (Nd_2Fe_{17}). The question arises as to the origin of these preferences. Figure 5 shows that the observed preferences in the alloys studied to date are correlated with site volume, however this in no way indicates a causal link. Many other possible parameters, including rare-earth coordination and site symmetry, may be expected to affect site occupations and be correlated with site volume. It is clear that sites with volumes above ~12 Å^3 are avoided by cobalt. The current work is being extended to the other RE_mFe_n binary alloys in order to obtain a more systematic data set.

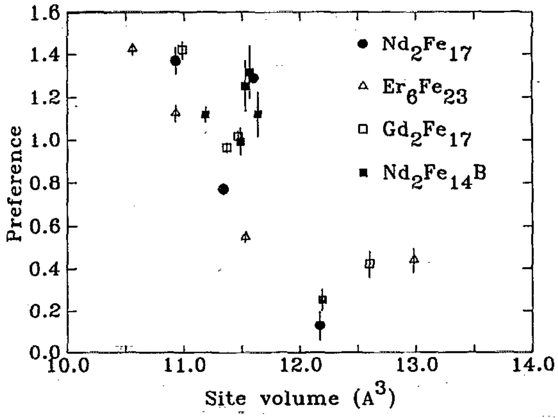

FIG. 5. Site preference (ratio of observed to statistical intensities) vs site volumes for the compounds studied to date.

ACKNOWLEDGMENTS

The research was supported by grants from the National Sciences and Engineering Research Council of Canada, Fonds pour la Formation de Chercheurs et l'aide à la Recherche, Québec, and the Faculty of Graduate Studies and Research of McGill University.

[1] D. H. Ryan, Z. Altounian, J. O. Ström-Olsen, and W. B. Muir, Phys. Rev. B 39, 4730 (1989).
[2] J. F. Herbst, J. J. Croat, and R. W. Lee, J. Appl. Phys. 53, 250 (1982).
[3] D. H. Ryan, Z. Altounian, L. X. Liao, J. O. Ström-Olsen, and W. B. Muir, J. Appl. Phys. 67, 4742 (1990).
[4] L. X. Liao, D. H. Ryan, and Z. Altounian (to be published).
[5] P. C. Gubbens, Ph.D. thesis, Delft University, 1977.
[6] K. Hardman, W. J. James, and W. B. Yelon, J. Phys. Chem. Solids 41, 1105 (1980).