
01 Feb 1992

Mössbauer and Neutron Diffraction Studies of $Y_2(Fe_{1-x}Mn_x)_{14}B$

Oran Allan Pringle

Missouri University of Science and Technology, pringle@mst.edu

Gaya Kanishka Marasinghe

Gary J. Long

Missouri University of Science and Technology, glong@mst.edu

William Joseph James

Missouri University of Science and Technology, wjames@mst.edu

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/phys_facwork/183

Follow this and additional works at: https://scholarsmine.mst.edu/phys_facwork

 Part of the [Chemistry Commons](#), and the [Physics Commons](#)

Recommended Citation

O. A. Pringle et al., "Mössbauer and Neutron Diffraction Studies of $Y_2(Fe_{1-x}Mn_x)_{14}B$," *Journal of Applied Physics*, vol. 64, no. 10, pp. 5580-5582, American Institute of Physics (AIP) Publishing, Feb 1992.

The definitive version is available at <https://doi.org/10.1063/1.342287>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Physics Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Mössbauer and neutron diffraction studies of $Y_2(Fe_{1-x}Mn_x)_{14}B$

O. A. Pringle, G. K. Marasinghe, Gary J. Long, and W. J. James
*Departments of Physics and Chemistry and the Graduate Center for Materials Research,
University of Missouri-Rolla, Rolla, Missouri 65401*

W. B. Yelon and D. Xie
University of Missouri Research Reactor, Columbia, Missouri 65211

F. Grandjean
Institut de Physique, Universite de Liege, B-4000 Sart Tilman, Belgium

We have used Mössbauer spectroscopy and neutron diffraction to study a series of $Y_2(Fe_{1-x}Mn_x)_{14}B$ samples in the composition range from $x = 0.0$ to 0.4 . $Y_2(Fe_{0.6}Mn_{0.4})_{14}B$ is paramagnetic at both room temperature and 85 K. The iron quadrupole splitting in this paramagnetic compound allows us to place an upper limit on the quadrupole shift in the magnetic $Y_2(Fe_{1-x}Mn_x)_{14}B$ alloys. Refinement of $Y_2(Fe_{1-x}Mn_x)_{14}B$ neutron diffraction data have been used to give the site occupancies of manganese on the transition-metal sublattice. Both neutron diffraction patterns and Mössbauer effect spectra indicate a marked preference for the manganese to occupy the $8j_2$ site, which is the largest volume transition-metal site. Both experimental techniques give completely consistent results for the site occupancies in $Y_2(Fe_{1-x}Mn_x)_{14}B$.

INTRODUCTION

$R_2(Fe_{1-x}T_x)_{14}B$ compounds, where R is yttrium or a rare earth, and T is a transition metal or metalloid, are of interest for several reasons. Useful permanent magnets based on $Nd_2Fe_{14}B$ will contain a number of elements which replace part of the iron. Selected R and T substitutions in $R_2(Fe_{1-x}T_x)_{14}B$ alloys may also lead to a better understanding of the magnetic exchange pathways and the origins of the high magnetocrystalline anisotropy in these materials.

In this paper, we report the initial results of a neutron diffraction and Mössbauer effect study of manganese-substituted $Y_2Fe_{14}B$. The effect of manganese on the magnetic exchange in $R_2(Fe_{1-x}Mn_x)_{14}B$ is interesting, because manganese is generally believed to be antiferromagnetic seeking, and because antiferromagnetic iron-iron interactions have been suggested as one of the causes for the relatively low Curie temperature in the $R_2Fe_{14}B$ magnets.¹

We have carried out Mössbauer effect studies of $Y_2(Fe_{1-x}Mn_x)_{14}B$ with x equal to 0.0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.30, and 0.40. Neutron diffraction patterns, taken above the Curie temperatures for the samples with x equal to 0.20, 0.30, and 0.40, were used to determine the occupancy of the different transition-metal sites by manganese. The site populations from neutron diffraction were used as constraints in fitting the Mössbauer spectra, and the results from the two techniques are in excellent agreement.

EXPERIMENT

$Y_2(Fe_{1-x}Mn_x)_{14}B$ samples were prepared by induction melting 99.9% pure starting materials, followed by vacuum annealing at 950 °C for periods ranging from 96 to 120 h. The starting materials for induction melting contained 0.8 wt. % excess of manganese, in order to compensate for manganese loss due to its higher vapor pressure.

The preparation of the Mössbauer absorbers has been described previously.² Powder samples obtained from the

same ingot were used for both the Mössbauer effect and neutron diffraction measurements. Our measurements show that the samples consist of the $R_2T_{14}B$ phase, plus at most 5% of α -iron.

The procedure used to fit the Mössbauer spectra has also been described previously.² For $Y_2Fe_{14}B$, there is no *a priori* reason why the linewidths for the different iron sites should be different. Thus, we have constrained all of its linewidths to be the same. When manganese is partially substituted for iron, the resulting distribution of near-neighbor environments results in a range of hyperfine parameters. We simulate a distribution of hyperfine fields at each iron site by introducing an incremental linewidth parameter as described in Ref. 2.

Approximately 2 g of selected powdered samples were encapsulated in a thin-walled vanadium cell. Neutron diffraction data for these samples were collected at the University of Missouri Research Reactor. The neutron wavelength was approximately 1.3 Å, and each scan took about 24 h. The data were collected in three 25° intervals from $2\theta = 5^\circ$ to 80° , and rebinned into 0.1° steps for analysis using a modified Rietveld code.

RESULTS

The $Y_2(Fe_{1-x}Mn_x)_{14}B$ samples all crystallized in the $Nd_2Fe_{14}B$ structure.³ Neutron diffraction refinements for $Y_2(Fe_{1-x}Mn_x)_{14}B$ with x equal to 0.20, 0.30, and 0.40, taken above their Curie temperatures, show a marked preference for manganese to occupy the $8j_2$ site, and a slight preference for iron to occupy the two $16k$ sites and the $4e$ site. These occupancies are close to those observed in the $Er_2(Fe_{1-x}Mn_x)_{14}B$ alloys,⁴ and are generally consistent with occupancies expected on the basis of site volumes. Manganese is expected to occupy the larger-volume $8j_2$ site and to avoid the smaller volume $16k_2$ and $8j_1$ sites.

Table I gives the site occupancies, obtained from neu-

TABLE I. Manganese occupancies for the transition-metal sites in $Y_2(Fe_{1-x}Mn_x)_{14}B$, as determined by neutron diffraction. Random substitution values are also given for comparison.

Site	$Y_2(Fe_{0.80}Mn_{0.20})_{14}B^a$		$Y_2(Fe_{0.70}Mn_{0.30})_{14}B^a$		$Y_2(Fe_{0.60}Mn_{0.40})_{14}B^a$	
	Neutrons	Random	Neutrons	Random	Neutrons	Random
$16k_1$	0.68	1.44	2.66	4.00	4.30	5.28
$16k_2$	0.88	1.44	2.71	4.00	3.26	5.28
$8j_1$	0.78	0.72	2.26	2.00	3.24	2.64
$8j_2$	2.24	0.72	5.05	2.00	5.48	2.64
$4e$	0.16	0.36	0.59	1.00	0.85	1.32
$4c$	0.26	0.36	0.83	1.00	1.45	1.32

^a Nominal composition.

^b Composition determined by neutron diffraction.

tron diffraction, in the form of manganese populations for each of the transition metal sites. The total manganese content, as refined in the neutron diffraction analysis, is consistently less than expected. Manganese loss must have occurred at a higher rate than anticipated. Nevertheless, x-ray, neutron diffraction, and Mössbauer effect measurements fail to show the presence of significant amounts of any impurity phase, other than a few percent of α -iron, so our results are useful, although the sample compositions are somewhat different than planned. Because we have neutron diffraction results for only three of the samples, we specify all samples in terms of their nominal manganese content, rather than in terms of their manganese content determined by neutron diffraction.

We obtained Mössbauer spectra for all of our samples at both room temperature and 85 K. $Y_2(Fe_{0.7}Mn_{0.3})_{14}B$ is paramagnetic at room temperature, but shows the onset of slow magnetic relaxation at 85 K, while $Y_2(Fe_{0.6}Mn_{0.4})_{14}B$ is paramagnetic at both room temperature and 85 K. The $Y_2(Fe_{0.6}Mn_{0.4})_{14}B$ spectra are quite useful, because the iron quadrupole doublets in this paramagnetic compound allow us to place an upper limit of 0.95 mm/s on the quadrupole splitting in the magnetic $Y_2(Fe_{1-x}Mn_x)_{14}B$ alloys. Figure 1 shows the room-temperature Mössbauer spectrum and fit

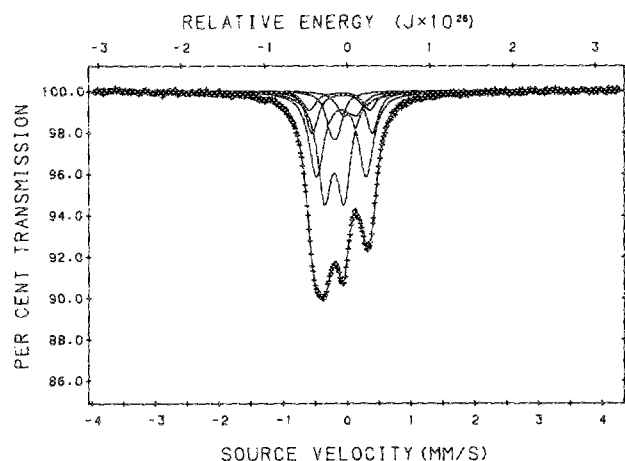


FIG. 1. Room-temperature Mössbauer spectrum of $Y_2(Fe_{0.6}Mn_{0.4})_{14}B$.

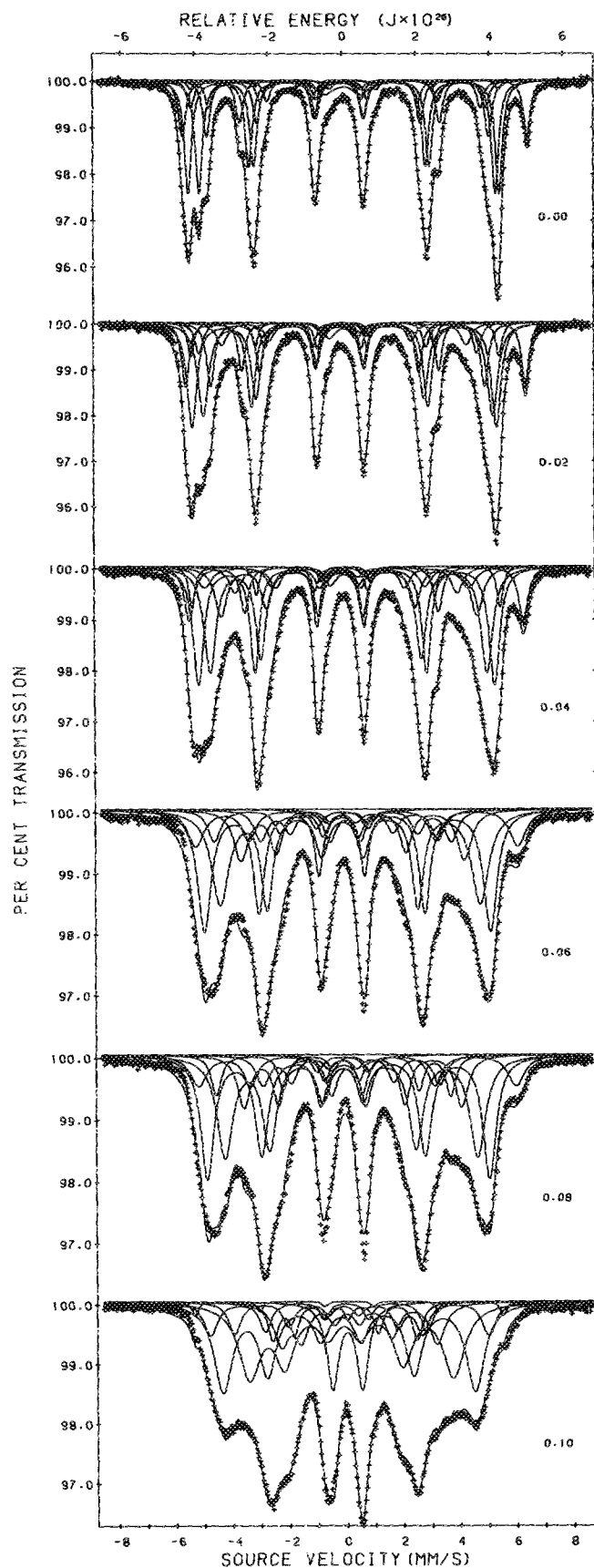


FIG. 2. Mössbauer spectra of $Y_2(Fe_{1-x}Mn_x)_{14}B$, obtained at 85 K.

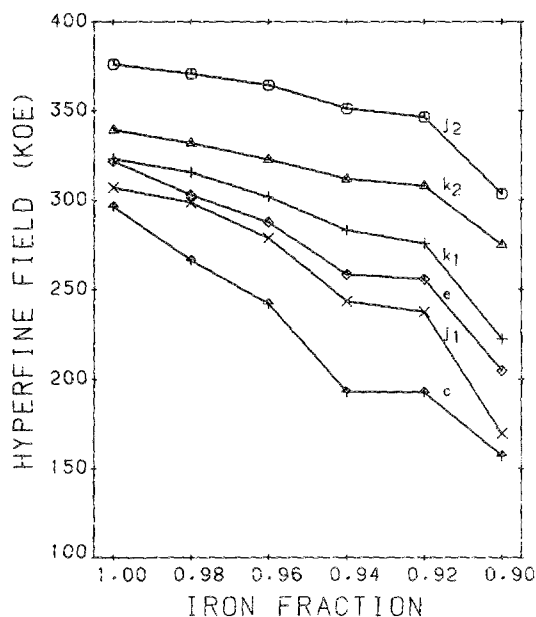


FIG. 3. Internal hyperfine field as a function of manganese composition at 85 K for $Y_2(Fe_{1-x}Mn_x)_{14}B$.

for $Y_2(Fe_{0.6}Mn_{0.4})_{14}B$. Analysis of this spectrum included the use of site populations as given in Table I.

We extrapolated the transition-metal site populations from neutron diffraction, as given in Table I, to lower manganese content. This extrapolation gives us relatively reliable site populations for use in the Mössbauer fits. Figure 2 shows the observed Mössbauer spectra and fits for $Y_2(Fe_{1-x}Mn_x)_{14}B$, taken at 85 K, with x equal to 0.0, 0.02, 0.04, 0.06, 0.08, and 0.10. Small amounts of α -iron, contributing from 3% to 5% of the total absorption, were included in some of these fits. The only modification to the neutron diffraction site populations has been to assign slightly larger manganese occupancies to the $8j_1$ and $8j_2$ sites.

Mössbauer spectra for the $Y_2Fe_{14}B$ sample, obtained at the magic angle,⁵ suggest a slight tendency for the tetragonal c axis of the $Y_2Fe_{14}B$ crystallites to lie in the plane of the absorber. The fits shown in Fig. 2 allow for a small degree of preferred orientation. The areas of the lines in each sextet are constrained in a ratio of $3x:1:1:x:3$, where x ranges from 2.08 to 2.30 over the series of samples, but is fixed at one value for all sextets in any given sample. A value of x equal to 2 would correspond to a Mössbauer absorber with no texture. Figure 3 shows a plot of the internal hyperfine field for each of the iron sites in the $Y_2(Fe_{1-x}Mn_x)_{14}B$ spectra presented in Fig. 2.

DISCUSSION

Prior work on the $Nd_2(Fe_{1-x}Co_x)_{14}B$ system has resulted in disagreement on the site occupations of cobalt and iron. Different Mössbauer effect studies have been used to show that iron preferentially occupies the $8j_2$ and the $16k_2$ sites,⁶ that there is no preferential site occupancy,⁷ and that iron preferentially occupies the $8j_1$ and $8j_2$ sites while cobalt prefers the $16k_1$ and $16k_2$ sites.⁸ In contrast, neutron diffraction indicates a strong preference of iron for the $8j_2$ site, and a

weak preference of cobalt for the $4e$ site and possibly for the $8j_1$ site.⁹

Our results from neutron diffraction and Mössbauer effect spectroscopy for $Y_2(Fe_{1-x}Mn_x)_{14}B$ are completely in accord on site populations. The fits shown in Fig. 2 can be improved only marginally by further varying the iron site populations. The neutron diffraction results are relatively unambiguous because over 400 reflections are used to extract a small set of parameters. The Mössbauer spectra of substituted samples are broadened, partly because the magnetic splittings all decrease as iron is removed, and partly because a range of hyperfine parameters results from the distribution of near-neighbor environments. As a result of the broader absorption linewidths in the substituted samples, more than one set of Mössbauer hyperfine parameters can be found which adequately fit the observed spectra. We have demonstrated that a consistent set of parameters can be found which fit both the Mössbauer spectra and neutron diffraction patterns, and we suggest that discrepancies reported for related compounds could be resolved through a similar combination of investigations using identical samples.

The inability to reach agreement on a model for the hyperfine parameters in $Nd_2Fe_{14}B$ has been well documented.^{10,11} The $Y_2(Fe_{1-x}Mn_x)_{14}B$ Mössbauer spectra shown in Fig. 2 are fit well by a model consistent with that recently proposed for $Nd_2Fe_{14}B$ (Ref. 12) and $Y_2Fe_{14}B$.¹³ The upper limit of 0.95 mm/s on the $Y_2(Fe_{1-x}Mn_x)_{14}B$ quadrupole splitting, as given by the $Y_2(Fe_{0.6}Mn_{0.4})_{14}B$ sample, is useful in assessing the validity of the different models, and supports the model proposed by Grandjean *et al.*,¹² in which the location of the rare-earth near neighbor directly determines the orientation of the electric field gradient at the iron sites.

ACKNOWLEDGMENTS

This work was supported by a University of Missouri Weldon Spring Grant and a NATO cooperative scientific research grant (86/685).

- ¹D. Givord, H. S. Li, and R. Perrier de la Bathie, *Solid State Commun.* **55**, 857 (1984).
- ²Y.-C. Yang, D. E. Tharp, G. J. Long, O. A. Pringle, and W. J. James, *J. Appl. Phys.* **61**, 4343 (1987).
- ³J. F. Herbst, J. J. Croat, F. E. Pinkerton, and W. B. Yelon, *Phys. Rev. B* **29**, 4176 (1984).
- ⁴C. D. Fuerst, G. P. Meisner, F. E. Pinkerton, and W. B. Yelon, *J. Less-Common Met.* **133**, 255 (1987).
- ⁵T. Ericsson and R. Wüppling, *J. Phys. (Paris) Colloq.* **37**, C6-719 (1976).
- ⁶H. M. van Noort and K. H. J. Buschow, *J. Less-Common Met.* **113**, L9 (1985).
- ⁷M. Matsui, M. Doi, and T. Shimizu, *IEEE Trans. Magn.* **MAG-23**, 3113 (1987).
- ⁸H. Honma and H. Ino, *IEEE Trans. Magn.* **MAG-23**, 3116 (1987).
- ⁹J. F. Herbst and W. B. Yelon, *J. Appl. Phys.* **60**, 4224 (1986).
- ¹⁰H. Onodera, A. Fujita, H. Yamamoto, M. Sagawa, and S. Hirokawa, *J. Magn. Magn. Mater.* **68**, 6 (1987).
- ¹¹O. A. Pringle and G. J. Long, in *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, edited by G. J. Long and F. Grandjean (Plenum, New York), Vol. 3, Chap. 2 (in press).
- ¹²F. Grandjean, G. J. Long, D. E. Tharp, O. A. Pringle, and W. J. James, *J. Phys. (Paris) Colloq.* (in press).
- ¹³D. E. Tharp, G. J. Long, O. A. Pringle, G. K. Marasinghe, W. J. James, and F. Grandjean (these proceedings).