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A Neutron Diffraction and Mössbauer Effect Study of the Magnetic Structure of $Y_2(Fe_{1-x}Mn_x)_{14}B$

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A neutron diffraction and Mössbauer effect study of the magnetic structure of $Y_2(Fe_{1-x}Mn_x)_{14}B$

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The magnetic structures of a series of $Y_2(Fe_{1-x}Mn_x)_{14}B$ samples, with x equal to 0.03, 0.10, 0.25, and 0.37, have been studied by powder neutron diffraction and Mössbauer spectroscopy. $Y_2(Fe_{0.97}Mn_{0.03})_{14}B$ and $Y_2(Fe_{0.9}Mn_{0.1})_{14}B$ are ferromagnetic at both 295 and 85 K, $Y_2(Fe_{0.63}Mn_{0.37})_{14}B$ is paramagnetic at both 295 and 85 K, whereas $Y_2(Fe_{0.75}Mn_{0.25})_{14}B$ is paramagnetic at 295 K and is partially ordered at 78 K. The magnetic structure of $Y_2(Fe_{0.75}Mn_{0.25})_{14}B$ is explained in terms of the preferential Mn occupancy of the transition metal $8j_2$ site in the $Y_2Fe_{14}B$ structure. Small amounts of Mn located in this site are very effective in disrupting the long-range ferromagnetic coupling.

Antiferromagnetic interactions have been suggested as one of the reasons for the low Curie temperatures of the $R_2(Fe_{1-x}T_x)_{14}B$ compounds.[1] We have previously reported[2] a Mössbauer analysis of a series of $Y_2(Fe_{1-x}Mn_x)_{14}B$ compounds with $x < 0.1$, and a neutron diffraction study of the crystal structure of $Y_2(Fe_{1-x}Mn_x)_{14}B$ solid solutions with x equal to 0.10, 0.25, and 0.37. The neutron diffraction results indicated a strong preference for Mn to occupy the $8j_2$ site in the $Y_2Fe_{14}B$ structure, and fits of the Mössbauer spectra were consistent with this preference. Moze et al.[3] have reported that both $Y_2(Fe_{0.93}Mn_{0.07})_{14}B$ and $Y_2(Fe_{0.79}Mn_{0.21})_{14}B$ are ferromagnetic at room temperature, with Mn magnetic moments coupled ferromagnetically with the iron moments. In this paper we report the magnetic structures of $Y_2(Fe_{1-x}Mn_x)_{14}B$ with x equal to 0.03, 0.10, 0.25, and 0.37.

Synthesis of the samples, preparation of the Mössbauer absorbers, and the Mössbauer experimental techniques have been previously described.[4,5] Neutron diffraction data for x equal to 0.10, 0.25, and 0.37 were obtained at 8 K with a wavelength of 1.2891 Å. Data for $Y_2(Fe_{0.97}Mn_{0.03})_{14}B$ were obtained at a wavelength of 1.5472 Å at temperatures of 538 K, which is above its Curie temperature, and at 295 K. The lattice constants, iron and Mn occupancies, atomic positions, scale factor, instrumental zero point, individual isotropic thermal parameters for yttrium, transition metals, and boron, and the iron magnetic moments were refined. Refinements were carried out in which the Mn was allowed to have either ferromagnetic or antiferromagnetic moments, but the best fits were obtained with no moments on the Mn.

The refinement of the powder neutron diffraction pattern obtained at 538 K for $Y_2(Fe_{0.97}Mn_{0.03})_{14}B$ (Fig. 1) shows that the tetragonal $Nd_2Fe_{14}B$-type phase was formed and that impurity phases, if present, are negligible. Atomic positions and occupancies are given in Table I. The atomic positions and lattice parameters agree well with those obtained by Moze et al.[3] As seen previously[2,3] Mn prefers the $8j_2$ transition metal site. The refined Mn concentrations of 0.03, 0.10, 0.25, and 0.37 for the four samples are below the corresponding starting concentrations of 0.08, 0.20, 0.30, and 0.40, respectively, indicating that some Mn loss occurred during induction melting. Such a Mn deficiency will result in excess Y and B in the sample. In the worst case ($x = 0.2$ nominal), excess Y and B accounts for 2 and 1 at. % of the sample, respectively. No significant amount of impurity phase was found when we searched our neutron diffraction patterns for peaks corresponding to known phases containing Y, Fe, Mn, or B.

The nuclear parameters for $Y_2(Fe_{0.97}Mn_{0.03})_{14}B$, and those obtained earlier[2] for related $Y_2(Fe_{1-x}Mn_x)_{14}B$ samples, were used as starting parameters for refining the neutron diffraction data obtained below T_c. The results of
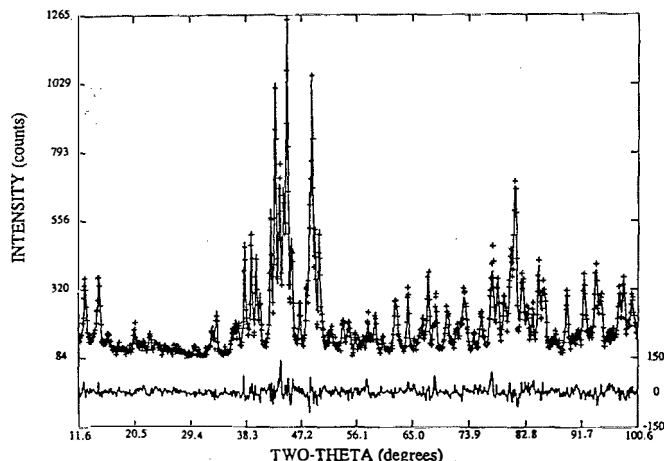

FIG. 1. Calculated (solid line) and experimental (points) powder neutron diffraction patterns for $Y_2(Fe_{0.97}Mn_{0.03})_{14}B$, obtained at 538 K.

TABLE I. Refined atomic positions and iron occupancies for $Y_2(Fe_{0.97}Mn_{0.03})_{14}B$, obtained from powder neutron diffraction data measured at 538 K.

Site	x	y	z	Fe occup.	% Fe occup.
Y, $4f$	0.2678(8)	0.2678(8)	0.0	...	...
Y, $4g$	0.1380(9)	$-0.1380(9)$	0.0	...	...
Fe, $16k_1$	0.2241(5)	0.5862(5)	0.1280(3)	16.0	100
Fe, $16k_2$	0.0358(5)	0.3607(5)	0.1742(4)	15.9(1)	99.1
Fe, $8j_1$	0.0994(6)	0.0994(6)	0.2015(5)	7.5(1)	93.8
Fe, $8j_2$	0.3174(6)	0.3174(6)	0.2470(6)	6.9(1)	86.6
Fe, $4e$	0.5	0.5	0.1159(7)	4.0	100
Fe, $4c$	0.0	0.5	0.0	3.9(05)	98.2
B, $4g$	0.3677(1)	$-0.3677(1)$	0.0	...	...

these refinements are given in Table II. A similar trend for the Mn occupancy was found in $Pr_2(Fe_{1-x}Mn_x)_{14}B$[7] and in $Er_2(Fe_{1-x}Mn_x)_{14}B$.[8]

The Mössbauer spectra and fits for some of the $Y_2(Fe_{1-x}Mn_x)_{14}B$ samples are shown in Fig. 2. Only the $Y_2Fe_{14}B$ spectrum shows a significant amount of α-Fe. The paramagnetic Mössbauer spectra have been fit with six doublets. Spectra which exhibit ferromagnetic ordering have been fit with six sextets. In these fits, a first-order perturbation of the magnetically split levels by a small quadrupole interaction is assumed.[7]

$Y_2(Fe_{0.75}Mn_{0.25})_{14}B$ is paramagnetic at 295 K, but shows partial magnetic ordering at 78 K. The best fit for the 78 K spectrum of $Y_2(Fe_{0.75}Mn_{0.25})_{14}B$ was obtained

TABLE II. Refined occupancies and magnetic parameters for $Y_2(Fe_{1-x}Mn_x)_{14}B$.

|			x		
		0.03	0.10	0.25	0.37
T, K		295	8	8	8
T_c, K[a]		530	435	215	60
Lattice	a, Å	8.7441(1)	8.7105(1)	8.7023(1)	8.7101(2)
Parameters	c, Å	12.0108(7)	11.9587(2)	11.9612(3)	11.9616(2)
Cell volume	V, Å³	918.35(1)	907.33(3)	905.83(5)	907.50(5)
% Mn	$16k_1$	0	2.5	15.8	29.0
occupancy	$16k_2$	0.9	5.0	16.3	22.8
	$8j_1$	6.2	12.9	27.8	39.9
	$8j_2$	13.4	30.0	62.5	69.6
	$4e$	0	3.5	11.3	22.2
	$4c$	1.8	7.9	20.9	32.8
Magnetic	$16k_1$	1.7(2)	1.3(2)	0.7(2)	...
moments	$16k_2$	2.2(2)	2.1(2)	1.1(2)	...
μ_B	$8j_1$	1.7(3)	1.4(3)	0.4(4)	...
	$8j_2$	3.2(3)	3.4(4)	2.9(4)	...
	$4e$	1.4(3)	1.5(3)	0.8(4)	...
	$4c$	1.0(3)	1.4(3)	0.9(4)	...
Net/f.u.,μ_B		27.0	23.0	10.4	...
μ_x/f.u.[a],μ_B		23.3	22.2	9.0	...
R (overall)		5.8	4.9	6.6	6.83
R (nuc.)		5.66	4.82	6.51	6.83
R (mag.)		9.58	7.08	7.56	...
Residual		1.8	2.6	3.8	3.6

[a]Obtained by extrapolating results from Ref. 6.
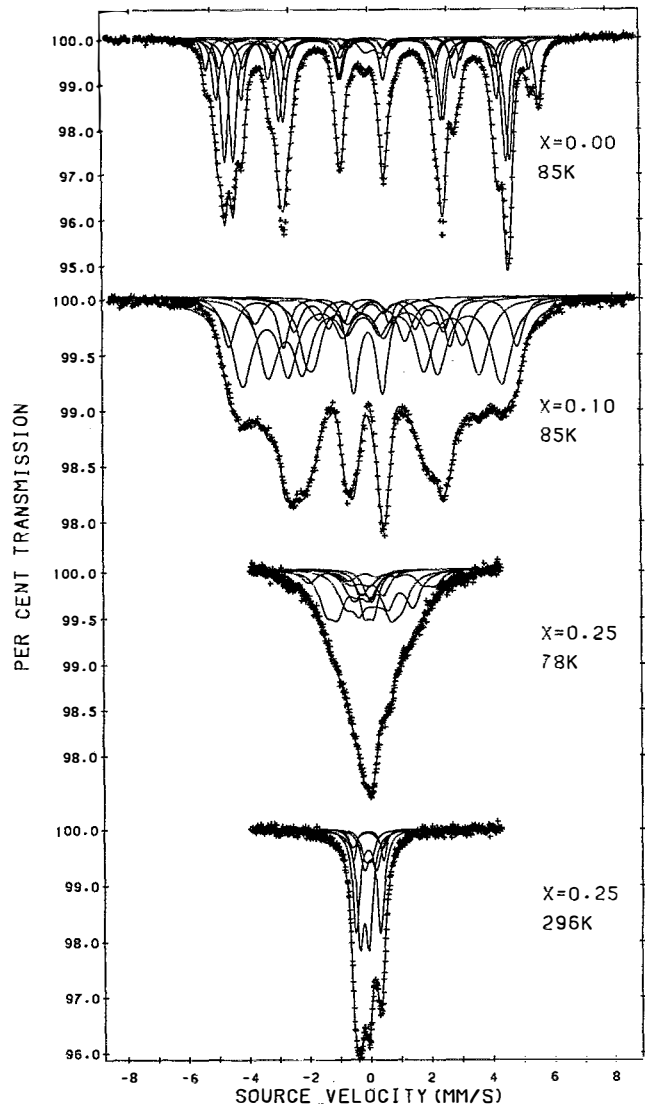
FIG. 2. Mössbauer spectra and fits for $Y_2(Fe_{1-x}Mn_x)_{14}B$ obtained at the indicated temperatures.

with a model which allowed ferromagnetic ordering only on the $8j_2$, $16k_1$, and $16k_2$ sites. The neutron diffraction refinements for this compound, Table II, indicate that only these three sites have appreciable magnetic moments. The refined moments for the $4c$ and $4e$ sites are nonzero, but their small site multiplicities make the refined moments less accurate than for the remaining sites. Thus, paramagnetic doublets have been used for the $8j_1$, $4c$, and $4e$ sites. The observed Mössbauer spectral absorption areas for the $16k_1$ and $16k_2$ sextets are smaller than those expected from their iron occupancy. This suggests that some of the $16k_1$ and $16k_2$ iron atoms order ferromagnetically, while the remainder are unordered at 78 K. To account for the missing absorption area, two additional doublets, representing those $16k_1$ and $16k_2$ iron atoms which are not ferromagnetically ordered, have also been incorporated into the fit. 56% of the total $16k_1$ absorption area and 60% of the total $16k_2$ absorption area correspond to unordered Fe atoms.

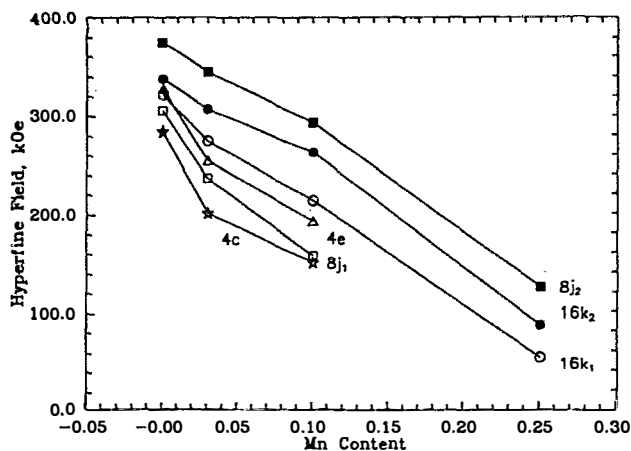Such a partially ordered structure can be explained by

FIG. 3. Hyperfine fields for $Y_2(Fe_{1-x}Mn_x)_{14}B$, with x equal to 0.03, 0.10, and 0.25, measured at either 78 or 85 K.

a distribution of the number of Fe atoms having different numbers of Mn near neighbors. The sextets for each Fe site are split into subspectra whose relative areas also follow a binomial distribution. The subspectra corresponding to the Fe atoms having the larger numbers of Mn near neighbors will have smaller hyperfine fields. At higher Mn concentrations, when the average field at an Fe site is already quite low, it is possible for the Fe atoms with large numbers of Mn near neighbors to have zero or very small moments, giving rise to a "partially ordered" site.

Hyperfine fields as a function of Mn content are shown in Fig. 3. The hyperfine fields decrease rapidly with increasing Mn content, and even at 78 K, $Y_2(Fe_{0.63}Mn_{0.37})_{14}B$ shows no indication of ferromagnetic ordering. This is consistent with the neutron diffraction results discussed above. The $8j_1$ and $4e$ sites have the largest proportions of $8j_2$ near-neighbor sites, 3/9 and 2/9, respectively.[9] Because Mn preferentially substitutes on the $8j_2$ site, the rapid decrease of the magnetic moments on the $8j_1$ and $4e$ sites can be attributed to their higher percentage of Mn near neighbors. The percentages of Mn near neighbors for each site can be calculated by assuming a binomial distribution. The percentages are 26%, 26%, 31%, 18%, 28%, and 16% for the $16k_1$, $16k_2$, $8j_1$, $8j_2$, $4e$, and $4c$ sites, respectively, for $Y_2(Fe_{0.75}Mn_{0.25})_{14}B$.

Based on the above percentages, the iron moments on the $8j_2$ and $4c$ sites should be least affected by Mn substitution, whereas the iron moments on the $8j_1$ site should be the most affected. The $8j_1$ and $8j_2$ moments follow this pattern, but the $4c$ moment is significantly reduced. This indicates that the $4c$ site, which in these compounds has only $16k_1$ and $16k_2$ transition metal near neighbors as well as nonmagnetic rare earth near neighbors, is particularly susceptible to the breakdown of the long range magnetic order caused by the Mn substitution.

We have also used the binomial distribution model for fitting the Mössbauer spectra of the $Y_2(Fe_{1-x}Mn_x)_{14}B$ samples. This approach assigns to each iron site both a maximum hyperfine field H_{max} when there are no Mn near neighbors, and a reduction ΔH for each Mn atom substi-

tuted in the near-neighbor environment.[10] Analysis of the 295 K Mössbauer spectra of $Y_2(Fe_{0.9}Mn_{0.1})_{14}B$ with this model indicated that H_{max} was largest for the $8j_2$ site and smallest for the $8j_1$ site. As would be expected from the near-neighbor environments, the largest ΔH was obtained for the $4c$ and $4e$ sites and the smallest ΔH was obtained for the $8j_2$ site. The $8j_2$ site has the largest number of iron near neighbors, and it also has the largest Wigner–Seitz cell volume.[10] Thus when an $8j_2$ near-neighbor iron site is substituted by Mn, only 1/12 of the near-neighbor iron atoms are replaced. Also, because the site volume is large, the transferred hyperfine field will be relatively small. In contrast the $4c$ and $4e$ sites have only eight and nine iron near neighbors, respectively, and with each Mn substitution, 1/8 or 1/9 of the iron atoms are replaced. In addition the site volumes are smaller for these two sites when compared with the $8j_2$ site, and, as a result, the transferred hyperfine field will be larger.

In $Er_2(Fe_{1-x}Mn_x)_{14}B$ for values of x above 0.25, the Er–Mn coupling results in an antiferromagnetic coupling of the moments on the Mn atoms occupying the $8j_2$ site.[8] The magnetic ordering of the iron atoms is also quite different than in $Y_2(Fe_{1-x}Mn_x)_{14}B$. The difference between $Er_2(Fe_{1-x}Mn_x)_{14}B$ and $Y_2(Fe_{1-x}Mn_x)_{14}B$ apparently arises because the transition metal-transition metal exchange dominates at low values of x, but the rare earth-transition metal exchange dominates at high values of x.[8] In the case of $Y_2(Fe_{1-x}Mn_x)_{14}B$, where there is no rare earth-transition metal magnetic exchange, two reasonable alternatives in addition to antiferromagnetic Mn ordering, are to either assign zero moments to the Mn atoms, or to assume that they couple ferromagnetically with the iron moments. In their analysis of $Y_2(Fe_{0.93}Mn_{0.07})_{14}B$ and $Y_2(Fe_{0.79}Mn_{0.21})_{14}B$, Moze et al.[3] chose to use the second approach. We find no evidence in the weak magnetic scattering for either ferromagnetic or antiferromagnetic[6] coupling of Mn moments with those of the Fe. The large drop in magnetization with increasing Mn content suggests the presence of "paramagnetic" Mn which would effectively disrupt the long range magnetic order.

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