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# A Mössbauer effect study of the structural and magnetic properties of $Y_2(Fe_{1-x}Al_x)_{14}B$

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The crystallographic and magnetic properties of  $Y_2(Fe_{1-x}Al_x)_{14}B$ , where  $x$  equals 0.00, 0.02, 0.04, 0.06, and 0.08, have been investigated by Mössbauer spectroscopy and magnetic measurements at room temperature and 85 K. Magnetic anisotropy and magnetization changes with aluminum substitution indicate that, because of size, the aluminum preferentially occupies the  $j_2$  site over the remaining five crystallographically nonequivalent iron sites. This preferential occupation has been confirmed by Mössbauer spectral studies, which indicate that the compositional variation of the hyperfine field for each site is related to the number of near-neighbor aluminum atoms for the site. This compositional variation is helpful in assigning the different spectral components in these alloys as well as in the related  $Nd_2(Fe_{1-x}Co_x)_{14}B$  and  $Y_2(Fe_{1-x}Co_x)_{14}B$  alloys. In all cases these assignments are consistent with the local symmetry and coordination environment for each site.

## INTRODUCTION

The new permanent magnets based on the  $R_2Fe_{14}B$  compounds, where  $R$  is yttrium or a rare earth, exhibit the highest energy product yet achieved in a permanent magnet.<sup>1</sup> Substitution of cobalt for iron has been shown to increase the Curie temperature but lower the coercivity of these compounds.<sup>2,3</sup> In contrast, substitution of aluminum for iron has been shown to increase both the coercivity and anisotropy field in  $Y_2Fe_{14}B$ , with only slight decreases in the saturation magnetization and Curie temperature.<sup>4</sup> This is of considerable interest because appropriate substitution of cobalt and aluminum in the  $Nd_2Fe_{14}B$  magnets might increase both their Curie temperature and coercivity while retaining the high energy product.

We have carried out a Mössbauer effect study of  $Y_2(Fe_{1-x}Al_x)_{14}B$  with  $x$  equal to 0.00, 0.02, 0.04, 0.06, and 0.08, to determine the effect of aluminum substitution on the magnetic properties of  $Y_2Fe_{14}B$ . The  $R_2Fe_{14}B$  space group is  $P4_2/mnm$ , with four formula units per unit cell. Table I lists the iron atomic sites and occupancies, as determined for  $Nd_2Fe_{14}B$  by neutron diffraction.<sup>5</sup>  $Y_2(Fe_{1-x}Al_x)_{14}B$  also crystallizes in the  $P4_2/mnm$  space group provided  $x$  is less than 0.1, the solubility limit of aluminum in  $Y_2Fe_{14}B$ . Apparently because of internal void size, the aluminum atoms substitute preferentially on the  $j_2$  site.<sup>4</sup> Our Mössbauer effect studies confirm this preferential occupation and indicate a much larger decrease in the iron hyperfine field than can be accounted for by stoichiometric dilution with aluminum. In addition, the relationship between the iron coordination environment in  $Y_2(Fe_{1-x}Al_x)_{14}B$  and the observed compositional dependence of the various hyperfine fields permits us to assign the  $j_2$ ,  $k_2$ ,  $k_1$ , and  $j_1$  sites (the major Mössbauer spectral components), and to tentatively assign the  $c$  and  $e$  sites in our Mössbauer spectra.

## EXPERIMENTAL METHODS

The samples of  $Y_2(Fe_{1-x}Al_x)_{14}B$  were prepared by arc melting 99.9% pure starting materials, followed by vacuum

annealing at 973 K for 6 h.<sup>4</sup> X-ray diffraction results indicated the samples were pure single-phase alloys. Mössbauer absorbers, consisting of 400-mesh (0.038-mm<sup>2</sup>) powders, were prepared under a pure nitrogen atmosphere. The absorber thicknesses were 36 mg/cm<sup>2</sup>. The Mössbauer spectra were obtained at room temperature and at 85 K by using a Harwell constant-acceleration spectrometer, which utilized a room-temperature rhodium matrix cobalt-57 source and was calibrated at ambient temperature with natural abundance  $\alpha$ -iron foil. Mössbauer spectra taken at the magic angle<sup>6</sup> for  $Y_2Fe_{14}B$  demonstrated the absence of preferred orientation effects in our samples. The Mössbauer spectra were fitted with six magnetic sextets composed of Lorentzian lines by least-squares computer minimization techniques. For each magnetic component, the variable parameters were the isomer shift  $\delta$ , the internal hyperfine field  $H_{int}$ , the quadrupole shift  $QS$ , the linewidth  $\Gamma$ , the incremental linewidth  $\Delta\Gamma$ , and the total absorption area. The linewidths of lines 2 and 5 were  $\Gamma + 0.5\Delta\Gamma$  and the linewidths of lines 1 and 6 were  $\Gamma + \Delta\Gamma$ , where  $\Delta\Gamma$  was determined from preliminary fits. Relative areas of the lines in each sextet were constrained in the ratio 3:2:1:1:2:3 as is required for a randomly oriented powder sample. The relative areas for each of the six

TABLE I. Atomic sites, occupancies, and the variation of the internal hyperfine field with composition for  $Y_2(Fe_{1-x}Al_x)_{14}B$ . (In the last column, RT denotes room temperature.)

Atom	Site	Occupancy	Slope (RT) <sup>a</sup>
Fe	$j_2$	8	— 5.7
Fe	$k_2$	16	— 6.7
Fe	$k_1$	16	— 8.2
Fe	$j_1$	8	— 9.6
Fe	$e$	4	— 10.9
Fe	$c$	4	— 3.1

<sup>a</sup> Units are kOe/(percent change in aluminum content).

magnetic spectral components were constrained to the relative occupation values determined from neutron diffraction refinements<sup>5</sup> on  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , as given in Table I, except that the area of the  $j_2$  site was made to satisfy the additional constraint that the aluminum atoms substitute entirely on that site. Where required, one paramagnetic doublet, due either to traces of an impurity or to a superparamagnetic component in the finely divided powder, was included in the fits.

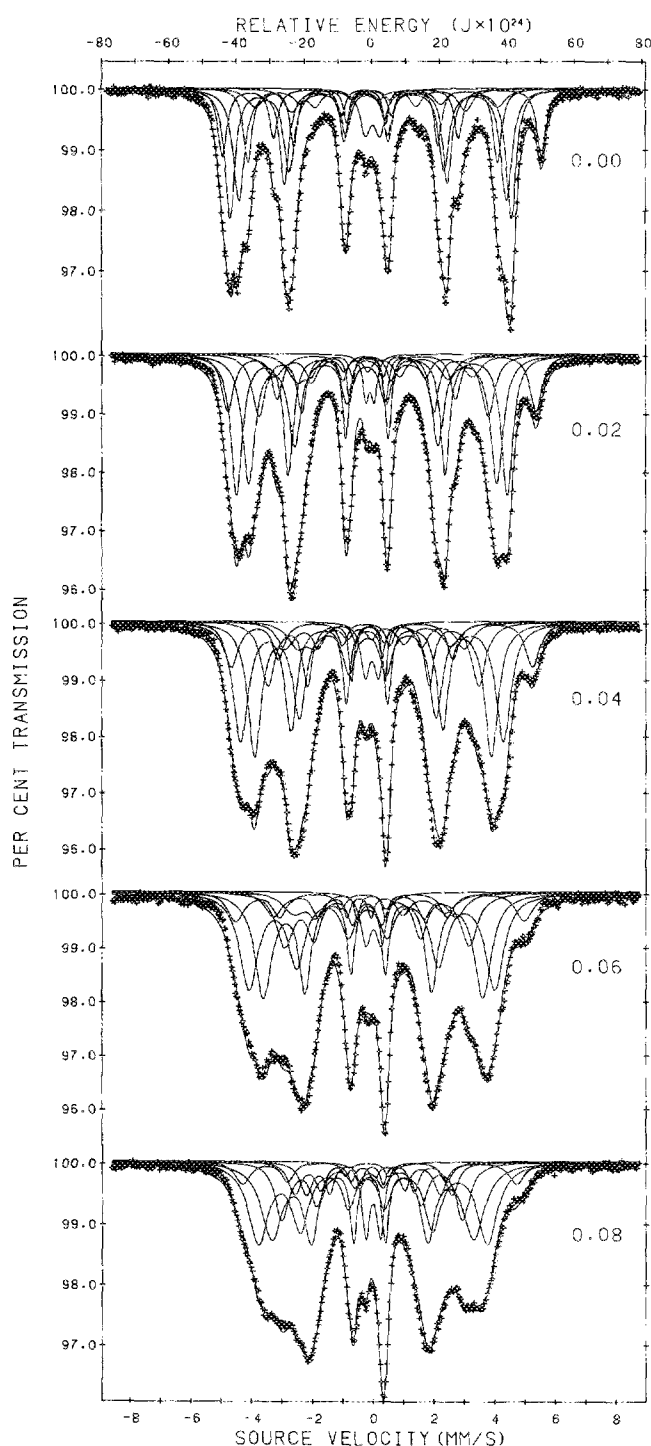


FIG. 1. Mössbauer spectra of  $\text{Y}_2(\text{Fe}_{1-x}\text{Al}_x)_{14}\text{B}$  obtained at room temperature.

## RESULTS AND DISCUSSION

The Mössbauer spectra of  $\text{Y}_2(\text{Fe}_{1-x}\text{Al}_x)_{14}\text{B}$  obtained at room temperature and their best fits are shown in Fig. 1. Comparable fits were obtained for the 85-K spectra, which are generally similar in appearance to the room-temperature spectra. The individual components shown in Fig. 1 represent the six crystallographically distinct transition-metal sites, as listed in Table I. Figure 2 illustrates the decrease of the iron hyperfine field per site as the iron magnetic sublattice in  $\text{Y}_2\text{Fe}_{14}\text{B}$  is diluted with aluminum. The slope of the compositional variation of  $H_{\text{int}}$  is given in Table I. The collapse of the magnetization with aluminum substitution is much faster than one would expect based only on dilution of magnetic iron with nonmagnetic aluminum. This is shown in Table II, which gives the variation with composition of the observed saturation magnetization and magnetic moment at 1.5 K,<sup>4</sup> the calculated decrease in moment expected upon dilution with aluminum, and the decrease in the average iron magnetic moment at room temperature and 85 K as determined from our Mössbauer spectral analysis. In the simple dilution model, the average iron moment is given by  $\mu = \mu_0(1 - x)$ , where  $\mu_0$  is the average iron moment for  $x = 0$ . The decrease in the internal hyperfine field, and hence magnetic moments, with the addition of aluminum is about 5 times larger than that found for substitution with cobalt.<sup>7</sup>

In our analysis of the hyperfine fields in  $\text{Y}_2(\text{Fe}_{1-x}\text{Al}_x)_{14}\text{B}$ , we take the order of the internal hyperfine fields to be  $j_2 > k_2 > k_1 > j_1 > e > c$ , where the assignment of the last two, weakest-intensity, fields is tentative. This assignment is consistent with our results<sup>7</sup> on

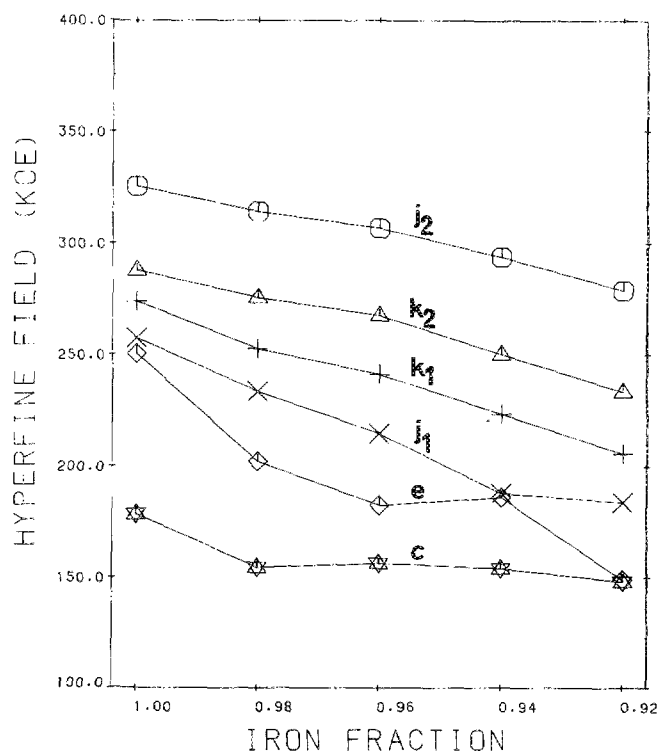


FIG. 2. Variation with composition of the internal hyperfine fields for  $\text{Y}_2(\text{Fe}_{1-x}\text{Al}_x)_{14}\text{B}$  at room temperature.

TABLE II. The saturation magnetization and magnetic moment for  $Y_2(Fe_{1-x}Al_x)_{14}B$  at 1.5 K (Ref. 4), the calculated decrease in moment for dilution only, and the decrease in the average iron magnetic moment at room temperature (RT) and 85 K as determined from our Mössbauer spectral analysis.

$x$	$\sigma$ (emu/g)	$\mu$ (obs.) ( $\mu_B$ /atom)	$\mu$ (calc.) ( $\mu_B$ /atom)	$\mu$ (RT) ( $\mu_B$ /iron)	$\mu$ (85 K) ( $\mu_B$ /iron)
0.00	156.0	1.94	1.94	1.78	2.07
0.02	148.6	1.89	1.90	1.70	1.99
0.04	144.2	1.79	1.86	1.62	1.88
0.06	134.8	1.71	1.82	1.50	1.77
0.08	129.2	1.65	1.78	1.38	1.67

$Nd_2(Fe_{1-x}Co_x)_{14}B$  and  $Y_2(Fe_{1-x}Co_x)_{14}B$ , and the assignment of the four stronger-intensity fields is also generally consistent with previous Mössbauer and neutron diffraction studies of  $Nd_2Fe_{14}B$  and  $Y_2Fe_{14}B$ .<sup>7</sup> The assignments of the hyperfine fields on the  $j_2$ ,  $j_1$ ,  $e$ , and  $c$  sites can be justified by arguments based on the structure and the preferred occupation by aluminum of the  $j_2$  site in  $Y_2(Fe_{1-x}Al_x)_{14}B$ .

As shown in Table I, of the four major sites in  $Y_2(Fe_{1-x}Al_x)_{14}B$ , the  $j_2$  site has the smallest compositional variation of its internal field when compared to the  $k_2$ ,  $k_1$ , and  $j_1$  sites. Exactly the opposite variation with composition was found<sup>7</sup> in  $Y_2(Fe_{1-x}Co_x)_{14}B$  and  $Nd_2(Fe_{1-x}Co_x)_{14}B$ . Further, one of the weak-intensity sites with a small field, which we assign to the  $c$  site, has little variation with composition in its internal field. We can understand these differences by using arguments based on the different local site coordination environments. The  $j_2$  site has no iron  $j_2$  near neighbors amongst its twelve iron near neighbors. Consequently, if all the aluminum occupies  $j_2$  sites, any  $j_2$  site occupied by iron will see only iron and no aluminum near neighbors. The  $j_2$  site will thus be only indirectly affected by the aluminum substitution, due to the weaker fields at the remaining sites. Hence the decrease in  $H_{int}$  should be less for the  $j_2$  site compared to all other sites except the  $c$  site. This can be seen in Fig. 2 and the values for the slopes given in Table II, and is even obvious in the experimental data, where the  $j_2$  site appears as the wing or shoulder at the extreme

right in the spectra. The only other iron site with no  $j_2$  near neighbors is the  $c$  site. This site should be affected even less than the  $j_2$  site by the aluminum substitution because only eight of its near neighbors are iron. The remaining four iron sites all have iron  $j_2$  atoms as near neighbors, and will experience reduced hyperfine fields due to interruption of magnetic exchange when aluminum substitutes on the  $j_2$  site. Of the four strong-intensity iron sites, the  $j_1$  site, with the largest number of  $j_2$  near neighbors, experiences the largest decrease in hyperfine field with aluminum substitution. We assign the  $e$  site, which has two  $j_2$  near neighbors, to the weak sextet which changes the most with aluminum substitution.

There remains some ambiguity regarding the relative magnitudes of the hyperfine fields at the  $c$  and  $e$  sites. These components have the smallest occupancy and hence contribute the least to the spectral intensity. The fits are ambiguous in that either  $H_{int,c} > H_{int,e}$  or the reverse both produce satisfactory fits, where we identify the  $c$  site as the one which has the smallest variation with composition. In other words, our spectral results demand one site, which we identify as the  $c$  site, with little or no compositional dependence, but are ambiguous concerning the exact value of the hyperfine field for that site. Further studies are being undertaken in an attempt to determine the relative ordering of the  $c$  and  $e$  sites.

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