

## Mössbauer spectroscopy study of the rhombohedral phase $Y_2Fe_{17}N_x$ with intermediate nitrogen content ( $0 \leq x \leq 2.8$ )

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Mössbauer spectra were obtained at 15 K from samples of rhombohedral  $Y_2Fe_{17}$  and its nitrides  $Y_2Fe_{17}N_x$ , with nominal nitrogen contents of  $x=0.6, 1.2, 1.8, 2.4,$  and  $2.8$ . The spectra have been analyzed using a model which is consistent with the crystallographic structure and with magnetization that lies along a general direction in the hexagonal basal plane. The hyperfine field values for the four crystallographically inequivalent Fe sites change differently upon nitrogenation. For each of the  $Y_2Fe_{17}N_x$  samples with intermediate N content, the spectrum can be described as a superposition of two components, one from the nitrated shell of the sample particle and one from the outer portion of its unnitrated core. These results, along with earlier  $^{57}Fe$  nuclear magnetic resonance measurements, yield a consistent picture for the two-phase configuration of  $Y_2Fe_{17}N_x$  and its hyperfine field behavior. © 1999 American Institute of Physics. [S0021-8979(99)55808-8]

### I. INTRODUCTION

Rare-earth iron nitrides  $R_2Fe_{17}N_x$ , where R is a rare-earth element or yttrium, have exhibited improved hard magnetic properties in comparison to their corresponding binary parent  $R_2Fe_{17}$ .<sup>1</sup> Because yttrium is nonmagnetic,  $Y_2Fe_{17}N_x$  provides an excellent opportunity for isolating the Fe sublattice and for studying hyperfine field (HF) behavior at the various Fe sites. Although there have been several previous reports of Mössbauer effect (ME) studies on  $Y_2Fe_{17}N_x$ , their main focus has been on the hexagonal parent  $Y_2Fe_{17}$  and fully nitrated compound  $Y_2Fe_{17}N_x$  with  $x \approx 2.6-2.8$ .<sup>2-5</sup> Detailed information concerning how the HF at a particular Fe site changes as nitrogen enters the  $Y_2Fe_{17}$  particle is needed for a better understanding of the nitrogenation process and the effect of the N atoms on the Fe magnetic moment. In this work, Mössbauer spectra for rhombohedral  $Y_2Fe_{17}N_x$  with intermediate nitrogen content  $x$  have been obtained systematically at 15 K. The analysis shows that, upon nitrogenation, the HF values at inequivalent Fe sites change differently, which is consistent with earlier  $^{57}Fe$  nuclear magnetic resonance (NMR) experiments.<sup>6</sup> The ME spectra for  $Y_2Fe_{17}N_x$  with  $x < 2.8$  provide direct evidence that, before reaching the fully nitrated state, each sample particle has a two-region configuration with a fully nitrated outer shell and a nearly unnitrated core.

### II. EXPERIMENTAL APPARATUS AND PROCEDURE

The  $Y_2Fe_{17}N_x$  samples with nominal N contents of  $x = 0.6, 1.2, 1.8, 2.4,$  and  $2.8$  used in this work were the same samples used in earlier  $^{57}Fe$  and  $^{89}Y$  NMR studies.<sup>6,7</sup> A par-

ent  $Y_2Fe_{17}$  ingot was prepared by arc melting, annealed in vacuum at approximately 950 °C for 7 days, ground into a powder, and passed through sieves to obtain five samples with average particle diameters of 50, 40, 34, 28, and 17  $\mu m$ . These samples were nitrogenated simultaneously at 480 °C under 1 bar of  $N_2$  gas for 17 h. X-ray diffraction (XRD) using Cu  $K\alpha$  radiation showed the rhombohedral  $Th_2Zn_{17}$ -type structure, with no trace of the hexagonal  $Th_2Ni_{17}$ -type structure. However, there was some precipitation of body-centered-cubic (bcc)  $\alpha$ -Fe ( $\approx 6\%$  for  $Y_2Fe_{17}N_{2.8}$ ). In addition, for this work, several  $Y_2Fe_{17}$  powders were similarly prepared and checked by XRD in order to obtain a parent sample. There was some amount of hexagonal phase in all of these parent powders, but no bcc  $\alpha$ -Fe precipitation.

Mössbauer spectra were obtained using an Austin Science Associates constant-acceleration spectrometer with a 30 mCi source of  $^{57}Co$  in a rhodium matrix. A 15 K sample temperature was obtained using a closed-cycle two-stage Displex helium refrigerator with a DMX-20 vibration-isolation interface (APD Cryogenics). The velocity scale was calibrated using an  $\alpha$ -Fe absorber at room temperature.

### III. RESULTS AND DISCUSSION

In rhombohedral  $Y_2Fe_{17}N_x$ , there are four crystallographically inequivalent Fe sites,  $6c, 9d, 18f,$  and  $18h$ , together with an easy magnetization direction in the hexagonal basal plane, but not in general along the crystallographic  $a$  direction.<sup>8</sup> Consequently, each of the  $9d, 18f,$  and  $18h$  Fe sites is divided into three magnetically inequivalent subsites due to different angles between the principal axis of the electric field gradient and the magnetization direction. Therefore, a Mössbauer effect spectrum for  $Y_2Fe_{17}N_x$  consists a total of

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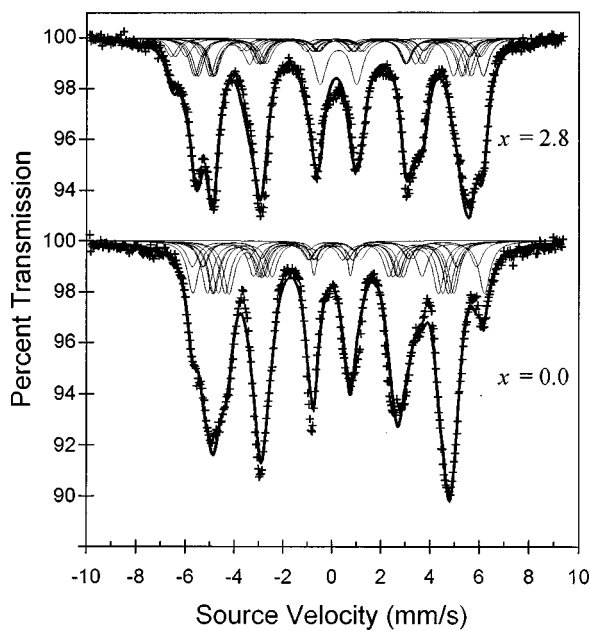


FIG. 1. Mössbauer spectra for the parent  $Y_2Fe_{17}$  and fully nitrated  $Y_2Fe_{17}N_{2.8}$  at 15 K. The data points represent the experimental spectrum, the thin lines represent the subspectra sextets, and the thick line represents the fit to the spectrum.

ten sextets with a population ratio of 6:3:3:3:6:6:6:6:6:6 for  $6c$ ,  $9d$ ,  $18f$ , and  $18h$ . However, these 10 sextets are not completely independent since the three subsites for each of the  $9d$ ,  $18f$ , and  $18h$  Fe atoms have the same crystallographic environment and, thus, the same isomer shift. Also, the hyperfine field values should not be very different for the three subsites within the same crystallographic site because the variation in the dipolar interaction is expected to be small.

Figure 1 shows ME spectra for a typical parent  $Y_2Fe_{17}$  sample and the fully nitrated  $Y_2Fe_{17}N_{2.8}$  sample at 15 K. Both spectra have been fit with ten magnetic sextets, each having the following parameters: a magnetic hyperfine field, an isomer shift, and a quadrupole splitting. One uniform line-width value of 0.27 mm/s was used for all sextets. The expected intensity ratio of 3:2:1 for lines 1, 2, and 3 as well as for lines 6, 5, and 4 was maintained for each sextet. The assignment of the sextets to the various Fe sites was based on a combination of previous Mössbauer studies<sup>3,8</sup> and  $^{57}Fe$  NMR measurements.<sup>6</sup>

TABLE I. Hyperfine field values (in tesla) obtained from fitting the Mössbauer spectra at 15 K for the rhombohedral parent  $Y_2Fe_{17}$  and fully nitrated  $Y_2Fe_{17}N_{2.8}$ .

Site	$x=0.0$	$x=2.8$
$6c$	37.0	36.6
$9d_a$	36.0	39.0
$9d_b$	32.5	37.4
$9d_c$	32.1	37.4
$18f_a$	30.6	33.4
$18f_b$	30.6	32.1
$18f_c$	30.1	30.4
$18h_a$	27.9	34.9
$18h_b$	27.9	34.3
$18h_c$	27.6	32.1

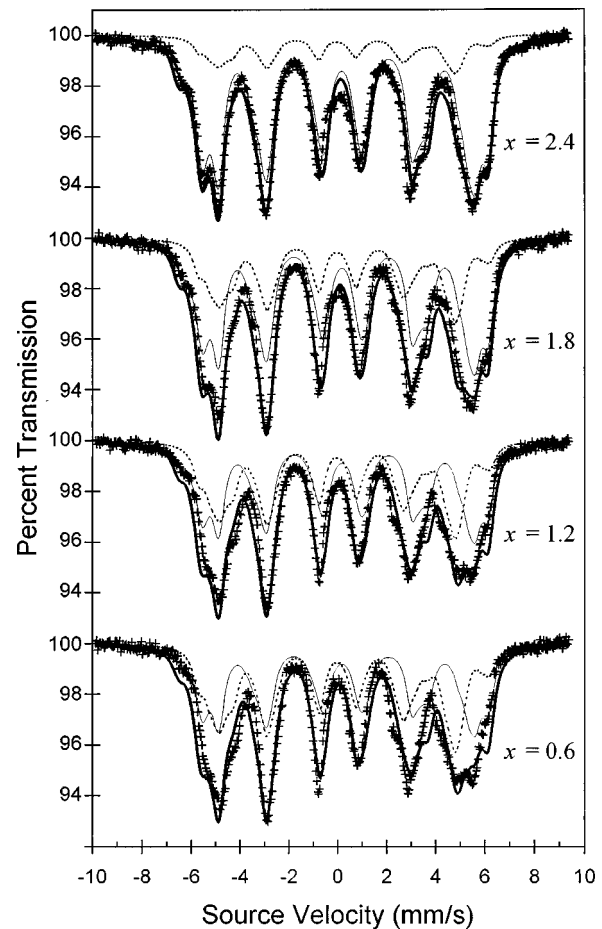


FIG. 2. Mössbauer spectra for  $Y_2Fe_{17}N_x$  at 15 K. The data points represent the experimental spectrum, the dashed line represents the unnitrated component, and the thin solid line represents the nitrated component. The thick solid line represents the superposition of the two components.

Table I lists the hyperfine field values obtained by fitting the ME spectra for the parent  $Y_2Fe_{17}$  and the fully nitrated  $Y_2Fe_{17}N_{2.8}$  samples. It can be seen that the HF for the “dumbbell”  $6c$  Fe site (37.0 T) remains essentially unchanged upon nitrogeneration. There are three HF values for each of the  $9d$ ,  $18f$  and  $18h$  sites, and all of them increase with nitrogeneration; the largest increase occurs at the  $9d$  and  $18h$  sites. For the  $Y_2Fe_{17}$  parent reported here, the average HF values for the four crystallographic Fe sites are in descending order,  $6c > 9d > 18f > 18h$ , which is consistent with an earlier assignment for hexagonal  $Y_2Fe_{17}$ .<sup>3</sup> After nitrogeneration, the new order is  $9d > 6c > 18h > 18f$  with changes in place between  $9d$  and  $6c$  and between  $18h$  and  $18f$ . These results are in complete agreement with  $^{57}Fe$  NMR measurements.<sup>6</sup> In addition, the ME results reported here complement the NMR data because some of the  $^{57}Fe$  peaks in the parent  $Y_2Fe_{17}$  NMR spectrum were obscured by a large  $^{89}Y$  peak covering a spectral region from 38 to 43 MHz.<sup>6</sup> Using the  $^{57}Fe$  gyromagnetic ratio of 1.38 MHz/T and average hyperfine field values of 30.4 and 27.8 T for the  $18f$  and  $18h$  sites in  $Y_2Fe_{17}$ , the corresponding NMR peaks are 42.0 and 38.4 MHz, respectively. Also, the  $^{57}Fe$  peak in the parent  $Y_2Fe_{17}$  NMR spectrum at 50.1 MHz (36.3 T), which was assigned to the  $6c$  Fe site,<sup>6</sup> actually contains a contribution from one third of the  $9d$  sites.

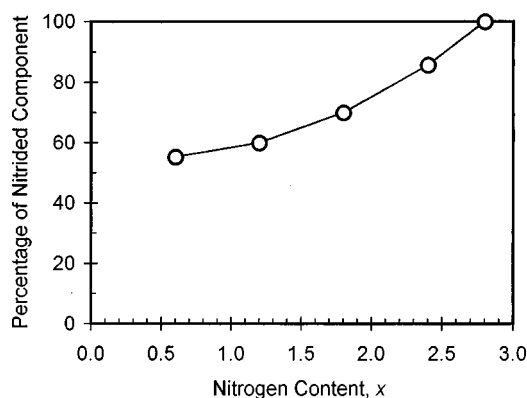


FIG. 3. Percentage of the nitrified component observed in the Mössbauer spectra vs nitrogen content  $x$ .

Figure 2 shows the ME spectra obtained from  $Y_2Fe_{17}N_x$  with intermediate N contents of  $x=0.6, 1.2, 1.8,$  and  $2.4$ . Attempts to fit these spectra using a single ten sextet model with one set of hyperfine parameters were unsuccessful, which clearly demonstrates that the relevant hyperfine parameters do not simply vary monotonically as nitrogen is introduced into the 2:17 lattice. Instead, good fits to all four spectra in Fig. 2 could be obtained using a superposition model which involved a linear combination of the spectra for the unnitrified  $Y_2Fe_{17}$  parent and the fully nitrified  $Y_2Fe_{17}N_{2.8}$  compound (Fig. 1). The superposition model uses only two adjustable parameters: one which is a measure of the contribution to the spectrum due to the unnitrified component and another which is a measure of the contribution due to the fully nitrified component. From Fig. 2, it can be seen that the fits are quite good except for some minor deviation with the sixth line.

Figure 3 shows the percentage of the ME spectrum that is attributed to the nitrified component for each  $Y_2Fe_{17}N_x$  sample as a function of N content  $x$ . The monotonic increase to the limiting value for  $Y_2Fe_{17}N_{2.8}$  is apparent. The above analysis provides direct evidence for the two-region configuration that exists in a sample particle during the nitrogenation process. The nitrified component results from the outer shell of the particle where all of the unit cells contain some maximum number of N atoms, whereas the unnitrified component is due to the inner core which is devoid of N atoms. This nitrified–unnitrified shell-core configuration is a consequence of the strong chemical effect between a nitrogen atom and the lattice, which results in the N atom becoming immobile once it enters an octahedral interstitial site.<sup>9</sup> The nitrogenation process can be described as the gradual growth of the nitrified shell at the expense of the unnitrified core. If the percentage of the volume of the nitrified region is calculated based on an ideal shell-core model, one obtains values of 21%, 43%, 64%, 86%, and 100% for  $x=0.6, 1.2, 1.8, 2.4,$  and  $2.8,$  respectively. The data in Fig. 3 agree with the calculated percentages for  $x=2.4$  and  $1.8,$  but are progressively higher for  $x=1.2$  and  $0.6$ . The fact that the percentage of the unnitrified core is underrepresented for the lower N content samples arises from the finite penetration of the 14.4 keV  $\gamma$  rays used in the  $^{57}Fe$  Mössbauer experiments. A detailed

calculation using the radiation penetration depth and absorption cross sections<sup>10</sup> revealed that the samples with  $x=0.6$  and  $1.2$  (particle radii of 25 and 20  $\mu m$ , respectively) would not have the entire core exposed to the radiation, resulting in the apparent larger ratio of the nitrified component to the unnitrified component.

#### IV. SUMMARY AND CONCLUSIONS

A detailed analysis of the Mössbauer spectra obtained at 15 K from rhombohedral phase  $Y_2Fe_{17}N_x$  with intermediate N content was presented. It was found that for the dumbbell  $6c$  site, the hyperfine field values were essentially unchanged upon nitrogenation, while the HF values for the  $9d$  and  $18h$  sites experienced relatively large increases of approximately 5 T and the value for the  $18f$  site experienced a relatively small increase of 1.6 T. As a result, the HF sequence (averaged over the subsites) changed from  $6c > 9d > 18f > 18h$  for  $Y_2Fe_{17}$  to  $9d > 6c > 18h > 18f$  for  $Y_2Fe_{17}N_{2.8}$ . This is consistent with, and complements, the hyperfine field results from earlier  $^{57}Fe$  NMR experiments.<sup>6</sup> In particular, hyperfine field values are now clearly obtained for the  $18f$  and  $18h$  Fe sites whose NMR peaks are obscured by a large  $^{89}Y$  peak over the same spectral region in the NMR spectrum of the parent compound. For the  $Y_2Fe_{17}N_x$  samples with an intermediate N content of  $0.6 \leq x \leq 2.4$ , the Mössbauer spectra can be fit quite well by using a superposition which involves a linear combination of the spectra for the unnitrified  $Y_2Fe_{17}$  and the fully nitrified  $Y_2Fe_{17}N_{2.8}$ . This strongly supports the nitrified–unnitrified shell-core model which was proposed earlier for the sample particles as N atoms enter the 2:17 lattice and become trapped in the interstitial sites.<sup>11</sup> During the nitrogenation process, the nitrified shell grows at the expense of the unnitrified core, and this is reflected in the relative amounts of the two components in the ME spectra.

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