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A neutron diffraction and Mössbauer effect study of the magnetic properties of $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ ^{a)}

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The neutron diffraction powder patterns of $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ have been measured at 295 K and refined within the $\text{Th}_2\text{Zn}_{17}$ structure type to give the structural changes which occur upon nitrogenation; changes which include a 6.4% expansion of the unit cell volume. The Mössbauer spectra of $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ have been measured between 85 and 295 K and analyzed with a model which is based on the Wigner-Seitz cell environment of each iron site, the basal orientation of the magnetization, and a comparison with the Mössbauer spectra of $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$. Upon nitrogenation of $\text{Pr}_2\text{Fe}_{17}$, the 85 K-weighted average isomer shift increases from 0.049 to 0.156 mm/s, and the isomer shifts of the four crystallographically distinct iron sites increase in agreement with the increase found in their Wigner-Seitz cell volumes and the presence of a nitrogen near-neighbor for the 18*f* and 18*h* sites. The temperature dependence of the isomer shifts indicates an increase in covalency upon the formation of the nitride. Upon nitrogenation of $\text{Pr}_2\text{Fe}_{17}$, the 85 K-weighted average hyperfine field increases from 286.2 to 331.9 kOe, however, as is the case for the nitrogenation of $\text{Nd}_2\text{Fe}_{17}$, the increases on the 6*c* and 18*f* sites are much smaller than those observed on the 9*d* and 18*h* sites. These changes provide support for the band structure calculations of changes in the magnetic moments upon nitrogenation of Y_2Fe_{17} , $\text{Nd}_2\text{Fe}_{17}$, and $\text{Gd}_2\text{Fe}_{17}$.

I. INTRODUCTION

The search for new hard permanent magnet materials has recently concentrated on the ternary nitrides $\text{R}_2\text{Fe}_{17}\text{N}_{3-\delta}$ (Refs. 1–4). It is known¹ that interstitial nitrogen atoms substantially increase the Curie temperature of the corresponding R_2Fe_{17} compounds. The crystallographic and magnetic properties of the R_2Fe_{17} compounds have been known for many years,^{5–7} and in a recent paper,⁸ we have reported in detail on the microscopic magnetic properties of $\text{Nd}_2\text{Fe}_{17}$ and their changes upon nitrogenation to form $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$. In this paper, we will concentrate on $\text{Pr}_2\text{Fe}_{17}$ and its nitride, $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$.

The crystallographic and magnetic structures of $\text{Nd}_2\text{Fe}_{17}$ (Refs. 7 and 9), $\text{Pr}_2\text{Fe}_{17}$ (Ref. 10), $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.4}$ (Ref. 11), and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.9}$ (Ref. 10) have been studied by powder neutron diffraction and all four compounds crystallize in the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure in which the iron atoms occupy the four inequivalent 6*c*, 9*d*, 18*f*, and 18*h* crystallographic sites.^{7,9,10} The 6*c* site, the “dumbbell site,” plays an important role in determining the magnetic properties of the R_2Fe_{17} compounds and their nitrides because the short iron 6*c*–iron 6*c* distance in the R_2Fe_{17} compounds is believed to be responsible for their low Curie temperatures, and the increase in this bond distance upon

nitrogenation leads to the higher Curie temperatures observed for $\text{R}_2\text{Fe}_{17}\text{N}_{3-\delta}$ (Ref. 1).

In all four compounds, the magnetization and hence magnetic moments were found to be parallel with the hexagonal basal plane, in agreement with the sign of the A_2^0 crystal field parameter and the α_J second-order Stevens coefficient for both praseodymium and neodymium.^{12–14} Unfortunately, the orientation of the magnetic moments within the basal plane of the rhombohedral structure cannot be determined from powder neutron diffraction studies. However, Gubbens and his coworkers^{12,15} have concluded that in $\text{Nd}_2\text{Fe}_{17}$, the easy axis of magnetization, and hence presumably the moments, lies along the *a* axis in the basal plane; a conclusion which was supported by our Mössbauer effect work⁸ on both $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$. In contrast, the magnetization in $\text{Pr}_2\text{Fe}_{17}$ was believed^{12,15} to lie along the *b* axis in the basal plane. Although the signs of the α_J and β_J Stevens coefficients are the same for both praseodymium and neodymium, their values and the resulting angular distribution of the 4*f* charge density are quite different. Further the γ_J sixth-order Stevens coefficient differs in sign for neodymium and praseodymium and, as a result, it is quite possible that the easy-axes and moments adopt different orientations in the neodymium and praseodymium compounds.

The structural results^{7,10,11} indicate that, in both $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.9}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$, the nitrogen atoms are located on the pseudooctahedral 9*e* site and have only 18*f*

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TABLE I. Lattice parameters, positional parameters, and average bond distances in $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$.

Parameter		Pr ₂ Fe ₁₇	Pr ₂ Fe ₁₇ N _{2.6}	% change	% change Nd	
Lattice parameters	<i>a</i> , Å	8.621(4)	8.8223(5)	2.3	2.4	
	<i>c</i> , Å	12.518(6)	12.7079(9)	1.5	1.8	
	<i>c/a</i>	1.452	1.440	−0.8	−0.6	
	<i>V</i> , Å ³	805.0(1)	856.6(1)	6.4	6.8	
Positional parameters	Pr, 6 <i>c</i> , <i>z</i>	0.3449(5)	0.3409(14)			
	Fe, 6 <i>c</i> , <i>z</i>	0.0964(2)	0.0967(5)			
	Fe, 18 <i>f</i> , <i>x</i>	0.2871(2)	0.2819(3)			
	Fe, 18 <i>h</i> , <i>x</i>	0.1692(1)	0.1732(3)			
	Fe, 18 <i>h</i> , <i>z</i>	0.4896(1)	0.4863(3)			
Average bond distance, Å	Fe, 6 <i>c</i> to	Fe, 6 <i>c</i>	2.412	2.458	1.9	0.9
		Fe, 9 <i>d</i>	2.640	2.698	2.2	2.6
		Fe, 18 <i>f</i>	2.754	2.774	0.7	0.1
		Fe, 18 <i>h</i>	2.652	2.669	0.6	0.6
		Pr, 6 <i>c</i>	3.111	3.103	−0.3	2.7
	Fe, 9 <i>d</i> to	Fe, 18 <i>f</i>	2.450	2.487	1.5	1.6
		Fe, 18 <i>h</i>	2.474	2.505	1.2	1.1
		Pr, 6 <i>c</i>	3.342	3.375	1.0	2.5
		Fe, 18 <i>f</i> to	Fe, 18 <i>f</i>	2.475	2.487	0.5
	Fe, 18 <i>f</i> to	Fe, 18 <i>h</i>	2.620	2.681	2.3	2.7
		Pr, 6 <i>c</i>	3.096	3.193	3.1	3.7
		N, 9 <i>e</i>	...	1.924
		Fe, 18 <i>h</i> to	Fe, 18 <i>h</i>	2.540	2.669	5.1
	Pr, 6 <i>c</i>		3.201	3.284	2.6	2.5
	N, 9 <i>e</i>		...	1.946

and 18h near-neighbors.¹⁶ In addition, the iron 6c-iron 6c distance is increased by 0.022 Å or 0.9% upon nitrogenation of $\text{Nd}_2\text{Fe}_{17}$. However, this increase is approximately the same as that induced by hydrogenation of $\text{Nd}_2\text{Fe}_{17}$, whereas the increase in Curie temperature is twice as large in the nitride as in the hydride. Therefore, there must be additional factors which account for the large increase in Curie temperature and magnetization in the nitrides. As will be shown in this paper, Mössbauer spectroscopy, which probes on a microscopic basis the iron atoms on the four inequivalent crystallographic sites, is essential in understanding the effect of the interstitial nitrogen on the magnetic properties of $\text{R}_2\text{Fe}_{17}\text{N}_x$.

II. EXPERIMENTAL

Samples of $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ were prepared as described previously.¹⁷ Neutron diffraction data were collected at 295 K on approximately 2g samples using the position sensitive detector diffractometer at the University of Missouri Research Reactor. The neutron wavelength was 1.4766 Å as obtained from a pressure bent perfect silicon (511) monochromator. The data were measured from 5° to 105° in 2θ . Mössbauer absorbers of 36 mg/cm² thickness were prepared from powdered samples which had been sieved to a 0.045 mm or smaller diameter particle size. Mössbauer spectra were obtained between 85 and 295 K on a constant-acceleration spectrometer which utilized a rhodium matrix cobalt-57 source and was calibrated at room temperature with α -iron foil. The resulting spectra have been fit as discussed below and elsewhere¹⁸ and the

estimated errors are at most ± 1 kOe for the hyperfine fields, ± 0.005 mm/s for the isomer shifts, and ± 0.01 mm/s for the quadrupole shifts.

III. NEUTRON DIFFRACTION RESULTS

The neutron diffraction powder patterns were analyzed by the Rietveld method with the GSAS program¹⁹ for multiphase materials. The magnetic scattering was very small at 295 K even in $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ and was ignored in the refinements. $\text{Pr}_2\text{Fe}_{17}$ showed no detectable second phase whereas $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ showed several percent of a second phase, a phase which is most likely nitrated iron. All of the remaining lines were indexed and refined on the basis of the $\text{Nd}_2\text{Fe}_{17}$ structure and the results of the Rietveld analysis are presented in Table I. The last column in this table gives the related percentage change in structural parameters upon nitrogenation of $\text{Nd}_2\text{Fe}_{17}$ (Ref. 7) to form $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.9}$ (Ref. 11). With one exception, a comparison of the percentage changes of the neodymium and praseodymium compounds upon nitrogenation reveals that the changes are very similar. The major difference is in the average bond distance between the iron 6c site and the praseodymium or neodymium 6c site; a distance which decreases in praseodymium but increases substantially in neodymium upon nitrogenation. Hence, although the iron-iron bonding in the two series of compounds is quite similar, a change in the rare-earth metal does have a distinct influence on the bonding, especially to the iron 6c site and, to a lesser extent, to the iron 9d site.

After the initiation of our neutron diffraction study of $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$, Isnard *et al.*¹⁰ reported a detailed

study of these materials at 2, 300, and 655 K. Although their results are quite similar to ours, we have chosen to report and use our 295 K results for several reasons. The work of Isnard *et al.*¹⁰ was particularly concerned with the low-temperature magnetic properties of these compounds and, hence, their refinement of the neutron diffraction data emphasized the determination of the magnetic moments at various temperatures. As a result, they did not study the two compounds under identical conditions at room temperature. In contrast, our data were obtained with high resolution and an extended q -range and were more useful for a close comparison of the room temperature structural details. Consequently, our refinement²⁰ shows a slightly different trend in the Wigner-Seitz cell volumes at room temperature than do the results of Isnard *et al.*¹⁰ In particular, we find a 1.9% expansion of the iron 6c to iron 6c bond distance upon nitrogenation, a value consistent with both the observed lattice expansion upon nitrogenation and the related value for $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$. The relative Wigner-Seitz cell volumes based on our refinement show exactly the same trends for $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$.

IV. MÖSSBAUER SPECTRAL RESULTS

Figures 1 and 2 show the Mössbauer spectra of $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ measured between 85 and 295 K. These spectra are similar to those reported by Hu *et al.*,²¹ but show a substantially better resolution because of a narrower spectral linewidth. Hu *et al.*²¹ report linewidths in the range of 0.28 to 0.36 mm/s, whereas the linewidths of the spectra measured herein are in the range of 0.26 to 0.28 mm/s. The small spectral linewidths observed for $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ indicate that the nitrogenation has led to a uniform but random distribution of the nitrogen on the 9e site in the sample. The 295 K spectra of $\text{Pr}_2\text{Fe}_{17}$ shows no α -iron impurity. In contrast, the spectra of $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ show the presence of an iron containing impurity phase, as was also observed in the neutron diffraction results. The relative intensity of this phase amounts to ca. 7% at all temperatures, in good agreement with the neutron diffraction results. The hyperfine parameters of this phase are consistent with a nitrided iron alloy.

The spectra shown in Figs. 1 and 2 were fit with a least-squares program which was previously described¹⁸ and applied to both the $\text{R}_2\text{Fe}_{14}\text{B}$ and $\text{R}_2\text{Fe}_{14}\text{C}$ compounds²²⁻²⁴ and to $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (Ref. 8). Because of the basal orientation of the iron magnetic moments in $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$, seven sextets, with relative intensities 6:6:3:12:6:12:6, corresponding to the magnetically inequivalent 6c, 9d₆, 9d₃, 18f₁₂, 18f₆, 18h₁₂, and 18h₆ sites, are necessary to fit the Mössbauer spectra shown in Figs. 1 and 2, as was the case for $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (Ref. 8). In the final fits, it was found that an increase of ca. 2% in the relative intensity of the 6c site from the constrained ratio yielded substantially improved fits, as was the case for the analogous neodymium compounds. This indicates a slightly larger recoil free fraction for the 6c site, as might be expected from the short iron 6c-iron 6c distance. Several additional constraints on the

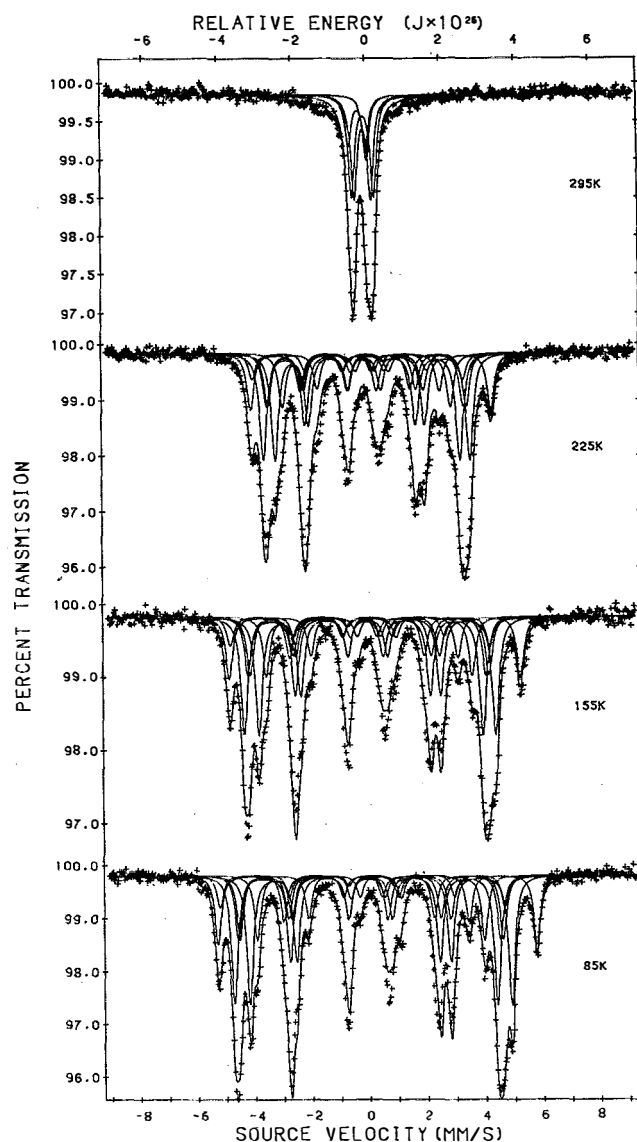


FIG. 1. The Mössbauer effect spectra of $\text{Pr}_2\text{Fe}_{17}$ obtained at the indicated temperatures.

hyperfine parameters were used in these fits. Specifically the isomer shifts for the pairs of crystallographically equivalent sites, 9d₆ and 9d₃, 18f₁₂ and 18f₆, and 18h₁₂ and 18h₆ sites were constrained to be equal. The hyperfine fields for these pairs of sites are expected to differ at most by a small amount, the difference representing the variations in the dipolar and orbital contributions to the magnetic hyperfine fields. However, as already noted by Gubbens *et al.*¹⁵ and Hu *et al.*,²¹ a comparison of the spectra of $\text{Nd}_2\text{Fe}_{17}$ (Ref. 8) with those of $\text{Pr}_2\text{Fe}_{17}$, and a comparison of the spectra of $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (Ref. 8) with those of $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$, indicates that the iron magnetic moments have different basal orientations in the praseodymium and neodymium compounds. This different orientation shows up as different quadrupole shifts for the two magnetically inequivalent sites arising from the 9d, 18f, and 18h crystallographic sites.

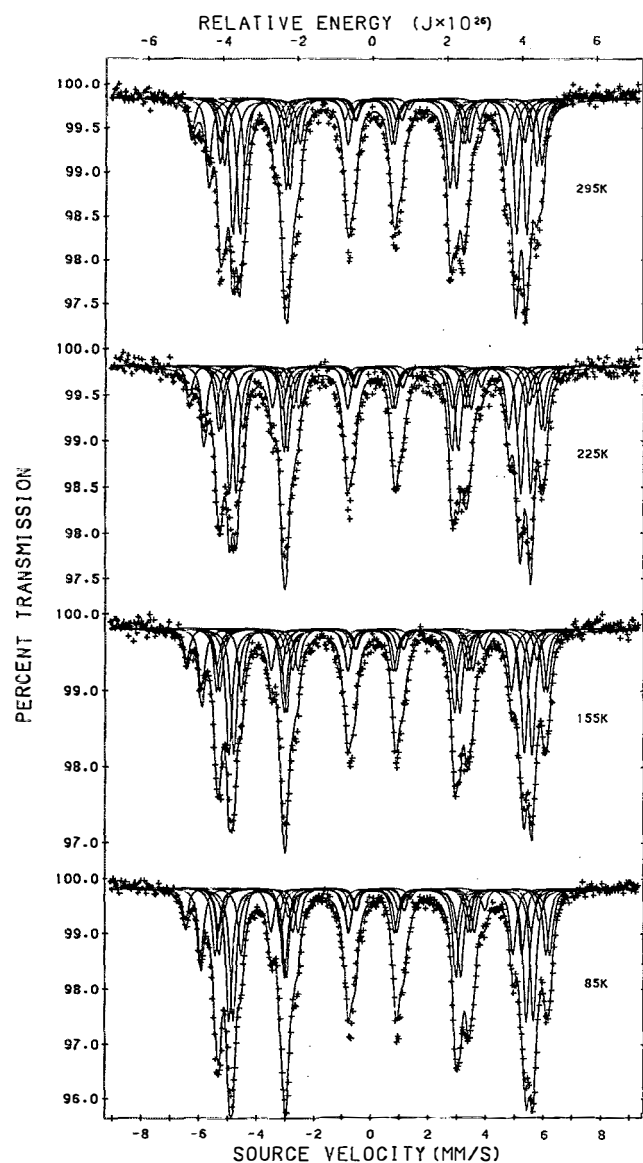


FIG. 2. The Mössbauer effect spectra of $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ obtained at the indicated temperatures.

TABLE II. Mössbauer spectral hyperfine parameters for $\text{Pr}_2\text{Fe}_{17}$.

	<i>T</i> , K	6 <i>c</i>	9 <i>d</i> ₆	9 <i>d</i> ₃	18 <i>f</i> ₁₂	18 <i>f</i> ₆	18 <i>h</i> ₁₂	18 <i>h</i> ₆	Wt. Ave.
<i>H</i> , (kOe)	85	343	282	306	298	264	266	263	286.2
	155	313	256	279	270	239	241	239	259.8
	225	259	212	227	222	198	199	197	214.3
δ , ^a (mm/s)	85	0.240	−0.095	−0.095	0.065	0.065	0.040	0.040	0.049
	155	0.202	−0.125	−0.125	0.020	0.020	0.000	0.000	0.009
	225	0.130	−0.160	−0.160	−0.030	−0.030	−0.060	−0.060	−0.045
	295	0.040	−0.210	...	−0.080	...	−0.090	...	−0.092
<i>QS</i> , ^b (mm/s)	85	−0.03	0.14	−0.36	0.06	0.58	0.16	−0.62	...
	155	−0.03	0.15	−0.34	0.05	0.60	0.17	−0.50	...
	225	−0.03	0.20	−0.30	0.05	0.60	0.18	−0.40	...
	295	−0.03	−0.59	...	+0.72	...	−0.62

^aRelative to room temperature α -iron foil.

^bThe values at 295 K and all values for the 6*c* site are the quadrupole interaction, $e^2Qq/2$. The remaining values are the quadrupole shift.

As noted⁸ for the 6*c* site in both $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$, the principal axis of the electric field gradient tensor is expected to lie along the crystallographic *c* axis and, hence, for this site θ , the angle between the principal axis of the electric field gradient tensor and the easy magnetization axis, is 90° and the asymmetry parameter η is zero. The quadrupole shifts for the remaining six sextets were treated as in the case of $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (Ref. 8). One common linewidth was used for the seven sextets and the total absorption area as well as the 6*c* relative area were the only other adjustable parameters. Thus there were a total of 21 adjustable parameters for each spectrum.

The solid lines shown in Figs. 1 and 2 are the result of the fits with the constraints described above and the resulting hyperfine parameters are given in Tables II and III. The paramagnetic spectrum of $\text{Pr}_2\text{Fe}_{17}$, obtained at 295 K, was fit with four symmetric doublets of equal linewidth and with relative areas constrained equal to the crystallographic site population, i.e., 6:9:18:18. The isomer shifts and quadrupole splittings were initially chosen in agreement with the values obtained at 225 K and subsequently refined to yield the hyperfine parameters given in Table II.

V. ISOMER SHIFTS AND SITE ASSIGNMENTS

In the assignment of the seven sextets to the four crystallographically and seven magnetically inequivalent sites, we have used the approach already successfully applied to $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (Ref. 8). This approach is based on the Wigner-Seitz cell volumes¹⁶ for the crystallographically inequivalent 6*c*, 9*d*, 18*f*, and 18*h* sites in the $\text{Th}_2\text{Zn}_{17}$ -type structure of these compounds. The Wigner-Seitz cell volumes, which are computed from the atomic positional parameters, and the 12-coordinate atomic radii of 1.82, 1.26, and 0.92 Å for praseodymium, iron, and nitrogen, respectively, are given in Table IV.

There is no ambiguity in the assignment of the 6*c* sextet, which has both the the largest isomer shift and the largest Wigner-Seitz cell volume in both $\text{Pr}_2\text{Fe}_{17}$ and

TABLE III. Mössbauer spectral hyperfine parameters for $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$.

	T, K	$6c$	$9d_6$	$9d_3$	$18f_{12}$	$18f_6$	$18h_{12}$	$18h_6$	Wt. Ave.
$H, (\text{kOe})$	85	359	371	380	315	325	327	292	331.9
	155	355	368	376	312	323	326	290	329.4
	225	350	363	370	306	318	323	285	324.6
	295	342	352	360	294	310	313	280	315.1
$\delta,^a (\text{mm/s})$	85	0.300	0.025	0.025	0.140	0.140	0.190	0.190	0.156
	155	0.280	0.000	0.000	0.110	0.110	0.160	0.160	0.128
	225	0.260	-0.020	-0.020	0.080	0.080	0.130	0.130	0.101
	295	0.210	-0.040	-0.040	0.050	0.050	0.100	0.100	0.071
$QS,^b (\text{mm/s})$	85	-0.36	0.09	-0.70	0.30	-0.34	0.30	0.01	...
	155	-0.36	0.09	-0.70	0.30	-0.34	0.30	0.01	...
	225	-0.36	0.09	-0.70	0.30	-0.34	0.30	0.01	...
	295	-0.36	0.09	-0.70	0.30	-0.34	0.30	0.01	...

^aRelative to room temperature α -iron foil.^bThe values for $6c$ are the quadrupole interaction, $e^2Qq/2$. The remaining values are the quadrupole shift.

$\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$. Similarly, the two $9d$ sextets have both the smallest isomer shift and the smallest Wigner-Seitz cell volume in both $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$. The isomer shifts for the $18f$ and $18h$ sites in $\text{Pr}_2\text{Fe}_{17}$, which are actually quite similar, do not correlate exactly with the Wigner-Seitz cell volume, in contrast to the case of $\text{Nd}_2\text{Fe}_{17}$ (Ref. 8). Although we could reverse the assignment of the $18f$ and $18h$ sites, this would lead to major difficulties in understanding the hyperfine fields, as will be discussed in the next section. The correlation between the Wigner-Seitz cell volumes and the 85 K isomer shifts, shown in Fig. 3, is similar to that found in the analogous neodymium compounds.⁸

Figure 3 also illustrates the changes in the individual isomer shifts upon nitrogenation of $\text{Pr}_2\text{Fe}_{17}$; changes which may be understood both on the basis of the unit cell volume expansion, presented in this figure in terms of the Wigner-Seitz cell volume, and on the presence of a nitrogen near-neighbor. Although neither the $6c$ nor the $9d$ site has nitrogen near-neighbors in the nitride, they do exhibit increases in both their Wigner-Seitz cell volumes and their isomer shifts. As proposed by Hu *et al.*²¹ the increases in the isomer shift, $\Delta\delta$, and the Wigner-Seitz cell volume,

V_{WS} , may be compared as the ratio, $\Delta\delta/\Delta\ln V_{\text{WS}}$. The $6c$ and $9d$ sites show similar values of this ratio, as is shown in Table IV. However, because of the comparatively small volume expansion upon nitrogenation of $\text{Pr}_2\text{Fe}_{17}$, these values are larger than those observed for the nitrogenation of $\text{Nd}_2\text{Fe}_{17}$ (Ref. 8). Although both the $18f$ and $18h$ sites have one nitrogen near-neighbor, only the $18h$ site experiences a substantial increase of its Wigner-Seitz cell volume. Hence, the 0.075 mm/s isomer shift increase for the $18f$ site is entirely due to the presence of a nitrogen near-neighbor. In contrast, the larger 0.150 mm/s isomer shift increase for the $18h$ site is due to both the volume expansion and the presence of a nitrogen near-neighbor. If we divide this increase into two contributions, the first arising from a nitrogen near-neighbor and equal to 0.075 mm/s, as observed for the $18f$ site, and the second arising from the volume expansion and equal to 0.075 mm/s, this latter adjusted increase for the $18h$ site is similar to the increases observed for the $6c$ and $9d$ sites and leads to a $\Delta\delta/\Delta\ln V_{\text{WS}}$ value of 2.3 mm/s; a value which is similar to those observed for the $6c$ and $9d$ sites, see Table IV. The value of $\Delta\delta/\Delta\ln V_{\text{WS}}$, given in Table IV for the $18f$ site is very large because of the very small increase in Wigner-Seitz

TABLE IV. Isomer shifts and related quantities for $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$.

Parameter	Compound	$6c$	$9d$	$18f$	$18h$	Wt. Ave.
$\delta, 85 \text{ K}$ (mm/s)	$\text{Pr}_2\text{Fe}_{17}$	0.240	-0.095	0.065	0.040	0.049
	$\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$	0.300	0.025	0.140	0.190	0.156
$\Delta\delta, (\text{mm/s})$ $(d\delta/dT) \times 10^4,$ (mm/s.K)	$\text{Pr}_2\text{Fe}_{17}$	0.060	0.120	0.075	0.150	0.107
	$\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$	-7.9	-5.4	-6.9	-6.4	-6.6
$M_{\text{eff}} (\text{g/mol})$	$\text{Pr}_2\text{Fe}_{17}$	-4.1	-3.1	-4.3	-4.3	-4.1
	$\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$	53	77	60	65	64
Nitrogen nn	$\text{Pr}_2\text{Fe}_{17}$	100	135	97	97	104
	$\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$	0	0	1	1	-
$V_{\text{WS}}, 295 \text{ K}$ (\AA^3)	$\text{Pr}_2\text{Fe}_{17}$	12.53	11.43	11.94	12.25	12.03
	$\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$	12.91	11.93	11.95	12.66	12.31
$\Delta V_{\text{WS}} (\text{\AA}^3)$ $\Delta V_{\text{WS}}/V_{\text{WS}}, (\%)$	$\text{Pr}_2\text{Fe}_{17}$	0.38	0.50	0.01	0.41	0.28
	$\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$	3.1	4.4	0.1	3.3	2.3
$\Delta\ln V_{\text{WS}}$ $\Delta\delta/\Delta\ln V_{\text{WS}}, (\text{mm/s})$	$\text{Pr}_2\text{Fe}_{17}$	0.030	0.043	0.001	0.032	0.023
	$\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$	2.0	2.8	107.0	4.7	3.5 ^a

^aIn this weighted average the large $18f$ site value has been ignored.

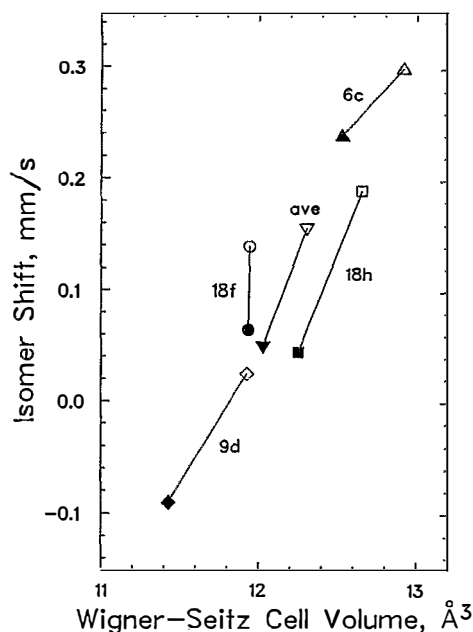


FIG. 3. The correlation between the Wigner-Seitz cell volume and the 85 K isomer shift for each site and their weighted average in going from $\text{Pr}_2\text{Fe}_{17}$, closed symbols, to $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$, open symbols.

cell volume for this site and is given simply for comparison.

Table IV also gives the weighted average isomer shifts for $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$, and indicates an average increase of 0.107 mm/s upon nitrogeation, an increase which is almost identical to the 0.104 mm/s value observed upon nitrogeation of $\text{Nd}_2\text{Fe}_{17}$ (Ref. 8). The weighted average isomer shift and its increase may be compared with the values measured by Hu *et al.*^{21,25} Their increase in the weighted average isomer shift upon nitrogeation amounts to 0.13 mm/s and is the largest they observed in their series of 12 R_2Fe_{17} compounds. This value leads to a ratio $\Delta\delta_{\text{ave}}/\Delta\ln V$, where V is the unit cell volume, of 2 mm/s, which is the largest in their R_2Fe_{17} series and is substantially

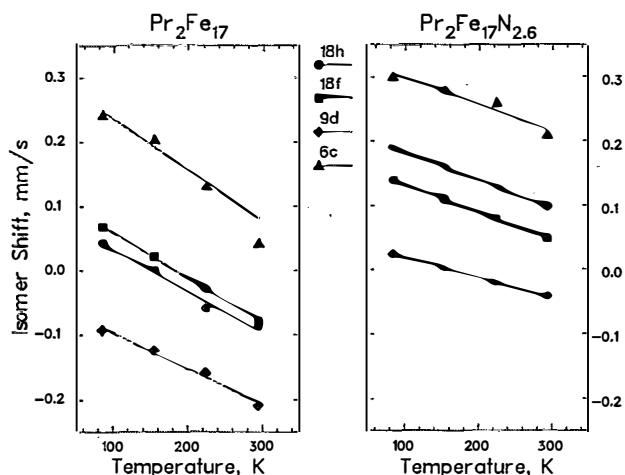


FIG. 4. The temperature dependence of the Mössbauer effect isomer shifts in $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$.

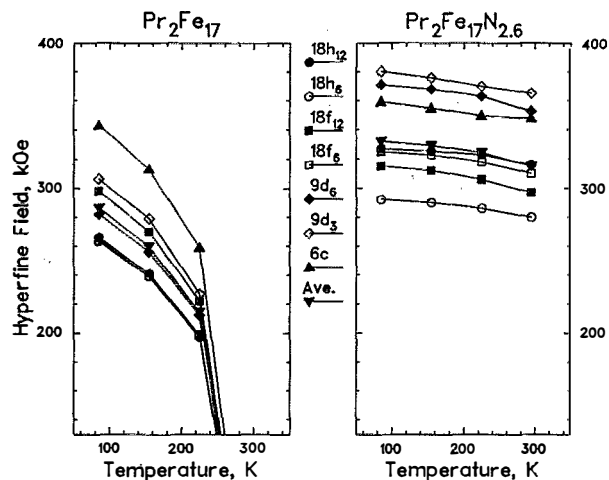


FIG. 5. The temperature dependence of the Mössbauer effect hyperfine fields in $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$.

larger than the value of 1.31 mm/s measured for α -iron.²⁶ Our increase in the weighted average isomer shift of 0.107 mm/s leads to a ratio $\Delta\delta_{\text{ave}}/\Delta\ln V$ of 1.7 mm/s, in excellent agreement with the other ratios²¹ and in better agreement with the value for α iron.

The temperature dependence of the individual isomer shifts in $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ is also given in Table IV and is shown in Fig. 4. The slopes of the straight lines are normal for the second-order Doppler shift and the corresponding effective recoil masses, given in Table IV, may be obtained as explained by Herber.²⁷ We believe that the larger slopes of -5.4×10^{-4} and -3.1×10^{-4} mm/(s.K), found for the 9d site, are not an artifact of the fits because attempts to force the temperature dependence to be more negative led to substantially poorer fits. A similar difference was also observed for $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (Ref. 8). These larger slopes lead to larger effective recoil masses which may be related to the smaller Wigner-Seitz cell volume of the 9d site in the R_2Fe_{17} and $\text{R}_2\text{Fe}_{17}\text{N}_x$ compounds. In other words, the iron nucleus is more effectively bound into the 9d site than into the other three sites of the crystal structure. It should be noted that both the effective recoil mass for each site and the weighted average effective recoil mass increase upon nitrogeation, presumably because of the added covalency of the bonding with the nitrogen atom. Such covalent bonding has been observed by Jaswal in the band structure calculations for Y_2Fe_{17} and $\text{Y}_2\text{Fe}_{17}\text{N}_3$ (Ref. 28). In conclusion, the individual isomer shifts and the weighted average isomer shift and their changes upon nitrogeation of $\text{Pr}_2\text{Fe}_{17}$ are well understood in terms of the individual Wigner-Seitz cell volumes, the volume changes upon nitrogeation, and the presence of a nitrogen near-neighbor.

VI. MAGNETIC HYPERFINE FIELDS

The magnetic hyperfine fields for each site in $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ are given in Tables II and III and are shown as a function of temperature in Fig. 5. In this figure,

TABLE V. Hyperfine fields and related quantities in $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$.

Parameter	Compound	6c	9d ₆	9d ₃	18f ₁₂	18f ₆	18h ₁₂	18h ₆	Wt. Ave.
H, 85 K	$\text{Pr}_2\text{Fe}_{17}$	343	282	306	298	264	266	263	286.2
(kOe)	$\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$	359	371	380	315	325	327	292	331.9
ΔH , (kOe)	Pr^a	16	89	74	17	61	61	29	45.7
	Nd^a	11	82	96	14	3	57	67	41.5
ΔH_{ave} , (kOe)	Pr^a	16	84.0		31.7		50.3		45.7
	Nd^a	11.0	86.4		10.5		60.1		41.5
μ , (μ_B)	$\text{Pr}_2\text{Fe}_{17}^b$	2.17	2.17		2.17		2.17		2.17
	$\text{Pr}_2\text{Fe}_{17}\text{N}_{2.9}^c$	2.45	2.45		2.45		2.45		2.45
$\Delta\mu$, (μ_B)	Pr^a	0.28	0.28		0.28		0.28		0.28
	$\text{Nd}^{a,d}$	-0.20	0.73		-0.51		-0.15		-0.12
	$\text{Gd}^{a,e}$	0.05	0.26		-0.14		0.38		0.14
	$\text{Y}^{a,f}$	0.12	0.61		-0.24		0.57		0.23
H/ μ , (kOe/ μ_B)	$\text{Pr}_2\text{Fe}_{17}$	158.0	133.6		132.1		122.1		131.9
	$\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$	146.5	152.7		129.9		128.7		135.4
Fe nn		13	10		10		9		...
Nd nn		1	2		2		3		...
N nn		0	0		1		1		...
Total nn		14	12		13		13		...

^aThe increase upon nitrogenation for the indicated rare-earth atom in R_2Fe_{17} and $\text{R}_2\text{Fe}_{17}\text{N}_x$.^bMeasured at 2 K.^cMeasured at 295 K.^dData taken from Ref. 30.^eData taken from Ref. 28.^fData taken from Ref. 29.

the rapid decrease in the hyperfine fields of $\text{Pr}_2\text{Fe}_{17}$ contrasts with the slow decrease in the hyperfine fields of $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ and clearly illustrates the large increase of the Curie temperature upon nitrogenation.¹ For $\text{Pr}_2\text{Fe}_{17}$ there is a direct correlation between the observed hyperfine field and the number of iron near-neighbors, as defined by the Wigner-Seitz cell for each site. Such a correlation was also observed in $\text{Nd}_2\text{Fe}_{17}$ (Ref. 8) and the $\text{R}_2\text{Fe}_{14}\text{B}$ and $\text{R}_2\text{Fe}_{14}\text{C}$ compounds.²²⁻²⁴ Unfortunately, individual magnetic moments have not been determined by neutron diffraction, and only an average iron magnetic moment of $2.17 \mu_B$ at 2 K has been reported.¹⁰ Therefore, among the H/μ values given in Table V, the average value of 132 kOe/ μ_B is the most meaningful. This value is lower than the typical 150 kOe/ μ_B value usually observed in intermetallic compounds,²² because the hyperfine field is measured at 85 K and the magnetic moment at 2 K. The hyperfine fields given in Table II for $\text{Pr}_2\text{Fe}_{17}$ at 85 K agree rather well with those reported by Hu *et al.*²¹ at 15 K.

For $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ there is not a direct correlation between the observed hyperfine fields and the number of iron near-neighbors, as determined by the Wigner-Seitz cell of each site. The hyperfine fields given in Table III for $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ at 85 K do not agree with those reported by Hu *et al.*²¹ at 15 K because these authors used a different model to analyze their data. However, their weighted average hyperfine field of 333 kOe at 15 K is in perfect agreement with the value of 331.9 kOe that we measure at 85 K, see Table III. The observed changes in the hyperfine fields upon nitrogenation of $\text{Pr}_2\text{Fe}_{17}$ follow a trend similar to that observed for $\text{Nd}_2\text{Fe}_{17}$ (Ref. 8) and also are in agreement with the results of various calculations²⁸⁻³⁰ for similar compounds, as will be discussed in the next paragraph. Unfortunately, only an average iron magnetic moment of $2.45 \mu_B$

at 300 K was determined¹⁰ by neutron diffraction for $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.9}$. This value gives an average H/μ ratio of 135 kOe/ μ_B , a value similar to the 143 kOe/ μ_B obtained^{8,29} for $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$.

As shown by the ΔH and ΔH_{ave} values given in Table V, the changes in hyperfine fields upon nitrogenation of $\text{Pr}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}$ are very similar. It is very interesting to see that the large increases of the 9d and 18h hyperfine fields, previously observed in $\text{Nd}_2\text{Fe}_{17}$ (Ref. 8), are definitely confirmed in this study. Indeed, there is no doubt about the hyperfine field of the weak 9d₃ site in $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ because of the clearly visible absorption line at ca. -6.5 mm/s, see Fig. 2, and the shoulder at +4 mm/s. The constraint that the 9d₆ site should have a hyperfine field similar to the 9d₃ site and the intensity of the line at -6.0 mm/s, in Fig. 2, strongly support the assignment of the 9d₆ sextet. There is also little doubt about the hyperfine field of the weak 9d₃ site in $\text{Pr}_2\text{Fe}_{17}$ because the intensity of the line at -5.5 mm/s indicates that it must contain both the 9d₃ and the 6c line. The positions of the 9d₆ and 9d₃ sextets were less clearly defined in the spectra of $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (Ref. 8) and the present study confirms our earlier assignments. The present assignment of the 9d₆ and 9d₃ sextets is also well supported by the associated quadrupole effects as will be discussed in the next section. As already noted for the neodymium compounds,⁸ the increases in the 9d and 18h hyperfine fields confirm the increase in magnetic moment predicted from band structure calculations on $\text{Nd}_2\text{Fe}_{17}$ (Ref. 30), $\text{Gd}_2\text{Fe}_{17}$ (Ref. 29), and Y_2Fe_{17} (Ref. 28) and their nitrides. A similar small increase upon nitrogenation for the 6c hyperfine field is observed in both $\text{Pr}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}$, in agreement with the small calculated increase in magnetic moment.^{28,29} The increase in hyperfine field of the 18f site upon nitrogenation

TABLE VI. Quadrupole shifts in R_2Fe_{17} and $\text{R}_2\text{Fe}_{17}\text{N}_{2.6}$ at 85 K.

Compound	$6c^a$	$9d_6$	$9d_3$	$18f_{12}$	$18f_6$	$18h_{12}$	$18h_6$
$\text{Pr}_2\text{Fe}_{17}$	-0.03	0.14	-0.36	0.06	0.58	0.16	-0.62
$\text{Nd}_2\text{Fe}_{17}$	-0.05	-0.10	0.34	0.44	-0.10	-0.42	0.48
$\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$	-0.36	0.09	-0.70	0.30	-0.34	0.30	0.01
$\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$	-0.38	-0.18	0.36	0.10	0.38	-0.20	0.38

^aThe value reported for the $6c$ site is $e^2Qq/2$, the quadrupole splitting.

is larger in $\text{Pr}_2\text{Fe}_{17}$ than in $\text{Nd}_2\text{Fe}_{17}$. This difference may result from the relative importance of the different core, orbital, and dipolar contributions to the hyperfine field.

VII. QUADRUPOLE INTERACTIONS

In $\text{Pr}_2\text{Fe}_{17}$ (Ref. 15) and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ (Ref. 10) the magnetization and the magnetic moments are known to be in the basal plane and are usually assumed to be along the b axis¹⁵ of the hexagonal representation of the rhombohedral unit cell. For the $6c$ site, the principal axis of the electric field gradient tensor is parallel to the c axis of the unit cell and, consequently, makes an angle of 90° with the hyperfine field and the asymmetry parameter is zero. Thus, the QS values reported in Tables II, III, and VI for the $6c$ site are the values of $e^2Qq/2$, the quadrupole splitting. There is an excellent agreement between the values obtained for the praseodymium and neodymium compounds as shown in Table VI. In all of our fits, as expected, for both $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$, there is little if any indication of any temperature dependence of the measured quadrupole shifts, see Tables II and III.

It is clear from the Mössbauer spectra in Fig. 1 and 2 that the relative orientation of the hyperfine field and of the principal axis of the electric field gradient tensor is different from that observed in $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (Ref. 8). This change is related to the rotation of the magnetization in the basal plane from parallel to the a axis in the neodymium compounds to parallel to the b axis in the praseodymium compounds. This rotation is very clearly observed as a change in the sign of the quadrupole shifts observed for the $9d_6$ and $9d_3$ sextets for the praseodymium and neodymium compounds, as shown in Table VI. The changes in quadrupole shifts for the $18f$ and $18h$ sites, on going from praseodymium to neodymium, are also related to this rotation of the magnetization in the basal plane.

The paramagnetic spectrum of $\text{Pr}_2\text{Fe}_{17}$ at 295 K, see Fig. 1, can be used to deduce the quadrupole splitting and θ angles of the $9d$, $18f$, and $18h$ sites. For the $9d$ site, a quadrupole splitting of ± 0.59 mm/s is measured at 295 K. The $+0.59$ mm/s value is inconsistent with the quadrupole shift of -0.36 mm/s observed for the $9d_3$ site. The value of -0.59 mm/s leads to θ values of 65° and 31° for $9d_6$ and $9d_3$ sites, respectively. For the $18f$ site, a quadrupole splitting of ± 0.72 mm/s is observed at 295 K. The -0.72 mm/s value is inconsistent with the quadrupole shift of $+0.58$ mm/s measured at 85 K for the $18f_6$ site. If the quadrupole shift of $+0.72$ mm/s is used θ values of 52° and 19° are found for the $18f_{12}$ and $18f_6$ sites, respectively. For the $18h$ site, a quadrupole splitting of ± 0.62 mm/s is mea-

sured at 295 K. The $+0.62$ mm/s value is inconsistent with the value of -0.62 mm/s measured at 85 K for the quadrupole shift of the $18h_6$ site. The value of -0.62 mm/s leads to θ angles of 66° and 0° for $18h_{12}$ and $18h_6$ sites, respectively.

VIII. CONCLUSIONS

In this paper, we have measured and analyzed the Mössbauer effect spectra of $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ at various temperatures between 85 and 295 K, with a model which is based on crystallographic and magnetic data and which is compatible with, and hence provides support for, band structure calculations on related R_2Fe_{17} compounds and their nitrides.

The assignment of the seven sextets to the four inequivalent crystallographic iron sites in $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ is based on the isomer shifts, the sequence of which agrees closely with the Wigner-Seitz cell volume sequence for the four iron sites. The increase in the isomer shifts of an individual iron site upon nitrogenation may be understood in terms of the increase in unit cell volume and the presence of a nitrogen near-neighbor for a specific site. The individual effective recoil masses of iron-57, obtained from the temperature dependence of the individual isomer shifts indicate an increase in the covalent bonding of the iron upon nitrogenation; an increase which is in agreement with the calculations of Jaswal.²⁸

The hyperfine fields found for the four iron sites are very reasonable for both $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ and correlate well with the number of iron near-neighbors of a specific site. The changes in hyperfine field upon nitrogenation of $\text{Pr}_2\text{Fe}_{17}$ are in agreement with the unit cell volume expansion and the band structure calculated changes in magnetic moments in $\text{Nd}_2\text{Fe}_{17}$, $\text{Gd}_2\text{Fe}_{17}$, and Y_2Fe_{17} (Refs. 28–30). The Mössbauer effect spectra of $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ differ from those of $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ because of the different orientation of the magnetic moments in the basal plane. However, the changes in isomer shift and hyperfine field upon nitrogenation show very similar trends in the praseodymium and neodymium compounds.

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