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# Structural, Magnetic, and Mössbauer Spectral Properties of $Pr_2Fe_{17}H_x$ Where X Is 1, 2, and 3

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# Structural, magnetic, and Mössbauer spectral properties of $Pr_2Fe_{17}H_x$ where $x$ is 1, 2, and 3

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The 295 K unit cell parameters of $Pr_2Fe_{17}H_x$, where $x$ is 0, 1, 2, and 3, have been determined by x-ray diffraction. Upon hydrogenation, the unit cell volume expands anisotropically with a 1.2% expansion of the $a$ axis and no expansion of the $c$ axis for $x=3$. The Curie temperatures are 286, 374, 440, and 484 K, for $x=0$, 1, 2, and 3, respectively. The Mössbauer spectra have been measured between 4.2 and 295 K, and the spectra of $Pr_2Fe_{17}H$ and $Pr_2Fe_{17}H_2$, obtained above 80 K, and those of $Pr_2Fe_{17}H_3$, obtained above 120 K, have been analyzed with a seven sextet model, a model which corresponds to basal magnetic anisotropy. The Mössbauer spectra of $Pr_2Fe_{17}H_3$ change dramatically upon cooling below 80 K, and between 4.2 and 75 K they are well fit with a four sextet model which corresponds to axial magnetization. Between 80 and 120 K, the spectra are very complex and, hence, the Mössbauer spectra reveal a spin reorientation which occurs between 80 and 120 K in $Pr_2Fe_{17}H_3$. © *1999 American Institute of Physics.* [S0021-8979(99)55908-2]

## I. INTRODUCTION

The influence of the insertion of hydrogen or deuterium upon the structural and magnetic properties of the $R_2Fe_{17}$ rare-earth compounds has been studied[1–6] by different techniques over the past 10 years. In particular, the Mössbauer spectra[2,5] of both $Nd_2Fe_{17}H_x$, with $x \leqslant 3$, and $Pr_2Fe_{17}D_3$ have been analyzed in terms of the spectra of $Nd_2Fe_{17}$ and $Pr_2Fe_{17}$ and their nitrides. A spin reorientation was discovered[5] in $Pr_2Fe_{17}D_3$ at $105\pm5$ K and the observed changes in the Mössbauer effect spectra were explained in terms of a rotation of the iron spins within the basal plane of the rhombohedral unit cell. In view of this spin reorientation, we decided to investigate the structural, magnetic, and Mössbauer spectral properties of the partially hydrided compounds, $Pr_2Fe_{17}H_x$, where $x$ is 1, 2, and 3.

## II. EXPERIMENT

The $Pr_2Fe_{17}H_x$ compounds, where $x$ is 1, 2, and 3, have been prepared as described earlier.[5]

The x-ray diffraction patterns were obtained with a Guinier focusing camera by using iron $K\alpha_1$ radiation in order to avoid fluorescence from the iron. Silicon was used as an internal standard and the lattice parameters were refined by using all the observed reflections. The ordering temperatures were derived from thermomagnetic studies carried out on a Faraday balance. When necessary, the samples were sealed in silica tubes to avoid oxidation or hydrogen loss upon heating.

Mössbauer absorbers of 36 $mg/cm^2$ were prepared from powdered samples which had been sieved to a 0.045 mm or smaller diameter particle size. The Mössbauer spectra were obtained between 4.2 and 295 K on a constant-acceleration spectrometer which utilized a rhodium matrix cobalt-57 source and was calibrated at room temperature with $\alpha$-iron foil. The spectra were fit as discussed in Sec. IV and the estimated errors were at most $\pm1$ kOe for the hyperfine fields, $\pm0.005$ mm/s for the isomer shifts, and $\pm0.01$ mm/s for the quadrupole shifts.

## III. STRUCTURAL AND MAGNETIC PROPERTIES

X-ray diffraction patterns reveal that the samples all crystallize in the $Th_2Zn_{17}$ rhombohedral structure and have the lattice parameters given in Table I. As indicated by the increase in $a$ with $x$, the lattice expansion upon hydrogenation is concentrated within the basal plane of the unit cell. The relative expansion of $a$ between $x$ values of 0 and 3 amounts to 1.2%. The Curie temperatures, given in Table I, reveal an increase of 200° between $x$ values of 0 and 3.

## IV. MÖSSBAUER SPECTRA

The Mössbauer spectra of $Pr_2Fe_{17}H_3$, obtained at 4.2, 75, 135, and 295 K, are shown in Fig. 1. It is immediately apparent that the spectra form two groups; the 4.2 and 75 K

TABLE I. Lattice parameters and Curie temperatures for $Pr_2Fe_{17}H_x$.

| $x$ | $a$ (Å) | $c$ (Å) | $T_C$ (K) |
|---|---|---|---|
| 0 | 8.585(2) | 12.465(2) | 286 |
| 1 | 8.623(2) | 12.466(2) | 374 |
| 2 | 8.653(2) | 12.459(2) | 440 |
| 3 | 8.686(2) | 12.466(2) | 484 |

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FIG. 1. Mössbauer spectra of $Pr_2Fe_{17}H_3$ obtained at 4.2, 75, 135, and 295 K.



FIG. 2. Temperature dependence of the isomer shifts in $Pr_2Fe_{17}H_3$. The values for the $18f$ site (●) and for the weighted average (▼) are very similar. The error bars for all values are approximately the size of the data points.

α-iron. The excellent fit of these spectra with four sextets indicates that the iron moments, and hence the magnetization, in $Pr_2Fe_{17}H_3$ are parallel to the $c$ axis below 85 K. Above 120 K, the spectra are well fit with seven sextets, with relative areas of 6:6:3:12:6:12:6 assigned to the seven magnetically inequivalent iron $6c$, $9d_6$, $9d_3$, $18f_{12}$, $18f_6$, $18h_{12}$, and $18h_6$ sites. An eighth sextet, with a relative area of ~4%, is assigned to α-iron. The existence of seven sextets in these spectra indicates that the iron moments, and hence the magnetization, in $Pr_2Fe_{17}H_3$ are within the basal plane above 120 K. Between ~80 and 120 K, the spectra are a superposition of the low and the high temperature spectra. Hence, the spin reorientation, from axial at low temperature, to basal at high temperature, takes place over a range of ~40°.



FIG. 3. Temperature dependence of the hyperfine fields in $Pr_2Fe_{17}H_3$. The error bars for all values are approximately the size of the data points.

spectra shown and all the spectra obtained below 85 K are sharper and simpler than the spectra obtained above 120 K. Furthermore, the low and high temperature spectra of $Pr_2Fe_{17}H_3$ resemble those of $Pr_2Fe_{17}D_3$ measured below and above 105 K, respectively.

As shown in Fig. 1, the spectra obtained below 80 K are well fit with four sextets, with relative areas of 6:9:18:18 assigned to the four crystallographically inequivalent iron $6c$, $9d$, $18f$, and $18h$ sites, respectively. A fifth sextet, with a relative area of less than 4% and with hyperfine parameters constrained to be equal to those of α-iron, is assigned to
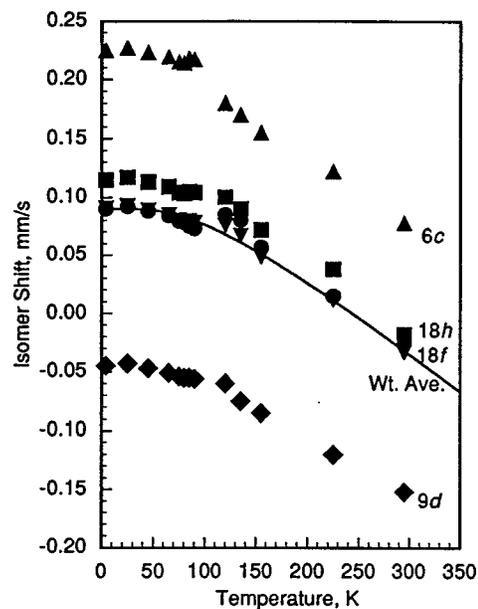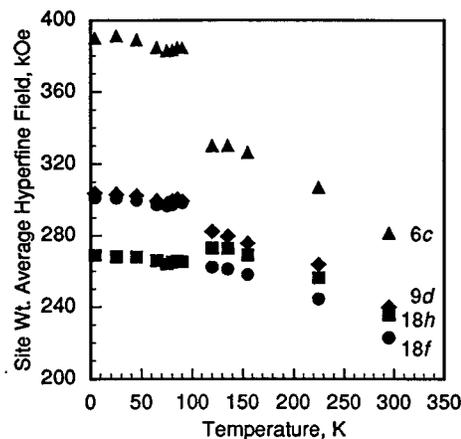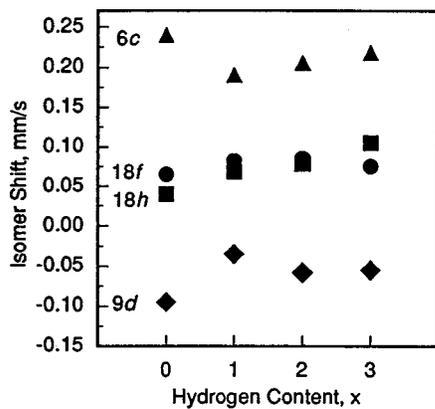
FIG. 4. Isomer shifts in $Pr_2Fe_{17}H_x$ as a function of hydrogen content, $x$. The error bars for all values are approximately the size of the data points.



FIG. 5. Hyperfine fields in $Pr_2Fe_{17}H_x$ as a function of hydrogen content, $x$. The error bars for all values are approximately the size of the data points.

The temperature dependences of the individual site and the weighted average isomer shifts in $Pr_2Fe_{17}H_3$ are shown in Fig. 2. As is also shown in Fig. 2, the temperature dependence of the weighted average isomer shift has been fit[7] under the assumption that $Pr_2Fe_{17}H_3$ behaves like a Debye solid; the resulting Debye temperature and effective recoil mass are 370 K and 61 g/mol. This mass is similar to the 64 g/mol observed[8] for $Pr_2Fe_{17}$ and the Debye temperature is somewhat larger than the 352 and 311 K observed[2] for $Nd_2Fe_{17}$ and $Nd_2Fe_{17}H_3$, respectively.

The temperature dependence of the site average hyperfine fields is shown in Fig. 3. As expected, there is an abrupt change in the fields at the spin reorientation. Specifically, the $6c$ hyperfine field decreases by ~50 kOe between 90 and 120 K, but above 120 K all four hyperfine fields follow a typical Brillouin curve. The quadrupole shifts are temperature independent above 120 and below 90 K and show the expected abrupt changes at the spin reorientation.

Because of the similarity between the low temperature spectra of $Pr_2Fe_{17}H_3$ and the 85 K spectrum[5] of $Pr_2Fe_{17}D_3$, a fit of the latter spectrum with four sextets has been successfully carried out. This model was not used in our earlier work[5] because, at the time, the axial alignment of the spins could not be confirmed from the three spectra available at 85, 90, and 95 K. Further studies of the Mössbauer spectra of $Pr_2Fe_{17}D_3$ below 85 K are in progress.

The Mössbauer spectra of $Pr_2Fe_{17}H$ and $Pr_2Fe_{17}H_2$, obtained between 85 and 295 K, are similar to those of $Pr_2Fe_{17}H_3$ above 120 K and, hence, they have been analyzed with a similar seven sextet basal magnetization model. The temperature dependences of the isomer shifts and the hyperfine fields in both compounds are smooth and exhibit the expected second-order Doppler and Brillouin law behaviors, respectively. A study of $Pr_2Fe_{17}H$ and $Pr_2Fe_{17}H_2$ below 85 K is in progress in order to determine whether a spin reorientation occurs in these compounds.

A visual inspection of the 85 K spectrum[3] of $Pr_2Fe_{17}$ and the spectra of $Pr_2Fe_{17}H$ and $Pr_2Fe_{17}H_2$ reveals gradual changes in the first and fifth absorption lines with increasing hydrogen content. Further, the $6c$ hyperfine field is the largest in $Pr_2Fe_{17}$. The similarities and differences in the spectra upon hydrogenation are emphasized in Figs. 4 and 5, which show, as a function of hydrogen content in $Pr_2Fe_{17}H_x$, the
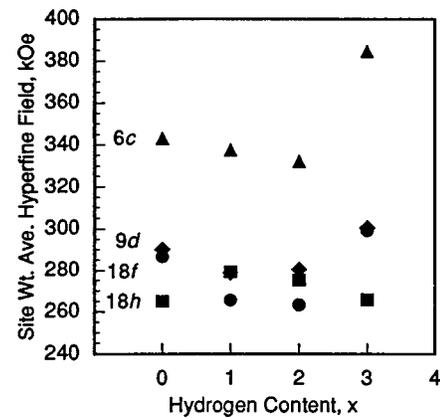
isomer shifts and hyperfine fields, respectively. The $9d$, $18f$, and $18h$ site isomer shifts increase upon hydrogenation in agreement with the lattice expansion and the presence of one hydrogen near neighbor for the $18f$ and $18h$ sites. The $6c$ isomer shift decreases from $Pr_2Fe_{17}$ to $Pr_2Fe_{17}H$ and is virtually identical in the three hydrides. This behavior may well be related to the absence of expansion along the $c$ axis upon hydrogenation and, hence, to an invariant short Fe $6c$–Fe $6c$ dumbbell bond distance. It is interesting to note that the $18h$ site isomer shift in $Pr_2Fe_{17}H_3$ is larger than the $18f$ site isomer shift, as is shown in Fig. 4. This difference is no doubt related to the lattice expansion within the basal plane and crowding of the $18f$ site with the addition of hydrogen. Similar behavior was observed[2] for $Nd_2Fe_{17}$ and $Nd_2Fe_{17}H_3$.

The visually observed decrease in the average hyperfine field between $Pr_2Fe_{17}$ and $Pr_2Fe_{17}H$ is confirmed in Fig. 5. In $Pr_2Fe_{17}H_3$ the 85 K hyperfine fields are substantially higher than in the other three compounds because of the spin reorientation. The decreasing order of the hyperfine fields, i.e., $6c > 9d \geqslant 18f > 18h$, agrees[2,8] with the order of the decreasing number of iron near neighbors, i.e., $12 > 10 = 10 > 9$.

## ACKNOWLEDGMENTS

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