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A spin reorientation in $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ as revealed by Mössbauer spectroscopy

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The Mössbauer effect spectra of $\text{Pr}_2\text{Fe}_{17}\text{D}_3$, which have been measured between 85 and 295 K, indicate the presence of a spin reorientation of the iron magnetic moments at 105 ± 5 K. At this magnetic transition a large increase of ~ 50 kOe in the $6c$ iron magnetic hyperfine field and abrupt changes in all of the remaining hyperfine fields are observed. A study of the changes in the quadrupole shifts at the transition indicates that this spin reorientation takes place within the basal plane of this rhombohedral compound. As expected, the temperature dependence of the isomer shifts does not show any anomaly at the transition. The origin of this spin reorientation is attributed to competing effects between lattice expansion upon deuteration and lattice contraction upon cooling.

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I. INTRODUCTION

As Coey and Sun¹ first showed in 1990, insertion of nitrogen into R_2Fe_{17} , where R is a rare earth, improves their magnetic properties and dramatically increases their Curie temperatures. We have previously studied^{2,3} the Mössbauer spectra of $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ and the hydrides of $\text{Nd}_2\text{Fe}_{17}$. Hence, it is useful to study the deuterides of $\text{Pr}_2\text{Fe}_{17}$ and to compare their Mössbauer spectral properties with those of the nitride, $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$, and the related hydrides. In this article, we will report the interesting and unexpected behavior of $\text{Pr}_2\text{Fe}_{17}\text{D}_3$. $\text{Pr}_2\text{Fe}_{17}\text{D}_5$ will be discussed in a future article⁴ along with various other deuterides and hydrides of R_2Fe_{17} .

II. EXPERIMENT

$\text{Pr}_2\text{Fe}_{17}\text{D}_3$ was prepared as described⁵ earlier and its deuterium content is known to an accuracy of $\sim 3.0 \pm 0.1$. Mössbauer absorbers of 36 mg/cm^2 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 fitted as discussed below and the estimated errors are at most ± 1 kOe for the hyperfine fields, $\pm 0.005 \text{ mm/s}$ for the isomer shifts, and $\pm 0.01 \text{ mm/s}$ for the quadrupole shifts.

III. MÖSSBAUER SPECTRAL RESULTS

The Mössbauer spectra of $\text{Pr}_2\text{Fe}_{17}\text{D}_3$, obtained between 85 and 295 K, are shown in Fig. 1. It is immediately apparent that dramatic changes occur in the spectra between 95 and

120 K. A closer examination of the spectra indicates that between 120 and 295 K they are similar but different from those obtained below 95 K. Additional spectra obtained between 95 and 120 K show a superposition of the high and low temperature spectra.

Because in both $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{D}_5$, the magnetic moments are oriented⁵ ferromagnetically in the basal plane of the $\text{Th}_2\text{Zn}_{17}$ rhombohedral unit cell, we assume that the magnetic moments in $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ have the same orientation. Because of this basal orientation of the moments and because of the point symmetry of the four iron crystallographic sites in the $\text{Th}_2\text{Zn}_{17}$ structure, the spectra were fitted² with seven sextets, with relative areas of 6:6:3:12:6:12:6, for the seven magnetically inequivalent, $6c$, $9d_6$, $9d_3$, $18f_{12}$, $18f_6$, $18h_{12}$, and $18h_6$ sites. The constraints applied to the hyperfine parameters have been described in detail elsewhere.² The most important constraint is that the isomer shifts of crystallographically equivalent, but magnetically inequivalent, sites be equal. Furthermore, all lines in a spectrum have been fit with a single linewidth, of between 0.28 and 0.30 mm/s. Finally, a sextet corresponding to α -iron with a relative area of $\sim 5\%$ was required to fit the observed spectra.

Figure 2 shows the temperature dependence of the four site averaged hyperfine fields. Clearly between 120 and 95 K there is a large increase of ~ 50 kOe in the $6c$ magnetic hyperfine field and there are abrupt changes in all of the remaining hyperfine fields. These changes indicate the presence of a magnetic transition in $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ at 105 ± 5 K. The nature of this transition, which does not show any obvious hysteresis, may be elucidated through the study of the quadrupole shifts, as discussed below.

The weighted average hyperfine fields are larger than those found in $\text{Pr}_2\text{Fe}_{17}$ but smaller than those found in $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.6}$ at the corresponding temperatures.² This trend parallels the evolution of the magnetic moment^{2,5} upon hy-

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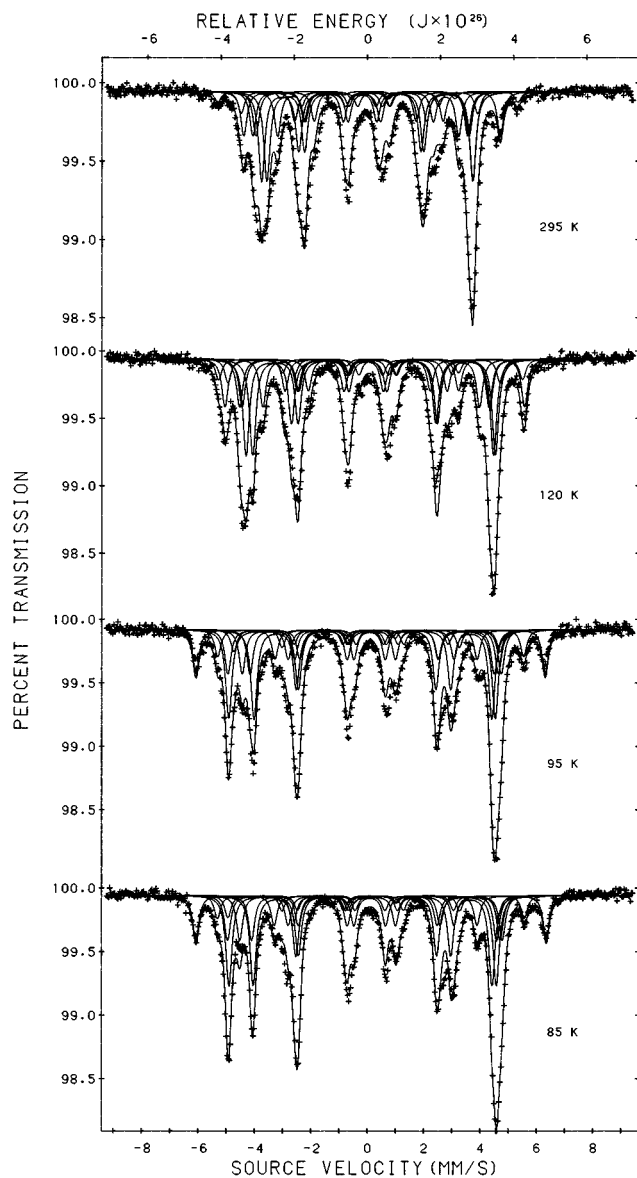


FIG. 1. The Mössbauer spectra of $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ obtained at the indicated temperatures.

drogenation and nitrogenation. The hyperfine fields at the four crystallographic iron sites decrease in the order $6c > 9d > 18f > 18h$, an order previously observed^{2,6-8} in the R_2Fe_{17} compounds, where R is Pr, Nd, Sm, Ho, and Th, and an order which agrees with the decreasing number of iron near neighbors for each site.

The spectra of $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ in both magnetic states are different from those of $\text{Nd}_2\text{Fe}_{17}\text{H}_3$. This difference indicates that the orientation of the magnetic moments within the basal plane is different in the two compounds, a difference already noted² for $\text{Pr}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}$. The weighted average hyperfine fields in $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ at 155, 225, and 295 K are ~ 5 kOe smaller than those observed³ at the same temperature in $\text{Nd}_2\text{Fe}_{17}\text{H}_3$. In contrast, the weighted average hyperfine field at 85 K is 15 kOe larger. Hence, the magnetic transition which occurs in $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ at ~ 105 K increases the low temperature average magnetic moment above the value in $\text{Nd}_2\text{Fe}_{17}\text{H}_3$.

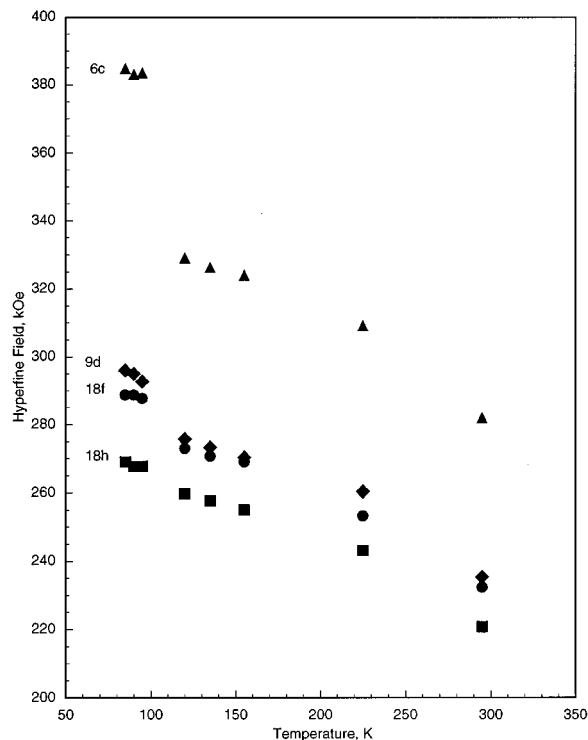


FIG. 2. The temperature dependence of the hyperfine fields in $\text{Pr}_2\text{Fe}_{17}\text{D}_3$.

Figure 3 shows the temperature dependence of the isomer shifts of the four crystallographically distinct iron sites and their weighted average. It is clear that none of the isomer shifts, nor their weighted average, show any anomaly in their

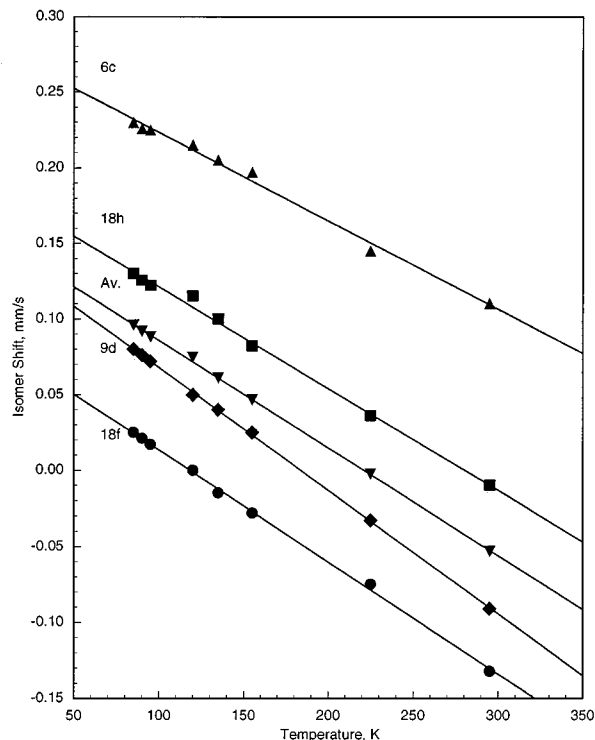


FIG. 3. The temperature dependence of the four isomer shifts in $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ and their weighted average.

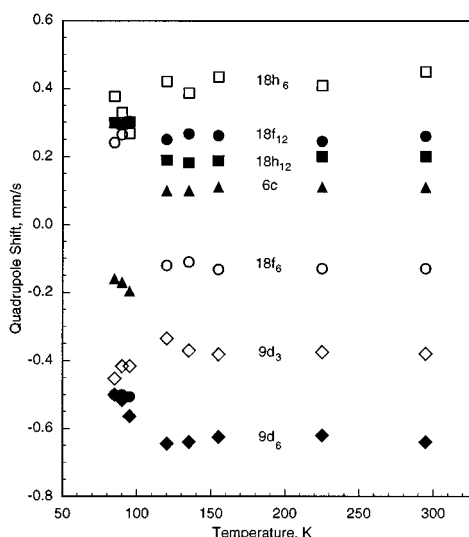


FIG. 4. The temperature dependence of the seven quadrupole shifts in $\text{Pr}_2\text{Fe}_{17}\text{D}_3$.

temperature dependence around 105 K. Of course, no anomaly in the isomer shift would be expected at a magnetic transition. This behavior supports our fitting model both above and below the magnetic transition. The slopes of the straight lines in Fig. 3 range between -5.85×10^{-4} and -8.30×10^{-4} mm/(s K) and are similar to those measured² in $\text{Pr}_2\text{Fe}_{17}$.

The weighted average isomer shift of $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ is larger than that of $\text{Pr}_2\text{Fe}_{17}$ at the same temperature in agreement with the unit cell expansion upon deuteration. A similar increase of ~ 0.05 mm/s was observed³ upon hydrogenation of $\text{Nd}_2\text{Fe}_{17}$. The correlation between the Wigner-Seitz cell volume and the isomer shift for each iron site in going from $\text{Pr}_2\text{Fe}_{17}$ to $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ shows a behavior similar to that observed for $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{H}_3$ and will be discussed in detail elsewhere.⁴

Figure 4 shows the temperature dependence of the seven quadrupole shifts in $\text{Pr}_2\text{Fe}_{17}\text{D}_3$. It is immediately apparent that at the magnetic transition at 105 K the quadrupole shifts of the 6c and 18f sites change sign and that those of the 9d and 18h sites change their values. These abrupt changes cannot result from a sudden change in the electric field gradient value, because no change in crystallographic structure is observed⁹ at low temperature. Hence, they can only result from a change in the angle between the hyperfine field and the principal axis of the electric field gradient tensor, or, in other words, a change in the direction of the magnetic moments at 105 ± 5 K. In $\text{Pr}_2\text{Fe}_{17}$, the magnetic moments are believed^{10,11} to lie along the *b* axis or $[1, -1, 0]$ in the basal plane of the unit cell. Because the signs of the quadrupole shifts of the 6c, 18f, and 18h sites are the same in $\text{Pr}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ above 105 K, we conclude that the moments lie along the *b* axis in $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ in the high temperature magnetic phase. Because the spectra below 105 K are still well fit with seven sextets, the magnetic moments still lie in the basal plane but the changes in quadrupole shifts at the magnetic transition indicate that the moments have rotated within the basal plane. Unfortunately, it is not possible to deduce the direction of the moments from the values of the

quadrupole shifts. The measurement of a Mössbauer spectrum above the Curie temperature of $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ may help to solve this question, if the compound does not lose deuterium upon heating and if the spectrum shows enough resolution to permit a reliable fit with four doublets.

The magnetic anisotropy in the R_2Fe_{17} compounds is determined¹² by the rare-earth single ion anisotropy through the interaction between the aspherical crystal field potential at the rare-earth sites and the aspherical charge density of the rare-earth 4*f* shell, described by the Stevens coefficients of the second, fourth, and sixth order, α_J , β_J , and γ_J . The Stevens coefficients are characteristic of the rare-earth atom and do not vary with temperature. Hence, the spin reorientation in $\text{Pr}_2\text{Fe}_{17}\text{D}_3$ at 105 K can only result from changes in the crystal field potential, changes probably resulting from the competing effects of lattice expansion, atomic rearrangement upon deuteration, and lattice contraction upon cooling. No similar spin reorientation was observed³ in $\text{Nd}_2\text{Fe}_{17}\text{H}_3$, between 85 and 295 K, but, of course, it could occur below 85 K and Mössbauer measurements between 4.2 and 85 K will be carried out in the near future to check this possibility. However, it is known^{6,10,11} that the magnetic moments in $\text{Nd}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}$ lie in different directions in the basal plane, probably because the sixth order Stevens coefficients γ_J have different signs. Because the three deuterium atoms are located in the basal plane, they may change dramatically the high order crystal field terms and, in particular, the sixth order term γ_J . Mössbauer spectroscopy is a unique technique to observe this spin reorientation because of its sensitivity to the quadrupole shift. Such a spin reorientation within the basal plane cannot be observed by powder neutron diffraction.

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