

Dynamics of hydrogen in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$

Eugene Mamontov^{1,2}, Terrence J. Udovic¹, John J. Rush¹, and Olivier Isnard^{3,4}

¹NIST Center for Neutron Research, National Institute of Standards & Technology, 100 Bureau Dr., MS 8562, Gaithersburg, MD 20899-8562, U.S.A.

²Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115, U.S.A.

³Laboratoire de Cristallographie, CNRS, associé à l'Université J. Fourier, BP 166X, F-38042 Grenoble Cedex, France

⁴Institut Universitaire de France, Maison des Universités, 103 Boulevard Saint-Michel, F-75005 Paris, Cedex France

ABSTRACT

We describe a study of the dynamics of hydrogen in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$, where isolated hexagons formed by the interstitial tetrahedral (t) sites of the metal lattice are populated by mobile hydrogen atoms. An activation energy of 0.10 eV has been determined for a localized jump process involving the hopping of these hydrogen atoms among adjacent vertices of each hexagon, slightly lower than that for hydrogen hopping in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$, where each hexagon is occupied by two hydrogen atoms.

INTRODUCTION

The dramatic increase in Curie temperature and magnetization resulting from insertion of small atoms such as hydrogen into the host metal matrix of R_2Fe_{17} makes these materials attractive candidates for hard magnet materials [1-3]. Among them, one of the most promising compounds is $\text{Pr}_2\text{Fe}_{17}\text{H}_x$ [4-7]. Similar to other R_2Fe_{17} compounds with lighter rare-earth atoms, $\text{Pr}_2\text{Fe}_{17}$ crystallizes in the $\text{Th}_2\text{Zn}_{17}$ rhombohedral R-3 m structure [8]. The host metal structure is retained in the hydride. Initially, hydrogen atoms in $\text{Pr}_2\text{Fe}_{17}\text{H}_x$ fill interstitial 9e distorted octahedral (o) sites, with four Fe atoms and two Pr atoms at the corners [9], and at $x = 3$, all o sites become populated. Further hydrogenation leads to filling the interstitial 18g tetrahedral (t) sites, with two Fe atoms and two Pr atoms at the corners [8]. The t sites form arrays of isolated hexagons in the basal plane of the hexagonal structure normal to the c -axis, with a side dimension of $\approx 1.16 \text{ \AA}$. The small size of the hexagons explains why the maximum hydrogen uptake in $\text{Pr}_2\text{Fe}_{17}\text{H}_x$ corresponds to $x = 5$, with one-third of the available t sites in the $\text{Pr}_2\text{Fe}_{17}$ host structure filled. Isnard *et al.* [3] proposed that a pair of hydrogen atoms occupies two diametrically opposed vertices of the hexagons in order to comply with Switendick's empirical criterion of $\approx 2.1 \text{ \AA}$ minimum H-H separation in ordered metal hydrides. Such a minimum has been ascribed to a repulsion interaction [10]. All but the opposite vertices of these hexagons in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ are separated by less than 2.1 \AA . We have suggested earlier [11] that the jumps of these two H atoms must be correlated in order to reconcile the dynamics of hydrogen hopping in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ with the Switendick criterion. In the work described here, we have extended our earlier study to include the compound with a composition of $\text{Pr}_2\text{Fe}_{17}\text{H}_4$. In this case, an isolated hexagon contains, on average, only one hydrogen atom, which allows assessing the impact of a second hydrogen atom on the hopping dynamics.

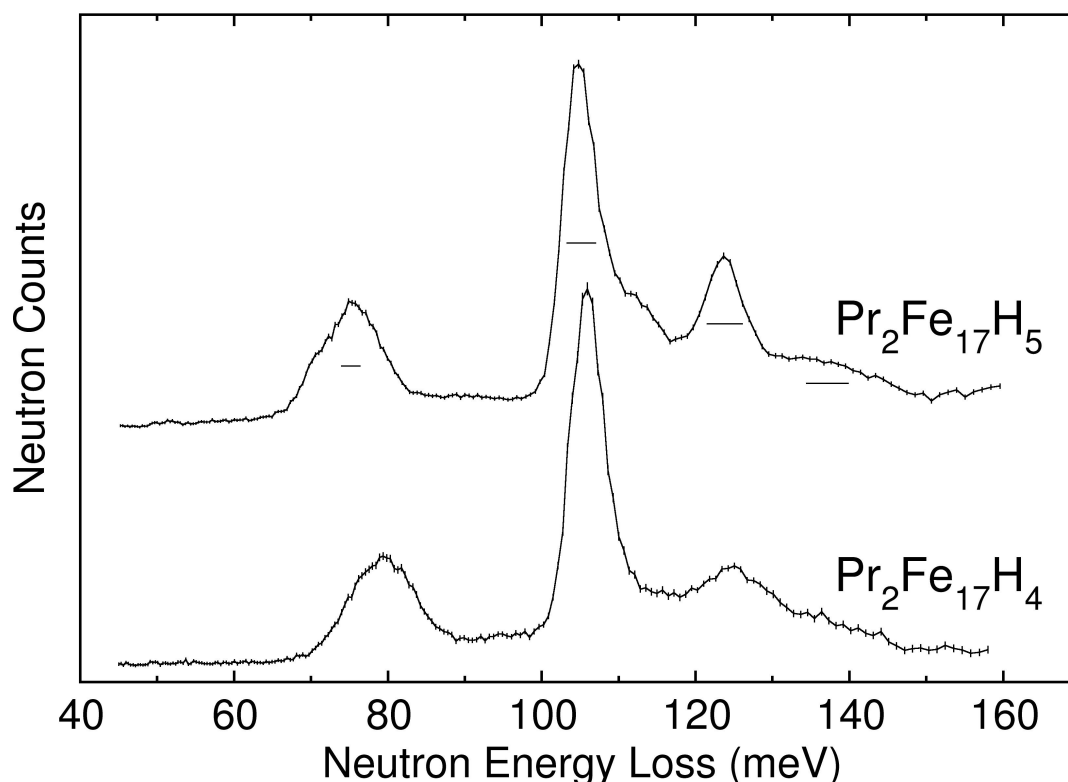


Figure 1. The neutron vibrational spectra of $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ measured at 10 K. The resolution (FWHM) is denoted by the horizontal bars beneath the spectra.

EXPERIMENTAL DETAILS

The synthesis procedure for $\text{Pr}_2\text{Fe}_{17}$ samples has been described elsewhere [7, 12, 13]. Hydrogen was loaded by means of gas absorption. Vibrational spectroscopy measurements were performed with the Filter-Analyzer Neutron Spectrometer (FANS) [14] using the Cu(220) monochromator and horizontal collimations of 20 and 40 minutes of arc before and after the monochromator, respectively. Quasielastic neutron scattering (QENS) experiments were carried out on the high flux backscattering spectrometer (HFBS) [15] at the NIST Center for Neutron Research. The HFBS provides $\approx 1 \mu\text{eV}$ energy resolution and the dynamic range of up to $\pm 35 \mu\text{eV}$ at a fixed final wavelength of 6.27 \AA . The sample was placed in an annular Al sample holder in a He atmosphere, sealed with an indium o-ring, and mounted onto a closed-cycle refrigerator. The thickness of the sample was chosen to ensure 90 % neutron transmission and thus minimize multiple scattering. Data were collected at 260 K, 240 K, 220 K, 200 K, and 5 K with the HFBS. The spectrum measured at 5 K was used as the resolution function.

RESULTS AND DISCUSSION

The neutron vibrational spectra for $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ at 10 K are shown in Figure 1. In both spectra, the two main peaks below 110 meV reflect the vibrations of the three

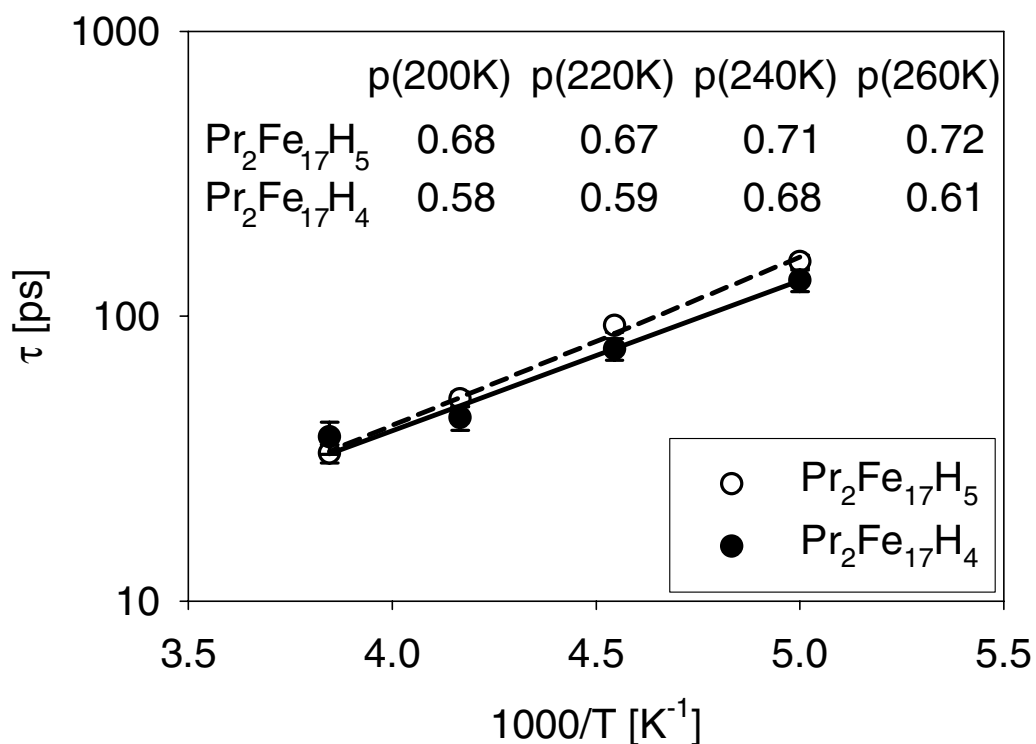


Figure 2. Arrhenius fits of the temperature dependence of the residence time between jumps, τ , for $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ (this work, solid line fit) and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ ([11], dashed line fit). For $\text{Pr}_2\text{Fe}_{17}\text{H}_5$, only the data obtained at the backscattering spectrometer were used for the fitting. Also shown are the parameters $p(T)$ (the mobile fraction of hydrogen atoms in the tetrahedral sites) for $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ (this work) and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ [11]. Errors on $p(T)$ values are of the order of 0.1.

o-site H atoms per $\text{Pr}_2\text{Fe}_{17}$ formula unit. The two additional features evident at ≈ 112 meV and 123.7 meV for $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ reflect the vibrations of the two additional t-site H atoms per hexagon [11]. The decreased intensity of these features for the $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ spectrum is consistent with the lower concentration of one hydrogen per hexagon for this stoichiometry.

Since hopping between well-separated hexagons is unlikely, we have fitted the QENS data with a model scattering function describing a hopping between the six sites of an isolated hexagon. The model scattering function describing the hopping between six sites on a circle of radius r [16] was modified to account for the immobile hydrogen atoms. Our previous work [11] has indicated that all H atoms in the o sites and some H atoms in the t sites are immobile on the time scale of the backscattering spectrometer and contribute to the elastic scattering. The fraction of the immobile H atoms in the t sites relative to all H atoms in the t sites is commonly described by a temperature-dependent parameter, $1 - p(T)$. In $\text{Pr}_2\text{Fe}_{17}$ hydrides, some H atoms in the t sites may be trapped, for example, by anti-site defects in the host lattice. The resulting model scattering function is given in Ref. 11, except that the coefficients for the elastic and quasielastic terms have to be adjusted to reflect the fact that the H atoms in the t sites account for two-fifths and one-fourth of the total hydrogen content in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ and $\text{Pr}_2\text{Fe}_{17}\text{H}_4$, respectively. We used only two fitting parameters, $p(T)$

and the residence time between hydrogen jumps, τ , with a fixed value of $r = 1.16 \text{ \AA}$ because, for six equidistant sites on a circle, the distance between two neighboring sites is equal to the circle radius. Figure 2 shows the comparison of the fitting parameters obtained for $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ [11] and $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ (this work). The temperature dependence of τ for $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ can be fit with an Arrhenius-type law with an activation energy of 0.10 eV. Using only the data collected on the HFBS to obtain the activation energy for $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ as shown in figure 2 provides a more direct comparison between the measurements of $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ and yields an activation energy of 0.12 eV for $\text{Pr}_2\text{Fe}_{17}\text{H}_5$, which is not dramatically higher than that for $\text{Pr}_2\text{Fe}_{17}\text{H}_4$. As we have suggested previously [11], only the correlated jumps in the same direction that keep the H atoms on the opposite vertices of the hexagon should be possible, whereas uncorrelated jumps that place the H atoms within a distance where repulsive H-H interactions become appreciable are unlikely. With a weaker H-H repulsive interaction allowing the placement of hydrogen atoms not necessarily on the opposite vertices of a hexagon, a stronger influence of the t-site occupation on the activation energy of the hopping process could be expected. At each of the measured temperatures, the fraction of mobile H atoms in the tetrahedral sites is slightly lower for $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ compared to $\text{Pr}_2\text{Fe}_{17}\text{H}_5$, which is not entirely understood.

CONCLUSION

We have studied the dynamics of hydrogen atoms in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$, where three hydrogen atoms per formula unit fully occupy the $9e$ distorted o sites of the host metal lattice, and one hydrogen atom per formula unit fills one sixth of the $18g$ t sites. We have observed the hopping of the hydrogen atoms between such t sites that constitute arrays of isolated hexagons in the basal plane perpendicular to the c -axis. The residence time of H atoms between jumps shows an Arrhenius-type temperature dependence with an activation energy of 0.10 eV, which is only about 20 % lower compared to that in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$, where each hexagon is occupied by a pair of hydrogen atoms. This finding is consistent with our previous assertion that the jumps of the paired H atoms on a hexagon in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ are correlated; that is, only the simultaneous jumps of two atoms in the same direction occur. In such a scenario, the direct H-H repulsive interaction between the atoms constituting a pair on a hexagon prohibits uncorrelated jumps, and, therefore, has only minor influence on the activation energy for the correlated jumps.

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