Neutron vibrational spectroscopy of the Pr$_2$Fe$_{17}$-based hydrides

T.J. Udovic$^{a,*}$, W. Zhou$^{a,b}$, H. Wu$^{a,c}$, C.M. Brown$^{a,d}$, J.J. Rush$^{a,c}$, T. Yildirim$^{a,b}$, E. Mamontov$^{a,c,1}$, O. Isnard$^{e,f}$

$^a$ NIST Center for Neutron Research, National Institute of Standards and Technology, 100 Bureau Drive, MS 8562, Gaithersburg, MD 20899-8562, USA
$^b$ Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut St., Philadelphia, PA 19104-6272, USA
$^c$ Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115, USA
$^d$ Indiana University Cyclotron Facility, 2401 Milo B. Sampson Lane, Bloomington, IN 47408, USA
$^e$ Laboratoire de Cristallographie, CNRS, associé à l’Université J. Fourier, BP 166X, F-38042 Grenoble Cedex, France
$^f$ Institut Universitaire de France, Maison des Universités, 103 Boulevard Saint-Michel, F-75005 Paris, Cedex, France

Received 6 December 2006; accepted 13 December 2006

Available online 27 December 2006

Abstract

Neutron vibrational spectroscopy measurements of Pr$_2$Fe$_{17}$H$_x$ and Pr$_2$Fe$_{17}$D$_x$ ($x \leq 5$) reveal dynamic features consistent with the interstitial hydrogen locations previously determined by neutron diffraction. In particular, for Pr$_2$Fe$_{17}$H$_3$, two peaks centered at $\approx$85.4 and 106.0 meV correspond to the normal-mode vibrational energies of hydrogen in octahedral (o) sites comprised of a near-square planar arrangement of four Fe atoms and two apical Pr atoms. Based on bond distances and preliminary first-principles calculations, the lower-energy feature is assigned to the Ho vibration along the $c$-oriented Fe–Ho–Fe axis. The higher-energy feature is assigned to the other two normal-mode H o vibrations along the orthogonal Fe–Ho–Fe and Pr–Ho–Pr axes in the basal plane. For Pr$_2$Fe$_{17}$H$_4$ and Pr$_2$Fe$_{17}$H$_5$, the lower-energy Ho mode softens considerably by $\approx$6 and 10 meV, respectively. This is in part due to the $c$-axis expansion to accommodate the additional hydrogen occupying the neighboring distorted tetrahedral (t) sites comprised of two Fe atoms and two Pr atoms. For Pr$_2$Fe$_{17}$H$_5$, in addition to slightly softened Ho basal-plane modes centered at $\approx$104.7 meV, there is extra scattering intensity evident near $\approx$112 and 123.7 meV due to two of the Ht normal modes. The analogous Pr$_2$Fe$_{17}$D$_5$ spectrum suggests that the third H t normal mode is located near 103.3 meV, obscured by the 104.7 meV Ho peak. A comparison of Pr$_2$Fe$_{17}$H$_x$ and Pr$_2$Fe$_{17}$D$_x$ vibrational energies indicates that the o-site bonding potential is largely harmonic, whereas the t-site bonding potential is more anharmonic.

Keywords: Interstitial alloys; Hydrogen storage materials; Magnetically ordered materials; Gas–solid reactions; Neutron scattering; Diffraction

1. Introduction

Hydrogen has a profound influence upon the structural and magnetic properties of the R$_2$Fe$_{17}$ rare-earth (R) compounds. Typical of such compounds, Pr$_2$Fe$_{17}$ crystallizes in the Th$_2$Zn$_{17}$ rhombohedral ($R\bar{3}m$) structure. Hydrogen can insert into Pr$_2$Fe$_{17}$ to form the hydrides Pr$_2$Fe$_{17}$H$_x$ ($0 \leq x \leq 5$) (see Fig. 1). Neutron diffraction results [1–3] indicate that the first three hydrogen atoms occupy the interstitial 9e distorted octahedral (o) sites, each comprised of four Fe atoms in a near-square planar configuration and two Pr atoms at the apices. Above $x = 3$, these o sites are completely filled, and the extra hydrogen atoms occupy up to one third of the available interstitial 18g tetrahedral (t) sites, each comprised of two Fe atoms and two Pr atoms at the corners. This is consistent with the fact that the lattice parameter $a$ increases almost linearly with $x$, whereas the lattice parameter $c$ remains unchanged up to $x = 3$ and then increases with further increases in $x$ [3]. The t sites form arrays of isolated, partially hydrogen-occupied hexagons in the basal plane of the Pr$_2$Fe$_{17}$ structure. The t-site hydrogen (Ht) atoms jump readily among adjacent vertices of each hexagon, as evidenced initially by Mössbauer spectroscopy [4] and subsequently in greater detail by quasielastic neutron scattering measurements [5,6]. This interesting Ht dynamical behavior is dictated by the details of the hydrogen binding potentials. To better understand these
potentials, we have performed neutron vibrational spectroscopy (NVS) measurements of both Pr$_2$Fe$_{17}$H$_x$ and Pr$_2$Fe$_{17}$D$_x$ ($x=3, 4, 5$).

2. Experimental

Pr$_2$Fe$_{17}$ samples were synthesized as reported previously [2]. Hydrogen and deuterium were loaded via gas-phase absorption. All neutron scattering measurements were performed at the NIST Center for Neutron Research. Samples were cooled with closed-cycle, He-refrigerated displacement systems. NVS measurements were performed with the Filter-Analyzer Neutron Spectrometer (FANS) [7] using the Cu(220) monochromator and horizontal collimations of either 40 or 20 min of arc before and either 20 or 10 min of arc after the monochromator. The resulting instrumental resolutions (full width at half maximum) are denoted by horizontal bars beneath the spectra. Lower-energy acoustic vibrational mode measurements (not shown here) were performed using the Fermi–Chopper time-of-flight spectrometer (FCS) [8] with an incident wavelength of 4.8 Å.

3. Results and discussion

Fig. 2 shows NV spectra for Pr$_2$Fe$_{17}$H$_x$ ($x=3, 4, 5$). The Pr$_2$Fe$_{17}$H$_3$ spectra reflect the three normal-mode vibrations of the single type of interstitial o-site hydrogen (H$_o$). The relative intensities for the 10 K spectrum suggest that the lower-energy 85.4 meV feature reflects one mode and the higher-energy 106.0 meV feature reflects the other two. One of the high-energy modes was assigned to the H$_o$ vibration along the basal-plane-oriented Fe–H$_o$–Fe axis, while the other two normal modes reflect the presence of the main 106.0 meV peak. Comparing these results with the higher-hydride spectra in Fig. 2, the H$_o$ vibration along the c-directed Fe–H$_o$–Fe axis shifts considerably lower by 10 meV (from 85.4 to 75.4 meV) for Pr$_2$Fe$_{17}$H$_4$ and by 10 meV (from 85.4 to 75.4 meV) for Pr$_2$Fe$_{17}$H$_5$. This is at least in part due to a lattice expansion along the c direction caused by the extra t-site hydrogens (H$_t$) (i.e., a 1.2% expansion upon going from Pr$_2$Fe$_{17}$H$_3$ to Pr$_2$Fe$_{17}$H$_5$ [3]). Yet, such a large relative shift may also reflect an H$_t$-induced perturbation of the H$_o$ bonding potential. The existence and extent of such a perturbation will require more detailed x-dependent first-principles...
calculations. Nonetheless, it seems likely that the addition of Ht atoms is responsible for the increased peak width evident for the lower-energy Ho mode, since the presence of Ht sublattice disorder [2,5] provides a distribution of Ht interactions with the Ho atoms.

In addition to the slightly softened, orthogonal Ho modes now maximized at ≈104.7 meV for Pr2Fe17H5, the two new higher-energy vibrational features at ≈112 and 123.7 meV are assigned to two of the three expected Ht normal modes. The increased energies for these modes are consistent with the relatively smaller size of the t site compared to the o site, with Pt–Ht and Fe–Ht bond distances of 2.32 and 1.72 Å, respectively [2]. In β-PrH2, for comparison, the H atoms reside in regular t sites with a slightly larger Pr–Ht bond distance of 2.38 Å, yielding an Ht normal-mode energy of 108 meV [15].

Unlike β-PrH2, the presence of both Pr and Fe neighbors with different bond distances to Ht complicates the exact assignments of the observed Ht features in Pr2Fe17H5. Such assignments will also require additional first-principles calculations. The relatively larger integrated intensity of the 104.7 meV Ht scattering band for Pr2Fe17H3 compared with the corresponding band for Pr2Fe17H5 at 10 K suggests that the third Ht normal-mode vibration is most likely located somewhere beneath this band. Our preliminary results from first-principles phonon calculations for Pr2Fe17H3 are in qualitative agreement with the locations of the three Ht normal-mode vibrations and suggest that the two higher-energy modes are associated with Ht vibrations in the basal plane and the lowest-energy mode with out-of-plane Ht vibrations.

The 10 K Pr2Fe17D3 spectrum in Fig. 2 also indicates the presence of Ht features but of lower intensity. Although the weaker lower-energy Ht feature is now more obscured by the surrounding Ho-related scattering bands, the more distinct higher-energy Ht peak displays a slight upshift to ≈125 meV, consistent with the somewhat smaller lattice constants at this hydrogen concentration compared to Pr2Fe17H5 [3]. For both Pr2Fe17H4 and Pr2Fe17H5, broad multiphonon scattering is also evident ≈14 meV above the lowest-energy and highest-energy normal-mode peaks.

The Pr2Fe17H3 and Pr2Fe17H5 spectra at higher temperatures (200 and 300 K) in Fig. 2 reflect an attenuation of normal-mode intensities due to the temperature dependence of the significant Debye-Waller factors for hydrogen. Moreover, the appearance of multiphonon bands also on the lower-energy side of the normal-mode peaks at these higher temperatures is due to opto-acoustic combinations involving 14 meV acoustic-mode de-excitations. The observed downward shift in the higher-energy Ht modes with increasing temperature is consistent with a temperature-induced lattice expansion. (N.B., the 200 and 300 K spectra for Pr2Fe17D3 in Fig. 3 indicate similar expected trends in peak attenuations and energy shifts as for Pr2Fe17H3 upon increasing the temperature above 10 K.)

Fig. 3 shows NV spectra for Pr2Fe17Dx (x = 3, 4, 5). Similar to the Pr2Fe17H3 spectra, the Pr2Fe17D3 spectrum reflects the vibrational peaks of interstitial o-site deuterium (Do) at ≈60.0 and 75.1 meV, roughly scaled down by a harmonic factor of 1/√2 with respect to those of the half-as-massive Ho atoms.

For Pr2Fe17D4 and Pr2Fe17D5, there is a softening (analogous to Pr2Fe17H4 and Pr2Fe17H5) of the Do vibrations with the appearance of t-site deuterium (Dt). Again, this softening is much more dramatic for the lower-energy mode, decreasing to ≈54.9 and 52.7 meV for Pr2Fe17D4 and Pr2Fe17D5, respectively. The corresponding higher-energy Do mode decreases less dramatically to ≈74.9 and 74.2 meV, respectively. A more complex, broadened peak shape for the lower-energy Do mode for Pr2Fe17D4 and Pr2Fe17D5 again suggests a distribution of force constants due to concentration-dependent Dt–Do interactions originating from Dt sublattice disorder.

The Dt modes in Fig. 3 are evident at ≈84.4 and 90.1 meV for Pr2Fe17D4 and at ≈85.0 and 91.0 meV for Pr2Fe17D5. Unlike the largely harmonic o-site potential, these values reflect a t-site potential that is considerably anharmonic, with H/D normal-mode energy ratios of around 1.33 and 1.37 for the lower-energy and higher-energy modes, respectively. The contrast between o-site and t-site potentials is seen more clearly in the somewhat higher-resolution spectra in Fig. 4, where the ratio of energy-loss scales for Pr2Fe17H4 and Pr2Fe17D4 spectra is adjusted to equal the harmonic value of √2. It is interesting to note that a definite higher-energy shoulder near 77 meV emerges above the 74.2 meV Do peak for Pr2Fe17D4. This shoulder, which is absent from the 75.1 meV Do peak for Pr2Fe17D3 (see Fig. 3), is clear evidence of a third Dt normal-mode peak. A multipeak fit of this Do + Dt combined feature for Pr2Fe17D5 places the Dt peak more precisely at 76.5 meV. Assuming an anharmonic H/D normal-mode energy ratio of 1.35 (the average for the other two observed Dt peaks) places the corresponding third Ht normal-mode energy for Pr2Fe17H5 at ≈103.3 meV, which would indeed largely obscure it beneath the 104.7 meV Ho peak.
4. Summary

Neutron vibrational spectroscopy measurements of Pr$_2$Fe$_{17}$H$_x$ and Pr$_2$Fe$_{17}$D$_x$ ($x=3, 4, 5$) have allowed assignment of the normal-mode vibrations of H and D in the octahedral and tetrahedral-type interstices. These results are consistent with the hydrogen locations determined from earlier diffraction results. A comparison of Pr$_2$Fe$_{17}$H$_x$ and Pr$_2$Fe$_{17}$D$_x$ vibrational energies indicates a largely harmonic o-site bonding potential, yet a considerably anharmonic t-site bonding potential. More thorough analyses of the hydrogen bonding potentials and their relationship to the rapid H$_t$ hopping dynamics observed in this alloy await more detailed first-principles calculations.

References