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Hydrogen dynamics in the hexagonal $Ho_2Fe_{17}H_4$ and $Y_2Fe_{17}H_{4.2}$: Inelastic and quasielastic neutron scattering studies

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ABSTRACT

The vibrational spectra of hydrogen and the parameters of H jump motion in the hexagonal Th_2Ni_{17}-type compounds $Ho_2Fe_{17}H_4$ and $Y_2Fe_{17}H_{4.2}$ have been studied by means of inelastic and quasielastic neutron scattering. It is found that hydrogen atoms occupying interstitial $Ho(Y)_2Fe_2$ sites in both compounds participate in the fast localized jump motion over the hexagons formed by these tetrahedral sites. The temperature dependence of the H jump rate is well described by the Arrhenius law over wide T ranges (100–340 K for $Ho_2Fe_{17}H_4$ and 140–360 K for $Y_2Fe_{17}H_{4.2}$) with the activation energies of 54 (4) meV and 84 (7) meV, respectively. For $Ho_2Fe_{17}H_4$, the localized hydrogen jump motion is found to be the fastest among all R_2Fe_{17} hydrides studied so far. At room temperature, the H jump rate in $Ho_2Fe_{17}H_4$ derived from our quasielastic neutron scattering data reaches 6.4×10^{11} s^{-1}.

1. Introduction

Intermetallic compounds R_2Fe_{17} (where R is yttrium or rare-earth element) are known to adopt either the rhombohedral Th_2Zn_{17}-type or the hexagonal Th_2Ni_{17}-type structure. Owing to their interesting magnetic properties, these compounds have been extensively studied since the late sixties [1–5]. The renewed interest to the R_2Fe_{17} intermetallics is related to the discovery of dramatic changes in their magnetic properties upon hydrogen uptake [6–8]. In particular, hydrogenation of the R_2Fe_{17} compounds leads to a strong increase in the Curie temperature and magnetization [6–12], which makes these materials attractive candidates for permanent magnet applications. The structural aspects of hydrogenated $R_2Fe_{17}H_x$ compounds have been summarized by Isnard et al. [6,8,11]. For materials of both structural types, the host lattice retains its structure after hydrogenation, showing anisotropic expansion with increasing H content. Initially, H atoms fill the distorted octahedral (o) interstitial sites formed by four Fe atoms and two R atoms, and at $x = 3$, these sites are fully occupied. Further hydrogenation leads to a partial filling of the tetrahedral (t) interstitial sites coordinated by two Fe and two R atoms. In materials of both structural types, the sublattice of these tetrahedral sites consists of regular hexagons in the basal plane with a side dimension of ~1.1–1.2 Å. Because of the repulsive interaction between hydrogen atoms in metals, H atoms cannot simultaneously occupy the sites separated by the distances of ~2.1 Å or less (the "blocking" effect) [13]. Therefore, each t-site hexagon can accommodate up to two H atoms, so that the maximum occupancy of t sites is 1/3. The maximum H content in $R_2Fe_{17}H_x$ is $x = 5$, which corresponds to the complete filling of o sites and a one-third filling of t sites. Experimentally, this maximum H content was attained for the rhombohedral Th_2Zn_{17}-type hydrides, while for the hexagonal Th_2Ni_{17}-type hydrides the maximum attainable value of x remains lower than 5 and decreases along with the lanthanide contraction. It has been shown by both *in situ* neutron diffraction and differential scanning calorimetry investigations that the octahedral sites are more stable than the tetrahedral ones [14,15], the hydrogen desorption occurring first for the smaller tetrahedral positions.

The peculiar sublattice of partially occupied interstitial sites in $R_2Fe_{17}H_x$ may be responsible for unusual hydrogen dynamics in these compounds. Since the t-site hexagons are well separated

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from each other and from *o* sites, one may expect a localized motion of H atoms over these hexagons. The existence of fast H jump motion in the rhombohedral $Pr_2Fe_{17}H_x$ was first revealed by Mössbauer spectroscopy [16]. Subsequent quasielastic neutron scattering (QENS) experiments in Th_2Zn_{17}-type $Pr_2Fe_{17}H_x$ [17,18] and $Ce_2Fe_{17}H_5$ [19] gave the direct evidence that this fast jump process corresponds to localized H motion over the *t*-site hexagons. The most intriguing feature of the QENS results [17–19] is that the localized H motion is not suppressed by the repulsive H–H interaction due to the presence of two hydrogen atoms at each hexagon. Thus, the jump motion of two H atoms occupying the opposite vertices of the same hexagon should be correlated, as if these atoms formed a bound pair. In the hexagonal Th_2Ni_{17}-type compounds, hydrogen dynamics has not been studied thus far. The aim of the present work is to investigate both the vibrational spectrum of hydrogen and the jump motion of H atoms in the hexagonal Th_2Ni_{17}-type compounds Ho_2Fe_{17} and Y_2Fe_{17} using inelastic and quasielastic neutron scattering measurements. The results will be compared to those obtained for the rhombohedral Th_2Zn_{17}-type compounds. We shall also discuss the effects of changes in dimensions of the *t*-site hexagons and in occupancy of these hexagons on the parameters of H jump motion in the R_2Fe_{17} intermetallics.

2. Experimental details

Intermetallic compounds Ho_2Fe_{17} and Y_2Fe_{17} were prepared by arc melting in an argon atmosphere followed by annealing in argon at 1273 K for 72 h. According to X-ray diffraction analysis, the annealed sample of Ho_2Fe_{17} was a single-phase compound with the hexagonal Th_2Ni_{17}-type structure (space group $P6_3/mmc$) and the lattice parameters $a = 8.451$ Å and $c = 8.292$ Å. For the annealed Y_2Fe_{17} sample, the dominant phase also had the hexagonal Th_2Ni_{17}-type structure with $a = 8.464$ Å and $c = 8.362$ Å; this sample contained traces of residual α-Fe. Both samples were hydrogenated in a Sieverts-type apparatus using $LaNi_5$ hydride as a source of pure hydrogen at a temperature of 488 K and a hydrogen pressure of 15 bar. The host lattice of both hydrogenated samples was found to retain the Th_2Ni_{17}-type structure with the increased lattice parameters: $a = 8.547$ Å and $c = 8.341$ Å for $Ho_2Fe_{17}H_x$, and $a = 8.565$ Å and $c = 8.362$ Å for the dominant phase of $Y_2Fe_{17}H_x$. The lattice parameters of the residual α-Fe phase did not change after hydrogenation; this means that α-Fe does not absorb hydrogen under the present conditions. The hydrogen content per formula unit, *x*, estimated gravimetrically was 4.0 (1) H atoms per formula unit for $Ho_2Fe_{17}H_x$ and 4.2 (1) H atoms per formula unit for $Y_2Fe_{17}H_x$. Note that the lattice parameters of $Ho_2Fe_{17}H_4$ and $Y_2Fe_{17}H_{4.2}$ are consistent with the corresponding previous results on the hydrides with similar compositions [6,8].

All neutron scattering experiments were performed at the NIST Center for Neutron Research (Gaithersburg, Maryland, USA). The inelastic neutron scattering measurements of the hydrogen vibrational spectra at 4 K were made on a filter-analyzer neutron spectrometer (FANS) [20] using the Cu(220) monochromator and horizontal collimation of 20 min of arc before and after the monochromator. The measured range of neutron energy loss was 40–160 meV, and the energy resolution was about 3% of the energy transfer. Measurements of QENS spectra $S_{exp}(Q,\omega)$ (where $\hbar\omega$ is the energy transfer and $\hbar Q$ is the elastic momentum transfer) were performed on the time-of-flight disk-chopper spectrometer (DCS) [21] and the high-flux backscattering spectrometer (HFBS) [22] using the incident neutron wavelengths λ of 6.0 Å (DCS) and 6.27 Å (HFBS). These two spectrometers complement each other with respect to the energy resolution and the accessible range of energy transfer. In our experiments, the energy resolution full widths at half-maximum (FWHM) were 67 μeV (DCS) and 1.0 μeV (HFBS). The ranges of the elastic momentum transfer studied corresponded to *Q* ranges of 0.39–1.70 $Å^{-1}$ (DCS) and 0.25–1.75 $Å^{-1}$ (HFBS). The powdered $Ho_2Fe_{17}H_4$ and $Y_2Fe_{17}H_{4.2}$ samples were studied in annular geometry in a hollow-cylinder Al container, the sample thickness being about 0.3 mm. The sample thickness was chosen to ensure ~90% neutron transmission and thus minimize multiple-scattering effects. For analysis of the DCS data, the detectors were binned into eight groups. The scattering angles corresponding to the Bragg reflections were excluded from the analysis. The instrumental resolution functions $R(Q, \omega)$ were determined from the measured QENS spectra for $Ho_2Fe_{17}H_4$ and $Y_2Fe_{17}H_{4.2}$ at low temperatures (25 K for DCS and 4 K for HFBS).

It should be noted that statistical uncertainties in all figures, if not explicitly indicated by error bars, are commensurate with the observed scatter in the data.

3. Results and discussion

3.1. Neutron vibrational spectroscopy

A schematic view of the hexagonal Th_2Ni_{17}-type structure of $Ho_2Fe_{17}H_x$ with the octahedral (6*h*) and tetrahedral (12*i*) hydrogen sites is shown in Fig. 1(a). Fig. 1(b) represents a hexagon formed by the tetrahedral 12*i* sites in the basal plane. The experimental low-temperature INS spectra for $Ho_2Fe_{17}H_4$ and $Y_2Fe_{17}H_{4.2}$ are shown in Figs. 2 and 3, respectively. The H incoherent neutron scattering cross section overwhelmingly dominates those for Ho, Y, and Fe, so that the INS spectrum from a filter-analyzer-type spectrometer, such as FANS, approximates the H vibrational density of states (VDOS) averaged over *Q* space [20]. As can be seen from Figs. 2 and 3, INS spectra for both compounds have similar shapes in the studied energy transfer range. The strongest peak in the spectrum is observed near 85 meV for $Ho_2Fe_{17}H_4$ and near 87 meV for $Y_2Fe_{17}H_{4.2}$. At higher energy transfers, there are additional scattering features between 90 and 130 meV. For metal – hydrogen systems, low-temperature INS spectra in the energy transfer range 40–160 meV are usually dominated by the fundamental modes of H optical vibrations. The simplest approach to the description of these vibrations is based on the model of a three-dimensional Einstein oscillator [23,24]. For the ħω range of fundamental modes, this model predicts three peaks of nearly equal intensity. Depending on the point symmetry of H sites, all or two of these peaks may be degenerate. For hydrogen in both 6*h* and 12*i* sites of the Th_2Ni_{17}-type compounds, the local symmetry is lower than axial; therefore we may generally expect three peaks for hydrogen in each of these sites. Although this simple Einstein oscillator model might be sufficient for description of an isolated interstitial H atom in a metallic lattice, in reality, hydrides are often far from dilute. Hence, significant interactions between neighboring and even more distant H atoms often result in noticeable dispersion in the measured VDOS. Indeed, in the more extensive prior INS studies of $Pr_2Fe_{17}H_x$ and their deuterated analogues [25], there was clear evidence of phonon dispersion due to various H–H interactions as well as additional overlapping yet minor contributions from broad combination bands involving low-energy (~14 meV) acoustic modes and the fundamental optical-mode transitions. Nonetheless, by measuring multiple spectra as functions of H and D concentrations, the various H normal-mode vibrations could be assigned, and a significant anisotropy was deduced for the potential wells associated with H atoms in the interstitial *t* sites [25]. For the present hexagonal hydrides, all the observed peaks are considerably broader than the instrumental resolution (see Figs. 2 and 3); therefore, phonon dispersion effects should also be significant for $Ho_2Fe_{17}H_4$ and $Y_2Fe_{17}H_{4.2}$. Even though the range of INS data for the