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Hydrogen dynamics in Laves-phase hydride $YFe_2H_{2.6}$: Inelastic and quasielastic neutron scattering studies

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ABSTRACT

The vibrational spectrum of hydrogen and the parameters of H jump motion in the C15-type compound $YFe_2H_{2.6}$ have been studied by means of inelastic and quasielastic neutron scattering. It is found that hydrogen atoms occupying tetrahedral interstitial *g* (Y_2Fe_2) sites participate in the fast localized jump motion. The behavior of the elastic incoherent structure factor as a function of momentum transfer (measured up to $Q_{max} \approx 4$ Å^{-1}) is consistent with the two-site motion of H atoms within pairs of closely spaced *g* sites. In the studied *T* range of 140–390 K, the temperature dependence of the jump rate of this localized motion is found to be non-Arrhenius; however, it can be described by two Arrhenius-like terms with the activation energies of 42 and 10 meV in the ranges 295–390 K and 140–240 K, respectively. Our results also indicate that hydrogen dynamics in $YFe_2H_{2.6}$ is affected by considerable local lattice distortions resulting from hydrogenation of YFe_2.

1. Introduction

Laves phase intermetallics composed of yttrium (or rare-earth element) and a transition metal can absorb large amounts of hydrogen forming hydrides with interesting physical properties [1]. Among these compounds, the YFe_2–H(D) system is of particular interest due to the rich variety of crystal structures derived from the cubic C15-type structure of the parent intermetallic at different hydrogen concentrations [2]. Seven different crystal structures have been reported for this system, starting from the tetragonal structure for $YFe_2D_{1.2}$ to the orthorhombic structure for the deuterium-rich YFe_2D_5 [3,4]. Such a complex phase diagram is expected to originate from the ordering of H(D) atoms that can be accompanied by lattice distortions and/or superstructures below the ordering temperature. The processes of hydrogen redistribution among the available interstitial sites require certain mobility of H atoms. However, the dynamical properties of hydrogen in YFe_2 have not been investigated so far. In the present work, we use inelastic and quasielastic neutron scattering to study H dynamics in the hydride $YFe_2H_{2.6}$ retaining the cubic C15-type host-metal structure of the YFe_2 intermetallic.

One of the most unusual features of hydrogen diffusion in Laves phase compounds is the coexistence of two types of H jumps with different characteristic rates. It has been found [5,6] that in those C15-type Laves phases AB_2 where hydrogen atoms occupy only tetrahedral interstitial *g* sites (with A_2B_2 coordination), the faster jump process corresponds to the localized H motion within the regular hexagons formed by *g* sites, and the slower process is associated with H jumps from one *g*-site hexagon to another. The difference between the characteristic rates of these jumps is expected to originate from the difference between the nearest-neighbor *g*–*g* distances r_1 (within the hexagons) and r_2 (between the nearest hexagons), see Fig. 1. The value of r_2/r_1 is determined by the positional parameters of H atoms at *g* sites; these parameters are found to depend strongly on the ratio of the metallic radii R_A and R_B of the elements *A* and *B* [6]. The localized H motion has been investigated mostly in C15-type compounds with $R_A/R_B \leqslant 1.25$ where $r_2/r_1 > 1$ (changing from 1.07 for $ZrCr_2H_x$ to 1.45 for TaV_2H_x [6]). For compounds with $R_A/R_B > 1.3$, the *g*–*g* distance r_2 is expected to become shorter than r_1. This may give rise to a qualitative change in the microscopic picture of H motion: the faster jump process should be transformed into the back-and-forth jumps within *pairs* of *g* sites separated by r_2. The only C15-type system where such a two-site localized motion has been observed experimentally [7,8] is YMn_2H_x with $r_2/r_1 = 0.82$. The results of the neutron diffraction study [2] of $YFe_2D_{2.6}$ at room temperature have

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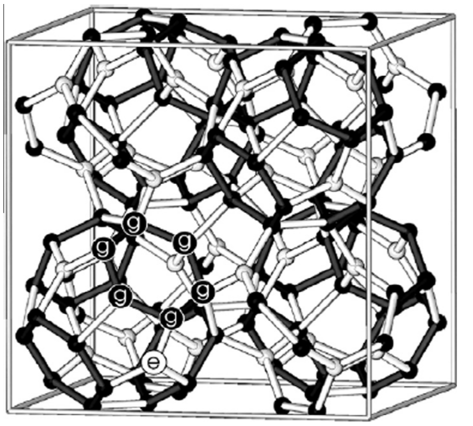

Fig. 1. The spatial arrangement of interstitial *g* sites (dark spheres) and *e* sites (light spheres) in the cubic C15-type AB_2 compound. Each *g* site has three *g*-site neighbors: two *g* sites on the same hexagon at a distance of r_1 (dark bars) and one *g* site on the adjacent hexagon at a distance of r_2 (light bars). Metal atoms are not shown. Each *g* site is coordinated by 2 *A* and 2 *B* atoms, and each *e* site is coordinated by 1 *A* and 3 *B* atoms.

shown that D atoms in this compound randomly occupy *g* sites with the positional parameters $x_g = 0.339$, $z_g = 0.141$. Using these structural data for $YFe_2D_{2.6}$, we find that $r_2 = 0.79$ Å, $r_1 = 1.50$ Å, and $r_2/r_1 = 0.53$. It should be noted that the value of r_2 for $YFe_2D_{2.6}$ is the shortest *g*–*g* distance ever found for hydrogen-absorbing Laves phases. Thus, the YFe_2–H(D) system offers a good opportunity to verify the relation between r_2/r_1 and the microscopic picture of localized H motion in cubic Laves phase compounds. In the present work, quasielastic neutron scattering (QENS) is applied to study the mechanism and parameters of hydrogen jump motion in $YFe_2H_{2.6}$ over a wide temperature range. QENS experiments are complemented by an inelastic neutron scattering (INS) measurement of the hydrogen vibrational spectrum, which is sensitive to the local environment of H atoms in $YFe_2H_{2.6}$.

2. Experimental details

The sample preparation was analogous to that described in Refs. [9] and [10]. The intermetallic compound YFe_2 was prepared by induction melting of pure Y (99.9%) and Fe (99.99%) followed by annealing in vacuum for 12 days at 1163 K. The composition and homogeneity of the intermetallic compound were checked by electron probe microanalysis and X-ray diffraction. According to X-ray diffraction analysis, the resulting YFe_2 sample was a single-phase compound with the cubic C15-type structure (space group $Fd\bar{3}m$) and the lattice parameter $a = 7.362$ Å. Before hydrogen absorption, the powdered sample was activated by heat treatment at 363 K in vacuum. The hydride was prepared by solid–gas reaction at 408 K using a Sieverts-type apparatus. In order to avoid sample amorphisation or decomposition, the rate of H_2 admission was kept low. The hydrogen content was measured by recording the pressure variation in calibrated and thermostated volumes. According to X-ray diffraction, the resulting $YFe_2H_{2.6}$ hydride retained the single-phase state with the same C15-type host-metal lattice, but with larger lattice parameter ($a = 7.782$ Å). This value of a is in good agreement with previous data [2] for the same composition.

All neutron scattering experiments were performed at the NIST Center for Neutron Research (Gaithersburg, Maryland, USA). The inelastic neutron scattering measurement of the hydrogen vibrational spectrum at 4 K was made on a filter-analyzer neutron spectrometer (FANS) [11] using the Cu(2 2 0) monochromator and horizontal collimation of 20 min of arc before and after the monochromator. The measured range of neutron energy loss was 50–210 meV, and the energy resolution was about 4–5% 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) [12] using the incident neutron wavelengths λ of 5.0 Å and 2.75 Å. The energy resolution full widths at half-maximum (FWHM) were 105 μeV ($\lambda = 5.0$ Å) and 270 μeV ($\lambda = 2.75$ Å). The ranges of the elastic momentum transfer studied corresponded to Q ranges of 0.63–2.01 $Å^{-1}$ ($\lambda = 5.0$ Å) and 1.17–3.94 $Å^{-1}$ ($\lambda = 2.75$ Å). The powdered $YFe_2H_{2.6}$ sample was studied in annular geometry in a hollow-cylinder Al container, the sample thickness being ~0.3 mm. The sample thickness was chosen to ensure ~90% neutron transmission and thus minimize multiple-scattering effects. QENS spectra were recorded at $T = 30$, 140, 170, 200, 240, 270, 295, 330, 360 and 390 K with $\lambda = 5.0$ Å, and at $T = 30$, 240 and 360 K with $\lambda = 2.75$ Å. For analysis of the DCS data, the detectors were binned into eight or nine 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 $YFe_2H_{2.6}$ at low temperature (30 K).

3. Results and discussion

3.1. Neutron vibrational spectroscopy

The experimental low-temperature INS spectrum for $YFe_2H_{2.6}$ is shown in Fig. 2. It consists of two broad peaks centered at ~97 and ~150 meV with a nearly 1:2 intensity ratio. The simplest approach to the description of INS spectra due to localized hydrogen vibrations is based on the model of a three-dimensional Einstein oscillator [13,14]. For the $\hbar\omega$ range of fundamental modes, this model predicts three peaks of nearly equal intensity. Depending on point symmetry of H sites, all or two of these peaks may be degenerate. For hydrogen at *g* sites of the C15-type lattice, we expect three non-degenerate peaks, since the point symmetry (m) of these sites is lower than axial. General features of the experimental INS spectrum for $YFe_2H_{2.6}$ can be ascribed to H atoms at *g* sites (two unresolved peaks in the range 125–170 meV and a third peak in the range 82–117 meV). Comparing the shape of INS spectrum for $YFe_2H_{2.6}$ with those for other Laves-phase hydrides with partially occupied *g* sites [15–18], we can conclude that $YFe_2H_{2.6}$ exhibits the largest width of the main two peaks. While the broadening of the spectral features can be usually attributed to the dispersion of the corresponding bands due to H–H interactions, the large width of the peaks for $YFe_2H_{2.6}$ also suggests that the host-metal lattice in this compound is locally distorted, although it retains the average C15-type structure. This is consistent with the results of extended X-ray absorption fine structure (EXAFS) studies [19] for C15-type YFe_2D_x ($x = 2.5$ and 2.9) showing the presence of considerable distributions of Fe–Fe distances in these deuterides.

3.2. Quasielastic neutron scattering

Since the incoherent scattering cross-section of hydrogen is very large, the observed neutron scattering from our $YFe_2H_{2.6}$ sample is dominated by the incoherent nuclear scattering on protons. We have found that at $T \geqslant 140$ K the measured QENS spectra are satisfactorily described by a sum of two components: an 'elastic' line represented by the spectrometer resolution function and a resolution-broadened Lorentzian 'quasielastic' line. The relative intensity of the 'quasielastic' component increases with increasing

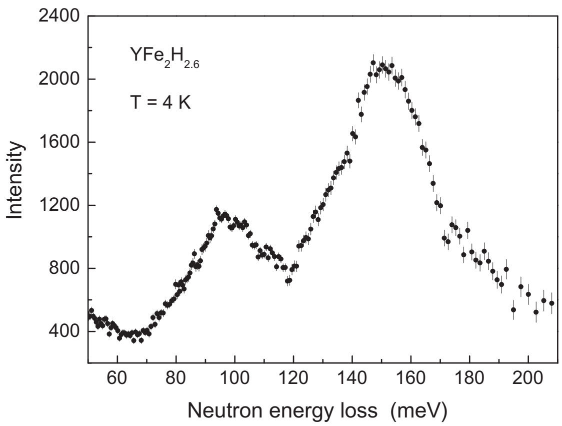

Fig. 2. The low-temperature inelastic neutron scattering spectrum for $YFe_2H_{2.6}$. Vertical error bars correspond to one standard deviation.