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Neutron spectroscopy of localized modes in $CeD_{2-x}H_y$

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Abstract

Localized modes of H in $CeD_{1.93}H_{0.07}$ and $CeD_{2.00}H_{0.07}$ have been measured by inelastic neutron scattering. Assignment of the observed peak positions and intensities in the measured spectra was obtained with a lattice dynamical treatment of an extended ‘‘supercell’’, modelling the crystal structure of the samples.

Keywords: Neutron scattering; Crystal structure; Localized modes

1. Introduction

The analysis of vibrational spectra for hydrogen in metals provides information on the strength of metal–hydrogen and, if present, of hydrogen–hydrogen interactions, both essential for the understanding of many other properties of metal–hydrogen systems (MH_x). Inelastic neutron scattering (INS) is the most powerful technique to investigate lattice dynamical properties of MH_x. It allows for two different types of measurements: (a) phonon dispersion curves, containing the most detailed information, but only obtainable by coherent INS from deuterated single crystals and (b) phonon density of states, using incoherent INS, typically with more easily synthesized poly-crystalline samples.

With respect to H vibrations in the hydride (β-)phase of the rare-earth metals, coherent inelastic neutron scattering investigations on single crystal samples are, up to now, limited to CeD_x for which the favourable low melting point of Ce permits hydrogenation in the melt. Like for other light rare-earth metals, the CeD_{2+x} β-phase has a cubic fcc metal lattice with (ideally) all tetrahedral sites occupied at $x=0$ and additional D ($x>2$) on octahedral sites. Phonon dispersion relations have been measured for $CeD_{2.12}$ [1,2] and $CeD_{2.72}$ [3], and have both been analysed with a lattice dynamical (Born–von Karman) model based on the stoichiometric compositions CeD_2 and CeD_3, respectively. An extension of this lattice dynamical model for a ‘‘supercell’’, which accounts for non-stoichiometry, has later been applied to describe measured phonon lineshapes in $CeD_{2.12}$ [4].

Very recently, optical vibrations of H and D in isotope-diluted $YD_{2-x}H_x$ (isostructural with $CeD_{2-x}H_x$) have been investigated by INS from polycrystalline samples [5]. Simple mass-defect theory was applied to analyse the data for low H ($x=0.04$) and for low D ($x=1.8$) concentrations of defect atoms within the otherwise pure host lattice of the companion isotopes.

We have performed INS experiments on the system $CeD_{2-x}H_y$ with small hydrogen concentrations y for the following reasons: (a) The availability of a supercell formulation [4] allows us to model the system $CeD_{2-x}H_y$ with the Born–von Karman set of force constants [2] for the host lattice. (b) The supercell formulation should not only model the case $y=x$ (to which the analysis by mass-defect theory for $YD_{2-x}H_x$ [5] refers), but also the case $y>x$. For $y=x$, both D and H (ideally) occupy tetrahedral sites, whereas, for $y>x$, excess atoms occupy octahedral sites. In the latter case, due to minimising the total system energy [6], the octahedral sites should preferentially be occupied by H. (c) In contrast to yttrium, the cubic hydride β-phase of cerium does not transform to a hexagonal γ-phase for concentrations up to the trihydride, thus, in principle, allowing the investigation of a larger concentration range of interstitial H within the same phase.

2. Experimental

Two samples of nominal compositions, $CeD_{2.00}H_{0.07}$ and $CeD_{1.93}H_{0.07}$, were prepared from high-purity Ce ingots (99.99 at.%) by first deuterium loading, followed by

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hydrogen loading, at 600 °C. Both samples were kept at this temperature for about 15 h before they were cooled to room temperature. Annular shaped sample holders were filled under He atmosphere.

INS data were collected with the Time-of-Flight Spectrometer FDS at the Manuel Lujan Jr. Neutron Scattering Center of Los Alamos National Laboratory, at sample temperatures of 15 and 300 K. The measured data were corrected for the asymmetric resolution function of the spectrometer by a deconvolution procedure [7].

As the experimental data taken at 15 K show more pronounced features than those at room temperature (where multiphonon effects become more important), only the low temperature data for both samples are shown in Fig. 1(b) and Fig. 1(c), respectively. Fig. 1(a) shows data for a $CeH_{1.94}$ sample, taken under identical experimental conditions, but transformed (changing the energy scale by $1/\sqrt{2}$) to a fictive ''$CeD_{1.94}$'' spectrum. With respect to the ''pure'' sample spectrum, the isotopically mixed samples give additional peaks at 52, 94 and 111 meV, the intensities of which are composition dependent. Fig. 1(d) gives the result when both spectra are subtracted, indicating significant changes with composition. The peak at 52 meV is known to correspond to vibrations of D on octahedral sites (D_o, the occupation of which already in CeD_2 is related to sample preparation [8]). The pronounced peak at 111 meV resembles that found at 126 meV in $YD_{1.96}H_{0.04}$ and corresponds to localized modes of H on tetrahedral sites (H_t).

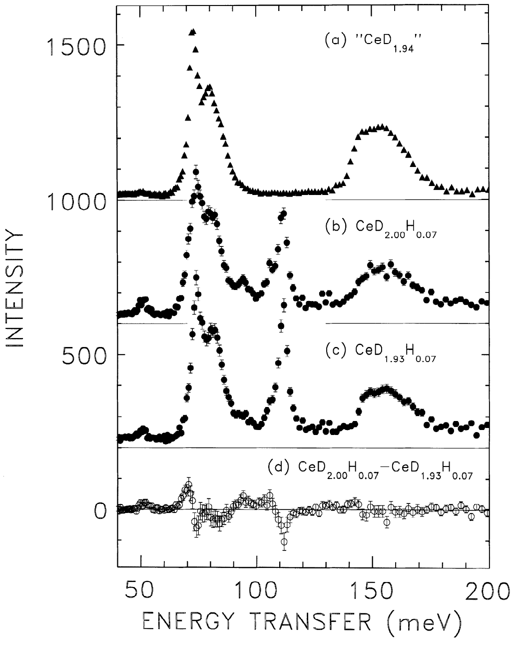

Fig. 1. INS spectra of (a) ''$CeD_{1.94}$'' (obtained from a measured $CeH_{1.94}$ spectrum by energy scale transformation), (b) $CeD_{2.00}H_{0.07}$, (c) $CeD_{1.93}H_{0.07}$ and (d) the difference spectrum ($CeD_{2.00}H_{0.07}$–$CeD_{1.93}H_{0.07}$).

3. Analysis

The original version [4] of the lattice dynamics program for a ''supercell'' has been further extended to achieve a finer sampling of phonon wavevectors (uniformly distributed within the irreducible element of the Brillouin zone) and to optionally assign different masses to the (in total 96) interstitial positions of the metal lattice (which is represented by 32 atoms in the ''supercell'').

In incoherent approximation and for one-phonon (creation) scattering, the contribution of atom k in the supercell to the neutron scattering function is

$$S_k(Q,\omega) = (\sigma_k/4\pi)\,(\hbar Q^2/2M_k)\,[g_k(\omega)/\omega]\,(n_B+1) \\ \times \exp(-2W_k)$$

where σ_k is the neutron scattering cross-section, $g_k(\omega)$ the normalized contribution of atom k to the phonon density of states, n_B the Bose occupation number and $\exp(-2W_k)$ the Debye–Waller factor. With respect to the experimental conditions under which the INS data were taken, the neutron energy transfer $\hbar\omega$ is proportional to the square of the neutron momentum transfer $\hbar Q$, and other factors not strongly varying within the considered energy transfer range, resulting in

$$S_k(Q,\omega) \sim (\sigma_k/M_k)\,g_k(\omega)$$

The lattice dynamics program calculates this expression and sums separately for k being cerium, deuterium or hydrogen, in order to identify their contribution to the total intensity. (The cerium contribution in the range of optical frequencies is negligible, however.)

Fig. 2(a) and Fig. 2(b) show results of this simulation with the original set of force constants for the host lattice CeD_2 [2] and one additional (central) force constant for the coupling of the (interstitial) octahedral atoms to this lattice. The computed scattering functions are convoluted with the resolution function of the spectrometer. The H-concentration $y=0.07$ corresponds in the ''supercell'' to 2H, which are in one case both assumed to be H_t and in the other one split into $1H_t$ and $1H_o$. Whereas the part of the two measured spectra corresponding to the host lattice vibrations is not exactly reproduced by the simulation, the main features of measured and simulated spectra agree. An interesting observation is the assignment of the 94 meV peak (beside the one at 52 meV) being due to deuterium on octahedral sites, strongly coupled to those on tetrahedral sites by a high nearest-neighbour force constant value (3450 g sec^{-2} in the notation of [2]). Consequently, replacing D_o by H_o, leads to two peaks at about 70 and 110 meV. The latter peak, in energy close to that of H_t, is the reason for not reducing the intensity at 111 meV by a factor of two when comparing the simulations for $CeD_{1.93}H_{0.07}$ and $CeD_{2.00}H_{0.07}$. This complication prevents any more accurate determination of site occupation numbers from peak areas in this (isotopically mixed) system.

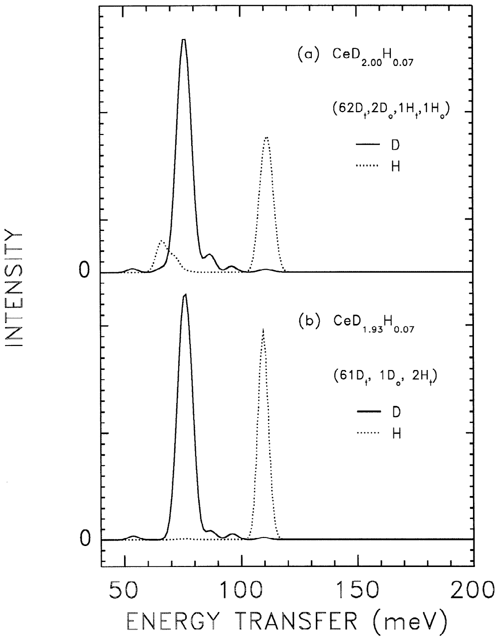

Fig. 2. Supercell simulations for (a) $CeD_{2.00}H_{0.07}$ and (b) $CeD_{1.93}H_{0.07}$.

Though a Born–von Karman model is based on force constants which do not give any direct information about the origin of the interaction, it allows conclusions with respect to the strength of dominant interactions. For the system under study it was found —in agreement with our previous analysis of phonon dispersion curves, but now through the analysis of localized mode spectra for H in CeD_{2-x}—that the dominant interaction for H on tetrahedral lattice sites is that with the metal atoms, and for H on octahedral lattice sites is that with the deuteriums on tetrahedral positions.

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