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Neutron spectroscopic evidence of concentration-dependent hydrogen ordering in the octahedral sublattice of β-TbH_{2+x}

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The octahedrally coordinated hydrogen (H_o) of the superstoichiometric rare-earth dihydrides β-TbH_{2+x} ($0.03 < x < 0.25$) has been probed by incoherent inelastic neutron scattering. The H_o sublattice arrangements and associated optical vibrations are sensitive to the value of x. For $x = 0.03$ at low temperature, the majority of the low-concentration *o*-site hydrogens are isolated in a local cubic environment and exhibit a relatively sharp vibrational density of states at 80.8 meV, in accord with the presence of triply degenerate normal modes. In contrast, for $x = 0.25$, a broad bimodal band peaking at ~ 76.7 and 83.1 meV is evident, consistent with the type of long-range order that is known to occur in the H_o sublattice at this higher concentration. Increasing the temperature above the long-range ordering transition leads to a more disordered H_o sublattice and a density of states similar to that at low values of x but broadened, most likely by the persistence of some short-range order.

The rare-earth dihydrides β-RH_{2+x} possess an fcc metal lattice. Ideally, for $x = 0$, the hydrogen occupies all of the tetrahedral (*t*-site) interstices. In the superstoichiometric region $0 < x < x_{\max}$, the excess hydrogen occupies the octahedral (*o*-site) interstices [see Fig. 1(a)]. Further addition of hydrogen above $x_{\max}$ leads to the precipitation of the hexagonal γ-RH_3 phase. In recent years, there has been interest in more thoroughly characterizing the physical properties of the different rare-earth dihydrides throughout the superstoichiometric region where the excess hydrogen causes concentration-dependent changes in the electronic band structure. For example, β-TbH_{2+x} [$x_{\max} \approx 0.25$ (Ref. 1)] has been shown to possess several x-dependent magnetic-ordering phases at low temperatures below ~ 40 K.[1,2] At higher temperatures (~ 150–200 K), an x-dependent anomaly was found in the electrical resistivity,[1–3] strikingly similar to that observed for the various rare-earth–hydrogen α-phase systems[4] and attributed to the onset of structural ordering within the octahedral hydrogen sublattice. Very recently, neutron diffraction studies[5] of β-TbD_{2+x} ($0.08 \le x \le 0.18$) have shown that *o*-site hydrogens (H_o) undergo long-range ordering for $x > 0.1$ into a Ni_3Mo-type structure (*I4/mmm*) in which three consecutive empty (042) planes are followed by one occupied plane [see Fig. 1(b)], ideally yielding the stoichiometric compound β-$TbH_{2.25}$. Below this concentration, the diffraction studies confirm the absence of long-range order although the growth of short-range order with increasing x is suggested by the resistivity measurements. In this report, we present incoherent-inelastic-neutron-scattering (IINS) results for β-TbH_{2+x}, which illustrate the utility of the virbrational density of states as a sensitive probe of the changes in H_o bonding states accompanying the appearance of the structural ordering in the H_o sublattice at the higher H_o concentrations.

Starting with high-purity Tb (99.99 at. %, Johnson Matthey), a series of β-TbH_{2+x} samples ranging from 4–10 g each were prepared with different H_o concentra-

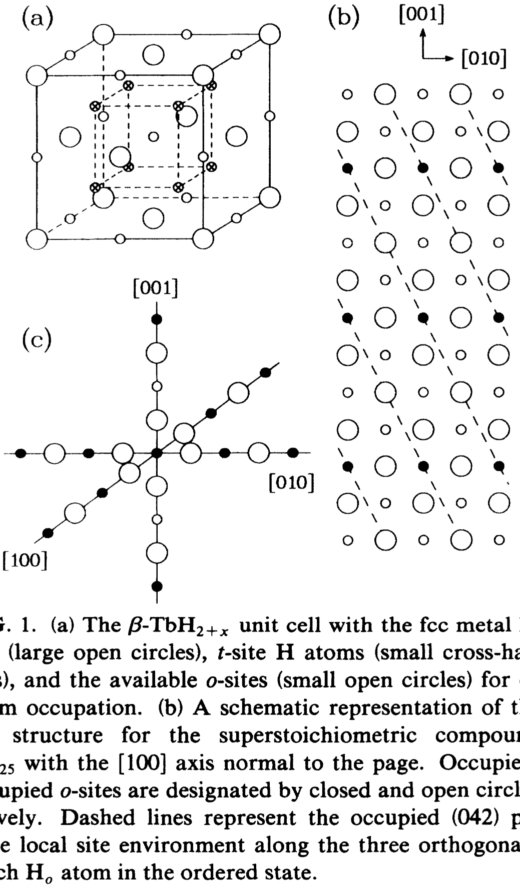

FIG. 1. (a) The β-TbH_{2+x} unit cell with the fcc metal lattice atoms (large open circles), *t*-site H atoms (small cross-hatched circles), and the available *o*-sites (small open circles) for excess H atom occupation. (b) A schematic representation of the ordered structure for the superstoichiometric compound β-$TbH_{2.25}$ with the [100] axis normal to the page. Occupied and unoccupied *o*-sites are designated by closed and open circles, respectively. Dashed lines represent the occupied (042) planes. (c) The local site environment along the three orthogonal axes for each H_o atom in the ordered state.

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tions from $x=0.3$ to 0.25 using a procedure similar to that established by Vajda, Daou, and Burger.[2] For each sample, hydrogen (Matheson Research grade, >99.9995 at.% purity) was loaded by gas-phase absorption at 873 K in a quartz tube to the nominal stoichiometry β-$TbH_{2.005}$; some uncertainty exists about the exact stoichiometry, since this is dependent on the purity of the starting material. To obtain an "ideal" β-$TbH_{2.00}$ baseline compound, excess o-site hydrogen was removed by vacuum evacuation at 773 K, where it is known that the dihydride is stable, while the o-site hydrogen is unstable.[2] After evacuation, hydrogen was again added to the pure dihydride at 773 K to synthesize the desired superstoichiometric compound, and the sample was allowed to cool slowly over an 8-h period to an x-dependent temperature in the range of 400–450 K and held there for 24–48 h. After this stage, the small hydrogen vapor pressure above the sample was evacuated simultaneously with a rapid cooling to room temperature. Each sample was then transferred to a glove box where it was pulverized and loaded into an Al cell having a thin plate geometry to minimize the effects of multiple scattering. The vibrational spectra were measured at the Neutron Beam Split-Core Reactor (NBSR) at the NIST using the BT-4 spectrometer. The Cu(220) monochromator with precollimations and postcollimations of 20′ in combination with the Be-graphite-Be-filter analyzer provided a resolution ranging from 1.8 meV full width at half maximum (FWHM) at 75 meV to 2.2 meV FWHM at 90 meV.

The vibrational spectrum due to o-site hydrogen can be easily separated from that due to t-site hydrogen, since the latter modes are in the region of 120 meV, while the former are observed close to 80 meV. A comparison of the low-temperature vibrational densities of states of the o-site hydrogens for the superstoichiometric compounds in Fig. 2 illustrates dramatic differences in both peak widths and peak shapes. For $x=0.03$, the o-site band at 80.8 meV is relatively sharp and possesses only minor low- and high-energy shoulders. Indeed, as the H_o concentration increases, the intensity contributions of the shoulders increase relative to the central peak. For $x=0.25$, the band, now totally devoid of the sharp central peak, is broad and clearly bimodal with the higher-energy peak at ~83.1 meV twice the intensity of the lower-energy feature at ~76.7 meV.

For β-$TbH_{2.03}$, the H_o atoms are predominantly isolated, and thus reside in a locally cubic environment. The narrow vibrational band reflects the close to triply degenerate eigenstates expected for nearly independent oscillators. The sideband contributions are attributed to the small fraction of the H_o atoms that are not isolated, but rather are situated together in small clusters of short-range order. As the H_o concentration increases, these short-range-ordered clusters evolve into the long-range order indicated by the diffraction studies. This is reflected by the growth and development of the sidebands from minor shoulders at low concentration to fully developed spectral features at high concentration concomitant with the disappearance of the sharp central band due to isolated H_o oscillators. In the fully ordered

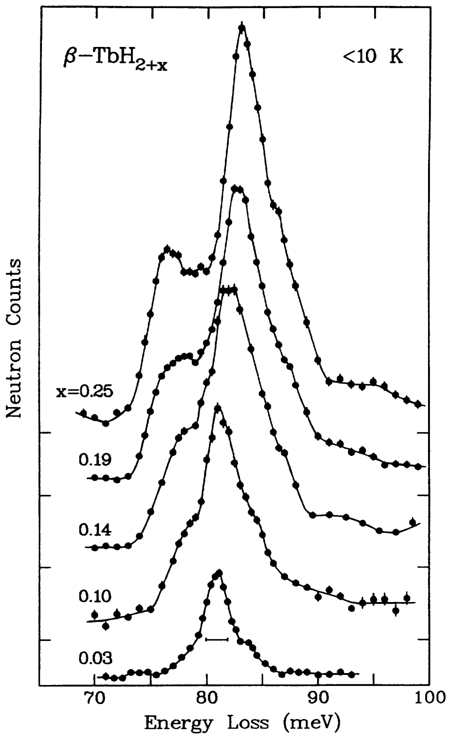

FIG. 2. The vibrational densities of states of the H_o sublattice in β-TbH_{2+x} for different values of the excess hydrogen x. Solid lines are intended only as guides to the eye. The instrumental resolution (FWHM) is denoted by the horizontal bar accompanying the spectra.

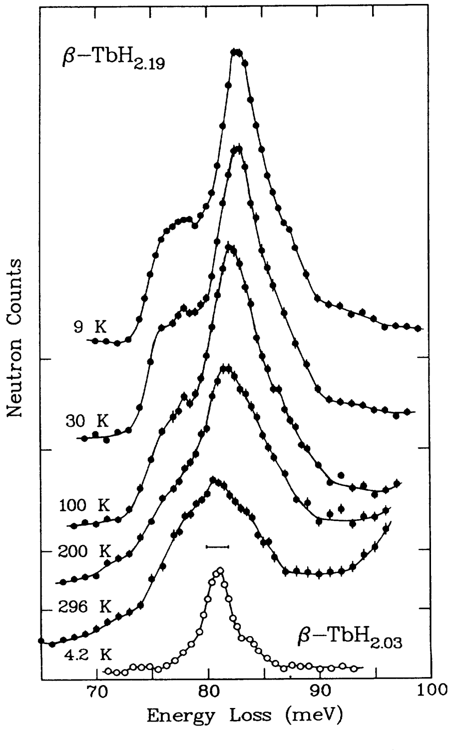

FIG. 3. The vibrational densities of states of the H_o sublattice in β-$TbH_{2.19}$ at different temperatures compared to that in β-$TbH_{2.03}$ at 4.2 K. Solid lines are intended only as guides to the eye.

stoichiometric compound, β-$TbH_{2.25}$, which marks the β-γ phase boundary, each *o*-site hydrogen is an intersecting member of identical $(\text{-}H_o\text{-Tb-})_n$ chains in the [100] and [010] directions and a $(\text{-}H_o\text{-Tb-}\square\text{-Tb-})_n$ chain (where □ represents an *o*-site vacancy) in the [001] direction [see Fig. 1(c)]. The accompanying bimodal line shape reflects the three orthogonal normal-mode vibrations of the H_o atoms along the primary crystallographic axes. By symmetry considerations, the vibrational energies of the modes in the [100] and [010] directions are degenerate and thus correspond to the higher-intensity feature at ~83.1 meV. The remaining lower-energy feature at ~76.7 meV would then correspond to the singlet mode in the [001] direction. The considerable width of the two major components are very likely associated with dispersion of the phonon branches due to H-H interactions. The correlation of the *o*-site density of states with the H ordering is also clearly illustrated in Fig. 3, which shows the temperature dependence for β-$TbH_{2.19}$. The bimodal line shape, observed in the ordered phase at 9 K, gives way to a broad band centered at ~81 meV as the temperature is raised to 296 K, above the order-disorder transition. The central feature in the high-temperature band corresponds to the peak observed at low H_o concentrations, indicating a disordered phase. However, the width of the band strongly suggests that some degree of short-range order is still present.

Thus, we have observed a vibrational splitting associated with the ordering of the hydrogen residing in the *o*-site sublattice in β-TbH_{2+x}, which demonstrates the importance of the H-H interactions at least out to second-nearest-neighbor (H_o) distances in this system. Note that in the ordered structure, a repulsive H_o nearest-neighbor interaction favors vacancies around each occupied *o* site. The observed modes exhibit broad complex line shapes, reflecting dispersion due to longer-range interactions and/or imperfect ordering. In closing, we have found that the presence of H_o atoms also perturbs the vibrational dynamics of the tetrahedrally coordinated H atoms. This is currently under investigation, and a full analysis of the vibrational dynamics of both β-TbH_{2+x} and β-TbD_{2+x} will be the subject of a future paper.

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