

Brief Reports

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Evidence of mode splitting for *c*-axis-polarized hydrogen vibrations in α -ScH_{0.34}

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The vibrational spectra of tetrahedrally bound hydrogen in polycrystalline α -ScH_{0.34} have been measured using incoherent-inelastic-neutron-scattering methods. Low-resolution spectra locate the *c*-axis and basal-plane-polarized normal-mode energies at 103.5 and 147.5 meV, respectively. A high-resolution measurement of the broad *c*-axis vibration peak exhibits evidence of a hydrogen-mode splitting, unlike previous spectroscopic results for α -ScH_{*x*} (*x* ≤ 0.25). This suggests that the low-temperature, short-range ordering of Sc-bridged hydrogen pairs along the *c* axis is more fully developed near the α/β -phase boundary than at lower hydrogen concentrations, which is generally consistent with behavior found previously for α -YH_{*x*}. As at lower hydrogen concentrations, however, the broader peaks for α -ScH_{0.34} indicate less extended order than in α -YH_{*x*}.

Scandium as well as several other rare-earth hcp metals (e.g., Lu, Y, Er, and Tm) are capable of forming α -phase solid solutions with hydrogen that remain stable at low temperatures approaching absolute zero.¹ The H atoms are known to reside in the tetrahedral interstices (i.e., *t* sites) of the metal host lattice.²⁻⁵ Recent results of diffuse-elastic-neutron-scattering (DENS) studies of α -ScD_{*x*},⁶ α -LuD_{*x*},^{7,8} and α -YD_{*x*} (Refs. 9 and 10) have revealed the existence of strong short-range H-pairing order in the α phase. The basic H-M-H unit consists of a *c*-axis-aligned pair of H atoms in second-nearest-neighbor *t* sites on either side of a metal atom. The observation of modulated ridges of diffuse scattering intensity in these studies indicate that these hydrogen pairs are arranged in zigzag chains (i.e., undergo a lateral displacement step after each consecutive hydrogen pair) along the *c* direction. The appearance of diffuse scattering peaks at low temperatures and high-H concentrations further indicate the onset of three-dimensional short-range order, apparently involving interchain correlations. A typical behavior of these solid solutions is a concentration-independent electrical resistivity anomaly occurring between 150 and 170 K.¹ Although originally attributed to the onset of short-range ordering of H atoms into pairs, the subsequent DENS results suggest that this anomaly is more likely due to the ordering of the H pairs themselves into chains.

Further evidence for H pairing along the *c* direction was obtained from incoherent-inelastic-neutron-scattering (IINS) measurements of the *c*-axis-polarized vibrational mode of H in α -YH_{*x*},^{11,12} which possessed a distinct 4–5-meV splitting at the higher-H concentra-

tions. A simple phenomenological model successfully explained the splitting behavior as due to the dynamic coupling of H pairs along the *c* direction, creating local lower-energy “acoustic” and higher-energy “optic” branches.¹² The “acoustic” branch is essentially independent of H concentration while the “optic” branch is strongly perturbed by the concentration-dependent distribution of H-H interactions and effectively disappears as the H concentration is reduced to low values. Hence, hydrogen pairing is itself a strongly concentration-dependent, cooperative phenomenon, showing a tendency toward unpaired hydrogen configurations at the lowest concentrations and highly correlated pair configurations at the highest concentrations.

Recently, an IINS study¹³ of hydrogen dynamics in α -ScH_{*x*} (*x* = 0.05, 0.16, and 0.25) revealed a *c*-axis vibrational peak at all hydrogen concentrations that was much broader (~ 14-meV FWHM intrinsic linewidth, *x* = 0.25) than the instrumental resolution, yet devoid of any resolved fine structure indicative of a distinct mode splitting as was observed previously for α -YH_{*x*}.¹² Although the broad widths of the α -ScH_{*x*} *c*-axis peaks were consistent with the presence of H pairing across Sc atoms along the *c* axis at low temperatures, the lack of a resolved splitting suggested that the ordering of the hydrogen pairs themselves along the *c* axis was less extensive at these H concentrations than in α -YH_{0.18}. This was in contrast to a previous IINS study¹⁴ of α -ScD_{*x*} (*x* = 0.19 and 0.33) under lower-resolution conditions, which reported a much narrower (~ 5-meV FWHM) intrinsic linewidth for the unsplit *c*-axis mode, even at the highest D concentration. In the present study, the H vi-

brational spectrum of $\alpha\text{-ScH}_{0.34}$ has been measured using IINS methods in order to further characterize the bonding potential of H in the t sites at high-H concentration, very close to the $\alpha\text{-ScH}_x/\beta\text{-ScH}_2$ phase boundary [$x_{\text{max}} \approx 0.35$ (Ref. 15)].

The sample consisted of two rectangular plates of polycrystalline scandium (99.97% metals purity) supplied by the Ames Laboratory Materials Preparation Center at Iowa State University.¹⁶ Each plate was approximately 9 g and measured $70 \times 20 \times 2$ mm³. The thin-plate geometry was necessitated by the significant neutron absorption cross section for Sc. For the IINS measurements, the plates were arranged side by side to create an effective sample size of $70 \times 40 \times 2$ mm³, thus, being able to take advantage of the full neutron beam cross section (63.5×25.4 mm²). Scattering measurements were taken in the reflection geometry with a 110° scattering angle. The angle between the neutron beam axis and the surface normal vector was chosen to maximize the scattering intensities of the c -axis and basal-plane vibrational modes. Preliminary angle-dependent measurements determined that the polycrystalline samples possessed some texture, with a tendency for the basal planes of the microcrystals to be approximately parallel to the sample surface plane. Hence, the best angle was determined to be 15° for measuring the c -axis mode and 57.5° for measuring the basal-plane modes. The hydrogen loading was accomplished (using Matheson¹⁶ Research grade H₂, greater than 99.9995% purity) in the normal fashion by gas-phase adsorption using a calibrated dose volume to titrate the desired concentration. Each plate was loaded separately at 973 K over a 1-h period, equilibrated for one additional hour at 1173 K, cooled slowly back to 973 K over a 2-h period (where there was a negligible H₂ partial pressure), further cooled to room temperature, and finally mounted into a low-temperature displacer for spectral analysis. The IINS measurements were performed at the Neutron Beam Split-Core Reactor (NBSR) at the National Institute of Standards and Technology using the BT-4 triple-axis spectrometer. Incident energies were selected using a Cu(220) monochromator. Low-resolution scans were taken using $40'$ pre- and post-monochromator collimations and a liquid-nitrogen-cooled Be filter before the neutron detector. In this configuration, the instrumental resolution varied from 6 to 12 meV (FWHM) for energy transfers of 80–180 meV. Characterization of vibrational line shape was accomplished in a high-resolution configuration consisting of $20'$ - $20'$ collimations and a liquid-nitrogen-cooled Be-graphite-Be composite filter. In this configuration, the instrumental resolution was 2.5 meV at 100-meV energy transfer.

In Fig. 1, the low-resolution H vibrational spectrum for $\alpha\text{-ScH}_{0.34}$ at 8 K illustrates the expected low-energy c -axis and high-energy basal-plane vibrational features. Gaussian fits of each feature with two peaks (one main peak and one multiphonon sideband at higher energy) yield an energy (FWHM peakwidth) of 103.5 ± 0.2 (16.9 meV) (and a 122.9-meV sideband energy) for the c -axis mode and 147.5 ± 0.1 (10.1 meV) (and a 168.3-meV sideband energy) for the doubly degenerate basal-plane modes. The values for the normal-mode energies and

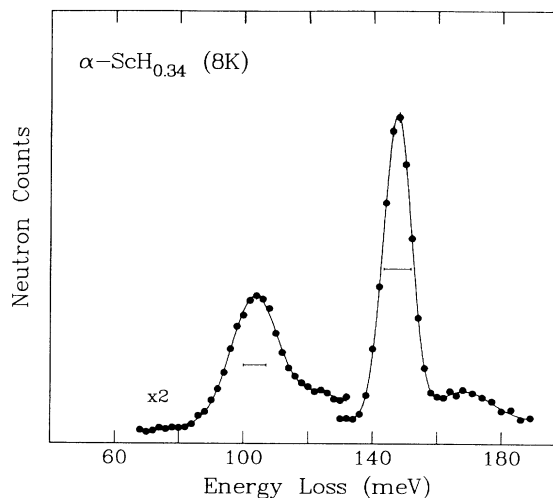


FIG. 1. Low-resolution IINS spectrum of $\alpha\text{-ScH}_{0.34}$ at 8 K. The spectrum was measured at two different sample/beam orientations as explained in the text. Solid lines are the result of Gaussian fits. The instrumental resolutions (FWHM) are illustrated by the horizontal bars beneath the spectral peaks.

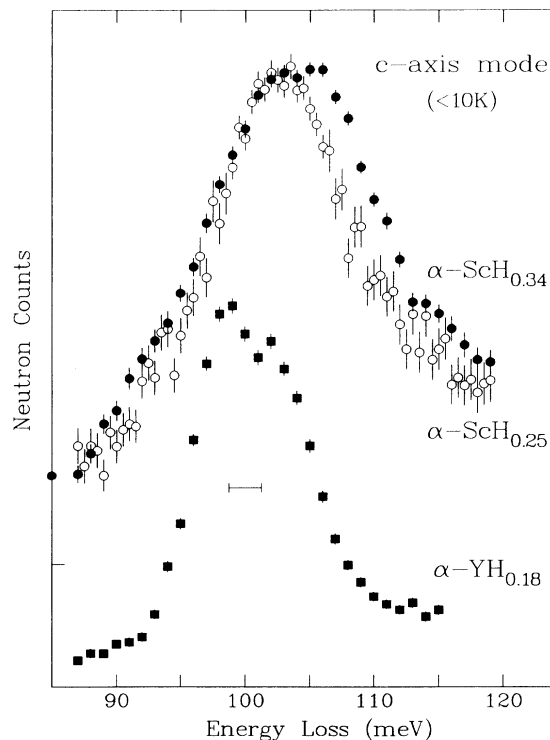


FIG. 2. High-resolution IINS spectrum of the c -axis mode for $\alpha\text{-ScH}_{0.34}$ (8 K, solid circles) from this study, compared with that for $\alpha\text{-ScH}_{0.25}$ (4 K, open circles) (Ref. 13) and $\alpha\text{-YH}_{0.18}$ (8 K, solid squares) (Ref. 12). To aid in the comparison of peakshapes, the $\alpha\text{-ScH}_x$ spectra are normalized to approximately the same peak intensity near 103 meV. The instrumental resolution (FWHM) is illustrated by the horizontal bar beneath the spectra.

peakwidths are comparable to the corresponding values of 102.5 (16.0 meV) and 147.5 (9.4 meV) found previously for α -ScH_{0.25}.¹³ Again, after resolution corrections, the soft *c*-axis mode is very broad (15.4-meV intrinsic FWHM) compared to the basal-plane mode (4.6-meV intrinsic FWHM), indicating considerable H-H pair interactions along the *c* direction. The somewhat larger peakwidths for α -ScH_{0.34} relative to α -ScH_{0.25} provide evidence of increased H-H interactions at the higher-H concentration, both along the *c* direction and laterally along the basal-plane direction.

More insight was provided by measuring the *c*-axis-mode line shape under high-resolution conditions. Figure 2 illustrates the high-resolution, low-temperature, *c*-axis vibrational spectrum for α -ScH_{0.34} compared with that for α -ScH_{0.25} and α -YH_{0.18}. It is clear that increasing the H concentration has led to the growth of scattering intensity predominantly on the higher-energy side of the *c*-axis peak, resulting in a more broadened feature centered at a slightly higher energy and the emergence of a faint yet distinct splitting of ~ 4 –5 meV, similar in magnitude to that observed for α -YH_{0.18}. In analogy with the α -YH_{*x*} results, the α -ScH_{0.34} spectrum suggests a more fully developed ordering along the *c* axis at the higher-H concentration. These results give further credence to the phenomenological model describing the concentration-dependent *c*-axis-mode splitting in α -YH_{*x*} (Ref. 12) mentioned above. As the H concentration is maximized in α -ScH_{*x*} (i.e., as the α -ScH_{*x*}/ β -ScH₂ phase boundary is approached), the importance of coherency strains leads to more highly correlated pair configurations and the growth of the “optic” branch of the spectral doublet. Moreover, the increase in H concentration leads to more significant interchain (i.e., lateral H-H) interactions as inferred by the increased broadening of the basal-plane mode. The increase in H concentration also appears to perturb the distribution of H-metal force constants, causing a slight broadening of the “acoustic” branch of the *c*-axis-mode peak as evidenced (in Fig. 2) by some additional scattering intensity on the lower-energy side for α -ScH_{0.34} compared to α -ScH_{0.25}.

Similar to α -YH_{0.18},¹³ fitting the entire α -ScH_{0.34} spectrum with two Gaussians required component linewidths too broad to reproduce the bimodal contour of the central portion of the peak. Although a rigorous deconvolution of the component line shapes is complicated by the presence of multiphonon structure on the higher-energy

side, both the α -YH_{0.18} and α -ScH_{0.34} spectra are found to be better fit by empirical, non-Gaussian component line shapes possessing much sharper maxima yet broadened more significantly than Gaussians by substantial intensity contribution in the wings. The required line shapes illustrate the non-Gaussian nature of the vibrational density of states for these high-H-concentration, rare-earth systems and reflect, in part, the predominance of particular local “acoustic” and “optic” mode energies favored by a significant fraction of the H-H pairs present in the *c*-axis-directed chains, most probably those H-H pairs populating the interior of the chains. It is reasonable to assume that the potentials experienced by H in these pairs are very similar to each other leading to similar vibrational energies. Moreover, increasing the H concentration of the α phase is believed to lead to a higher fraction or sharper distribution of long chains, and thus, a higher fraction of interior H-H pairs.

This reasoning is consistent with the spectral differences observed for α -ScH_{0.34} and α -YH_{0.18}. Although the magnitude of the *c*-axis-mode splitting is similar to that for α -YH_{0.18}, the much broader components of the spectral doublet observed for α -ScH_{0.34} compared to α -YH_{0.18} indicate less extended order of hydrogen pairs in α -ScH_{0.34}, in line with other indications^{6,17} that the chains in α -ScH_{*x*} are shorter than in the other rare-earth hydrogen systems. Moreover, the atomic volume for α -Sc is nearly 25% smaller than for α -Y.¹⁸ The shorter distances between atoms for α -ScH_{0.34} thus imply stronger perturbations on the *t*-site potentials from vicinal H either along the *c* direction or laterally from nearby chains, which is also in keeping with the broader line shapes observed.

The absence of splitting and the relatively narrow intrinsic linewidths found for the *c*-axis mode in α -ScD_{*x*} (*x* = 0.19 and 0.33),¹⁴ despite corresponding DENS evidence for deuterium pairing at these D concentrations,⁶ led the authors of these studies to conclude that local-mode splitting is not a necessary signature of pair formation and therefore cannot be taken generally as a characteristic measure for the evolution of the ordered state. In light of the *c*-axis-mode line shapes found for α -ScH_{*x*} and α -YH_{*x*} in our studies and the DENS evidence for pair formation in these systems, it seems clear that the detailed shape (i.e., splitting and/or broadening) of the *c*-axis vibrational peak is, indeed, a function of the short-range order associated with pairing and provides a useful qualitative measure of its extent.

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