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Concentration and temperature dependence of hydrogen vibrations along the *c* axis for hydrogen in yttrium: Evidence of dynamically coupled hydrogen pairs

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The *c*-axis vibrations of hydrogen in yttrium have been measured at various concentrations and temperatures using high-resolution neutron spectroscopy. The unusual splitting of these modes is revealed to be highly sensitive to both conditions and to isotopic dilution. The results indicate that the splitting is caused by hydrogen pairs dynamically coupled across metal atoms and that this interaction is modulated by concentration- and temperature-dependent occupation correlations along the *c* axis.

INTRODUCTION

The local-mode frequencies of hydrogen isotopes dissolved in metals provide direct information on the symmetry and strength of interatomic potentials. Recently improved neutron instrumentation has allowed such measurements to be extended to the solid-solution or low-concentration phases with higher resolution, where details of the potential in the dilute phases are evidenced.[1] Paralleling this, there has been increasing interest in the study of the dynamics of hydrogen in the rare-earth hcp metals, such as Y, Sc, Er, Tm, and Lu, which are characterized by their ability to retain hydrogen in solid solution up to relatively high concentration.[2] For the case of yttrium, neutron diffraction measurements[3,4] identified the preferred sites occupied by H in this phase as the tetrahedral (*T*) sites, which are arranged in pairs along the *c* axis with two such pairs per unit cell. Quasielastic neutron scattering studies[5] on polycrystalline samples of $YH_{0.18}$ confirmed the predominant occupation of *T* sites at 600 °C. However the results showed that long-range diffusion involved migration via the octahedral sites with an instantaneous occupation of less than 3%. Similar behavior has been observed in NMR studies of the comparable ScH_x system.[6]

In order to explain concentration-independent resistivity anomalies observed in this system (and in the comparable Lu-H and Tm-H systems) in the vicinity of 180 K, a pairing of hydrogens on the near-neighbor *T* sites was proposed.[7-9] However, the separation of such pairs in yttrium is approximately 1.3 Å, the exact value being dependent on the concentration, which is much less than the minimum separation between two hydrogens suggested by Westlake as a result of band calculations.[10] Thus it is reasonable to assume that the occupancy of adjacent (first-neighbor) sites is precluded, which suggests a maximum concentration of $YH_{1.0}$. This conclusion is supported by recent NMR measurements on $YH_{0.18}$ (Ref. 11). In practice, a phase separation occurs at concentrations above $x = 0.24$ and the fcc dihydride phase is precipitated.

Furthermore, diffuse elastic neutron scattering (DENS) measurements on $YD_{0.17}$ have shown that there is a tendency for deuterons to pair at second-neighbor distances, thus bridging a metal atom.[12] The model proposed to explain these results suggests that such pairs exist at all temperatures but that cooling through the observed anomaly temperature causes individual pairs to arrange themselves along the *c* axis, each such line of pairs having little or no correlation with neighboring lines. In this model the D concentration determines the number of ordered lines and not the transition temperature of a given line. A similar ordering has also been observed in the comparable Lu-H system, although in this case, the model put forward is based on a three-dimensional arrangement of the individual pairs[13] postulated as a mechanism for reducing the lattice distortion.

In addition, quasielastic-neutron-scattering (QENS) measurements[14] have demonstrated the existence of a rapid diffusion process between the two near-neighbor sites giving rise to local jump frequencies of approximately 3.5×10^{10} s^{-1} at 300 K. This local diffusion rate is orders of magnitude greater than the bulk diffusion at the same temperature. The elastic structure factor obtained from the QENS measurements, however, indicates a trapping of H which becomes more effective as the temperature is lowered and which may be related to the pairing mechanism observed in the DENS measurements.[15] It is interesting to note that the rather high activation energy for long-range diffusion of 0.57 eV as determined by both QENS and NMR measurements implies localization on the pair of *T* sites during a time scale of the order of several minutes at 180 K. This observation would suggest that long-range rearrangement of H at these temperatures is so slow compared to the measurement time that the transition becomes transport limited rather than reaching equilibrium. This argument is supported by recent resistivity studies on several rare-earth samples which had been subjected to quenching or low-temperature electron irradiation.[16]

Recently, measurements of the local-mode frequencies in single-crystal samples of $YH(D)_{0.18}$ (Ref. 17) demonstrated a highly unusual potential in this system which is much softer and anharmonic along the *c* axis than in the basal plane. The observation of a vibration frequency which is reduced by approximately 25% along the *c* axis is surprising since the *T* sites have nearly cubic local symmetry with a hexagonal c/a ratio which is only 3% less than the ideal value. Low-temperature results with improved energy resolution showed a novel splitting of the *c*-axis mode which was interpreted in terms of H pairing in this system.

In the present paper we present results of high-resolution measurements of the local-mode frequencies of hydrogen in yttrium at various concentrations and temperatures in order to further investigate the details of the hydrogen potential and pairing interactions in this system. We also report on the results of an isotope dilution study which confirms that dynamical coupling of hydrogen is responsible for the unusual *c*-axis mode splitting observed in this system.

EXPERIMENTAL DETAILS

The present measurements were performed on the BT4 spectrometer at the NBS reactor using a Cu(220) monochromator with 20′ collimators before and after to select the incident energy and a composite beryllium-graphite filter cooled to 77 K for final energy analysis. Operated in this way, the spectrometer has a resolution of 2.5 meV (FWHM) at 100 meV energy transfer.

The two samples of yttrium used for the measurements were supplied by the Materials Preparation Center of Iowa State University and contained less than 80 ppm atomic oxygen impurity. Hydrogen and deuterium were routinely added to the samples from the gas phase using a calibrated dose volume to attain the desired concentrations. The loading process was typically followed by annealing to 1330 K before cooling to room temperature. Each concentration was checked by gravimetric analysis. The first sample was a single crystal (16 g) oriented during the measurements such that the momentum transfer vector **Q** was approximately parallel to the *c* axis, enhancing the sensitivity to vibrations polarized in that direction. This sample was first loaded with 15 at. % hydrogen ($YH_{0.18}$) and the energy spectrum in the vicinity of 100 meV was measured at temperatures between 8 and 240 K. Subsequently 90% of the hydrogen was removed and replaced with deuterium, resulting in a sample of $YD_{0.17}H_{0.019}$. The energy spectrum of this sample was also measured at 8 K with **Q** along the *c* direction.

The concentration dependence of the splitting of the 100 meV H local mode was investigated using the second sample, which consisted of three polycrystalline rods (25 g total) stacked vertically and arranged with the cylinder axes (which is the preferred orientation for the *c* axis in these samples[18]) aligned approximately along the **Q** vector. A series of spectra were collected for hydrogen concentrations ranging from 1 to 15 at. %. The intrinsic background count rate was determined after each measurement and subtracted from the sample spectra after normalization.

RESULTS

Figure 1 shows the spectra taken from the single-crystal $YH_{0.18}$ at temperatures of 8, 220, and 240 K together with the data taken from the same crystal with composition $YD_{0.17}H_{0.019}$. At 8 K, the spectrum for

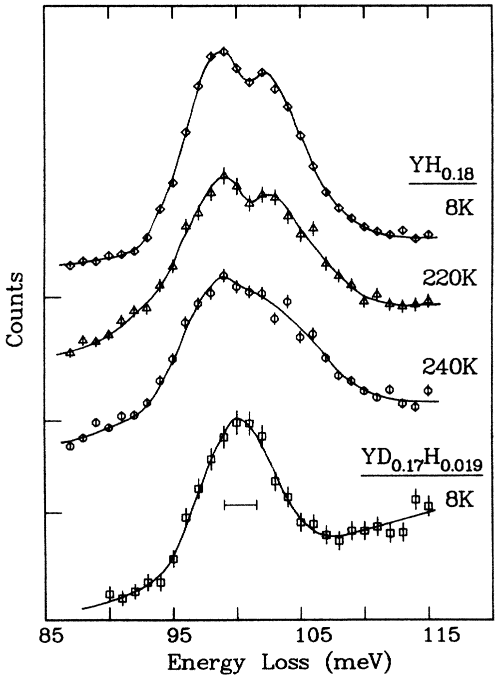

FIG. 1. Vibrational spectra for single-crystal $YH_{0.18}$ with **Q** parallel to the *c* axis as a function of temperature. (Solid lines are intended only to guide the eye.) Bottom spectrum for single-crystal $YD_{0.17}H_{0.019}$ at 8 K is shown for comparison with its corresponding Gaussian fit (6.6 meV FWHM).

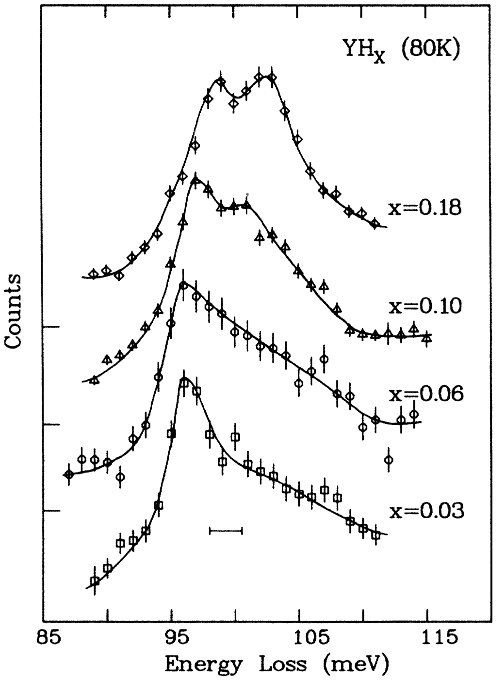

FIG. 2. Vibrational spectra for polycrystalline YH_x at 80 K as function of hydrogen concentration. (Solid lines are intended only to guide the eye.)

$YH_{0.18}$ shows two distinct peaks of roughly equal intensity centered at 99 and 102.5 meV, respectively. This observation of a splitting in the local-mode frequency polarized along the *c* direction for hydrogen parallels the earlier measurements of a similar splitting for $YD_{0.18}$. For both isotopes, a splitting of approximately 3.5–4 meV is observed, suggesting that the widths of the two peaks are of the order of the instrumental resolution. As the temperature is raised to 220 K, the overall width of the features increases, but two peaks can still be clearly distinguished in the spectrum at the same positions as observed in the 8-K spectrum. When the temperature is further increased to 240 K, the feature at 99 meV can still be observed, although the entire spectrum becomes more complex, and the second peak cannot be clearly distinguished.

The spectrum from the crystal loaded to a composition of $YD_{0.17}H_{0.019}$ at 8 K shows a striking contrast to that for the pure hydrogen sample in that only one peak is observed, which is centered at 100 meV. The uncorrected width of this peak is found to be 6.5 meV (FWHM). Although larger than the instrumental resolution, it is markedly smaller than the total width of approximately 11 meV measured for the $YH_{0.18}$ sample at the same temperature.

Turning to the concentration dependence of the local-mode frequencies, Fig. 2 shows the spectra taken for the polycrystalline sample of YH_x with $x=0.03$, 0.06, 0.10, and 0.18 at 80 K. Other spectra were also measured at $x=0.01$, 0.04, and 0.05, which follow the same general trend but are not included in the figure. At the highest concentration $x=0.18$, the spectrum is similar to that observed for the single crystal at low temperature showing two equally intense, sharp features centered at 99 and 102.5 meV. As the concentration is lowered, the peak initially seen at 99 meV remains prominent but the peak position shifts down to about 97 meV at $x=0.10$ and 96 meV at $x=0.06$. There is apparently no further significant shift with concentration below 96 meV within the precision afforded by the present statistics.

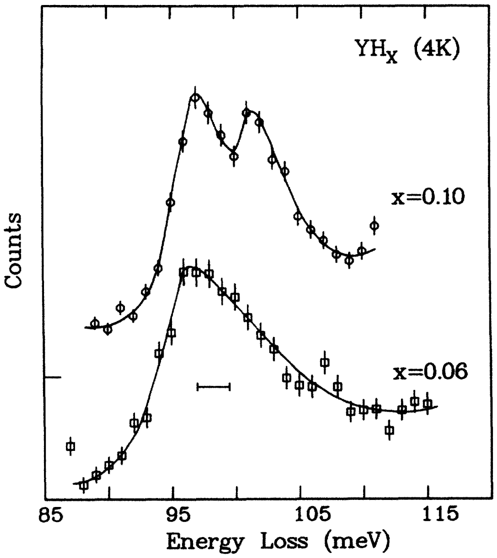

FIG. 3. Vibration spectra for polycrystalline YH_x at 4 K as a function of hydrogen concentration. (Solid lines are intended only to guide the eye.)

The behavior of the second peak is somewhat different. At $x=0.10$, a second maximum in the spectrum is still observable, centered at an energy of about 101 meV, although the width of this second feature does seem to have become distinctly broader. As the concentration is further lowered to $x=0.06$ the spectrum does not show a clearly defined second peak but rather a broad shoulder on the high-energy side of the 96 meV feature. The results at even lower concentrations suggest a further decrease in the intensity of this high-energy shoulder.

The spectra obtained from samples with $x=0.10$ and 0.06 measured at 4 K are presented in Fig. 3. The two peaks observed for $x=0.10$ at 80 K (Fig. 2) are sharper and better defined at 4 K with maxima situated at 97 and 101.5 meV. However, the 4 K spectrum taken for the $x=0.06$ is similar to the corresponding 80 K spectrum, showing only a broad asymmetric band with a peak at 96 meV but no other clearly discernible feature.

DISCUSSION

The results presented in the previous section reveal several novel aspects of the vibration spectrum of hydrogen in yttrium and shed some light on the nature of the interatomic potentials and interactions involved. Perhaps the simplest phenomenological model that correlates these spectroscopic observations is based on an elementary pair of coupled harmonic oscillators described by the potential function

$$V=\tfrac{1}{2}k(z_1^2+z_2^2)+\tfrac{1}{2}\kappa[d](z_1-z_2)^2\ , \tag{1}$$

where z_1 and z_2 refer to the displacements of a pair of hydrogens along the *c* axis. In (1) $\kappa[d]$ is a coupling "spring" constant that depends on the equilibrium separation *d* of the pair and allows the local "optic" mode of vibration to be split from the local "acoustic" mode described by the force constant *k*, which is dominated by the isolated hydrogen-metal interaction. We assume that $\kappa[d]$ is strongly dependent on hydrogen concentration *via* the coherent strain ordering mechanism apparent in these materials.[12] At high concentration hydrogen pairs are isolated from each other along the *c* axis, and *d* is effectively constrained to be $d=3c/4$. The next smallest separation is three times as large $d=9c/4$ (Refs. 12 and 13), as shown in Fig. 4(a). As the concentration is lowered, this ordering tendency presumably is reduced, even at very low temperature, and configurations having interparticle separations $d=c$, $5c/4$, $7c/4$, and $2c$ may also become populated to varying degrees along with more distant "pairing," as suggested by Fig. 4(b). Some "unpaired" hydrogen at any given temperature and concentration is also possible. Thus in this picture, $\kappa[d]$ is sharply distributed at high concentration but becomes more broadly distributed as the hydrogen concentration is decreased, at least at temperatures low enough for coherency strains to be important.

The fundamental pair vibration frequencies determined by (1) are

$$\omega^2=\frac{k+\kappa}{2\mu}\pm\frac{1}{2}\left[\frac{4\kappa^2}{M\mu}+\left[\frac{k+\kappa}{\mu}\right]^2\left[\frac{\Delta m}{M}\right]^2\right]^{1/2}, \qquad (2)$$

where $M=m_1+m_2$ is the total mass of the coupled pair, allowing for two different hydrogen isotopes, $\mu=m_1m_2/(m_1+m_2)$ is the reduced mass, and $\Delta m=m_1-m_2$ is the mass difference. Thus for $m_2=m_1=m$, corresponding to the Y-H experiments, one has the two nearly degenerate hydrogen frequencies $\omega=\omega_0$, $\omega_0+\Delta\omega$, where $\Delta\omega=\omega_0\kappa/k$ is assumed small compared with ω_0. We then associate the prominant peak at 99 meV with the ω_0 vibration, representing the dominant metal-hydrogen interaction. The observed high-concentration peak at approximately 103 meV (Fig. 1) is explained in the model by the hydrogen-hydrogen interaction across the bridged metal atom, with $\kappa[3c/4]\approx 0.04k$, producing a vibration at $\omega_0+\Delta\omega$. The effective broadening and collapse of this peak with decreasing concentration (Fig. 2) is then consistent with the hypothesized distribution of hydrogen-hydrogen interactions $\kappa[d]$, associated with a breakdown of short-range hydrogen order along the c axis. The concommitant small downward shift of ω_0 with decreasing concentration to 97 meV (evident in Fig. 2) is also expected as alternative hydrogen configurations become accessible which permit additional metal relaxation along the c axis and thus a larger average metal-hydrogen separation. Moreover, the observed proportionality between hydrogen concentration and the Debye temperature in Lu-H (Ref. 19) suggests that all interactions in these systems are dependent on concentration.

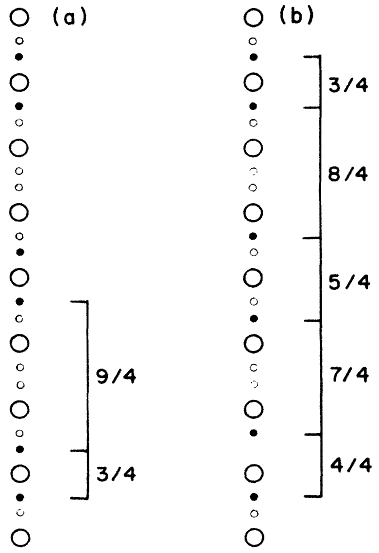

FIG. 4. Schematic representation of hydrogen occupation along the c axis, showing metal atoms (large circles) and interstitial T sites (small circles). Occupied T sites are shown as filled circles, and H-H distances are in units of c. (a) Short-range ordered fragment characteristic of high concentration and low temperature, according to Refs. 12 and 13, in which H-H pairs bridging a metal atom are separated by at least four unoccupied T sites. The picture is not intended to imply long-range order along the c axis or that neighboring lines are the same. (b) Disordered fragment showing H-H separations not allowed in (a). This fragment was obtained from (a) by moving three hydrogens to concisely exhibit the new separations and not to suggest a typical configuration, since depletion of hydrogen along the line, due to reduced concentration or elevated temperature, is not represented.

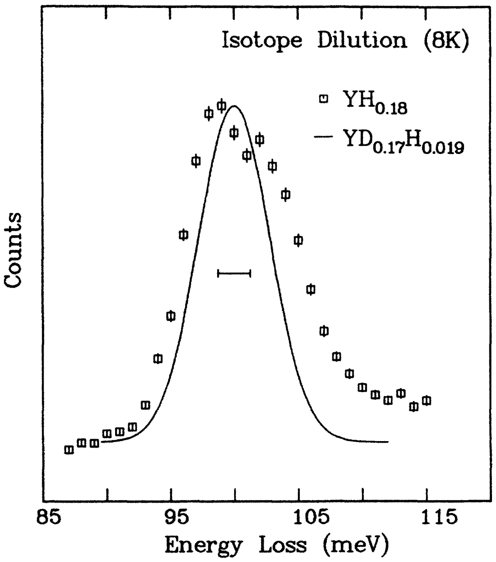

FIG. 5. Comparison of the vibrational spectra for single-crystal $YH_{0.18}$ and $YD_{0.17}H_{0.019}$ at 8 K. The solid line for $YD_{0.17}H_{0.019}$ represents the Gaussian fit without the sloped background evident in Fig. 1.

The isotope dilution spectrum in Fig. 1 offers further direct evidence for this general model. This is emphasized in Fig. 5, where the spectrum for $YD_{0.17}H_{0.019}$ is compared with that for $YH_{0.18}$. In the isotope-dilution experiment, the overall H + D concentration is similar ($x\approx 0.19$) to that in the high-concentration Y-H experiment in which pairing at $d=3c/4$ apparently is maximized, but now the hydrogen is sufficiently dilute that it can effectively pair only with deuterium across a metal atom. For this case we take $m_1=m$ and $m_2=2m$ in (2), giving frequencies $\omega=\omega_0+\Delta\omega/2$, $(\omega_0+\Delta\omega/2)/\sqrt{2}$, corresponding to small upward shifts of the nominal isotopic fundamentals. In particular, there is now only one excitation in the neighborhood of ω_0, at $\omega=\omega_0+\Delta\omega/2$. Hence, as a result of the mass defect, one should observe a single line near 101 meV in place of the doublet at 99 and 103 meV observed when hydrogen couples to hydrogen across a bridged metal atom. This predicted behavior is in good agreement with the observed single peak at 100 meV (presumably broadened by some H-H pairing at 10% H) in the isotope-dilution experiment (Fig. 1) and appears to confirm the suggestion that the 4 meV splitting in Y-H is caused by a dynamic coupling mechanism, as crudely modeled in (1), rather than by vibrations in a local potential statically perturbed by pairing.

CONCLUSIONS

The first neutron spectroscopic observation[17] of a splitting of the c-axis hydrogen vibration in concentrated Y-H(D) suggested that this splitting is the result of pairing of hydrogen in sites on either side of an yttrium atom. The current inelastic scattering experiments over a range of concentrations and temperatures, and the associated isotope-dilution experiment, appear to corroborate this connection between pairing and spectroscopic fine structure while pointing to a model in which the central effect of pairing correlations along the c axis is a concentration- and temperature-dependent modulation of dynamic coupling interactions between occupied hydrogen sites. As shown by the experiments summarized in Figs. 1 and 2, the two members of the spectroscopic "doublet" are not equivalent. Essentially, the lower energy peak is independent of concentration, except for the shift noted in the discussion, while the higher-energy peak is strongly perturbed and effectively disappears as the concentration is reduced to low values. This indicates that pairing is itself a strongly concentration-dependent, cooperative phenomenon, which suggests the importance of coherency strains in producing highly correlated pair configurations at the highest concentrations. Since an isolated occupied T site permits the maximum local-lattice relaxation (a bridged metal site is constrained against elastic relaxation) an elastic tendency toward unpaired sites with decreasing concentration is not unreasonable. If pairing at $d=3c/4$ remains the basic configurational entity even at low concentration, its spectroscopic "signature" should be insensitive to dilution, which does not appear to be supported by these data. Furthermore, within the resolution of our measurements, the isotope-dilution experiment does not favor a splitting mechanism based on the vibration spectrum of a static, single-particle potential unless the pairing environment is unexpectedly sensitive to the isotopic occupation of the T sites. Comparison of this work with the previous experiments[17] also suggests that the mechanisms for pair dissociation with decreasing concentration and with increasing temperature are not identical, as indicated by the different effects on the line shapes. In particular, at high concentration, raising the temperature beyond 200 K appears to rapidly increase the number of unpaired or weakly paired hydrogens (deuteriums), as indicated by the onset of a central line, while at lower temperatures, decreasing the concentration causes the effects we associate largely with a distribution of pairing interactions. Considering that, as the temperature is raised from 180 to 240 K, the diffusion residence time on the c axis decreases more than a 1000-fold from several minutes (see the Introduction) to a fraction of second, it seems reasonable that different pathways for pair dissociation are involved in the different temperature regimes. Furthermore, it is known[4] that the near-neighbor T-T distance decreases substantially with increasing temperature in $YD_{0.18}$, which would suggest the existence of additional disorder in the system at high temperatures.

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