Hydrogen Pairing and Anisotropic Potential for Hydrogen Isotopes in Yttrium

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The potential for H isotopes in α-phase (hexagonal) $YH(D)_{0.18}$ has been probed by neutron spectroscopy. The results reveal a highly unusual potential, which is considerably softer and anharmonic along the c axis than in the basal plane, even though the near-neighbor arrangement of metal atoms is only slightly distorted from regular tetrahedral symmetry. Low-temperature results show a splitting of the c-axis vibrational modes, consistent with the pairing of hydrogen on either side of yttrium atoms.

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The properties of the YH_x system in the α or solid-solution phases have been the subject of a great deal of study and controversy in recent years, especially since, for $x < 0.2$, the α phase persists down to very low temperatures, rather than precipitating to an ordered hydride phase as do other metal-hydrogen systems. In particular, the structure of the α phase has been the subject of some controversy, with neutron diffraction results indicating that only tetrahedral sites are occupied,[1] while resistivity and inelastic scattering studies have been interpreted in terms of partial octahedral-site occupancy.[2-4] Yttrium metal has a hexagonal-close-packed (hcp) structure, with a c/a ratio that differs from the ideal value of $(\frac{8}{3})^{1/2}$ by less than 3%. As a result, in the α phase the possible local symmetry of the H-atom sites is classified as either octahedral or tetrahedral, with only slight distortions from the perfect symmetry (actually the site symmetry of the "tetrahedral" interstices in the hcp lattice is 3 m). If one assumes that the character of the hydrogen vibrations is dominated by the geometry of near-neighbor metal atoms (which is the case, e.g., for H in bcc metals[5]), the local vibrational modes for such sites would be close to threefold degenerate and would provide a single vibration band in the neutron spectrum. On this basis, recent neutron spectroscopic data,[4] which show two widely separated peaks at 100 and 136 meV, have been interpreted as evidence for partial octahedral-site occupancy. The dependence of the relative intensities of these two peaks on sample history has been attributed to the presence of trapping centers, such as oxygen, which could vary in concentration with sample treatment. Moreover, a recent neutron diffuse scattering study[6] has suggested the formation of pairs of hydrogen, oriented along the c direction of the hexagonal lattice and separated by an yttrium atom, with the concentration of pairs increasing as the temperature is decreased.

In the present Letter, we present neutron spectroscopic results which show that the unusual and seemingly contradictory observations on this system are associated with a hydrogen-bonding potential which is strongly anisotropic, and anharmonic along the c axis. Our results also verify the existence of hydrogen pairing in yttrium, which is reflected in a splitting of the local mode polarized along the c axis. The model of partial occupation of octahedral sites proposed to interpret various data is shown to be incorrect.

The two Y samples used in these experiments were obtained from the Materials Preparation Center of Iowa State University. The first was a single crystal of approximately 25 g, containing less than 80 at. ppm O, while the second was a polycrystalline sample of approximately 80 g, with a similar O content. The samples were first loaded with 15 at.% H ($YH_{0.18}$). Later, this H was removed, and the samples were loaded with 15 at.% D ($YD_{0.18}$).

The measurements were performed on the BT-4 spectrometer at the National Bureau of Standards Research Reactor, with the filter technique for final energy analysis. Two different filters were used; the first was polycrystalline Be cooled to 77 K, which passes all neutrons with energies less than 5 meV, while the second was a composite filter of polycrystalline Be and graphite, cooled to 77 K, which passes all neutrons with final energies less than 1.8 meV. The incident energy was selected by a Cu(220) single crystal, with collimations of either 40′ or 20′ before and after the monochromator crystal.

Although the scattered wave vector is much smaller than the incident wave vector in the filter mode, thus making it impossible to measure at a fixed wave-vector transfer $\mathbf{Q}$, it was possible to arrange the conditions of the experiments so that $\mathbf{Q}$ was almost parallel or perpendicular to the c axis of the single-crystal sample during an energy scan. The results of such scans for $YH_{0.18}$ are shown in Fig. 1. For $\mathbf{Q}$ parallel to the c axis, a single prominent peak is observed at 100 meV, while for $\mathbf{Q}$ perpendicular to the c axis, a single prominent peak is observed at 134 meV. This result shows clearly that the local-mode energies in $YH_{0.18}$ for vibrations along and perpendicular to the c axis are split by 34 meV, and that the two peaks observed in previous studies of polycrystalline YH_x arose from these two nondegenerate modes, which are much more widely separated in energy than would be expected if the near-neighbor tetrahedral arrangement of metal atoms determined the character of

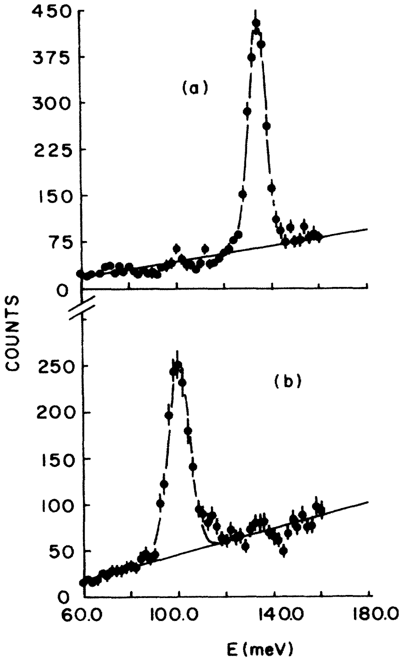

FIG. 1. Measured spectra for single crystal of $YH_{0.18}$ at 80 K, for (a) **Q** parallel to the *c* axis and (b) **Q** perpendicular to *c* axis. Lines are the result of fitting the data under the assumption of Gaussian peak shapes.

the vibration spectrum. Measurements on the polycrystalline sample have revealed that the seeming sample dependence of the previous results arose from the existence of preferred orientations in the supposedly polycrystalline samples.

The hydrogen was then removed from the samples, and 15 at.% deuterium was added, giving samples of $YD_{0.18}$. The results of scans parallel and perpendicular to the *c* axis are shown in Fig. 2. For the spectrum measured perpendicular to the *c* axis, two prominent peaks are observed at 96 and 186 meV, corresponding to excitations from the ground state to the first and second excited states, respectively. The value of the energy of the second excited state is close to the harmonic value of 192.6 meV. The weak peak observed at approximately 132 meV is likely the result of some residual H in the sample, while the weak peak at approximately 76 meV corresponds to the peak seen for *Q* parallel to the *c* axis, implying that the spectrometer resolution allows some sensitivity to modes of the wrong polarization. For *Q* parallel to the *c* axis, two prominent (and broad) peaks are observed at 75 and 137 meV, again corresponding to the first and second excited states, respectively. However, in this case, the energy of the second excited state is considerably displaced from the value 152 meV expected for a harmonic oscillator.

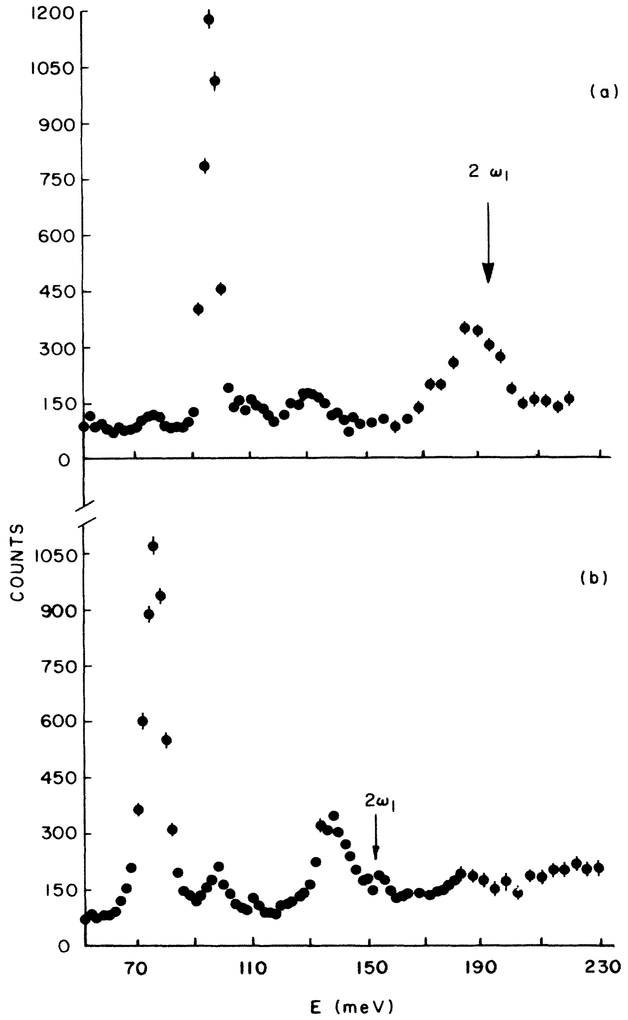

FIG. 2. Measured spectra for the single crystal of $YD_{0.18}$ at 80 K, for (a) **Q** perpendicular to *c* and (b) **Q** parallel to *c*. Peak positions predicted for a harmonic potential are indicated.

The spectra shown in Figs. 1 and 2 have been fitted by Gaussians, with the results given in Table I. It should be noted from these results that they not only are the modes parallel and perpendicular to the *c* axis widely separated in energy, but the widths are quite different as well. The resolution of the spectrometer for the 100- and 134-meV modes in $YH_{0.18}$ was 5.4 and 8.5 meV, respectively, so that the peak at 134 meV is almost resolution limited, while the peak at 100 meV has an intrinsic width of approximately 9.5 meV, implying that the potential along the *c* axis is strongly anharmonic. The same trend is shown for the $YD_{0.18}$ sample, where the intrinsic width for the mode polarized along the *c* axis is 7.1 meV. Also shown in Table I are ratios that emphasize the degree of anharmonicity in the potential by comparing the ratio of first to second excited-state energies for each polarization in $YD_{0.18}$, and the ratio of the first excited-state energies for the two isotopes for both polarizations. The

TABLE I. Results of fitting Gaussians to single-crystal data for $\mathrm{YH}_{0.18}$ and $\mathrm{YD}_{0.18}$. Note: All errors (in parentheses) are fitting errors only, and are the error in the last digit given.

		E_{0-1} (meV)	FWHM (meV)	E_{0-2} (meV)	FWHM (meV)	Ratio E_{0-1}/E_{0-2}
$\mathrm{YH}_{0.18}$	$Q \parallel c$	100.1(2)	11.3	. . .	. . .	. . .
	$Q \perp c$	134.2(5)	8.7	. . .	. . .	. . .
$\mathrm{YD}_{0.18}$	$Q \parallel c$	75.8(1)	8.5	137.8(4)	12.0	1.82
	$Q \perp c$	96.3(1)	5.8	186.5(6)	21.0	1.94
Ratio H/D	$Q \parallel c$	1.32		. . .	. . .	
	$Q \perp c$	1.39		. . .	. . .	

results of this comparison confirm that the potential along the c axis is strongly anharmonic, while that perpendicular to the c axis is much less so. This result shows that the vibration spectra cannot be explained on the basis of short-range forces as can be done,[5] e.g., for the bcc transition metals. The difference in the energies of vibration modes perpendicular and parallel to the c axis is also 6 times that which would be expected for protons bound in t sites in CaF_2-type metal hydrides, if one assumes a small difference (0.06 Å) in M—H bond distance equivalent to that observed in YD_x along the c axis. This comparison shows the inherent danger of placing too much physical significance in semiempirical results such as those of Ross, Martin, Dates, and Bakhsh,[7] and again emphasizes the unusual nature of the potential reflected in our spectroscopic results.

All of the above results were obtained with the normal Be filter analyzer, which produces an energy resolution width in excess of 5 meV. The composite Be/graphite filter analyzer allows us to increase the resolution substantially, to a full width of 1.85 meV (including the monochromator resolution, with 20-min collimation) for the modes at 75 and 96 meV. The single-crystal sample of $\mathrm{YD}_{0.18}$ was used to study the sharp peak at 96 meV (vibration perpendicular to the c axis), with the result that this peak was determined to have an intrinsic width of approximately 3.5 meV. For intensity reasons, the broader 75-meV peak was then studied in the larger polycrystalline sample as a function of temperature, with the results shown in Fig. 3 (the spectrum at 295 K was taken with an energy resolution of 2.5 meV).

Several points are immediately obvious from inspection of the results shown in Fig. 3 First, the spectrum at 295 K consists of a single broad peak centered at 74 meV, with a width in excess of 6 meV. Second, as the temperature is reduced to 240 K, the sepctrum clearly evolves into a more complex shape, that cannot be explained as a single peak. Third, at 8 K the spectrum has split into two separate peaks. Similar results have been obtained for $\mathrm{YH}_{0.18}$. Detailed analysis of these spectra reveal that at 8 and 200 K, the data can be well represented by two Gaussians centered at approximately 73 and 77meV. However, at 240 K, the results can only be fitted by three Gaussians, centered at 72.8, 74.7, and 76.5 meV. If this result is compared to that found at lower temperatures, it appears that the peaks at 72.8- and 76.5-meV correspond to the two peaks seen at low temperature, while the peak at 74.7 meV represents a different excitation energy. (It should be noted that the three-Gaussian form could also be used at 295 and 200 K; however, such fits are not particularly meaningful in view of the large number of parameters involved.)

We interpret these results in terms of the pairing proposed on the basis of diffuse scattering results. Within this model, the two tetrahedral sites on either side of an yttrium atom are preferentially occupied at low temperatures, with the fraction of paired H's decreasing as the temperature is increased. Then the peak observed at

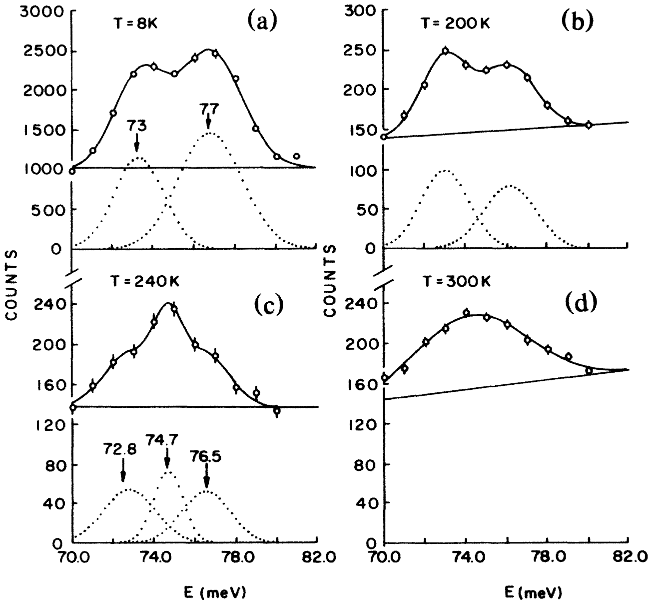

FIG. 3. Measured spectra for polycrystalline $\mathrm{YD}_{0.18}$ as a function of temperature; (a) 8 K, (b) 200 K, (c) 240 K, (d) 295 K. The solid lines are the results of Gaussian fits, as described in text. Note the evolution in shape from two peaks at 8 K to one broad peak at 295 K.

74.7 meV (240 K) corresponds to the vibration of that fraction of the deuterium atoms which are isolated, while the peaks at 72.8 and 76.5 correspond to a vibration level split by the interaction of the pairs. If we compare the intensities of the peak at 74.7 meV to those of the 72.8- and 76.5-meV peaks, we would say that 33% of the D atoms are involved in pairs at 240 K, a result in good agreement with the result from diffuse scattering.[6] From the latter data, we can then infer that the spectra measured at all temperatures consist of three peaks, with relative intensities corresponding to fraction of the deuterium involved in pairs. This conclusion is consistent with our data, although as mentioned above, only the spectrum at 240 K has adequate structure to justify fitting with such a form. We also note here that as part of our experiments we have measured neutron *quasielastic* scattering versus temperature for these samples and have observed two-component quasielastic peaks, a Gaussian shaped elastic component and a broadened Lorentzian component. These results again are consistent with the existence of both a trapped (relatively immobile) and a mobile species. Moreover the fraction of trapped (paired) to mobile species derived from deconvolution of the two-component peaks is again in good agreement with *both* the present results and the diffuse scattering results.

In summary, we have demonstrated the existence of a highly unusual potential for hydrogen dissolved in hcp yttrium, which is anisotropic and strongly anharmonic along the *c* axis, in spite of the nearly tetrahedral arrangement of the near-neighbor metal atoms. In addition, our results are consistent with the existence of pairing of hydrogen in sites on either side of an ytrrium atom at low temperatures, and provide a measure of the splitting in the local-mode energy caused by this interaction. This pairing is presumably responsible for the observation that hydrogen does not precipitate into an ordered hydride phase in this metal at low temperatures and must reflect a local electronic structure perturbation unlike that in any other metal-hydrogen system studied thus far.

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