

## Theory of Hydrogen Pairing in Yttrium

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(Received 6 April 1989)

The energetics of hydrogen atoms interacting with yttrium have been investigated using the self-consistent cluster model and the local-density approximation. Our results provide a theoretical understanding of a range of novel phenomena observed recently in resistivity, neutron scattering, NMR, and channeling experiments. These include pairing of hydrogen at low temperatures and the pairs' structural origin, the anomalous fast diffusion of hydrogen along the pairing axis compared to the bulk rate, and the lack of long-range order between the pairs in the metal matrix.

PACS numbers: 61.70.Bv, 66.30.Jt, 71.55.Dp, 82.30.Nr

In most metals hydrogen precipitates at low temperatures to form an ordered hydride phase. A departure<sup>1</sup> from this common occurrence was first observed in resistivity experiments in rare-earth metals (Sc, Y, Er, Tm, and Lu). The ability of these materials to retain hydrogen in solid solution down to absolute zero has led to numerous experimental studies involving neutron scattering,<sup>2-5</sup> nuclear magnetic resonance,<sup>6,7</sup> channeling,<sup>8</sup> and resistivity. However, the interpretation of these results has often been controversial. For example, while resistivity anomalies at low temperatures were initially interpreted in terms of partial occupancy of tetrahedral (*T*) and octahedral (*O*) sites, channeling and neutron scattering experiments clearly attributed the hydrogen occupancy to *T* sites. The resistivity anomalies were later shown to be due to the pairing of hydrogen,<sup>9</sup> although the structural origin of the pairs remained a debatable issue<sup>5,7,9</sup> for some time.

The experimental situation now seems to be clear. The general agreement is as follows: (1) Hydrogen preferentially occupies *T* sites. (2) The probability of hydrogen pairing increases with decreasing temperature<sup>5</sup> suggesting that pairing is a statistical problem rather than one associated with a phase transition. (3) The pairing occurs when the hydrogen atoms are separated by a metal atom, thus forbidding hydrogen atoms to occupy nearest-neighbor *T* sites. (4) At high temperatures hydrogen diffuses from *T* to *O* to *T* sites, with very little occupancy time at the *O* site. At low temperatures, the diffusion occurs between adjacent *T* sites and this rate is orders of magnitude faster than the bulk diffusion.<sup>10</sup> (5) The hydrogen pairs lack long-range order and thus form a "proton glass."<sup>6</sup> (6) An electronic transition concomitant with hydrogen pairing leads to an anomalous change in the proton spin-lattice relaxation rate.<sup>6</sup> (7) The pairing of hydrogen does not produce any displacement of the metal atoms. Instead, the hydrogen atoms are slightly displaced<sup>4</sup> from their *T* sites. To our knowledge, no theoretical studies of the above phenomena are yet available.

In this Letter, we present a comprehensive study of

hydrogen pairing in yttrium based upon electronic-structure and total-energy calculations. Our method involves a cluster model of the Y-H system. Using the linear combination of atomic orbitals (LCAO) and the local-density approximation, we have calculated the energetics of hydrogen in a number of  $Y_nH_m$  ( $4 \leq n \leq 9$ ,  $1 \leq m \leq 3$ ) clusters where Y atoms occupied bulk sites and hydrogen positions were varied within the cluster. The calculations reveal an unusual potential-energy curve along the hexagonal *c* axis with a double well and a small energy barrier. The potential energy along the *T-O* axis reveals no such unusual feature. From the energetics and electronic structure we are able to conclude the following. (1) Hydrogen prefers to occupy the *T* sites. (2) The pairing of hydrogen with a bridging Y atom is energetically preferred over any other combination. The potential-energy curve contains two minima

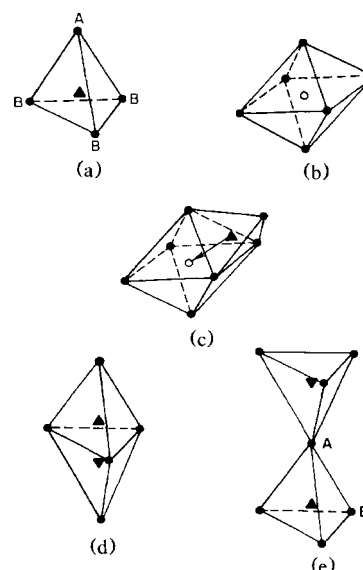


FIG. 1. Various clusters used in the calculations of energetics of H in Y. The triangles and circles mark the *T* and *O* sites, respectively.

yielding pair binding energies of 0.1 and 0.16 eV. (3) The motion of hydrogen between these two potential minima is orders of magnitude faster than the bulk diffusion rate. (4) A Jahn-Teller-type distortion gives rise to the displacement of hydrogen atoms from the  $T$  site. This results in a 4% increase of the H-H distance compared to the unperturbed value. (5) Both the electron density of states at the Fermi energy and the electron density at the proton site change when hydrogen forms pairs, indicating a change in the electronic structure. (6) The interaction between H and Y atoms is pairwise and remains unaltered when more hydrogen atoms are present. This mechanism leads to a very weak interaction between the hydrogen pairs and is responsible for the observed proton glass.

Our calculations are based upon a cluster representation of the host Y metal. To calculate the energetics of hydrogen in various positions, we have replaced the host metal by clusters of atoms. These are shown in Fig. 1.

The energies of these clusters were calculated using the discrete variational method<sup>11</sup> (DVM) and the local-density approximation to the exchange-correlation potential. The total energy is expressed as

$$E_{\text{tot}} = \sum_i f_i \epsilon_i - \frac{1}{2} \iint \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|} d\mathbf{r}'d\mathbf{r} + \int \rho(\mathbf{r})[E_{\text{xc}}(\mathbf{r}) - V_{\text{xc}}(\mathbf{r})]d\mathbf{r} + \frac{1}{2} \sum_{\mu\nu} \frac{Z_\mu Z_\nu}{R_{\mu\nu}}. \quad (1)$$

Here  $f_i$ ,  $\epsilon_i$ , and  $\rho$  are, respectively, the Fermi-Dirac occupation number, single-particle eigenvalue, and electron density.  $E_{\text{xc}}$  is the exchange-correlation energy and  $Z_\mu$  is the charge on the  $\mu$ th nucleus. In the DVM code, the cluster energy  $E_c$  is computed with reference to dissociated atoms, namely,

$$-E_c = E_{\text{tot}} - E_{\text{tot}}^{\text{ref}}, \quad (2)$$

where  $E_{\text{tot}}^{\text{ref}}$  is the total energy of free atoms constituting the cluster. In our present study, we are primarily interested in the energy of hydrogen atoms interacting with the metal matrix. Thus, for the remainder of the paper we concentrate on the difference energies,

$$\begin{aligned} -\Delta E_1 &= E_c(Y_n H) - E_c(Y_n), \\ -\Delta E_2 &= E_c(Y_n H_2) - E_c(Y_n). \end{aligned} \quad (3)$$

We shall refer to  $\Delta E_1$  and  $\Delta E_2$  as the binding energy of hydrogen and its pairs, respectively, for a particular cluster size  $n$ .

The present calculations were carried out by employing  $4s$ ,  $4p$ ,  $4d$ ,  $5s$ , and  $5p$  atomic valence orbitals on the Y atoms and  $1s$ ,  $2s$ , and  $2p$  valence orbitals on the H sites. The core orbitals  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ , and  $3d$  on Y were frozen. The effect of the rest of the bulk was simulated through an embedding scheme.<sup>11</sup> The Hamiltonian matrix elements entering the secular equation were obtained via numerical integration over a three-dimen-

sional grid of points. In the present studies, 3000 sampling points around Y and H sites were used. These points were found to be enough for the convergence of the electronic spectrum and energetics.

We first discuss the site preference of a single hydrogen atom. To determine this, we calculated the binding energy of hydrogen at the  $T$  site in the  $Y_4H$  cluster [Fig. 1(a)] and at the  $O$  site in the  $Y_6H$  cluster [Fig. 1(b)]. The binding energy at the  $T$  site is 1.5 eV higher than at the  $O$  site and is clearly preferred by hydrogen. In order to be assured that the above result is not influenced by our particular choice of cluster size and geometry, we also calculated the binding energies of hydrogen along the path joining the  $T$  and  $O$  sites in the  $Y_7H$  cluster [Fig. 1(c)]. The binding energy at the  $T$  site was found to be 1.3 eV higher than the energy at the  $O$  site—in good agreement with the 1.5 eV obtained before. This comparison puts a limit of about 0.3 eV on the accuracy of our calculation. It arises due to cluster-size and symmetry considerations. However, for a given cluster, the relative energetics of hydrogen moving along a path are more accurate than the above limit.

In Fig. 2(a) we plot the potential-energy curve for hydrogen moving along the  $c$  axis in the  $Y_4H$  and  $Y_7H$  [Fig. 1(e)] clusters. Note that the systematics in the energies are independent of cluster size and reveal the existence of two minima separated by a barrier height of approximately 0.15 eV. This small barrier height compared to the 1.5-eV barrier between  $T$  and  $O$  sites discussed earlier would lead to a motion of hydrogen along the  $c$  axis that is orders of magnitude faster than the bulk rate. This result is in agreement with both neutron scattering<sup>10</sup> and NMR data.<sup>6</sup> The physical origin of the two potential wells can be seen to be due to the bonding

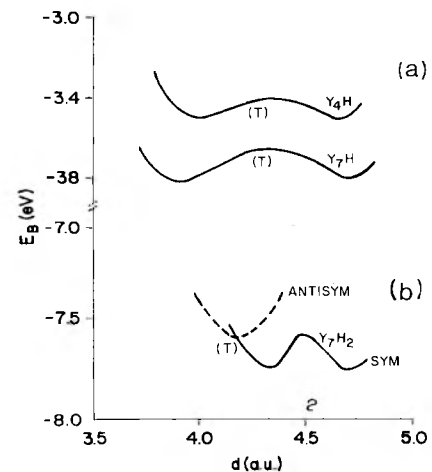


FIG. 2. (a) Potential energy of H as a function of its position along the  $c$  axis in the  $Y_4H$  and  $Y_7H$  clusters. (b) Potential energy of a H pair moving symmetrically and asymmetrically around the middle Y atom in the  $Y_7H_2$  cluster. The distance  $d$  is measured from atom A in Figs. 1(a) and 1(e).

of hydrogen to two types of Y atoms [marked *A* and *B* in Fig. 1(a)]. The first minimum occurs at  $3.9a_0$  from the Y atom marked *A*. The second minimum occurs at  $4.7a_0$  from the *A* atom. However, at this position the hydrogen atom is at a distance of  $4.0a_0$  from the Y atoms marked *B* in Fig. 1(a). To understand the significance of a  $3.9a_0$  distance between the Y and H atoms, we computed the potential-energy curve for the Y-H dimer. We observed that the bond length of the Y-H dimer is also  $3.95a_0$ . Thus, the interaction of hydrogen with Y atoms is found to be dominated by pairwise interaction. We shall return to this observation later in connection with the origin of the proton glass behavior of hydrogen pairs.

The pairing of hydrogen has been investigated first by confining the two hydrogen atoms to nearest-neighbor *T* sites [Fig. 1(d)] and to second-nearest-neighbor *T* sites bridged by a Y atom [Fig. 1(e)]. The binding energies for nearest and next-nearest pairing are, respectively, 6.9 and 7.6 eV suggesting that the pairing mediated by a metal atom is energetically favorable. Since these binding energies refer to two different clusters, it is legitimate to ask how sensitive are the relative strengths in binding to cluster sizes. We note, in this context, that the binding energy of a single hydrogen in the  $Y_4H$  cluster differed from that in the  $Y_7H$  cluster by 0.3 eV. We have, therefore, repeated these studies for  $Y_9H_2$  clusters formed by adding two Y atoms along the *c* axis in the  $Y_7H_2$  cluster shown in Fig. 1(e). The binding energy of two hydrogen atoms at the pairing site (i.e., occupying the *T* sites nearest to the bridging Y atom) is 0.44 eV higher than that at the nonpairing site (i.e., H atoms occupying *T* sites next nearest to the bridging Y atom). Both of the above results clearly reveal that pairing is energetically favorable.

The above studies, however, do not yield the true equilibrium separation between the pairs, for it is likely that hydrogen atoms may be displaced from the *T* sites in much the same way that we observed earlier in  $Y_nH$  systems. We have, therefore, calculated the potential-energy curves by moving the pair away from the bridging Y atom both symmetrically and asymmetrically. The results are plotted in Fig. 2(b). There are several interesting points to be noted. (1) The vibration of pairs in the asymmetric mode would be energetically inefficient. (2) Two minima similar to that in Fig. 2(a) do exist in the symmetric mode. The physics behind the double minima in Fig. 2(b) is the same as that discussed before. Thus, we could conclude that the pairing of hydrogen does not significantly alter the interaction between the hydrogen and the metal atom. (3) The first minimum is not at the *T* site, but is displaced from it by  $0.04c$ . Here *c* is the lattice constant along the *z* axis. This distortion, analogous to that in Fig. 2(a), can again be attributed to a Jahn-Teller-type mechanism. It should be noted that a displacement of  $0.02c$  of hydrogen atoms from the *T* site was required to fit the neutron

scattering data<sup>4</sup> in Lu. (4) The binding energy of the pair can be calculated by noting that in the  $Y_7H$  cluster, hydrogen gains 3.82 eV, whereas in the  $Y_7H_2$  cluster the energy gain (in one of the minima configurations) by two hydrogen atoms is 7.75 eV. Thus, the pairing energy is  $7.75 - 2 \times 3.82 = 0.11$  eV. Using this pairing energy, we have calculated the fraction  $f_p$  of hydrogen atoms involved in pairing at a given temperature within the framework of the lattice-gas model. We consider  $N_Y$  cells (one per Y atom) and  $N_H$  H atoms. Each cell has two equivalent (tetrahedral) sites available for H occupancy, the occupancy of each site being either 0 or 1. As a zeroth-order approximation, the cells were considered noninteracting. This should be a fairly good approximation at low concentrations. Noting the constraint of fixed  $N_H/N_Y$ ,  $\langle f_p \rangle$  can then be easily evaluated in the grand canonical ensemble. The behavior of  $f_p$  as a function of temperature is shown in Fig. 3 for  $YH_{0.18}$ . For this system, Anderson *et al.*<sup>5,12</sup> have estimated that  $f_p$  is  $\approx 0.67$  at 240 K; this compares favorably with our estimate of 0.80 from Fig. 3. No experimental results, to our knowledge, are available on the temperature dependence of pairing. Clearly such data would be very useful in understanding the extent to which simple statistical models can be applicable.

We next turn our attention to the NMR experiments of Lichty *et al.*,<sup>6</sup> who recently attributed the anomaly in the low-temperature behavior of the proton spin-lattice relaxation rate in  $ScH_{0.27}$  to an electronic-structure change. They concluded that the product of the electron density and density of states at the Fermi energy must change when hydrogen atoms form pairs. To verify this conclusion, we have calculated this product in the  $Y_9H_2$  cluster with two H atoms in the pairing and nonpairing positions. Here, the nonpairing position refers to the situation where each of the hydrogen atoms occupies the second-nearest *T* site with regard to the bridging Y atom in the  $Y_9H_2$  cluster. [See Fig. 1(e) for guidance.] The hydrogen pairing leads to an enhancement of the density

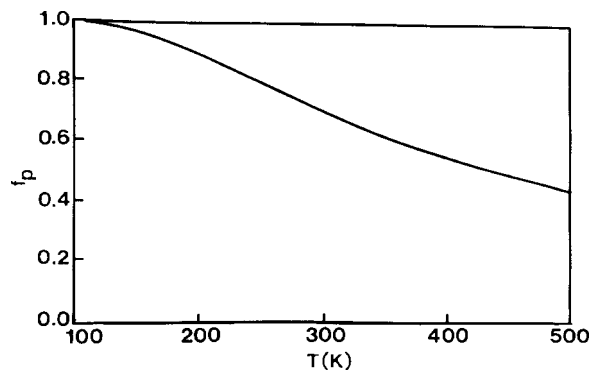


FIG. 3. Theoretical predictions for the temperature dependence of  $f_p$ , the fraction of H atoms involved in pairs, in the system  $YH_{0.18}$  using 0.11 eV as the pairing energy.

of states  $N(E_f)$  (calculated by broadening the molecular energy levels with a Lorentzian of 0.3-eV width) and the electron density at the hydrogen site  $n(0)$  by 0.9% and 2.7%, respectively. The change in the density of states, however, is not due to the  $d$  state as suggested by Lichty *et al.*,<sup>6</sup> but due to the Y  $5s$  states. The Korringa product in our calculation increases by 3.6% due to the pairing which is similar to the 4% change seen<sup>6</sup> in  $\text{ScH}_{0.27}$ .

Lichty *et al.*<sup>6</sup> also observed that the temperature and frequency dependences of the relaxation peak originating from the fast localized motion of hydrogen between closely spaced  $T$  sites are similar to those found in amorphous or disordered systems. This led them to conclude that the hydrogen pairs have little long-range order and constitute a proton glass within the metal lattice. To demonstrate further that the lack of strong interaction between hydrogen pairs emanates primarily from the strong pairwise interaction of hydrogen with the metal atom, we have carried out total-energy calculations of Y-H,  $\text{YH}_2$ , and  $\text{YH}_3$  clusters using the local-density approximation and Gaussian-type basis orbitals. Note that our prior calculations involved numerical orbitals. Computations of total-energy hypersurfaces are complicated and involve an enormous amount of computer time since the studies cannot use symmetry orbitals. The use of Gaussian orbitals enhances the computing efficiency.

We found that the bond lengths are nearly the same ( $\sim 1.9$  Å) as more hydrogen atoms decorate the Y atom. Secondly, the bond angle made by hydrogen atoms at the Y site in the  $\text{YH}_2$  trimer is  $122^\circ$ . The  $\text{YH}_3$  cluster is planar with the Y atom at the center and the bond angle is  $120^\circ$ . Thus, increasing decoration of hydrogen does not seem to affect the Y-H interaction. This would not be the case if the H-H interaction were strong. The binding energies of YH,  $\text{YH}_2$ , and  $\text{YH}_3$  are, respectively, 3.12, 6.16, and 9.76 eV. These results are in excellent agreement with available results using elaborate quantum chemical procedures<sup>13</sup> and vindicates our use of the local-density approximation. It is useful to compare the binding energies of the Y-H dimer obtained using the Gaussian and the DVM code. The DVM result yields a bond length of 2.06 Å and a binding energy of 3.6 eV in good agreement with those using the Gaussian scheme.

The minimal interaction between hydrogen atoms, as evidenced by the topologies of  $\text{YH}_3$  versus  $\text{YH}_2$ , is due to the fact that hydrogen always likes to draw electrons to become electronegative. It is easier to take electrons from a metal atom than from another hydrogen. The lack of long-range interaction between hydrogen atoms is responsible for the proton glass and originates at the molecular level.

In conclusion, our self-consistent calculations of the energetics of hydrogen in yttrium explain a range of phenomena starting with the tetrahedral-site occupancy of

hydrogen to hydrogen pairing and its structural origin. The calculations yield an unusual double-well potential along the  $c$  axis that explains the fast diffusion of hydrogen along the  $c$  axis and accounts for the peak in the proton relaxation rate. The lack of long-range order among hydrogen pairs has a molecular origin. We also demonstrated that the electronic structure changes when hydrogen forms pairs. This explains the increase in the Korringa product as primarily due to the change in the electron density at the proton site. It is gratifying that our cluster model gives results in good accord with available experimental data on Y-H systems. We look forward to the experimental confirmation of our prediction concerning the temperature dependence of the fraction of hydrogen atoms involved in pairing.

We are grateful to Dr. T. McMullen for many discussions. This work was supported in part by grants from the Army Research Office (DAAL 03-89-K-0015).

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