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Hydrogen in yttrium via first-principles total-energy calculations

B. J. Min and K. M. Ho
Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011
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The potential-energy surface of hydrogen in α-YH_x is obtained from first-principles total-energy calculations for the case of $YH_{0.5}$. Results on the localized vibration frequencies of hydrogen, the splitting of the hydrogen energy level, and the activation energy for hydrogen diffusion are presented and compared with available experimental data.

I. INTRODUCTION

Metal-hydrogen systems exhibit a variety of interesting physical phenomena. Topics such as the ordering of hydrogen in the host metal, localized hydrogen vibration modes, and the transport of hydrogen through the lattice, have been the subjects of many studies. The importance of understanding such phenomena in applications such as energy storage and the prevention of hydrogen embrittlement provides an additional impetus to these investigations.[1]

The behavior of hydrogen in hcp metals is distinguished from its behavior in the bcc and fcc metals by a number of unique features: A large amount of hydrogen can go into solid solution in the lattice at low temperatures without the precipitation of hydride phases.[2] Hydrogen remains in the disordered α phase up to atomic concentrations of $[H]/[Y] = 0.245$ at temperatures as low as 4 K.[2] This extraordinary stability of the disordered phase is fairly puzzling in view of the almost vanishing solubility for hydrogen in bcc and fcc metals at low temperatures. The occurrence of pairing of hydrogen atoms along the *c* axis[3–6] has also aroused much interest. A resistivity anomaly observed in the temperature range from 170 to 280 K (Ref. 2) in many hcp metals such as Lu (Ref. 7) and Sc (Ref. 8) has been attributed to hydrogen pairing along the *c* axis.[3–6] The vibrations of H (D) atoms in Y are noted for their unusual behavior: The local symmetry of the tetrahedral (T) site (Fig. 1) suggests threefold degenerate vibration frequencies for H (D). However, the inelastic neutron-scattering measurement of the localized vibration of H (D) in α-$YH_{0.18}$ ($YD_{0.18}$) by Anderson and co-workers[3,4] reported nondegenerate vibration frequencies. This indicates that the strong anharmonicity of the hydrogen potential plays an important role in determining the vibrational frequencies of hydrogen along the *c* axis. The long-range diffusion of hydrogen has also been studied for a long time.[9–13] However, theoretical modeling of the diffusion behavior has been limited by the lack of detailed knowledge of the potential energy surface of hydrogen in hcp metals. Strong isotope effects are also apparent in the low-temperature thermal expansion of the lattice with dissolved hydrogen.[15]

In this paper, first-principles total-energy calculations are performed to study the localized vibrational states of hydrogen (H) and deuterium (D) in the $YH_{0.5}$ ($YD_{0.5}$) system. First-principles total-energy calculation is a powerful tool for studying the structural and electronic properties of crystals. In particular, previous applications to various bcc and fcc metal-hydrogen systems[16] have been quite successful. In our previous total-energy calculation[17] of $YH_{0.5}$, with one H atom in the hcp primitive unit cell, we showed that H (D) atoms occupy the tetrahedral (T) sites of the hcp lattice, in agreement with the neutron-diffraction experiment of α-$YD_{0.18}$ by Khatamian *et al.*[18] Also the lattice expansion due to hydrogen and the heat of formation of $YH_{0.5}$ are in good agreement with experiments.[19,20] In this paper, we extend our investigations to study the dynamics of H (D) in $YH_{0.5}$.

Hydrogen is distinguished from the other interstitial atoms by its light mass. Thus quantum-mechanical effects are important in the dynamical behavior of the system at low temperatures. In this paper, we map out the potential felt by the hydrogen atom in the metal lattice by calculating the total-energy of the crystal as a function of the hydrogen position in the unit cell. We solve the Schrödinger equation for the vibrational states of hydrogen and its isotopes in the three-dimensional potential obtained from the first-principles calculations. We

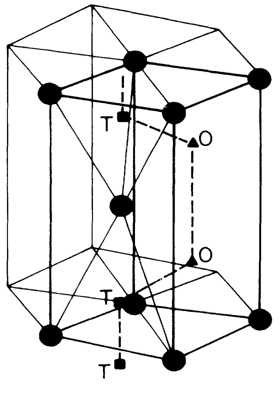

FIG. 1. The $YH_{0.5}$ primitive unit cell. The total-energy is calculated with the H atom located at symmetry directions connecting T-T-O-O sites.

put one hydrogen atom in each hcp unit cell in our calculations. While this reduces the computational effort in the first-principle calculations, it precludes the inclusion of lattice relaxation effects about the hydrogen atom other than by uniform change in the lattice. Further calculations with bigger unit cells and lower hydrogen concentrations are necessary to assess the effects of lattice relaxations as well as the effects of hydrogen-hydrogen interactions and pairing. The coupling of the hydrogen motion to lattice vibrations is another interesting problem difficult to include within the context of our present calculations. This is an area to be further explored in the future, possibly with tools such as molecular dynamics to include the effects of thermal motion of the lattice. First-principles calculations could provide the necessary data base for fitting more empirical potentials for use in such studies. In spite of these limitations, our calculation is able to provide information and insight into the above mentioned problems.

II. THE METHOD OF CALCULATION

Our calculation is performed with norm-conserving pseudopotentials[21] constructed directly from atomic calculations. The total-energy is calculated in a self-consistent way within the local density functional formalism[22] using the momentum space approach.[23] The Hedin-Lundqvist form of the exchange-correlation energy[24] was used. A mixed basis set of plane waves and Bloch sums of local orbitals are used to expand the electronic wavefunctions[25] The cutoff energy for the plane waves used in the expansion is 10.5 Ry. Local orbitals of the form

$$f_{lm}=Nr^{l}\exp(-\gamma r^{s})Y_{lm}(\theta,\phi) \qquad (1)$$

are used for Y. The values for γ are determined to maximize the convergence of the basis set. We used $l=1, s=3, \gamma=0.420$ a.u. for the $4p$ orbitals, and $l=2, s=2, \gamma=0.90$ a.u. for the $4d$ orbitals. The norm-conserving hydrogen pseudopotential used in the present calculation differs from that used in the previous calculation in that it has a smaller core radius of 0.7 a.u. to avoid problems with overlapping core radii. This is important because the path from a T site to the neighboring T site, the path from a T site to the adjacent octahedral (O) site (Fig. 1), and the direct path from an O site to the neighboring O site all pass through a triangular bottleneck consisting of three Y atoms. A local orbital is included in our basis to help represent the hydrogen 1s orbital. The local orbital is constructed to be the product of the hydrogen 1s pseudo-wave-function times a cutoff function of the form

$$f_{\text{cut}}=1-\exp[-\alpha(r_c-r)^2] \;, \qquad (2)$$

where the cutoff radius $r_c=0.7$ a.u. and $\alpha=4.40$ a.u. The charge calculations are performed with a recently developed mixed-basis charge symmetrization scheme.[26] The energy eigenvalues and the wave functions are sampled at 48 **k** points inside the irreducible Brillouin zone, and the Gaussian smearing method (with a Gaussian width of 0.05 eV) is used to determine the occupation of states near the Fermi level. Iteration to self-consistency is carried out until the total energy is stable to within 10^{-5} Ry and the difference between the input and the output screening potentials is smaller than 10^{-4} Ry.

We proceed to study the vibrational properties of H in YH_x by considering $YH_{0.5}$. We repeat the calculation of the total-energy of the $YH_{0.5}$ unit cell, changing the position of the H atom inside the unit cell. This describes the potential experienced by the hydrogen atom in the rigid metal lattice.

III. RESULTS AND DISCUSSIONS

Since we are using a new hydrogen pseudopotential with a smaller core, we have recalculated the equilibrium volume and c/a ratio of $YH_{0.5}$. The equilibrium volume decreases slightly from 462 to 457 a.u. per hcp primitive unit cell; the bulk modulus also decreases from 0.55 to 0.51 Mbar. The c/a ratio is 1.62, the same as our previous calculation.[17] At this fixed c/a ratio, the total-energy calculation is repeated for different locations of the H atom inside the unit cell. Seventeen points along the lines connecting the interstitial sites are considered. (See the dashed lines in Fig. 1.) Seven points on the line connecting a T site and the adjacent T site, five points on the line connecting an octahedral site (O site) and the neighboring O site, and five points in between a T site and the adjacent O site are taken.

The total energy as a function of hydrogen position is fitted to a periodic potential of the form

$$v(\mathbf{r})=\sum_{\mathbf{G}} v(\mathbf{G})\exp(i\mathbf{G}\cdot\mathbf{r}) \;. \qquad (3)$$

Since the hydrogen-hydrogen distance remains unaltered in the displacement of the hydrogen atoms, we assume that the hydrogen-hydrogen interaction stays constant and can be ignored in the above fit. The Fourier coefficients of the metal-hydrogen pair potential $v(\mathbf{G})$ are determined by minimizing the least-squares error in the potential energy surface. The error in the fitting is less than 3%. Ten independent $v(\mathbf{G})$'s are taken in the fitting and the results are listed in Table I. The fitted potential surface along the symmetry directions is shown with the first-principles points in Figs. 2–4.

The Schrödinger equation is solved for the motion of the hydrogen atoms in the three-dimensional potential

TABLE I. Fourier coefficients of the hydrogen-yttrium pair potential in mRy.

G			V(G)
−1	0	0	109.2936
0	0	−2	93.9058
−1	0	−1	87.7994
−1	0	−2	35.1398
−2	1	0	14.7772
−1	0	−3	6.0114
−2	0	0	2.9116
−2	1	−2	4.1378
−2	0	−1	3.0328
0	0	−4	0.2758

tron inelastic scattering measurement[3] gives 134.2 (96.3) meV. As expected, the vibration frequency is significantly higher in the basal plane than along the c axis. The good agreement between our results from experiment indicates that our approximations are indeed valid as far as the local vibrations are concerned.

There are splittings in the energy levels of the H (D) atom, which are related to quantum tunneling between two nearest-neighbor T sites. The splitting in the ground-state energy level will cause a peak to occur in the specific heat at a temperature corresponding to the magnitude of the splitting. There is no such experimental data for α-phase YH_x. However, in LuH_x,[27] which is also a hcp metal, such a peak occurs at 0.1 K, which corresponds to about 0.008 meV. For ScH_x, the ground state splitting is $0.37k_B$, or 0.031 meV.[28] We would expect a peak in the specific heat at about 0.6 K or slightly higher temperature for α-YH_x. For the $(0,0,1)_T$ state, the splitting is 4.1 meV in our calculation compared to about 5.0 ± 0.5 meV from the inelastic neutron scattering experiment.[29] The magnitudes of the splittings of the energy levels are summarized in Table III.

The consequences of including lattice relaxations in our calculations are twofold: Correlation of the H motion with the motion of the lattice atoms would lower the potential barrier between the two nearest-neighbor T sites. As the H atom moves toward the adjacent T site, the lattice atoms would move away from the H atom, opening up the triangular bottleneck, and lower the potential barrier. If we allow the c/a ratio of the lattice to relax fully for each hydrogen position, we find that the potential barrier is almost flattened out between the two T sites, increasing the splitting. On the other hand, relaxation of the lattice around the hydrogen interstitial site also increases the binding energy of the hydrogen atom and hence decreases the splitting. Since the Y-H distances are smaller at the bottleneck than at the T sites, the first effect is expected to be larger than the second effect if the lattice is allowed to relax fully at each hydrogen position. However, given that H is so light and moves much quicker than the metal atoms, the final result is difficult to estimate without further, more involved studies. There is also the possibility of coupling of hydrogen motion to the conduction electrons, which is also reported to increase the proton "hopping" rates.[30] Such coupling would be important at low temperatures. Coupled with the quantum nature of hydrogen motion, this poses a formidable problem at present. Since it is expected that such a process would have a strong dependence on the temperature, a quantum molecular dynamics simulation based on first-principles results may be needed for a study of this phenomena.

TABLE III. The splitting of the energy levels centered at the T sites in meV.

	H	D
J_{000}	0.053	0.001
J_{001}	4.103	0.183
J_{100}	0.015	0.001
J_{002}	33.519	6.078

Tunneling also complicates the analysis of the hydrogen diffusion problem in hcp metals. Since we do not have any splittings for the energy levels centered around the O site, there is practically no tunneling between a pair of O sites located along the c axis with a separation $c/2$. The tunneling is significant only between the pair of T sites separated by $c/4$. However, in the hcp lattice, the T sites occur in isolated pairs so that once the H atom has tunneled to the nearest-neighbor T site there is no other opportunity for tunneling other than back to the original T site. So the tunneling motion described above contributes only to a local rattling of the H atom and not to any long-range diffusion.

Possible long-range diffusion paths are shown in Fig. 1: between a pair of adjacent T sites, between a T site and an adjacent O site, and between a pair of O sites separated by $c/2$ along the c axis. Since the O site has more space around it, it is very easy to assume that the O-O path is very important in the long-range diffusion process. However, we find that the potential barrier height between a pair of O sites (850 meV) is significantly higher than the potential barrier height between an O site and an adjacent T site (460 meV), making direct O-O jumps not plausible at low temperatures. This is consistent with the findings from recent experiments that the interstitial site residence time for a jump from an O site to the above O site should be much larger than any other residence time.[12,13] Thus only T-O jumps and T-T jumps are significant in the long-range diffusion of hydrogen. This conclusion is supported by a recent report of isotropic diffusion coefficients by Gorsky effect measurements.[31] The nearly isotropic diffusion coefficient has been explained within the context of an atomistic jump model, which ignores the O-O jump. For a jump from a T site to an O site, the activation energy is 460 meV, while for the reverse process, the activation energy is 332 meV from our calculation. The NMR measurements by Lichty *et al.*[11] report 510 meV as the activation energy for α-phase $YH_{0.2}$. Other experiments report 530 meV (Ref. 12) and 570 meV (Ref. 13) as the activation energy for α-phase $YH_{0.215}$. The local deformation around the hydrogen interstitial could increase the activation energy by a self-trapping mechanism.[32]

The potential barrier between the T site and the O site is shown in Fig. 3. As stated earlier, the O site is higher than the T site by 128 meV. If a simple classical Boltzmann distribution is used to predict the occupation of an O site at temperature T, since there are four T sites and two O sites per primitive unit cell,

$$4f_T+2f_O=1\ , \tag{4}$$

$$f_O=f_T e^{-\Delta E/k_B T}\ , \tag{5}$$

where f_O and f_T are the probability of occupation for the T and O site, and $\Delta E=46$ meV for H and $\Delta E=68$ meV for D (it is important to include the contributions of zero-point energies in arriving at these values for ΔE). Then, 3.2% of D would occupy the O site at $T=300$ K and 10.8% of D would occupy the O site at 537 K. Experiments report that less than 5% of D occupies the O

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site at $T=300$ K,[18] and about 10% of D occupies the O site at $T=537$ K.[33] However, we have a large occupation of the O site by H compared to experiments that report that less than 3% of H occupies the O site at $T=873$ K.[5,12] Since the energy difference is small for H, it would be important to include the local deformations around the H, which would lower the T-site energy by a self-trapping mechanism.[32] Higher O-site occupations reported in earlier experiments are related to hydrogen trapping and can be reduced by annealing.

There is also an activation energy for a fast jump between the two nearest-neighbor T sites. We have 162 meV for the activation energy between the T sites compared to 90 meV from quasielastic neutron-scattering experiment.[13] Our value for the barrier height should represent an upper bound value, and the deviation may be explained by the coupling between the hydrogen motion and the host-metal lattice vibration. Again, a quantitative prediction cannot be made within the context of a first-principles frozen phonon calculation, and a quantum molecular dynamics study is due.

IV. SUMMARY

The potential energy surface for hydrogen in hcp yttrium metal is determined from first-principles total-energy calculations. The vibration frequencies of the hydrogen in $YH_{0.5}$ have been calculated in excellent agreement with the experiments. The activation energy of the diffusion of the hydrogen also agrees well with the experiments. From the splitting of the energy levels of H located at the T site, a peak in the specific heat is predicted at a temperature slightly higher than 0.6 K. Since the present study is limited by the Born-Oppenheimer approximation between the H and Y atomic motions, a quantum molecular dynamics simulation would be needed for a better understanding of hydrogen diffusion in hcp metals. Since such a simulation must include some empirical scheme in view of the present computing capacity, results from first-principles total-energy calculations will be useful for building such a scheme.

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