First-Principles Investigation of Metal-Hydrogen Interactions in NbH

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First-principles total-energy calculations have been performed for NbH in the β- and γ-phase structures. Lattice constants, bulk moduli, and heats of formation as well as the frequencies and second harmonics of the optical vibrations of hydrogen and deuterium in the lattice have been calculated and found to be in excellent agreement with experiment. Our calculated electronic densities of states resolve the discrepancy between previous band calculations and photoemission experiments.

Metal-hydrogen systems have been the subject of numerous investigations because of their technological importance and also because they serve as prototypes for understanding the behavior of interstitial atoms in metals. In particular, the hydrides of the group-VB metals (V, Nb, and Ta) have been studied extensively[1-17] because their properties are representative of most metal-hydrogen systems and the extremely high mobilities of the hydrogen in these metals have attracted many experimental[15-17] and theoretical[18] investigations. The key to a quantitative understanding of the properties of these systems is a detailed knowledge of the interaction of the dissolved hydrogen with the host metal lattice from which one can determine the vibration frequencies of the hydrogen at the interstitial site, the energy barrier for hopping between sites, as well as the probability for tunneling from one site to another: a mechanism which has been proposed to explain the high mobilities at low temperatures.[18]

In this paper, we report results of first-principles electronic-structure and total-energy calculations on NbH in the β- and γ-phase structures. We obtain accurate values for the heats of formation, the equilibrium lattice constants, and bulk moduli of the hydride phases as well as detailed information on the potential experienced by hydrogen in the metal lattice. This is the first time that modern *ab initio* band-structure techniques capable of accurate evaluation of total energies have been applied to investigate the hydrogen-metal potential. For the case of niobium and vanadium hydrides, previous investigations of the electronic structures have been performed only for a limited number of crystal structures,[19-21] and even with the most recent calculation, there is a discrepancy between the calculated density of states and photoemission data.[21]

Our calculations were made with use of the pseudopotential approach within the local density-functional formalism.[22] The only approximations involved in these calculations are the local density approximation[22] for treating the exchange-cor-

relation energy of the electrons (the Hedin-Lundqvist[23] form was used) and the use of the Born-Oppenheimer approximation in calculating the hydrogen-metal interaction potential. This method has been applied successfully in calculations of structural and dynamical properties of a wide variety of materials.[24-26] In particular, such calculations have been applied to the case of Nb and Mo, yielding excellent results for the cohesive energies, equilibrium lattice constants, bulk moduli, and the frequencies of selected phonon modes.[25,26] The pseudopotentials are generated with the norm-conserving approach.[27] The wave functions in the solid are expanded by use of a mixed basis[28] of local d orbitals for Nb plus plane waves up to a cutoff energy of 14.5 Ry. Sampling grids in the irreducible Brillouin zone contain 36 points for the γ phase and 24 points for the β phase.

Experimental investigations of the crystal structure of NbH_x indicate that for hydrogen concentrations $x \sim 1$, the hydrogen atoms are located in tetrahedral interstitial sites in the bcc Nb lattice.[1,6] At low temperatures, the hydrogen atoms are ordered in the β-phase structure or a mixture of β phase and γ phase. The arrangements in these phases are shown in Fig. 1. The structure for the β phase was deduced from neutron[6] and electron diffraction[7] experiments. The structure for the γ phase was proposed by Hauck[29] but has not been confirmed experimentally.

The total energy of the crystal was calculated as a function of volume for both crystal structures. The results were fitted to the universal binding curve proposed by Rose, Ferrante, and Smith[30] to obtain the cohesive energies, equilibrium volumes, and bulk moduli for both phases. The heat of formation of the hydride was then obtained by subtracting the cohesive energy of bulk Nb and the binding energy of molecular hydrogen from the cohesive energy of NbH. Because of the small value of the heat of formation, we have taken the following steps to obtain accurate results. The cohesive energy of the
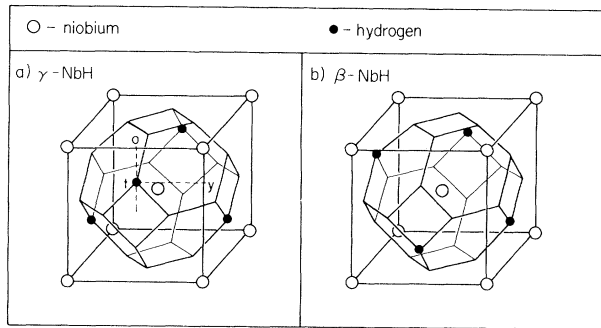
FIG. 1. Crystal structures of NbH in the (a) γ phase and (b) β phase.

FIG. 2. Calculated energy vs displacement curves for hydrogen in Nb. The displacements of the hydrogen for the tetrahedral site are $(0,0,a)$ [t-o in Fig. 1(a)] for the left-hand portion of the curve and $(0,a,0)$ [t-y in Fig. 1(a)] for the right-hand portion.

γ phase (which has a smaller unit cell) was calculated for several larger bases and the results extrapolated to full convergence of basis set size. A similar procedure was performed for bulk Nb. The difference in energies between the β phase and γ phase was calculated with use of the same unit cell and the same Brillouin zone grid to ensure maximum cancellation of error. For the binding energy of molecular hydrogen, we used the results of Gunnarsson and Lundqvist[31] as suggested by Williams, Kubler, and Gelatt.[32] The zero-point vibration energy of hydrogen is of the same magnitude as the final result; thus it has to be considered both in the solid and in the molecule. Our results are summarized in Table I. The agreement between calculation and experiment is quite satisfactory. It can be seen that at exact stoichiometry $x = 1$, the β phase is lower in energy than the γ phase. Experimentally, the γ phase is reported[33] to exist at low temperatures within a narrow concentration range for x between 0.88 and 0.92. Since the calculated energy difference is small ~ 2.5 mRy, we cannot rule out the possibility that the γ phase can be stabilized by interactions between hydrogen vacancies for
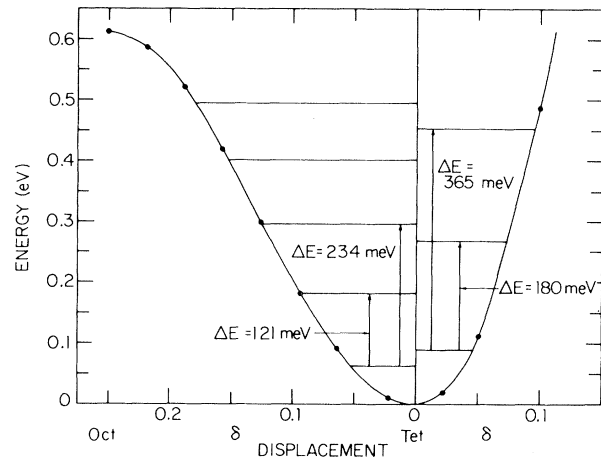
$x \sim 0.9$.

The phonon spectra of niobium hydrides and deuterides have been the subject of intensive investigations using neutron scattering to obtain information on the metal-hydrogen interactions.[10-14] It has been observed[11,12] that the optic modes in these systems are dispersionless even at high concentrations. This implies that hydrogen-hydrogen interactions are small and we can obtain a very good description of the metal-hydrogen potential by taking the stoichiometric compound and calculating the energy of the crystal as we displace the hydrogen sublattice relative to the metal sublattice. We have calculated the total energy of the crystal for different positions of the hydrogen atom in the unit cell. In Fig. 2 we show the energy versus displacement curves for moving the H atom from the tetrahedral site to the octahedral site along the

TABLE I. Bulk properties of NbH.

	Lattice constant (Å)	Bulk modulus (Mb)	Cohesive energy (eV)	Heat of formation (eV/H)
Calc. γ phase	3.47	1.91	10.16	0.15
Calc. β phase[a]	3.44	1.87	10.19	0.18
Expt. (Refs. 1, 2, and 5)[b]	3.46	1.79	$\cdots$	0.22

[a]Orthorhombic distortion is not included in the calculation.

[b]Quoted values of lattice parameter and heat of formation are for the α' phase. The bulk modulus is for $NbH_{0.78}$ in the β phase.

TABLE II. Optic-mode phonon energies of NbH and NbD. All values are in millielectronvolts.

	ω_{001}		$\omega_{010}, \omega_{100}$		ω_{002}	
	NbH	NbD	NbH	NbD	NbH	NbD
Expt. (Refs. 13 and 14)	122 ± 1	88.4 ± 0.3	166 ± 2	121.6 ± 0.4	231 ± 2	170
Calc. (with anharmonic effects)	121	87.5	180	127	234	171
Calc. (harmonic)	128	91	178	126	256	182

[001] direction (*t-o*) and also along the [010] direction (*t-y*) [see Fig. 1(a)]. These displacements correspond to the normal modes of a local harmonic oscillator centered at the tetrahedral site. Because of the light mass of hydrogen, anharmonic effects are important. The lack of dispersion of the optic modes allows us to adopt the Einstein model and solve for the energy levels of a hydrogen (or deuterium) atom[34] vibrating in the calculated potential wells. From the spacings of the energy levels we obtain the frequencies and also the second harmonics of the optic modes. [The deviation of the second-harmonic frequency (ω_{002}) from twice the value of the single-phonon frequency (ω_{001}) is a measure of the importance of anharmonic effects.] The results are listed in Table II and compared with the experimental measured values. Also listed are the values one would obtain if anharmonic effects are neglected and the phonon frequencies calculated following the usual frozen-phonon approach.[26] The agreement between our calculated results and experiment is excellent for the [001] mode but is less satisfactory for the [010] mode. This is probably due to the neglect of intermode coupling effects since the vibration levels are obtained from a one-dimensional well in the present calculations. Inclusion of such effects requires solving for the motion of the hydrogen atom in a three-dimensional well. Such calculations are in progress.

The electronic structure of NbH has been studied with photoemission spectroscopy.[21] The agreement between the experimental photoelectron energy distribution curves (EDC's) and the theoretical electron density of states (DOS) of previous band calculations[19-21] is rather poor. Since band theory has been successful in describing photoemission results of other hydrides,[35] this has led to speculation of a surface phase of high hydrogen concentration.[21] From our calculations, we find that the most probable reason for this discrepancy is that while under the experimental conditions, one would expect most of the NbH sample to be in the β phase, none

of the previous calculations were done with this geometry. We show in Fig. 3 our calculated electronic densities of states (DOS) for NbH in both the β- and γ-phase structures (solid lines). The DOS for the γ-phase structure agrees very well with the calculations of Peterman *et al.*,[21] but disagrees with the experimental EDC (dotted lines). On the other hand, the DOS of the β phase agrees very well with experiment. The hydrogen atoms are closer together in the β phases; this leads to a splitting in the hydrogen bands and produces the double-peak structure at -6.5 and -8.0 eV which is a characteristic feature of the experimental EDC. The shift between the experimental and the calculated position of the Fermi level is probably due to the effect of hydrogen vacancies—the experimental samples have compositions NbH_x with x between
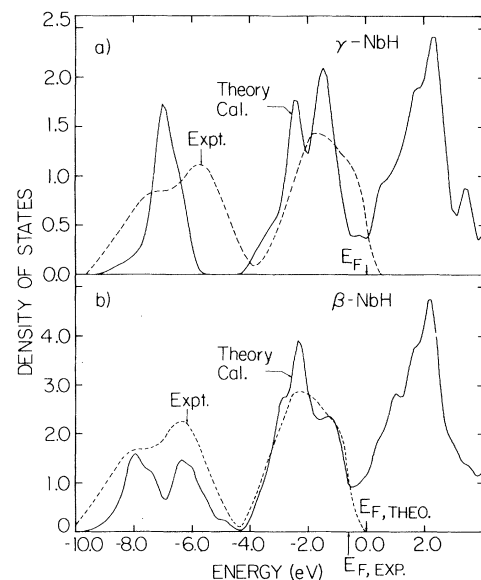

FIG. 3. Calculated DOS in units of (states/eV)/unit cell for (a) γ-NbH and (b) β-NbH (solid lines). The dotted lines indicate the photoelectron EDC from Ref. 21. The experimental curve has been shifted in (b) to line up with the DOS (see text).

0.6 and 0.8 whereas our calculations are performed for x exactly equal to 1.

The encouraging results that we have obtained show that first-principles total-energy calculations can give a very accurate description of the metal-hydrogen interactions in metal hydrides. Further investigations will be made on the effects of displacements of the metal atoms on the motion of hydrogen in the metal lattice and on the problem of hydrogen embrittlement in these systems.

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