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Theoretical Prediction of the Structure of Insulating YH_3

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Density functional calculations of the total energy have been used to determine minimum energy structures for YH_3. Small, symmetry lowering displacements of the hydrogen atoms lead to a structure with an energy which is lower than that of any other structure considered so far and the opening of a large band gap sufficient to explain the recently observed metal-insulator transition in the YH_x system. [S0031-9007(97)02331-4]

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There has recently been a breakthrough in the preparation and study of the physical properties of rare-earth hydrides [1]. By depositing thin films ($\sim$500 nm) of rare-earth metals on a transparent substrate and coating them with an optically thin protective layer of palladium through which hydrogen could diffuse, it was possible to observe a metal-insulator transition as a function of the H concentration optically as well as in electrical transport measurements. The transition could be cycled repeatedly without any apparent deterioration of the sample.

For $2 < x < 3$ Huiberts *et al.* [1] interpreted their extensive optical and electrical measurements on YH_x in terms of a cubic dihydride β phase and of a hexagonal trihydride γ phase. In the cubic YH_2 phase the two tetrahedral sites in the fcc Y lattice are (nominally) occupied and the octahedral sites unoccupied. This phase is quite well characterized from measurements on bulk samples and is metallic with a conductivity which is about a factor of 5 higher than that of yttrium metal. There have been detailed experimental studies of the optical properties [2] which could be interpreted in terms of conventional, self-consistently calculated one-electron band structures [3]. For $x > 2$ the octahedral sites are believed to become randomly occupied until the trihydride phase is nucleated when x exceeds 2.09 [4]. The properties of the hexagonal YH_3 phase were not well known until now because bulk samples disintegrate when x approaches three. To explain their measurements, Huiberts *et al.* required the hexagonal YH_3 phase to have a band gap of 1.8 eV and, for substoichiometric trihydrides $YH_{3-\delta}$, shallow donor states were assumed to be formed about 0.4 eV below the conduction band edge. This picture was supported by Hall measurements, a negative temperature coefficient of the electrical resistivity $(d\rho/dT)$, and the dependence of the resistivity on δ [1,5]. The metal-insulator transition in YH_x occurs on going from the cubic β phase to the hexagonal γ phase.

A number of electronic structure calculations have been performed for YH_3. In the most recent work [6,7] based on the HoD_3 structure derived from neutron scattering experiments [8–10], it was concluded that YH_3 should be metallic which is in disagreement with Huiberts' interpretation of his experiments. To reconcile these contradictory results, strong correlation effects have been invoked [1,7,11]. In this Letter we use Car-Parrinello calculations to determine minimum energy structures for hexagonal YH_3 [12]. We show that although YH_3 is metallic in the high symmetry HoD_3 structure, there exists a broken symmetry structure with a significant band gap whose energy is lower than that of the HoD_3 structure. This result suggests that correlations may be no more important in YH_3 than in a conventional semiconductor such as Si and may be treated perturbatively [13].

Our calculations were carried out within the local density approximation (LDA) for exchange and correlation [14]. The valence electron wave functions were expanded in a plane wave basis and soft [15] fully separable [16] norm-conserving pseudopotentials were used to describe the interaction of the valence electrons with the Y core. The Y $4p$ states were included in the core and nonlinear core corrections were made in the treatment of the exchange-correlation potential [17]. The Y pseudopotential included p and d nonlocal terms; the s component was chosen as the reference potential. The H pseudopotential included s nonlocality. The calculations were carried out with a tripled unit cell containing 6 Y and 18 H atoms and the corresponding full Brillouin zone (BZ) was sampled using 72 Chadi-Cohen points and a broadening parameter of 0.1 eV [18]. A plane wave kinetic energy cutoff of 30 Ry was used for most of the calculations. All important results were repeated using a 40 Ry cutoff, 0.01 eV broadening parameter, and 432 k-points in the full BZ. We were able to reproduce in

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detail the results of Wang and Chou [7,19] for elemental Y and for hexagonal YH_3.

A convenient starting point for our discussion is the ideal high symmetry structure of Y_2H_6 where the Y atoms form an hcp lattice and the H atoms occupy the two octahedral and four tetrahedral sites. This structure is unstable with respect to the formation of the LaF_3 structure where the octahedral atoms move vertically by $c/4$ into the metal plane and the tetrahedral atoms are shifted away from it. We find an energy gain of 965 meV per YH_3. The energy of the LaF_3 structure can be further lowered [7] by a Peierls distortion which results in the HoD_3 structure in which the unit cell in the basal plane is tripled in size as indicated by neutron powder diffraction studies [8–10]. The HoD_3 structure calculated by energy minimization is shown schematically in Fig. 1(a) in a representation in which the unit cell is divided into 6 layers perpendicular to the z axis at $z/c \sim \pm 0.09, \pm 0.25$, and ± 0.41. The structure in Fig. 1(a) has inversion symmetry about the origin, threefold rotation symmetry about the z axis through the origin, and the left- and right-hand panels of Fig. 1(a) are related by a glide plane. In each of the planes at $z/c = \pm 0.25$ there are 3 Y atoms per unit cell and, close to or in the plane, 3 "metal-plane" H atoms (H_{mp}). The H_{mp} atom at $x, y = (0, 0)$ remains in the metal plane while the other two H_{mp} atoms are displaced by $z/c \sim 0.07$ above and below the metal plane, respectively. The tetrahedral H atoms (H_{tet}) in the adjacent planes (at $z/c \sim \pm 0.25 \pm 0.16$) accommodate the displacements of the H_{mp} by relaxing towards the vertical displacement axis of those H_{mp} which move vertically away. In addition to this radial relaxation the H_{tet} triplets also undergo a rotation about the vertical displacement axes. To avoid steric hindrance, triplets of H_{tet} atoms in neighboring planes which share a rotation axis rotate in the same direction. The net gain in energy is 220 meV per Y_6H_{18}.

The energy bands calculated for the structure in Fig. 1(a) are shown in Fig. 2(a). The system is found to be metallic with two Fermi surface sheets in agreement with earlier work [6,7]. There is an electron band and a hole band, both with large dispersions along ΓK, ΓM, and ΓA. The electron band has mainly Y $d_{xz,yz}$ character, the hole band mostly H_{tet} s character. At Γ the hole band lies 1.1 eV above the electron band and along ΓK, ΓM, and ΓA the two bands can be classified as being either even or odd with respect to glide or glide-inversion symmetry [20]. The two bands have different symmetries and thus cross close to the Fermi level along ΓM and ΓA but not along ΓK where, however, the interaction is very small. The symmetry of the partly filled bands is such that they can interact when the glide symmetry is broken (but not when only the inversion symmetry is broken). Because the degeneracies occur so close to the Fermi level, the electronic energy can be lowered by breaking the symmetry and opening a gap.

The structure shown in Fig. 1(b) which we obtained on allowing the atoms to relax (from a number of different starting configurations) has an energy which is 70 meV per unit cell lower than that of the HoD_3 structure. The threefold rotation symmetry is found to be conserved but both the inversion and glide symmetries have been broken leading to the opening of a large gap in the band structure shown in Fig. 2(b). The valence band maximum and conduction band minimum are found along ΓA and ΓM, respectively, but the indirect band gap of 0.75 eV differs only slightly from the direct gap of 0.8 eV along ΓM. It is well known that the LDA underestimates the size of the fundamental band gap (e.g., by 0.65 eV for Si), and we expect a substantial enhancement of the LDA gap for YH_3 when the self-energy is accounted for, e.g., in the *GW* approximation [13,21,22]. The symmetry breaking can be reversed by applying hydrostatic pressure whereby the volume available to the H atoms decreases until eventually the glide symmetry is restored and the LDA band gap closes. This occurs when the volume is reduced to about 85% of the calculated equilibrium volume. (The calculated equilibrium volume and c/a ratio are within 2 and 1%, respectively, of the experimentally measured values.)

In the structure of Fig. 1(b) there are no longer any metal-plane hydrogen atoms actually in the metal plane, but there is still one H_{mp} at approximately $0.07c$ above and below each metal plane. The H_{tet}'s in the adjacent planes take advantage of these displacements to relax inwards towards the vertical displacement axis as in the HoD_3 structure. The remaining H_{mp} atom is found approximately $0.03c$ above the metal plane, and there is a small displacement of the three neighboring Y atoms away from it. The pattern of H_{mp} displacements shown in Fig. 1(b) results in steric hindrance of the rotational displacements of H_{tet}'s in adjacent planes. Because of the symmetry breaking, a single crystal with this structure will be either left handed or right handed, and a collection of crystals prepared at random will contain equal amounts of each. As a result it may not be possible to observe the symmetry breaking even in a careful powder diffraction experiment such as that published recently by Udovic *et al.* [10]. We believe that the structure illustrated in Fig. 1(b) provides a natural explanation for the large anisotropic temperature factors found in the refinement of the HoD_3 structure (or for the large occupancy of m' sites in models III, IV, and V of Ref. [10]).

In general, a measurement of the optical transmission coefficient is not enough to determine the size and nature of the fundamental band gap. Because the strength of optical transitions can be so strongly influenced by the matrix elements connecting initial and final states, we have calculated matrix elements for electric dipole transitions between occupied and unoccupied states for both the metallic and insulating structures of Fig. 2. In agreement with independent calculations by Chou and Wang [23] for the metallic HoD_3 structure, we find very small matrix elements for optical transitions between bands 18 and 19 along ΓK, ΓM, and ΓA. The hybridization

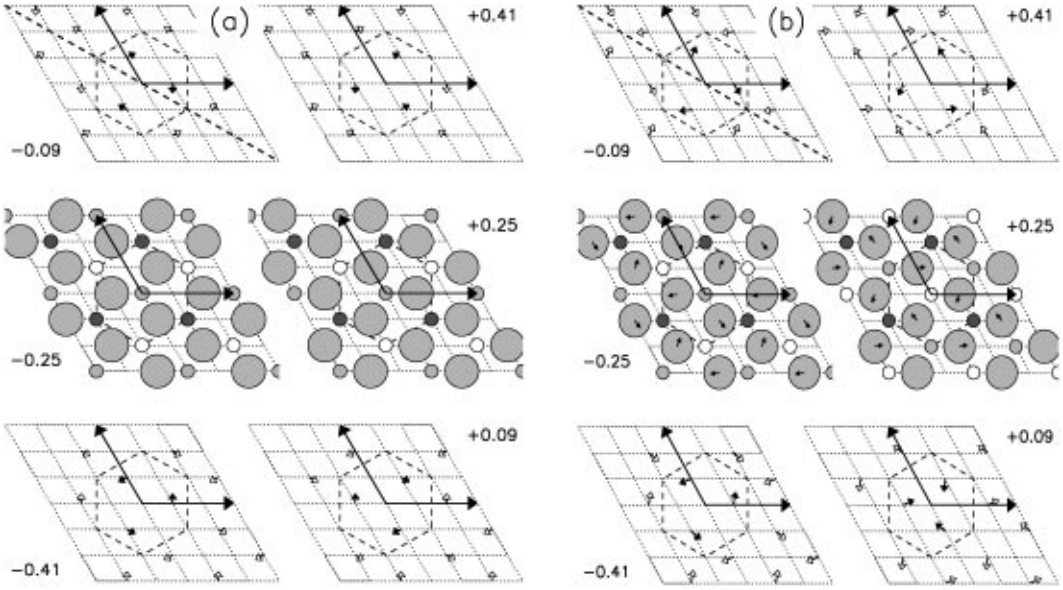


FIG. 1. Schematic drawings of (a) the HoD_3 structure and (b) of the lowest energy structure found, in a representation in which the unit cell is divided into six layers perpendicular to the z axis at $z/c \sim \pm 0.09, \pm 0.25$, and ± 0.41. The large arrows are the primitive lattice vectors and a hexagonal Wigner-Seitz cell is indicated by dashed lines. A reference grid is shown for convenience. The glide plane consists of reflection in the plane which contains the heavy dashed line shown in the top left-hand panels and the z axis, followed by a translation of $c/2$ along the z axis. The large grey circles in the $z/c \sim \pm 0.25$ planes represent the Y atoms, the smaller circles H_{mp} atoms. Shading indicates displacement of the H_{mp} atoms relative to the yttrium atom plane. The white (black) atoms are displaced upward (downward) by $z/c \sim 0.07$. In (a) the grey atoms are in the metal planes, in (b) they are $\sim 0.03c$ above the metal plane. The horizontal displacements of the H_{tet} atoms in planes separated from the metal plane by $\pm 0.16c$ are shown as arrows; the displacements are exaggerated by a factor of 5 to make them better visible. The small horizontal displacements of the yttrium atoms in (b) are exaggerated by a factor of 25.

associated with the symmetry lowering in Fig. 1(b) results in an increase in the oscillator strength between bands 18 and 19 by more than 2 orders of magnitude. We conclude that in both cases, an optical gap of at least 0.8 eV (LDA gap; substantially larger when corrected for self-energy effects) will be observed when measurements are performed for very thin samples as in Ref. [1].

The strongest evidence for the occurrence of a metal-insulator transition therefore comes from electrical transport measurements [5]. Unfortunately, the size of the gap could not be extracted reliably from experiment. From our calculations we find that the energy gained by opening a large gap is quite small because the density of states at the Fermi energy in Fig. 2(a) is so low. This raises the interesting question of the influence of temperature (and

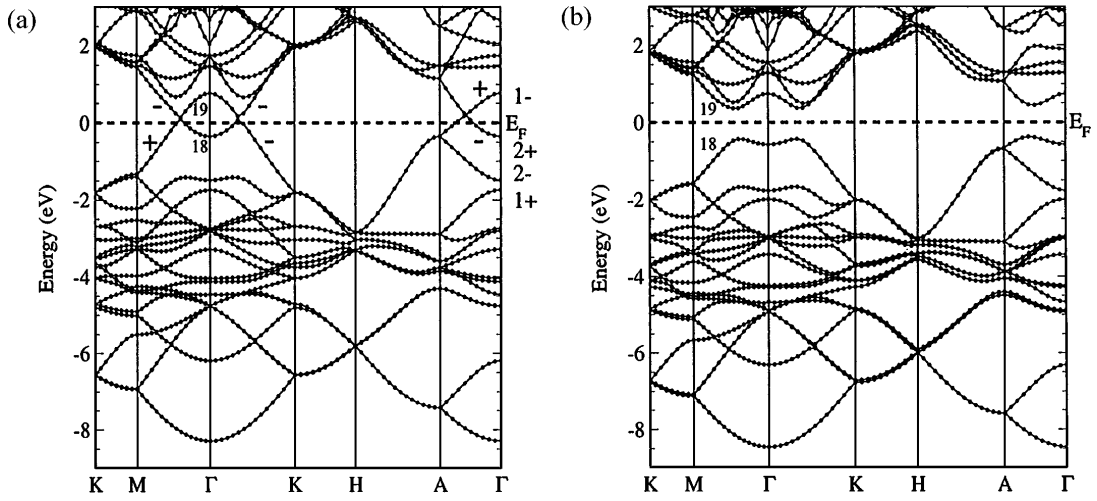


FIG. 2. (a) Energy bands of YH_3 for (a) the HoD_3 structure and (b) for the minimum energy structure. In (a) the parities of bands 18 and 19 are indicated and the irreducible representations according to which a number of states transform are given at Γ.

zero-point motion) on the calculated energy gap. In order to estimate the atomic displacements needed to close the band gap and the associated formation energies we have studied a large number of configurations with H atoms displaced from their equilibrium positions. Our findings can be summarized as follows: metallic configurations involving the displacement of only a small number of H atoms have large formation energies (of order 0.5 eV); metallic configurations with low formation energies (of order 0.1 eV) involve large numbers of H atoms displaced in a correlated fashion. Since the motion of the H atoms at room temperature may be expected to be uncorrelated, the statistical weight of the metallic state can be expected to be very small even though the energy required to reach the metallic state is relatively low [24]. In order to make a more reliable estimate of the time spent in the metallic state at room temperature, we are studying the temperature dependence of the band gap using *ab initio* molecular dynamics for YH_3. Experimentally, it is of the utmost importance to determine the size of the single-particle energy gap by, e.g., photoemission and inverse photoemission.

In conclusion, we have performed local density approximation calculations for hexagonal YH_3 and found a structure with a large band gap and a lower energy than any previously reported structure. We suggest that the small hydrogen displacements which lower the symmetry and give rise to a gap may have been overlooked in the past or interpreted in terms of disorder or large temperature factors. We propose that similar distortions may occur in other hydrogen metal systems and play a similarly important role there.

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