

## Peierls Distortion in Hexagonal $\text{YH}_3$

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A pseudopotential local-density calculation is performed for  $\text{YH}_3$  to study the unusual hydrogen displacements previously found in neutron diffraction. These displacements are identified as Peierls distortions associated with (hydrogen) lattice instability in this 3D system. The wave vector of these displacements is close to the vector connecting the electron and hole pockets in the undistorted system. With other electron and hole pockets at  $\Gamma$  that still overlap after distortion, the possibility of the existence of an excitonic insulator phase will be discussed.

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The hydrogen-metal systems have continuously attracted attention for being prototypes for studying certain basic physical properties such as fast solid-state diffusion, phase transitions of the lattice gas model, etc. [1]. In addition, a variety of immediate or potential applications in the energy industry have also been identified [1]. Among different hydrogen-metal systems, rare earth (RE) metals as well as Sc, Y, and La are of special interest because of their ability to absorb a large amount of hydrogen, up to three per metal atom. Several unusual features in these systems have been reported recently, including the pairing [2] and rapid low-temperature hopping [3] of hydrogen in the solid-solution phase, and a metal-semiconductor transition in  $\text{YH}_{2.10}$  [4].

Hydrogen normally occupies high-symmetry interstitial sites, namely, tetrahedral or octahedral sites, in a metal lattice. When additional hydrogen is absorbed by the heavy lanthanide and yttrium dihydrides, the metal atoms transform from the face-centered cubic (fcc) to the hexagonal close-packed (hcp) structure [5]. A neutron diffraction study of holmium trihydride  $\text{HoD}_3$  revealed some unexpected positions for the hydrogen atoms [6]. The tetrahedral sites are all occupied, but some correlated horizontal displacements away from the ideal positions were found. Instead of occupying the ideal octahedral sites, the additional hydrogen atoms move down to the metal plane and also exhibit some alternating vertical displacements. Later similar displacement patterns were also found for  $\text{YD}_3$  [7].

To our knowledge, these intriguing correlated displacements of hydrogen have never been seen in other groups of hydrides. In this Letter, we present a first-principles calculation and explain this behavior from the unique electronic structure of the material. In order to eliminate the complications caused by  $f$  electrons, we have chosen to investigate yttrium trihydride. We found that these hydrogen displacements are Peierls distortions [8] with two-dimensional wave vectors in this *three-dimensional* hexagonal crystal. They are connected with the special positions of the electron and hole pockets. The frozen-in hydrogen displacements lower the system energy and open a gap between two interacting electronic states near

the Fermi level. There are two remaining electron and hole bands that still overlap around  $\Gamma$  in the distorted structure and this may favor a ground state of an excitonic insulating phase [9]. The existence of an insulating state due to exciton condensation was speculated theoretically more than two decades ago [9]. Only recently has the first observation been reported in a semiconductor under pressure [10]. As will be discussed later,  $\text{YH}_3$  is likely to be another system approaching this insulating state from the semimetal side.

The calculations are performed using *ab initio* pseudopotentials with the local density approximation (LDA) [11]. Soft pseudopotentials [12] are generated for both Y and H and the wave functions are expanded by plane waves. We have tested the computational methods by studying the structural properties of elemental yttrium and the results are satisfying [13]. Good convergence was obtained with an energy cutoff of 36 Ry. Thirty-six special  $k$  points in the irreducible hcp Brillouin zone were used which, with Gaussian smearing [14], gave a convergence of about 0.5 mRy per  $\text{YH}_3$ . The calculated results of the cubic dihydride phase agree very well with the linear-augmented-plane-wave (LAPW) results [15].

We first determined the optimal interstitial sites for hydrogen by calculating the LDA total energies. The metal atoms are arranged in the hcp structure. With hydrogen placed at the perfect tetrahedral and octahedral sites, the energy turns out to be quite high, about 0.79 eV per  $\text{YH}_3$  higher than that of the fcc structure. The distance between two nearest neighbor tetrahedral sites (1.66 Å) is too small according to Switendick's criterion [16]. Hence vertical relaxations are favored which yield an energy drop of 0.18 eV per  $\text{YH}_3$  when the separation is increased from  $0.25c$  to  $0.3c$  ( $c$  is the vertical lattice constant). We found that the decrease mainly comes from the kinetic energy and the ion-ion interaction and is offset partly by an energy increase in the electron-ion interaction. An additional energy decrease of 0.80 eV is obtained by moving octahedral hydrogen down by  $c/4$  to the metal plane. This significantly reduces the energy to 0.19 eV per  $\text{YH}_3$  below the fcc trihydride. Therefore the hexagonal structure is stabilized by the occupation

of unconventional interstitial sites. The calculated equilibrium volume and  $c/a$  ratio are both within 2% of the observed values.

We will denote the hydrogen at the tetrahedral sites (relaxed) and on the metal plane by  $H(T)$  and  $H(M)$ , respectively.  $H(M)$  has three nearest-neighbor metal atoms at a distance of 2.12 Å, which is 10% shorter than the distance between  $H(T)$  and its nearest neighbors. It yields a stronger hydrogen-metal interaction and results in a considerable drop of certain energy bands compared with the configuration with hydrogen at the ideal octahedral sites. The Fermi energy also drops by about 1 eV.

The band structure of this geometry is shown in Fig. 1. It gives a semimetal with electron pockets centered at  $K$  and holes along  $\Gamma$  to  $A$ . The electron pocket at  $K$  is almost spherical, with an averaged effective mass of  $0.36m$  ( $m$  is the electron mass) and a 15% variation in different directions. This band consists of linear combinations of yttrium  $d$  functions  $xz$  and  $yz$ , and was pulled down across the Fermi level when  $H(M)$  drops to the metal plane. The hole pieces are around the central axis of the Brillouin zone ( $\Gamma A$ ) and there are two separated bands involved. One ( $\Gamma_4^-$ ) is almost cylindrical and associated with a linear combination of mainly the  $s$  states of both  $H(M)$  and  $H(T)$ . The other ( $\Gamma_2^-$ ) is of the "cigar" shape with the ratio of the radii at  $k_z = 0$  and  $\pi/c$  close to two. It consists of dominantly the  $s$  states of  $H(T)$  only. Both form open orbits in the repeated zone scheme. A cross section at  $k_z = 0$  is shown in Fig. 1.

Lattice instability associated with soft modes can occur depending on the details of the electron-phonon interactions and electronic structure [17, 18]. It is clear from

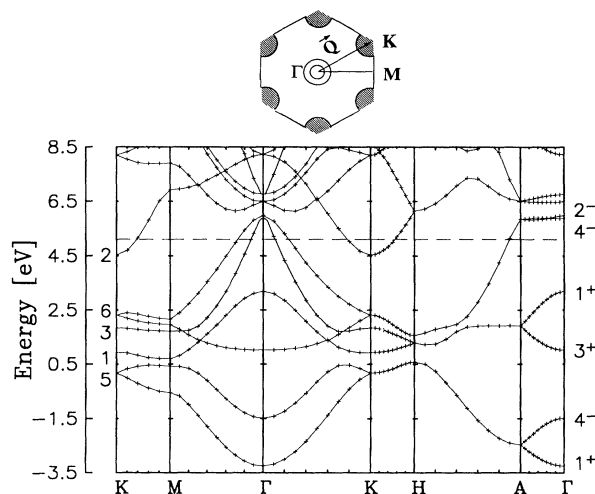


FIG. 1. Energy bands of hexagonal  $\text{YH}_3$  with  $H(M)$  on the metal plane and prior to wavelike distortions. The Brillouin zone is that of the hcp structure. Also sketched are the positions of the electron and hole pockets on the  $k_z = 0$  plane and the Peierls-distortion wave vector.

Fig. 1 that the electron and hole pockets are separated by a vector pointing from  $\Gamma$  to  $K$ . There are six equivalent vectors by symmetry. If permanent distortions should occur, these vectors will become the reciprocal lattice vectors for the new unit cell. The smallest unit cell satisfying this requirement has a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  unit in the horizontal plane which is exactly what was assigned in the neutron scattering experiment [6, 7]. It is 3 times larger than the original unit cell with the same lattice constant  $c$  in the  $z$  direction. Therefore we took the space group  $D_{3d}^4$  from Ref. [6] and calculated the total energies for various displacements.

The structure still follows the stacking sequence  $ABAB\dots$  with each stacking unit ( $A$  or  $B$ ) consisting of three groups of atomic layers: one layer of metal and  $H(M)$  associated with it, and two adjacent layers of  $H(T)$  above and below, respectively, as shown in Fig. 2. The hydrogen distortions are frozen-in displacement waves of wave vector  $\mathbf{Q}$  as indicated in the figure. For  $H(M)$  the displacements are vertical; 1/3 of them go up, 1/3 down by the same amount  $\Delta(M)$ , and 1/3 remain on the metal plane. For  $H(T)$  the displacements are horizontal. There are correlations in these displacements: when  $H(M)$  moves up (down), the three neighboring  $H(T)$  atoms in the layer below (above) move in

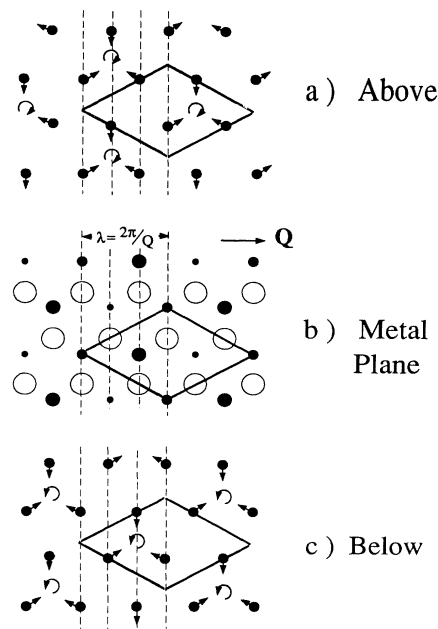


FIG. 2. Geometry of distorted hydrogen atoms in  $\text{YH}_3$ . Three atomic layers are shown: the metal plane and the layers of tetrahedral hydrogen above and below. The two-dimensional  $\sqrt{3} \times \sqrt{3}$  unit cell is marked. Metal (hydrogen) atoms are denoted by open (solid) spheres. The hydrogen atoms on the metal plane that move up (down) are marked by larger (smaller) solid spheres. Displacements of tetrahedral hydrogen are indicated by arrows.

together toward the center of gravity followed by a small rotation around the vertical axis.

We first did a search for the optimized displacements [ $\Delta(T)$  and  $\Delta(M)$ ] by computing the total energies at the experimental lattice constants. The rotation of  $H(T)$  was first neglected. We found that the equilibrium displacements for  $H(M)$  and  $H(T)$  are  $\Delta(M) = 0.055c$  (0.37 Å) and  $\Delta(T) = 0.017a$  (0.11 Å), respectively ( $a$  is the horizontal lattice constant of the tripled cell). These values are slightly different from those obtained in the neutron data, which are  $0.083c$  and  $(0.026-0.03)a$ , respectively [6, 7]. The corresponding total energy is lowered by 21 meV per  $\text{YH}_3$  after these distortions. It is a balance between several terms: the kinetic, Hartree, and Ewald energies are lowered by 194, 100, and 185 meV, respectively, while the electron-ion and exchange-correlation energies are increased by 402 and 56 meV, respectively. To show that this is associated with a lattice instability, the total energy as a function of the simultaneous displacements of  $H(M)$  and  $H(T)$  (scaled by the equilibrium value) is shown in Fig. 3. It is clearly seen that the energy is a local maximum at zero displacement. Finally the tetrahedral hydrogen  $H(T)$  atoms were rotated away from the symmetry directions with the magnitude of the displacement fixed at  $0.017a$ . A further decrease in energy of about 9 meV per  $\text{YH}_3$  was found. The optimal angle cannot be accurately determined since the small energy variation near the minimum (0.4 meV over a  $10^\circ$  range) is reaching the limit of the calculation. It is likely to be larger than that in  $\text{HoD}_3$  which is about  $10^\circ$  [6]. Because of the light mass of  $H(D)$ , the zero-point motion needs to be considered and will be the subject of future studies.

In Figs. 4(a) and 4(b), we show the calculated energy bands near the Fermi level before and after the distortions, respectively. They are labeled at  $\Gamma$  according to the irreducible representations of the point group  $D_{3d}$  [19]. Because of the symmetry change, the electron pocket at  $K$  in Fig. 1 is now at  $\Gamma$  in Fig. 4(a) and is doubly degenerate. By comparing Figs. 4(a) with 4(b), it is clear that the two crossing bands of the same symmetry ( $1^-$  at  $\Gamma$ ) are affected by the potentials arising from the hydro-

gen displacements and a gap is opened. These two bands are associated with yttrium  $xz$  and hydrogen [both  $H(T)$  and  $H(M)$ ]  $s$  functions, respectively. The distortions of  $H(T)$  and  $H(M)$  have similar effects and are added concurrently. As a result, the separation of the two  $1^-$  states at  $\Gamma$  have increased from 1.38 to 3.03 eV.

The other two bands have different symmetry ( $2^+$  and  $2^-$  at  $\Gamma$ ) and remain crossing near the Fermi level. Therefore, the LDA ground state is a compensated semimetal with an electron (hole) density of about  $5 \times 10^{20}/\text{cm}^3$ . This is not in contradiction with the photoemission results [20] which suggested this material to be poorly metallic or semiconducting. However, it is tempting to speculate that the true ground state may be an excitonic insulator [9] (a condensate of bound electron-hole pairs). It has been shown [21] that if a compensated semimetal has isotropic electron and hole bands, at  $0^\circ$  K the normal state is always unstable against the spontaneous formation of excitons. Using an effective mass of  $0.4m$  and an energy overlap of 1.3 eV [Fig. 4(b)] and assuming an interband dielectric constant of 10 (5), the energy gap expression in Ref. [21] yields a value of 0.30 (0.47) eV. With a BCS-like relation between the gap and the transition temperature [21], the transition temperature is of the order of 1000 K.

If the bands are anisotropic, the instability will occur only if the density of electrons and holes are not too large [9]. Although the carrier density in the present case is not too low, it is noted that the cross sections of the electron and hole pockets at  $k_z = 0$  are almost circular. It is also noted that the anisotropy of the hole pocket is greatly reduced by the hydrogen displacements, as shown in Fig. 4, which makes the final excitonic state more favorable. In addition, the energy bands affected by the hydrogen displacements (with  $1^-$  symmetry at  $\Gamma$ ) are within a few tenths of eV from the Fermi level on the  $\Gamma$ - $K$ - $M$  plane

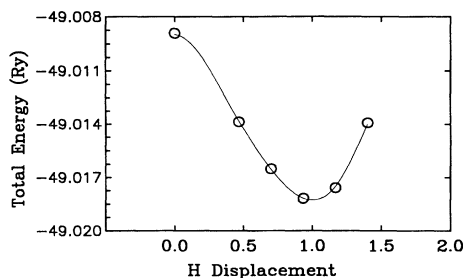


FIG. 3. Total energy per cell as a function of simultaneous displacements of  $H(M)$  and  $H(T)$  (scaled by the equilibrium values). The circles are the calculated values and the solid line is a fit.

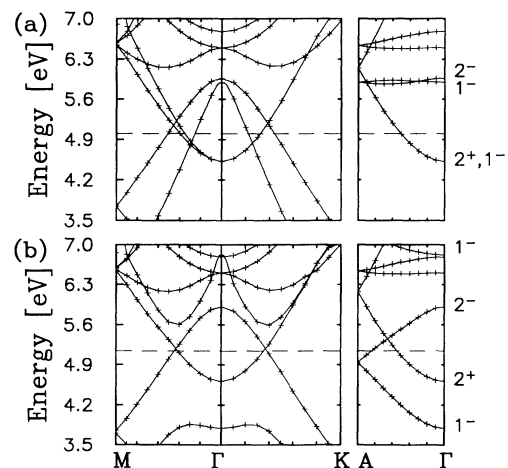


FIG. 4. Energy bands of  $\text{YH}_3$  in the Brillouin zone of the tripled cell (a) prior to and (b) after hydrogen distortions.

and around  $A$ . It may indicate that the electron-phonon interaction cannot be totally neglected in the study of the excitonic insulating phase.

It was speculated that the cubic trihydrides of early RE elements might be excitonic insulators and this was used to explain the metal-semiconductor transitions in highly nonstoichiometric La and Ce trihydrides [22]. However, there have been some disagreements in different calculations about whether there is a band overlap in these cubic trihydrides. In addition, the real situation is complicated by the nonstoichiometry and the occurrence of a cubic-tetragonal structural transition in the same temperature range. In comparison, in the present case the stoichiometric  $\text{YH}_3$  is shown to have a band overlap of over 1 eV and the hydrogen displacements are in agreement with the neutron diffraction data [6, 7]. It may be a promising system to investigate the possibility of an excitonic insulating state. Further experimental studies will be needed to resolve these issues.

In summary, we have studied yttrium trihydride in the hexagonal structure by pseudopotential local-density calculations. The calculation showed that the  $\text{HoD}_3$ -type structure is energetically more favorable than the cubic structure. The wavelike hydrogen displacements are identified as Peierls distortion connected to the unusual electronic structure of the system. The energy bands that are affected by these distortions open a gap at the Fermi level, while the remaining electron and hole pockets at  $\Gamma$  may favor an excitonic insulator phase.

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