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## On the dynamical stability and metallic behavior of $\text{YH}_3$ under pressure

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We report on the behavior of structural and electronic properties of yttrium trihydride under pressure using first principles calculations. We show that  $\text{YH}_3$  undergoes a structural transformation and its high pressure phase is dynamically stable under pressure since the peak at the imaginary frequencies of the phonon density of states, which account for the structural instability disappears at high pressure. Additionally, our GW calculations indicate a metallization of the high pressure cubic phase of  $\text{YH}_3$ . © 2009 American Institute of Physics. [DOI: 10.1063/1.3155505]

The understanding of the electronic structure of metal hydride systems is not only interesting from a fundamental point of view but it is also important to understand technologically important phenomena such as hydrogen desorption, catalysis, and storage. The present study is motivated by the fact that when yttrium and most of the rare-earth metals are exposed to a hydrogen atmosphere, they form hydrides that may exhibit a reversible metal-insulator transition, and this observation has attracted a great amount of attention over the past years. Huiberts *et al.*<sup>1</sup> reported that thin films of  $\text{YH}_x$  and  $\text{LaH}_x$  have valuable optical properties because they can be switched between shiny mirror and transparent window depending on the hydrogen content. Some interesting questions to be answered are as follows: What happens when an external pressure is applied on  $\text{YH}_3$ ? Does the energy band gap of  $\text{YH}_3$  decrease with pressure and if so, does it close completely toward a metallic state of  $\text{YH}_3$ ? In other words, does  $\text{YH}_3$  show a metal-insulator transition under pressure as yttrium does upon hydrogenation? In some way this question was put forward already a few years ago when Ahuja *et al.*<sup>2</sup> predicted that  $\text{YH}_3$  undergoes a structural phase transformation induced by pressure from hexagonal to cubic phase at 1.5 GPa. Additionally, they predicted a metallic state for the new high pressure cubic phase of  $\text{YH}_3$ . However, such prediction was ruled out by Wijngaarden *et al.*<sup>3</sup> who used high pressure diamond anvil cell and optical measurements. They have obtained neither the cubic phase nor the insulator-metal transition at pressures up to 25 GPa. By extrapolating their data they would expect the metallic behavior of  $\text{YH}_3$  at pressures only above 55 GPa. Latter, Palasyuk and Tkacz<sup>4</sup> found an evidence of the cubic phase of  $\text{YH}_3$  but unfortunately they were not able to stabilize a pure high pressure phase and reported the coexistence of hexagonal and cubic phases in the pressure range 5–25 GPa. The synthesis of the pure cubic phase of  $\text{YH}_3$  (Refs. 5 and 6) along with its Raman spectra at high pressure were recently reported.<sup>7,8</sup>

It was observed several years ago using x-ray and neutron-diffraction measurements that yttrium and most of the rare-earth elements form trihydrides, which crystallize in hexagonal,  $\text{HoD}_3$ -type, structure at ambient conditions.<sup>9,10</sup> However, there still exists a debate on the ambient crystal

structure of  $\text{YH}_3$ . Kelly *et al.*<sup>11</sup> using molecular dynamics simulations showed that the energy of another hexagonal structure having space group  $P6_3$  is lower than that of  $\text{HoD}_3$  structure and a gap opens up by lowering the symmetry. The  $P6_3$  structure was ruled out by neutron-diffraction experiments performed on powder samples and on epitaxial thin films.<sup>12–14</sup> Instead, the neutron data were more consistent with structures having space groups  $P\bar{3}c1$  and  $P6_3cm$ . Wolf and Herzig<sup>15</sup> performed *ab initio* calculations and showed that the energy difference for the  $P6_3$ ,  $P\bar{3}c1$ , and  $P6_3cm$  structures is about 0.001 eV per formula unit. They found that these structures are degenerated in energy and thus cannot be theoretically resolved just by total energy calculations. Here we focus our attention on the  $P\bar{3}c1$  ( $\text{HoD}_3$ ) structure because it was observed in recent neutron-diffraction experiments.<sup>16</sup> We would like to note that the three crystal structures possess almost the same total energy and a different choice would not change our main conclusions.

In this letter we show that  $\text{YH}_3$  undergoes a structural phase transformation from hexagonal to cubic phase under pressure and we explain the metallic behavior of cubic  $\text{YH}_3$  by calculating the electronic properties using the GW approximation to the self-energy. Additionally, we have performed lattice dynamics calculations to investigate the dynamical stability of  $\text{YH}_3$  at high pressure.

The phase stability of  $\text{YH}_3$  under pressure was studied by means of first principles calculations in the framework of density functional theory. Total energies for hexagonal and cubic phases of  $\text{YH}_3$  were calculated using the projected augmented wave (PAW) method as implemented in VASP code.<sup>17</sup> We have used the generalized gradient approximation for the exchange and correlation potential within the Perdew–Wang parametrization.<sup>18</sup> The PAW potentials<sup>19</sup> with the valence states  $1s$  for H and  $4s$ ,  $4p$ ,  $5s$ , and  $4d$  for Y and a basis set up to a kinetic-energy cutoff of 500 eV were used. For the sampling of the Brillouin zone we used an  $8 \times 8 \times 8$   $\mathbf{k}$ -points grid generated according to the Monkhorst–Pack scheme.<sup>20</sup> The crystal structures were optimized at each volume by force and stress minimization in which the atoms are moved toward their equilibrium positions. All the calculations were carried out until the Hellmann–Feynman forces become smaller than  $10^{-3}$  eV/Å and the total energies con-

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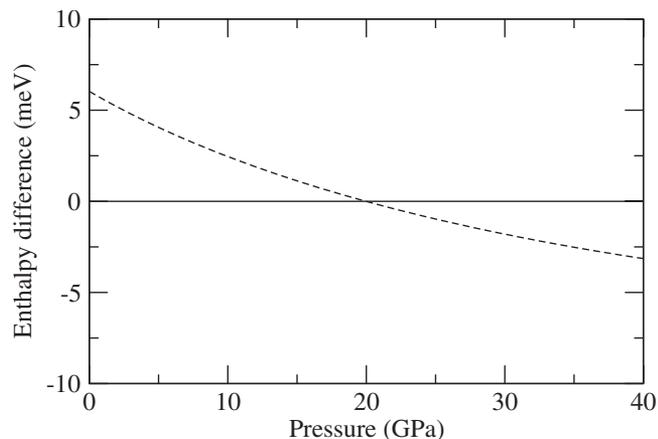


FIG. 1. Enthalpy difference as a function of pressure for  $\text{YH}_3$  in the hexagonal (full line) and cubic (dashed line) crystal structures. The enthalpy of hexagonal phase is taken as reference energy.

verged to below  $10^{-4}$  eV with respect to the Brillouin zone integration.

The total energies ( $E$ ) and volumes ( $V$ ) were fitted by a Murnaghan<sup>21</sup> equation of state (EOS), where the equilibrium volume ( $V_0$ ), bulk modulus ( $B_0$ ) at ambient pressure, and its first derivative ( $B'_0$ ) were determined for each structure. Using the EOS for the hexagonal structure, we obtained  $V_0 = 23.1 \text{ cm}^3/\text{mol}$ ,  $B_0 = 69 \text{ GPa}$ , and  $B'_0 = 3.6$ , whereas for the cubic structure we found  $V_0 = 21.2 \text{ cm}^3/\text{mol}$ ,  $B_0 = 95 \text{ GPa}$ , and  $B'_0 = 3.8$ . We have then calculated the hydrostatic pressure ( $P$ ), which is the first derivative of energy with respect to volume. The crystal phase stability is analyzed by evaluating the enthalpy ( $H = E + PV$ ). The most stable phase is thus the one which has the lowest enthalpy at a given pressure and the transition pressure is obtained at a pressure, which is the crossing point of enthalpy of the different crystal structures. To calculate the phonon band structure and density of states, the phonon software<sup>22</sup> with the *ab initio* force-constant method<sup>23</sup> was used. A series of small displacements corresponding to  $0.03 \text{ \AA}$  is required to calculate the

Hellmann–Feynman force constant properly. The conditions for translational and rotational invariance are applied to obtain the exact acoustic modes.

In Fig. 1, we show the calculated enthalpy difference as a function of pressure for the hexagonal and cubic phases of  $\text{YH}_3$ . Our calculations correctly describe the ground state of  $\text{YH}_3$  and we find that the hexagonal phase is energetically more favorable near the equilibrium volume. However, under compression the hexagonal  $\text{YH}_3$  undergoes a structural phase transformation and the cubic phase becomes energetically more stable. In the cubic phase, yttrium atoms occupy the positions of a face-centered-cubic lattice while the hydrogen atoms are located at the tetrahedral and octahedral sites. Similar phase transitions from  $\text{HoD}_3$ -type to cubic structure have been theoretically predicted and experimentally observed in some metal trihydrides such as  $\text{ErH}_3$ .<sup>24,25</sup> Our calculated transition pressure is at 20 GPa, which is one order of magnitude larger than the early result of 1.5 GPa reported by Ahuja *et al.*<sup>2</sup> Our value is in good agreement with the experimental result of 21 GPa observed by Watanuki and co-workers.<sup>5,6</sup> The main difference between the calculated values is likely due to the geometry optimization of the cells. By including relaxation effects, which were not taken into account in the early calculations, the total energy is lowered and the hexagonal phase remains stable for a wider pressure range and we suggest that this effect rises the transition pressure.

In Fig. 2, the phonon dispersion relations and the corresponding densities of states for cubic  $\text{YH}_3$  are shown at pressures below and above the phase transition. The phonon dispersion relations possess three distinct regimes. The highest vibrational modes are due to vibrations of H atoms whereas the vibrations of the Y atoms play the most prominent role in the lowest modes. The middle modes form a bridge of vibrations between Y–H atoms, which are stabilized at high pressure (28 GPa) but they become unstabilized when the pressure is lowered. The one optical mode at the  $L$  point gives rise to a high peak in the imaginary frequency regime and this could drive the dynamical instability.

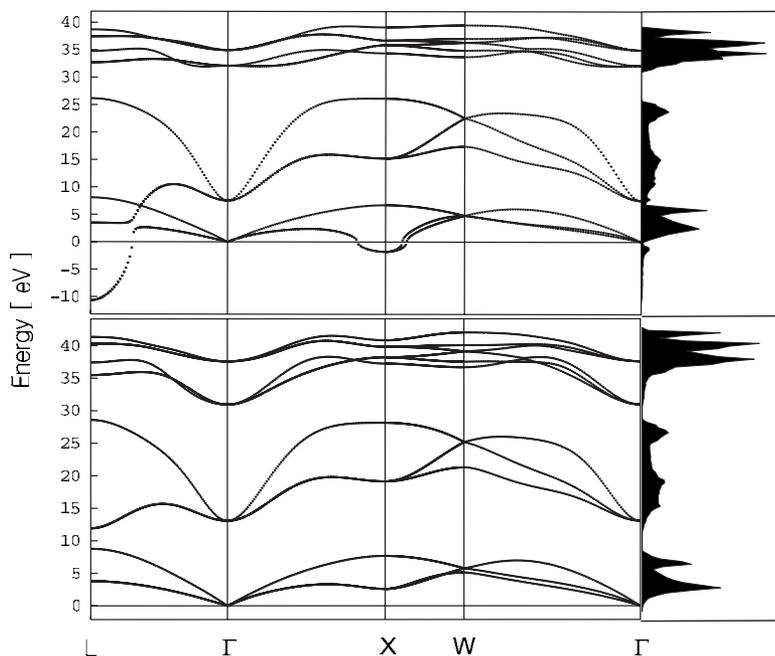


FIG. 2. The phonon dispersion relation at 11 GPa (upper panel) and 28 GPa (lower panel) of the cubic phase of  $\text{YH}_3$ . The shaded area plots at the right side represent the corresponding phonon densities of states.

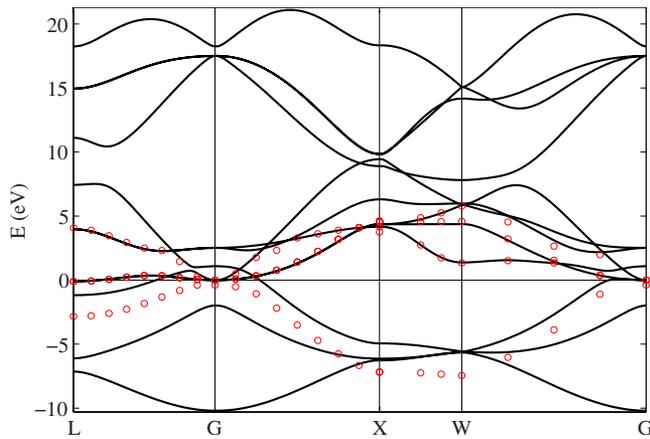


FIG. 3. (Color online) Electronic band structure (lines) and GW corrections (circles) along the high symmetry lines in the Brillouin zone for the cubic phase of  $\text{YH}_3$ . The Fermi level is set as zero energy and indicated by a horizontal full line.

The effect of pressure on the electronic properties of cubic  $\text{YH}_3$  is investigated through the band structure. In Fig. 3, we plot the electronic band structure along with the GW corrections<sup>26</sup> for the cubic phase of  $\text{YH}_3$  and we see that it is unlikely to open a gap. By analyzing Fig. 3, we found that the valence band is mostly due to the hybridization between Y  $d$  and H  $s$  states whereas the conduction band is primarily formed by Y  $d$  states. Clearly, we see that the Fermi level lies in the conduction band giving rise to a metallic state. In fact, the GW corrected band overlap at the  $\Gamma$  point is 0.38 eV. However, if the  $4p$  states of Y are taken into account in the calculations as semicore states, the overlap is reduced to 0.15 eV whereas if  $4s$  and  $4p$  states are included as semicore states, the overlap is further reduced to 0.12 eV. Therefore, our calculations indicate a metallization of the high pressure cubic phase of  $\text{YH}_3$ .

In conclusion, we show that  $\text{YH}_3$  undergoes a pressure-induced structural transformation to a cubic metallic phase. We show that relaxation effects are very important for the structural stability of  $\text{YH}_3$  under pressure and our calculated transition pressure is in good agreement with recent experimental results. The peak in the imaginary frequency regime of the phonon density of states disappears with increasing of pressure and the cubic phase becomes dynamically stable. Therefore, our findings explain the structural stability of the

cubic phase of  $\text{YH}_3$  and its metallic behavior at high pressure, confirming the earlier prediction and also recent experimental results.

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