

# Ab-initio Investigation of the Hydrogenation of Y

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## Abstract

We present an *ab-initio* electronic structure study of a face centred (fcc) cubic Y lattice, which is subsequently filled with hydrogen in tetrahedral and octahedral sites. The stoichiometry of the calculated compounds is Y,  $\text{YH}_2^{\text{tetra}}$ ,  $\text{YH}_3$  and  $\text{YH}_1^{\text{octa}}$ . Upon placement of hydrogen in tetrahedral sites we note for the  $\text{YH}_2^{\text{tetra}}$  phase a new, fully occupied hydrogen related band and a redistribution in the d-band manifold at the Fermi level. Interestingly during the fcc  $\text{Y} \rightarrow \text{YH}_2^{\text{tetra}}$  transition the overall topology of the Fermi surface (FS) is not changed, but we note a change in character from  $t_{2g}$  to  $e_g$  of the responsible band. It is this change to  $e_g$  character which allows subsequent H in octahedral sites to significantly interact with the FS, finally enabling the metal-insulator transition while reaching  $\text{YH}_3$ . A placement of hydrogen solely in octahedral sites does not affect significantly the  $t_{2g}$  d-band at the Fermi level.

## 1. Introduction

The valence electronic structure of rare earth hydrides is both technologically important and fundamentally interesting. Potential optical applications can be envisioned based on the recent discovery of Huiberts *et al.* [1] of a reversible (switchable) metal-insulator (Me-I) transition between the reflecting, metallic dihydride and the insulating, transparent trihydride. In a simple ionic picture this transition corresponds to a complete capture of the three Y valence electrons  $[\text{Ar}]4d^1 5s^2$  by the three, then negatively charged  $\text{H}^-$  ions. However, in a single particle picture hybridization will not allow the H atoms to remove all valence electrons and the system remains metallic. Indeed LDA calculations [2] show a metallic state for  $\text{YH}_3$ . The only way a (still insufficiently small) gap could be obtained was via a Peierls type symmetry breaking of the complicated  $\text{HoD}_3$  structure [2]. This argument certainly fails for the sister compound  $\text{LaH}_x$ , which does exhibit a similar Me-I transition without complicated crystal structure changes. Later on, various models [3,4] including strong electron correlations reproduced the insulating ground state and led to a deeper understanding of the electronic interaction between hydrogen and the metallic host lattice. Special emphasis was drawn to the peculiar properties of  $\text{H}^-$ , whose insufficient description within LDA, is believed to cause the wrong ground state for  $\text{YH}_3$ . The debate whether strong electron correlations play a role or not in this material are ongoing, since recent GW calculations are able to reproduce the insulating ground state without use of strong correlations [5–7].

In the present paper, we deliberately assume a very simple fcc based structure for  $\text{YH}_x$  (Fig. 1(a)). This assumption decouples effects arising from crystal structure changes (such as the complicated  $\text{HoD}_3$  structure proposed

for  $\text{YH}_3$ ) from the effects of hydrogenation as calculated via LDA. In this sense the paper follows the spirit of the pioneering calculations of Switendick [8] with the benefit of higher accuracy (self consistency) and recent experimental and theoretical developments, which initiate a critical assessment of the obtained LDA based band structures.

## 2. Computational details

The electronic structure calculations are based on Density Functional Theory (DFT) and the full potential linearized augmented plane wave code FPLAPW Wien2k [9] was employed. There the unit cell is divided into non-overlapping atomic spheres (muffin tin) and an interstitial region. In the muffin tin region the basis functions are comprised of atomic-like wavefunctions while the interstitial region is described with plane wave basis functions.

The crystallographic structure for the four studied compounds is derived from the published experimental structure of  $\text{YH}_2$  [10]. A lattice constant of 5.6201 Å was assumed for all calculated hydrides. The sole difference between the structures are the number and the positions of the incorporated hydrogen atoms. It is assumed that the Y sublattice is not distorted and remains fcc, independent of the degree of hydrogen filling. The fcc metal lattice and the octahedral and tetrahedral hydrogen lattice sites are sketched in Fig. 1(a). Figures 1(b) and (c) display calculated FSs of fcc Y and  $\text{YH}_2$ , respectively (see below).

With regard to the specific Wien2k related parameters, we used a muffin tin radius for rare earth atoms and hydrogen atoms of 1.16 and 0.85 Å, respectively. Self-consistency was judged to be, when the total energy change was less than 0.1 mRy in subsequent cycles. The calculation was based on 10 000 k-points, which corresponds to 286 k-points in the irreducible wedge of the Brillouin zone (BZ). After obtaining self-consistency, the eigenvalues were determined along some high symmetry lines as shown in Fig. 2.

## 3. Results

**Yttrium:** The computed band structure for fcc yttrium (Fig. 2(a)) is typical for a fcc transition metal. The trivalent Y gives rise to an sp-band (open dots), with a binding energy of  $-4.6$  eV at  $\Gamma$  and a partially occupied d-band manifold. A band with  $t_{2g}$  character (black dots) cuts the Fermi level between  $\Gamma$  and X, while the bands with  $e_g$  symmetry (grey ovals) remain above the Fermi level.

**$\text{YH}_2^{\text{tetra}}$ :** Experimentally an exposure of the clean metal to hydrogen leads to the formation of the dihydride phase,

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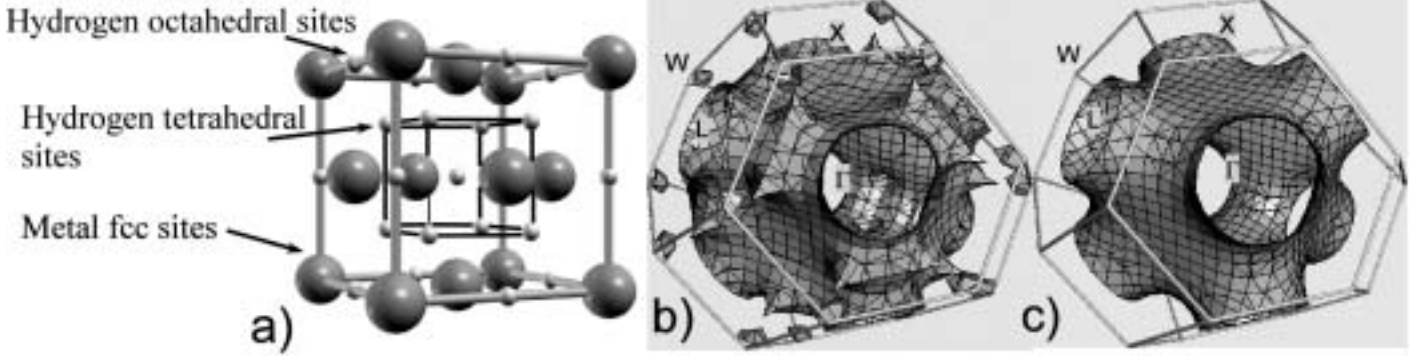


Fig. 1. (a) fcc lattice with occupied octahedral and tetrahedral sublattices. (b) FS for fcc Y and (c) YH<sub>2</sub>.

where hydrogen occupies tetrahedral sites. The corresponding band structure is shown in Fig. 2(b). The aforementioned Y *sp*-band (open dots) hybridizes with the H 1s state, leading to an almost rigid shift of this band by 3.4 eV to higher binding energies. Accordingly the position at the  $\Gamma$  point changes from  $-4.6$  to  $-8$  eV. A new band is formed above the Y *sp*-band of almost entirely H 1s character (open rectangles in Fig. 2(b)). It is found between the Y *sp*-band (open dots) and the *d*-band (grey ovals). There is an indirect energy overlap between this band at its maximum at the  $\Gamma$  point and Y *d*-bands at its minimum at the X point. Correspondingly the dihydride remains metallic, even for a considerable Fermi level lowering (in a rigid band model) upon further hydrogen uptake as suggested in an ionic picture. Furthermore, the hydrogenation affects very much the aforementioned *d*-band of *t*<sub>2g</sub> character (black dots), which was cutting the Fermi level between  $\Gamma$  and X for the pure metal (Fig. 2 (a)). This band (black dots in Fig. 2(b)) does not cut the Fermi level anymore and has acquired instead an upwards dispersion between  $\Gamma$  and X. Very importantly the FS is now formed solely by one *d*-band of *e*<sub>g</sub> symmetry (grey ovals in Fig. 2(b)). Recently it has been experimentally confirmed by angle-resolved photoemission that this single band hydride FS is indeed largely correct for ScH<sub>2</sub>, YH<sub>2</sub>, GdH<sub>2</sub> and LaH<sub>2</sub> [11]. This symmetry change due to the strong interaction between H in tetrahedral sites and the Y *t*<sub>2g</sub> band is exploited in the formation of the trihydride phase.

**YH<sub>3</sub>**: A further exposure to hydrogen leads to the formation of the trihydride phase, which is characterized by the hydrogen occupation of tetrahedral and octahedral sites. The calculated band structure for fcc YH<sub>3</sub> is shown in Fig. 2(c). The band bottom of the initial Y *sp*-band is now found at approximately  $-10$  eV (open dots in Fig. 2(c)) and the YH<sub>2</sub><sup>tetra</sup> related H 1s band (open rectangles) is virtually unaffected. The addition of octahedral hydrogen leads to an upwards dispersion of the *e*<sub>g</sub> band (grey ovals) between  $\Gamma$  and X. Again the introduction of hydrogen leads to the formation of one new band (black rectangles in Fig. 2(c)), which is partially unoccupied and overlaps with the *d*-derived bands (circled in Fig. 2 (c)). As explained in the introduction, this renders the trihydride a LDA metal, which is in disagreement to the experimental data.

**YH<sub>1</sub><sup>octa</sup>**: In order to deepen our band analysis, we calculated the electronic band structure for a fcc Y lattice with H solely in octahedral sites and the result is shown in Fig. 2(d). We note a very similar Y *sp*-band (black dots in Fig. 2(d)) for the YH<sub>1</sub><sup>octa</sup> structure (Fig. 2(d)) compared to the YH<sub>2</sub><sup>tetra</sup> (Fig. 2(b)) structure. Obviously, compared to fcc Y, the *t*<sub>2g</sub> derived *d*-band (black dots) between  $\Gamma$  and X remains at its position at the Fermi level, *E*<sub>F</sub>, similar to the pure metal (Fig. 2(a)). The *e*<sub>g</sub> derived band (grey ovals) is lowered in binding energy compared to the fcc Y case. For YH<sub>1</sub><sup>octa</sup> the largest changes appear for the  $\Gamma$ L direction and not for the  $\Gamma$ X direction. For  $\Gamma$ L we note a H 1s derived band (grey rectangles), which now cuts the Fermi level.

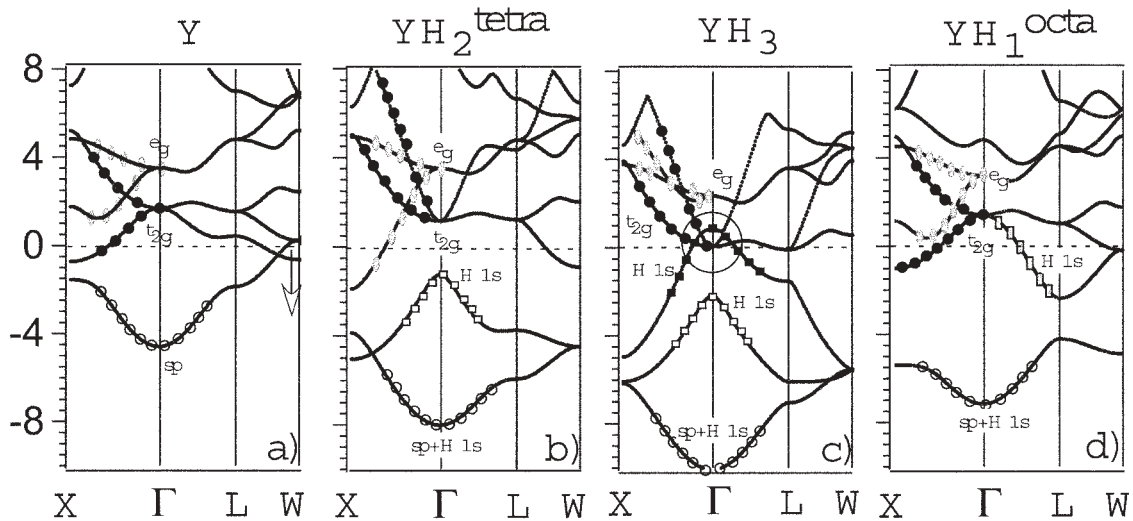


Fig. 2. Band structure along high symmetry directions for (a) fcc Y (b) fcc YH<sub>2</sub><sup>tetra</sup>. (c) fcc YH<sub>3</sub>. (d) fcc YH<sub>1</sub><sup>octa</sup>. Different symbols represent different orbital character (see text).

#### 4. Discussion

The preceding results illustrate a number of important hydrogen related electronic structure changes. We note a considerable lowering of the Y sp-band (open dots) by 3.4 eV for  $Y \rightarrow YH_2^{tetra}$  and by 2 eV for  $YH_2^{tetra} \rightarrow YH_3$ , which might explain the readiness of H-incorporation into the lattice. Furthermore, we observe a strong interaction between H in *tetrahedral* sites and Y d-states of  $t_{2g}$  symmetry (black dots), while *octahedral* sites interact mainly with  $e_g$  d-states (grey ovals). It is to be pointed out that the general shape of the FS is conserved during the transition between fcc Y and  $YH_2^{tetra}$ . The FSs for the pure metal and  $YH_2^{tetra}$  are shown in Fig. 1(b) and (c). The difference is just that the FS in the Y case is due to a  $t_{2g}$  band, while in the  $YH_2^{tetra}$  case it is derived from an  $e_g$  band (as compared with the corresponding band structures in Fig. 2(a) and (b)). In addition slight deviations occur in the vicinity of the W point, which could easily be removed by a rigid shift (arrow in Fig. 2(a)) of the Y sp-band (black dots) for the pure metal. The general shape of these FSs (Fig. 1(b) and (c)) is a warped cube with protruding necks extending in the  $\Gamma L$  direction. Contrarily the FS is largely different for  $YH_1^{octa}$  due to the  $E_F$  crossing of a H 1s related band between  $\Gamma$  and L. In addition to the very different FS, we note a partially unoccupied band of hydrogen character (grey rectangles Fig. 2(d)), which does not give rise to the same stability as the completely filled H 1s related band for the dihydride (open rectangles Fig. 2(b)). Accordingly the formation of  $YH_2^{tetra}$  is naturally preferred. The occupation of both, tetrahedral and octahedral sites then induces a new band, which overlaps only slightly with the Y d-band manifold. In this sense,  $YH_3$  is an “almost” insulator.

Since experimental probes of the occupied band structure in general do not detect major insufficiencies of the LDA band structure for the dihydride phase, it would be now quite tempting to ascribe the shortcomings of LDA to an insufficient description of H in octahedral sites. In terms of the many-body theoretical model of Ng *et al.* [3] for the related  $LaH_x$  system this is only partially correct. If one compares their band structure for  $LaH_2$  and  $LaH_3$  one notices as a major difference to the LDA based band structures a flattening (localization) of LDA bands. For the dihydride this affects primarily an unoccupied  $t_{2g}$  band, which does not give rise to a major change in the physical properties of the material. On the other hand for the trihydride, the flattening of the uppermost H related band leads to the aforementioned opening of a gap. One expects in this framework, that correlation effects are especially strong for the trihydride phase, since the calculated renormalization parameters of the overlap integrals are much larger for the interaction between H in tetrahedral and octahedral sites, compared to the coupling parameters via metal d-states. Nevertheless, the many-body band structure for the dihydride is modified compared to the LDA case as well. The correlation effects are simply not “visible” as they do not lead to a gap opening.

One could then ask, whether the dihydride phase is important at all for the switching of the material or if it (in light of its natural occurrence for all heavy rare earths)

even acts as a precursor state? We believe yes and one important feature turns up in our presented calculations. It is the hydrogen induced change of the d-band character at  $E_F$ . The strong interaction of tetrahedral hydrogen with  $t_{2g}$  d-bands leads to a FS which is comprised of states with strong  $e_g$  character. These states were shown to heavily interact with octahedral hydrogen states, as they are provided during the dihydride  $\rightarrow$  trihydride transition. One is tempted to interpret the fcc dihydride phase with a partially occupied  $e_g$  band as the natural template for hydrogen absorption in octahedral sites, which annihilates large parts of the dihydride FS. An “almost-insulator” state with a rather unstable partially filled H 1s related band (filled rectangles in Fig. 2(c)) is therefore reached and the various scenarios for the Me-I transition might or might not take place. This interpretation is supported by the natural occurrence of the dihydride phase for all the rare earths.

#### 5. Conclusion

We have presented *ab-initio* calculations for Y,  $YH_2^{tetra}$ ,  $YH_3$  and  $YH_1^{octa}$  all in the fcc structure. We found important changes in the spherical harmonics decomposition of the charge density at  $E_F$  upon hydrogenation. We identify the  $YH_2^{tetra}$  phase as the natural precursor for the trihydride formation. The observation of the transition from a  $t_{2g}$  derived Y FS to an  $e_g$  derived  $YH_2^{tetra}$  FS is an achievement of band theory and presents an extension of the simple ionic picture, which *a priori* does not distinguish between hydrogen in octahedral and tetrahedral sites.

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#### References

- Huiberts, J. N. *et al.*, Nature **380**, 231 (1996).
- Kelley, P. J., Dekker, J. P. and Stumpf, R. Phys. Rev. Lett. **78**, 1315 (1997).
- Ng, K. K., Zhang, F. C., Anisimov, V. I. and Rice, T. M., Phys. Rev. Lett. **78**, 1311 (1997).
- Eder, R., Penn, H. F. and Sawatzky, G. A., Phys. Rev. B **56**, 10115, (1997).
- van Gelderen, P., Bobbert, P. A., Kelly, P. J. and Brocks, G., Phys. Rev. Lett. **85**, 2989 (2000).
- van Gelderen, P., Bobbert, P. A., Kelly, P. J., Brocks, G. and Tolboom, R., Phys. Rev. B **66**, 075104 (2002).
- Miyake, T., Aryasetiawan, F., Kino, H. and Terakura, K., Phys. Rev. B **61**, 16491 (2000).
- Switendick, A. C., Sol. State Commun. **8**, 1463 (1970).
- Blaha, P. Schwarz, K. and Luitz, J., Comput. Phys. Commun. **59**, 399 (1990). Improved and updated UNIX version of the original copyrighted WIEN code by P. Blaha, K. Schwarz and P. Sorantin.
- Pearsson, “Pearson’s Handbook of Crystallographic Data for Intermetallic Phases,” American Society for Metals, Metals Park, OH 44073 (3000).
- Koitzsch, C., unpublished.