

## Parameter-Free Quasiparticle Calculations for $\text{YH}_3$

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Electronic structure calculations for  $\text{YH}_3$  within the local density approximation result in a metallic ground state with the bands at the Fermi energy overlapping by more than 1 eV, whereas a band gap of 2.8 eV is deduced from optical experiments. Here, we report the results of parameter-free *GW* calculations which predict a fundamental gap of 1 eV. When we take into account electric dipole matrix elements a large optical gap of almost 3 eV is obtained. A combination of photoemission and inverse photoemission spectroscopy could test the prediction of a small fundamental band gap.

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Recently, Huiberts *et al.* [1] discovered a spectacular metal-insulator (MI) transition in thin films of  $\text{YH}_x$  and  $\text{LaH}_x$  as  $x$  approaches 3. In the metallic dihydride phase these layers appear mirrorlike, whereas the insulating trihydride phase is transparent for visible light. The transition is reversible, and occurs at room temperature and at moderate hydrogen pressures, making it easy to observe experimentally. Because the hydrogen-to-yttrium ratio can be easily varied these layers can be used as “switchable mirrors,” which opens up the possibility of a range of interesting technological applications. Since the basic mechanism underlying the MI transition is still poorly understood, progress in trying to improve the performance of switchable mirror devices is made largely empirically.

The absorption edge of  $\text{YH}_3$  is found at 2.8 eV in optical reflection and transmission experiments [2]. Since these experiments probe only symmetry-allowed direct transitions, the fundamental band gap may be quite different. The strongest evidence for the existence of a fundamental band gap comes from the increase of the electrical resistivity by at least 2 orders of magnitude as the trihydride phase is formed [1]. The negative temperature coefficient of the resistivity and its inverse proportionality to  $\delta$  in substoichiometric  $\text{YH}_{3-\delta}$  support the conclusion that  $\text{YH}_3$  is a semiconductor. Unfortunately, it has not been possible to obtain an estimate of the size of the fundamental gap from the temperature dependence of the resistivity measurements [3].

It is the purpose of the present paper to provide a coherent picture of the electronic structure of  $\text{YH}_3$  consistent with all experimentally known data without introducing any unknown parameters. We will argue that the fundamental band gap of  $\text{YH}_3$  is only 1.0 eV and that vanishing electric dipole matrix elements prevent this transition from being seen in the optical experiments performed up till now. Our conclusions are based on calculations of the

single-particle excitation spectrum within the dynamically screened *GW* approximation [4].

There is a huge discrepancy between the measured gap of 2.8 eV and the value calculated using the local density approximation (LDA) of density functional theory. These calculations predict band *overlaps* of about 1.3 eV [5,6] for  $\text{YH}_3$  in the experimentally observed, so-called HoD<sub>3</sub> structure [7,8]. LDA calculations are known to severely underestimate the band gaps of many materials [9,10], but the present discrepancy is exceptionally large. Because this discrepancy is comparable to what is found in transition metal oxides such as NiO, where a strong Coulomb interaction between the transition metal *d* electrons plays an important role and is poorly described by the LDA, it has been suggested that a similarly strong Coulomb interaction between the electrons on hydrogen sites may be responsible for the large gap in  $\text{YH}_3$ . On the basis of parametrized model Hamiltonians for  $\text{LaH}_3$  and  $\text{YH}_3$ , respectively, Ng *et al.* [11] and Eder *et al.* [12] showed that such correlated models can indeed lead to the formation of large band gaps. These authors adopt an atomiclike viewpoint in which the metal ions donate their outer three electrons to the hydrogen atoms, and view these materials essentially as lattices of  $\text{H}^-$  ions perturbed by the metal ion sublattice. They argue that large correlation effects in a  $\text{H}^-$  ion are not well accounted for in an LDA calculation causing the H-derived valence bands in  $\text{YH}_3$  to overlap with the Y-derived conduction bands.

Apart from the issue of strong correlations, there is an obvious problem associated with the LDA description of atomic hydrogen even on the single-particle level. Although the LDA total energy of the single electron  $\text{H}^0$  is very close to the exact value, the 1*s* eigenvalue of the Kohn-Sham (KS) equation is only roughly half the exact 1*s* electron binding energy [13]. As a result, the position of the LDA bands derived from the atomic 1*s* state may

differ considerably from the true position of the corresponding one-electron levels. It is also well known that, in general, the KS eigenvalues—the conventional one-electron band structure—if interpreted as one-electron excitations, severely underestimate the electronic band gap, even for materials such as Si or Ge which are not strongly correlated [14,15]. In order to examine the one-particle excitation energies, one should solve Dyson's equation for the single-particle Green's function expressed in terms of the self-energy operator  $\Sigma$ . The self-energy operator can be expanded as a perturbation series in the Green's function  $G$  and the dynamically screened Coulomb interaction  $W$ . The so-called  $GW$  approximation introduced by Hedin [4] includes only the first term in this series, which is symbolically written as  $GW$ . In addition, one usually assumes a quasiparticle (QP) expression for the Green's function  $G$ . For a large number of semiconductors and insulators such calculations produce band gaps which are very close to experimental single-particle band gaps [9,10,16]. Even for transition metal oxides such as NiO [17] and MnO [18], where electron correlations play a considerable role,  $GW$  calculations produce gaps which are much closer to experiment than the values obtained in LDA calculations.

In our  $GW$  calculations we use the space-time approach suggested by Rojas *et al.* [19] and essentially follow the implementation described by van der Horst *et al.* [20]; details will be published separately later. Input data for the  $GW$  calculation consist of the electronic wave functions and energies obtained from LDA calculations [21]. For an  $Y_2H_6$  unit cell with the so-called  $LaF_3$  structure (see below) we used a  $(6 \times 6 \times 4)$   $\mathbf{k}$ -set, an  $(8 \times 8 \times 14)$  real-space grid, and a total of 200 bands in the  $GW$  calculation. By varying the size of the real space and reciprocal space grids we estimate that QP energies are converged within 0.1 eV. The convergence with respect to the time and frequency grids, and with respect to the number of unoccupied bands included in the calculation, is even better. For the  $Y_6H_{18}$  unit cell (the  $HoD_3$  structure, see below) we used a  $(4 \times 4 \times 4)$   $\mathbf{k}$ -set, a  $(12 \times 12 \times 12)$  real-space grid, and 300 bands. We have studied the effect of including the nondiagonal matrix elements of the self-energy operator (using the LDA wave functions as a basis set) when solving the QP equation. This does not significantly change the results as compared to a calculation in which only the diagonal elements of  $\Sigma$  are included, except in the case of the broken symmetry structure to be discussed later. This means that the QP wave functions are practically identical to their LDA counterparts. We iterate the  $GW$  scheme by updating the QP energies in both  $G$  and  $W$ .

The crystal structure of  $YH_3$  extracted from experiment has a  $Y_6H_{18}$  unit cell, which was first found for  $HoD_3$  [7,8]. This rather complex structure can be derived from a simple, hexagonal  $LaF_3$  structure with a  $Y_2H_6$  unit cell by means of a Peierls distortion which triples the unit cell in the basal plane [6]. We use our results for  $YH_3$

in the simpler  $LaF_3$  structure as a starting point, because they are easier to discuss and to interpret, yet still contain the essential features of the results for the actual ( $HoD_3$ ) structure.

The LDA bands for  $YH_3$  in the  $LaF_3$  structure are shown in Fig. 1(a). Throughout the Brillouin zone the bands around the Fermi level, marked by a circle and a triangle, are well separated by a direct gap. This separation is about 0.6 eV at  $\Gamma$  and 2.3 eV at  $K$ . However because the minimum of the upper band at  $K$  (circle) is lower than the maximum of the lower band at  $\Gamma$  (triangle) this leads to a semimetal. The indirect band overlap is about 1.3 eV. The unit cell of the  $HoD_3$  structure is 3 times larger than that of the  $LaF_3$  structure in the basal  $ab$  plane. When the  $LaF_3$  unit cell is tripled, the LDA bands originally at  $\Gamma$ , of course remain at  $\Gamma$ . In addition, two new bands appear at  $\Gamma$  which result from folding in the bands from  $K$  in the original larger Brillouin zone (BZ). The result of this folding is shown in Fig. 1(b) for the bands near  $\Gamma$ ,

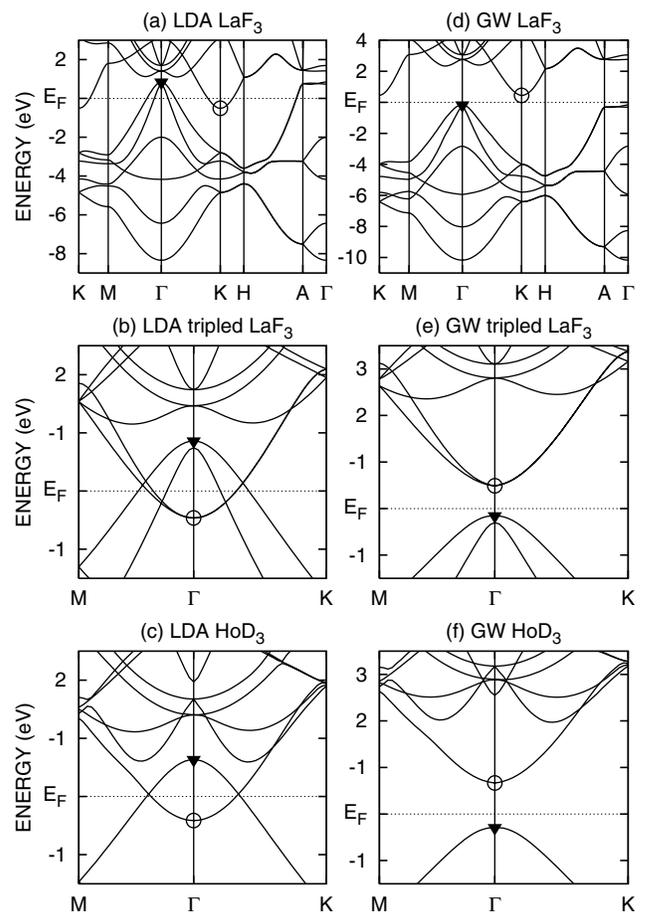


FIG. 1. LDA electron bands for  $YH_3$  in (a) the  $LaF_3$  structure, (b) the tripled  $LaF_3$  structure, and (c) the  $HoD_3$  structure. The corresponding  $GW$  band structures (d)–(f) are obtained from the LDA bands by linear interpolation of the calculated QP corrections found for the  $\mathbf{k}$  points included in the  $GW$  calculation. The circles refer to the bands which are folded back from  $K$  to  $\Gamma$  when the  $Y_2H_6$  unit cell is tripled. The triangles mark bands which are originally at  $\Gamma$ .

using the same symbols as in Fig. 1(a). The indirect band overlap between  $\Gamma$  and  $K$  in the  $\text{LaF}_3$  unit cell becomes a direct overlap at  $\Gamma$  in the BZ of the tripled unit cell. In the actual  $\text{HoD}_3$  structure small displacements of the hydrogen atoms lead to a lowering of the symmetry in the tripled unit cell. These symmetry-breaking hydrogen displacements move one pair of bands, which overlap at  $\Gamma$ , away from the Fermi level. The remaining symmetry in the  $\text{HoD}_3$  structure still allows for an overlap between the other pair of bands (which differ in symmetry). The result is shown in Fig. 1(c).

The results of our  $GW$  calculation for  $\text{YH}_3$  in the  $\text{LaF}_3$  structure are shown in Fig. 1(d). Compared to the LDA results of Fig. 1(a), the most prominent feature is that the separation between the valence and the conduction bands is increased and an indirect band gap of 0.6 eV opens between  $\Gamma$  and  $K$ . The  $GW$  calculation thus predicts  $\text{YH}_3$  to be semiconducting in the  $\text{LaF}_3$  structure in contrast to the semimetal obtained in LDA. The small indirect band gap (0.6 eV) is not easily measured in an optical experiment since the strongest optical transitions are  $\mathbf{k}$  conserving. The calculated direct gap at  $\Gamma$  is 2.9 eV, which corresponds very well to the experimentally observed optical gap. (This result is in fact quite similar to what is found for silicon, which has an indirect band gap of 1.2 eV but a direct optical gap of about 3 eV.) In the Brillouin zone of the tripled unit cell the small indirect  $\Gamma K$  gap is folded into a direct gap at  $\Gamma$  as shown in Fig. 1(e). In the absence of any structural change, the dipole matrix elements connecting the folded highest valence and lowest conduction bands vanish identically, so that the optical gap of 2.9 eV is between the highest valence band and the third conduction band at the  $\Gamma$  point in the reduced Brillouin zone; cf. Fig. 1(e).

We next perform a  $GW$  calculation for  $\text{YH}_3$  in the  $\text{HoD}_3$  structure, the results of which are shown in Fig. 1(f). As before, compared to the LDA calculation [Fig. 1(c)] we find that the conduction bands are shifted upwards and the valence bands are shifted downwards in energy. The overall valence bandwidth increases by some 9% to about 10 eV, as for the  $\text{LaF}_3$  structure. This is in contrast with the results for model calculations by Ng *et al.* [11] who find a large decrease of the valence bandwidth in  $\text{LaH}_3$ . The  $GW$  calculation gives a direct gap at  $\Gamma$  of 1.0 eV for  $\text{YH}_3$  in the  $\text{HoD}_3$  structure, which is substantially larger than the 0.6 eV found for the  $\text{LaF}_3$  structure (part of this difference is already present in the LDA calculation; the overlap of the corresponding LDA bands is 1.1 eV for the  $\text{HoD}_3$  and 1.3 eV for the  $\text{LaF}_3$  structure). Again, the symmetry-breaking hydrogen displacements in the  $\text{HoD}_3$  structure push some of the  $GW$  bands away from the Fermi level; compare Figs. 1(e) and 1(f). The QP wave functions are practically identical to the LDA wave functions, which implies that, in the absence of strong electron hole interaction (i.e., strong excitonic effects), the matrix elements for optical transitions are unchanged. The symmetry-breaking hydrogen displacements induce addi-

tional oscillator strength between some pairs of bands but, crucially for  $\text{YH}_3$ , not between the highest valence and the lowest conduction band. Between these two bands electric dipole transitions remain forbidden. The optical gap will therefore be given by the energy separation between the highest valence and the *second* conduction band, between which an electric dipole transition is allowed. This optical gap is 2.9 eV at  $\Gamma$ ; the gap is probably a few tenths of an eV smaller along the  $\Gamma M$  direction [22]. This result is in excellent agreement with experiment. The fundamental band gap of only 1.0 eV may be verified experimentally by means of a combination of photoemission and inverse photoemission spectroscopy.

Previous LDA total energy calculations predicted the existence of yet another structure in which additional displacements of the hydrogen atoms result in a further lowering of the symmetry of the  $\text{HoD}_3$  structure, without increasing the size of the unit cell [21]. The additional hydrogen displacements lower the total energy slightly and open up a band gap of 0.8 eV in the LDA band structure [21]. So far no evidence for this broken symmetry structure has been found experimentally [2,23,24]. At the same time, however, the  $\text{HoD}_3$  structure does not account for all details of the experimental structure determination of  $\text{YH}_3$  [25,26] so that the relevance of the structure found in Ref. [21] remains unclear. In order to test the sensitivity of our results to the structure, we have also performed a  $GW$  calculation for this broken symmetry structure. We find that in this case it is important to include non-diagonal elements of the self-energy  $\Sigma$  in the LDA basis functions when solving the QP equation. The  $GW$  bands of the broken symmetry structure around the Fermi level resemble the ones shown in Fig. 1(f), with a fundamental band gap at  $\Gamma$  of 1.4 eV. Breaking the symmetry will, in general, induce a finite oscillator strength between states for which it vanished by symmetry in the  $\text{HoD}_3$  structure. So compared to the latter, the broken symmetry structure has a larger fundamental, and a smaller optical gap. Since the  $GW$  calculations result in gaps for both the  $\text{HoD}_3$  and the broken symmetry structures, the latter no longer plays the pivotal role in the MI transition assigned to it by the LDA calculations [21].

Model calculations by Eder *et al.* focus on the (de)localization of the hydrogen orbital, which strongly depends upon the local charge or occupancy. Within a mean-field model this so-called “breathing” of the hydrogen orbitals results effectively in a downward shift of the on-site hydrogen levels [12]. At the mean-field level this breathing effect is already included in the LDA calculations (indeed it is included in any calculation that treats local charges/occupancies self-consistently). In our  $GW$  calculation, which treats exchange and correlation more accurately, we find that the wave functions are not significantly changed as compared to LDA. We conclude that the quasiparticle band structure adequately describes the band gap in  $\text{YH}_3$  and we do not need to invoke additional strong local correlations [11,12].

Roughly half of the large discrepancy between LDA calculations and the experimentally observed band gap is a consequence of the fact that in  $\text{YH}_3$  the optical and the fundamental gap are not the same due to vanishing matrix elements for optical transitions in the range between 1 and 3 eV (an effect which is neglected in Refs. [11] and [12]). The origin of the remaining discrepancy, which is well resolved by the *GW* method, can be traced to the failure of LDA to describe the  $1s$  eigenvalue of the neutral hydrogen atom. This is a well-understood artifact arising from the incomplete cancellation of the (fictitious) electron self-interaction by the local exchange-correlation potential [13].

The picture of  $\text{YH}_3$  which we derive from our parameter-free calculations is that of a simple compound semiconductor. We construct the solid with neutral  $\text{H}^0$  and  $\text{Y}^0$  atoms. Because the ionization energy of atomic  $\text{H}^0$  is twice as large as that of  $\text{Y}^0$ , charge is transferred from Y to H when the interaction between the neutral atoms is switched on. As a result, H acquires a negative charge (in agreement with electromigration experiments [27]). This causes the levels derived from the H  $1s$  states to shift upwards in energy and the Y-derived levels to move downwards. Overlap of the valence orbitals on neighboring atoms leads to covalent interaction and the atomic levels broaden into bands. The charge transfer to hydrogen also causes the atomic orbital to delocalize leading to increased bandwidth. These effects must be taken into account by a self-consistency procedure. However, because the LDA calculation for atomic  $\text{H}^0$  places the  $1s$  eigenvalue at  $-0.5$  Rydberg rather than at  $-1$  Rydberg the difference between the Y and H on-site energies is severely underestimated to start with. As a result the band centers of the valence and conduction bands are too close and the bands overlap.

Future research should focus upon the role of point defects (such as hydrogen vacancies) and their effect on the metal-insulator transition. We note, however, that electron correlations which are small in the host material cannot be automatically ignored when considering defects. For example, the states belonging to a vacancy in silicon are found to be very localized [28,29] and their charge dependent behavior is described well by an Anderson (negative-U) model Hamiltonian with  $U$  approximately equal to 0.3 eV [29]. This value of  $U$  is comparable in size to the band gap of Si and the energy change associated with the local lattice distortions. However, it can be safely ignored for bulk silicon because it is negligible compared to the valence bandwidth of 12 eV.

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*Note added:* After this work was accepted for publication we became aware of similar calculations for  $\text{YH}_3$  in

the cubic  $\text{BiF}_3$  and hexagonal  $\text{LaF}_3$  structures by Miyake *et al.* [30].

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