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The gap in YH_3 and its lattice structure

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Abstract. A systematic study has been carried out on the electronic structure of YH_3 . The attention was focused on the conditions for finding an energy gap, in accordance with experimental evidence. The calculations are made with a localized spherical wave (LSW) program, which is based on a first-principles tight-binding version of the augmented spherical wave method. No gap was found for the FCC structure in spite of the use of a great variety of model parameters. However, a non-self-consistent run of the program for this structure reproduced the gap of 2 eV found by Switendick. No gap was found for several versions of the HCP structure either, including the rather complicated HoD_3 structure. The separation of the bands around the Fermi level, as found for the LaF_3 structure, could explain the light transmission measurements.

1. Introduction

Until now it was believed that the semiconducting behaviour of $\text{YH}_{3-\epsilon}$ for small ϵ was fully understood. The non-self-consistent first-principles energy band calculations by Switendick (1970, 1971) on transition metal and lanthanide hydrides exhibited a clear gap of about 2 eV at the Fermi energy. Although Switendick knew about the HoD_3 structure for $\text{YH}_{3-\epsilon}$ proposed by Mansmann and Wallace (1964), for obvious reasons he did not extend his efforts beyond the BiF_3 structure, in which the metal atoms form a face centred cubic (FCC) lattice and the other atoms occupy the three interstitial sites, two tetrahedral sites and the octahedral site. His results were satisfactory; he was mainly looking for trends, and the HoD_3 structure would have been too complicated for implementation in those days. Furthermore, some of these hydrides indeed have the BiF_3 structure. So the precise lattice structure did not seem to be too important. In the present work we find that the good agreement between the band structure calculations for YH_3 by Switendick and experiment is fortuitous. For YH_3 with the BiF_3 crystal structure a gap can only be obtained by using *non-self-consistent* potentials.

Later, better and self-consistent calculations were already less successful in finding a convincing energy gap than his was. Kulikov and Zvonkov (1979) failed to find a gap, while Gupta and Burger (1980), Kulikov (1982, 1985) and Misemer and Harmon (1982) found a small or negligible gap. Since these activities were primarily directed towards the electronic structure of LaH_3 , which has the BiF_3 structure, a search for the influence of the lattice structure did not seem relevant. Only Kulikov (1985) and coworkers came with a suggestion of a tetragonal distortion and developed a description based on an excitonic dielectric model. As far as the present authors know neither the HoD_3 structure proposed

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by Mansmann and Wallace (1964) nor the LaF_3 structure proposed by Wyckoff (1966), both being hexagonal close packed (HCP) based structures, have been tried in the studies of the electronic structure of these hydrides.

In view of the unsatisfactory situation concerning the explanation of the semiconducting behaviour of YH_x for $x > 2$ (Daou and Vajda 1992) and a revived interest in trihydrides under pressure to achieve metallic hydrogen behaviour (Griessen 1992), we undertook a systematic study of the electronic structure of YH_3 in the search for a gap. First, model parameters, such as the sphere radii used in the atomic sphere approximation, were varied over a wide range for the BiF_3 structure. After that, a variety of modifications of the FCC and HCP structures were studied, all of them being inspired by different crystal structure proposals in the literature.

The paper is organized as follows. In section 2 the different structures studied are described. In section 3 the localized spherical wave (LSW) method used for the electronic structure calculations is discussed in comparison with the methods used in previous work. Some calculations are reported on, which were carried out to imitate Switendick's non-self-consistent calculation. Further information about k -space grids and computer time is given. In section 4 results are presented for the BiF_3 structure and crystallographic modifications of it. In addition, for the sake of comparison, some results will be given for ScH_3 and LaH_3 . Section 5 is devoted to the HCP-like structures. The paper ends with general conclusions and comments.

2. The lattice structures

2.1. The BiF_3 structure

In this relatively simple FCC structure, with a metal atom at the origin, the two tetrahedral sites at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ and the octahedral site at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ are occupied by hydrogen. The space group is O_h^5 . For the nomenclature we refer to Hahn (1987). The lattice parameter used in the majority of the calculations is 5.4645 Å, which corresponds to an expansion with respect to the pure metal of about 7%. Since the actual expansion is about 5%, a test calculation is done to find the lattice parameter dependence of the results, which in fact turns out to be small.

The LSW method used employs the well known atomic sphere approximation (ASA) as other scattered wave methods do. The total volume of the spheres around the atoms is equal to the volume of the compound, so that in the choice of the radii R_Y , R_{tet} and R_{oct} of the spheres around yttrium, tetrahedral and octahedral hydrogen, respectively, two degrees of freedom are left. Three series of calculations are made corresponding to three different relationships of the radii. In series I the yttrium sphere radius R_Y was kept at a constant value of 1.9327 Å, so that for a choice of R_{tet} the value of R_{oct} was fixed. The radii for the hydrogens were chosen to be bounded from below by the value of 1 Bohr (0.5292 Å). In series II the ratio $R_{\text{oct}}/R_{\text{tet}}$ was kept at the constant value of $\sqrt{2}$, which corresponds to a minimum overlap of neighbouring tetrahedral and octahedral ASA spheres. The increase in the value of the hydrogen radii was bounded by the requirement that the yttrium volume does not become smaller than the total hydrogen volume. In series III the ratio chosen by Switendick (1971), i.e. $R_Y/R_{\text{tet}} = 65/35$, was used. In figure 1 the three series and the twelve different actual choices are depicted. These numbers will be used in later sections in tables and figures. It is seen that choice 3 of series I coincides with a choice in series II. Also choice 6 of series I coincides with a choice in series III. For choice 10 in series II, R_Y takes its smallest value, corresponding to equal yttrium and total hydrogen volumes.

The curved line through point 10 parallel to the series I line represents the other values for the hydrogen radii compatible with the smallest R_Y value. It has to be pointed out that the different choices are not equally acceptable. First of all, those choices which lead to the lowest values of the total energy should be preferred (Moruzzi 1992). We will return to this criterion in presenting the results for the BiF_3 structure in section 4. Another criterion refers to the magnitude of the overlap between the different ASA spheres. Although these space-filling spheres overlap necessarily, for the choices 5, 6, 7, 10 and 12 and for points in figure 1 to the right of these choices some overlaps are unacceptably large. In view of this it appears that the acceptable choices are reasonably well represented in the three series.

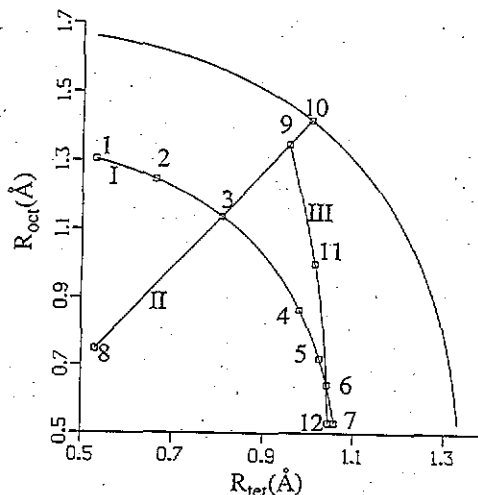


Figure 1. The ASA hydrogen radii used for the various band structure calculations.

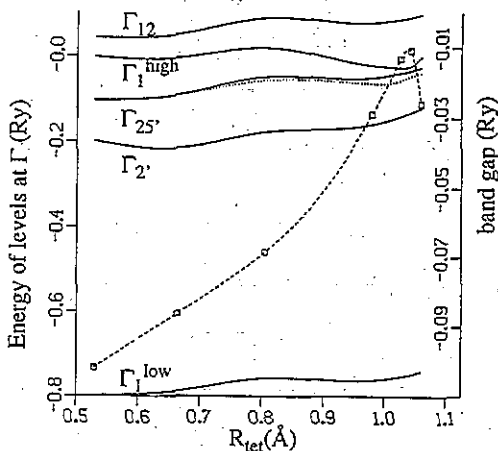


Figure 2. The energy of the levels at Γ for series I, in which the yttrium volume is held constant. The dotted curve gives the Fermi energy. The broken curve shows the band gap on the right-hand scale.

Some tetragonally distorted lattices, with a c/a ratio ranging from 0.97 to 1.05, according to suggestions of Kulikov (1985), were studied as well. This was done for choice 6 in series I, which turned out to give the smallest band overlap of all BiF_3 structure calculations.

The calculations for ScH_3 and LaH_3 were done for choice 9, which turned out to be the best compromise regarding the different criteria.

2.2. The HCP and LaF_3 structures

The four structures to be described now are HCP like. In the ordinary HCP structure the lattice parameters are $a = 3.673 \text{ \AA}$ and $c = 6.628 \text{ \AA}$, having a c/a ratio of 1.8045 (Mueller *et al* 1968). The tetrahedral and octahedral hydrogen atoms are denoted by H_{tet} and H_{oct} , respectively. The space group of this structure and the next two to be described is D_{6h}^4 .

According to Wyckoff (1966) YH_3 might have the LaF_3 structure. In that structure, besides a shift of the octahedral atoms into the yttrium plane, which atoms will be denoted by H_{plane} , the tetrahedral atoms are shifted away from the metal plane. The tetrahedral hydrogen atoms then lie closer to each other, but further from the other atoms.

In table 1 the positions of the three kinds of atom in these structures are given. An intermediate structure, indicated by HCP2, with the tetrahedral atoms as in HCP but the planar hydrogens as in the LaF_3 structure has been considered in the calculations as well. In this

Table 1. Positions of the three kinds of atom in the three hexagonal structures with a unit cell of Y_2H_6 .

	Y	H _{tet}	H _{oct}	H _{plane}
HCP	$\pm(\frac{1}{3} \frac{2}{3} \frac{1}{4})$	$\pm(\frac{1}{3} \frac{2}{3} \frac{1}{4} 0.6024)$ $\pm(\frac{2}{3} \frac{1}{3} \frac{1}{4} 0.1024)$	(000)(00 $\frac{1}{2}$)	—
LaF ₃	$\pm(\frac{1}{3} \frac{2}{3} \frac{1}{4})$	$\pm(\frac{1}{3} \frac{2}{3} \frac{1}{4} 0.57)$ $\pm(\frac{2}{3} \frac{1}{3} \frac{1}{4} 0.07)$	—	$\pm(00 \frac{1}{4})$
HCP2	$\pm(\frac{1}{3} \frac{2}{3} \frac{1}{4})$	$\pm(\frac{1}{3} \frac{2}{3} \frac{1}{4} 0.6024)$ $\pm(\frac{2}{3} \frac{1}{3} \frac{1}{4} 0.1024)$	—	$\pm(00 \frac{1}{4})$

Table 2. Positions of the atoms in the HoD₃ structure compared to those in the LaF₃ structure.

	HoD ₃	LaF ₃
Y	$\pm(\frac{1}{3} \frac{1}{3} \frac{1}{4})$ $\pm(\frac{2}{3} 0 \frac{1}{4})$ $\pm(0 \frac{2}{3} \frac{1}{4})$	$\pm(\frac{1}{3} \frac{1}{3} \frac{1}{4})$ $\pm(\frac{2}{3} 0 \frac{1}{4})$ $\pm(0 \frac{2}{3} \frac{1}{4})$
H _{tet}	$\pm(0.356 0.028 0.096)$ $\pm(0.972 0.328 0.096)$ $\pm(0.672 0.644 0.096)$ $\pm(0.972 0.644 0.596)$ $\pm(0.356 0.328 0.596)$ $\pm(0.672 0.028 0.596)$	$\pm(\frac{1}{3} 0 0.7)$ $\pm(0 \frac{1}{3} 0.07)$ $\pm(\frac{2}{3} \frac{2}{3} 0.07)$ $\pm(0 \frac{2}{3} 0.57)$ $\pm(\frac{1}{3} \frac{1}{3} 0.57)$ $\pm(\frac{2}{3} 0 0.57)$
H _{oct}	$\pm(\frac{1}{3} \frac{2}{3} \frac{1}{6})$ $\pm(\frac{2}{3} \frac{1}{3} \frac{1}{3})$	$\pm(\frac{1}{3} \frac{2}{3} \frac{1}{4})$ $\pm(\frac{2}{3} \frac{1}{3} \frac{1}{4})$
H _{plane}	$\pm(0 0 \frac{1}{4})$	$\pm(0 0 \frac{1}{4})$

table the positions are described relative to three basis vectors a , b , and c . The vectors a and b make an angle of 120° ; c is perpendicular to the plane spanned by the other vectors. Further, $|a| = |b| = a$, while c has length c .

2.3. The HoD₃ structure

The so-called HoD₃ structure is very intricate. It is described by Mansmann and Wallace (1964). Much symmetry is lost and the unit cell corresponds to the compound Y_6H_{18} . This makes the calculation a cumbersome and computer time consuming one. Instead of three there are now four kinds of atoms. The planar atoms are split into two classes. One consists of hydrogen atoms in the metal plane, to be called H_{plane}, just as in LaF₃. The other consists of atoms placed $0.08a$ above or below the metal plane. The latter will be called H_{oct} here, although they are closer to the metal plane than to the octahedral site. The tetrahedral atoms are slightly shifted from their position in the LaF₃ structure. So it is the planar hydrogen which destroys the symmetry. Because the unit cell is three times bigger the a and b axes are $\sqrt{3}$ times larger. This structure has space group D_{3d}^4 . In table 2 this structure is compared to the LaF₃ structure. The positions are rewritten relative to the basis of HoD₃. The basis vectors are also rotated somewhat with respect to the basis in the LaF₃ case. The relation between the primed HoD₃ basis vectors and the LaF₃ basis vectors is given by $a' = b - a$, $b' = 2a + b$ and $c' = c$.

3. Method and computational details

The LSW method used is a modification of the augmented spherical wave method of Williams *et al* (1979) in that the basis set has been transformed to the most localized one. This

transformation was introduced by Andersen and Jepsen (1984) for muffin-tin orbitals. The practical aspects are treated differently in the LSW method. The method has been described in a paper by Van Leuken *et al* (1990), to which we refer for more detailed information. The program is scalar relativistic. Exchange and correlation are treated according to Hedin and Lundqvist (1971). The program is devised to run to self-consistency, and that is the way it is applied in the present work. Self-consistent atomic potentials, generated with proper boundary conditions according to the ASA treatment of the space-filling requirement, are introduced at lattice sites in order to perform an electronic structure calculation for the system. The output leads to new potentials, which are first used to generate new self-consistent potentials at the atomic level, so that core levels are iterated as well. After that the iteration procedure for the system is continued.

However, not finding a gap by any choice of input parameters, it was tempting to simulate Switendick's non-self-consistent calculation. This was done by generating the band structure of YH_3 using the potential constructed in the first run, which usually initiates the iteration procedure to self-consistency. In addition to this calculation for the Hedin-Lundqvist exchange mentioned above, for comparison a similar calculation was performed for Slater exchange with $\alpha = 1$, as used by Switendick, and with $\alpha = \frac{2}{3}$. In all three calculations gap values were found as large as Switendick's gap obtained from a non-relativistic augmented plane wave (APW) calculation. The band structures were very much alike, although the bands are narrower for $\alpha = 1$, which is a well known general property. Apparently the LSW and the APW methods, both applied non-self-consistently, give quite comparable results as far as our main objective, the gap in YH_3 , is concerned. This proves that Switendick's finding of a gap is to be considered as a fortuitous result, only valid for non-self-consistent potentials.

Gupta and Burger (1980) used the same method but accounted for a warped muffin-tin potential in the interstitial region. They restricted their study to lanthanum hydrides. Kulikov and Zvonkov (1979) used a non-self-consistent linearized hybridized Korringa-Kohn-Rostoker (KKR) method, while in later work Kulikov (1982, 1985) ran his program to self-consistency, using different exchange potentials. In the latter case indirect gaps were found ranging from 0.10 to 0.95 eV, while the first calculation showed an indirect band overlap of 0.4 eV. Misemer and Harmon (1982) performed a self-consistent calculation using a semirelativistic KKR method. They found a very small indirect gap of 0.003 eV compared with the value of 0.53 eV obtained by Gupta and Burger. All these authors restricted their study to lanthanum hydrides and all found small gap values compared with the value of 1.6 eV that Switendick obtained for YH_3 .

For LaH_3 improvement of the calculation seems to lead to a smaller gap, apart from Kulikov's case. The latter found a small band overlap, but this may be due to his simplified calculational method. The improvement of Gupta and Burger compared with Switendick implies a proper treatment of the octahedral hydrogen and an account for a warped muffin-tin potential. The self-consistency achieved by Misemer and Harmon implies another improvement. They also considered the band structure at the first iteration and found a small band overlap. So the gap opened when running to self-consistency. In order to compare our self-consistent LSW method with the other methods used we performed some calculations for LaH_3 in the BiF_3 structure. In a non-self-consistent run we found a band overlap of 1 eV. After self-consistency an indirect gap of 0.2 eV developed, which tendency is in agreement with Misemer and Harmon. Note that for LaH_3 the self-consistency has an opposite effect on the gap compared with YH_3 . Further the band structure is very similar to the band structures found by others. We conclude again that the results obtained by means of different methods are well comparable. Thus, the results obtained by our LSW method

can be considered as being sufficiently reliable to draw conclusions about the influence of the lattice structure on the electronic structure.

The volume per k point in the FCC case was equal to $3.5 \times 10^{-5} \text{ \AA}^{-3}$. In the HCP, HCP2 and LaF₃ structures this volume was $1.8 \times 10^{-5} \text{ \AA}^{-3}$, while it was $3.4 \times 10^{-5} \text{ \AA}^{-3}$ in the HoD₃ structure.

All calculations were performed on an IBM3090 computer. For the simple BiF₃ structure self-consistency was achieved in half an hour. The complicated HoD₃ structure required that amount of time for just one iteration.

4. Results for the BiF₃ structure

For the three series of choices of the ASA spheres the band structures, densities of states (DOSS) and total energies were calculated. The DOS curves will not be shown, because in no case was a gap found and so a DOS curve does not contain additional information about the gap. Additional output, such as the charges within the atomic spheres, will be mentioned in comparing the results for the different structures. The attention is mainly focused on the behaviour of the energy levels at Γ , because a possible direct gap would develop at that point and the direct gap is always larger than the indirect gap. Further, it is helpful for the interpretation of the results that at this point the states can be characterized rigorously as linear combinations of atomic valence orbitals, transforming according to the irreducible representations of the cubic point group. In other k points this is not possible, because of complicated mixing of the states. The characterization given in table 3 is taken from Switendick. The states are composed of the yttrium s orbital, the d orbitals t_{2g} and e_g , the $1s$ orbitals h_1 and h_2 of the two tetrahedral hydrogens and the $1s$ orbital h_0 of the octahedral atom.

Table 3. Composition of the levels at Γ .

Level	Linear combination
Γ_1^{low}	$s \oplus (h_1 + h_2) \oplus h_0$
Γ_2'	$h_1 - h_2$
$\Gamma_{25'}$	$(t_{2g})^3$
Γ_1^{high}	$s \oplus (h_1 + h_2) \oplus h_0$
Γ_{12}	$(e_g)^2$

In figure 2 the levels at Γ , the Fermi energy (E_F) and the value of the gap, which is negative for all cases corresponding to band overlap, are plotted, for series I, as a function of R_{tet} . They are given with respect to the atomic zero. The squares correspond to the various choices of radii depicted in figure 1. The levels do not change monotonously with R_{tet} . They are almost parallel to each other and to the dotted E_F curve. Only the Γ_1^{high} level decreases strongly for R_{tet} between 0.81 \AA and 0.98 \AA , while all other levels are nearly constant. This almost causes the band overlap between Γ_1^{high} and $\Gamma_{25'}$ to vanish, but when R_{tet} exceeds 1.04 \AA , Γ_1^{high} increases faster than $\Gamma_{25'}$. It is not too surprising that the E_F curve is relatively constant. For this series the yttrium ASA radius is a constant, by which the yttrium contribution to the electronic structure is rather stable. The small oscillations of the E_F curve and the levels at Γ are due to variations in the spatial extension of the hydrogen ASA spheres. The strong decrease of the Γ_1^{high} level starts at R_{tet} values for which the octahedral ASA sphere no longer overlaps with an yttrium sphere, implying a decrease

of the contribution of the h_o level and, in view of table 3, of the separation between the Γ_1^{high} and Γ_1^{low} levels.

The minimum negative gap value occurs for choice 6 (see figure 1), having a ratio $R_Y/R_{\text{tet}}/R_{\text{oct}} = 65/35/21.6$. This point does not give a minimum in the total energy. It lies to the right of points 3, 4 and 5 for which the total energy curve remains in a slowly varying valley. It is interesting to notice that the 65/35 ratio was chosen by Switendick (1971) in his muffin-tin description of the potential in order to decrease the size of the discontinuity between the potentials within the muffin-tin spheres and the interstitial region of zero potential. In his muffin-tin description this ratio would have led to an $R_{\text{oct}}/R_{\text{tet}}$ ratio of 50/35. The latter ratio again is almost equal to $\sqrt{2}$, which was chosen to determine our series II. Remember that series III was determined by $R_Y/R_{\text{tet}} = 65/35$.

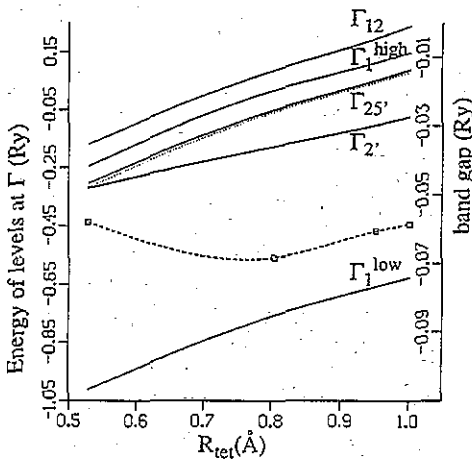


Figure 3. The energy of the levels at Γ , when the ratio of hydrogen radii is held constant, $R_{\text{oct}} : R_{\text{tet}} = \sqrt{2}$ (series II).

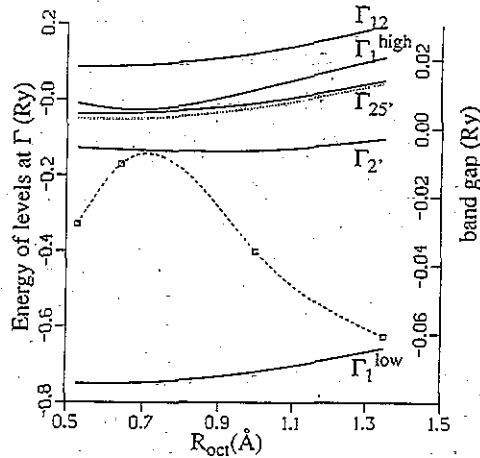


Figure 4. The energy of the levels at Γ , when the ratio of radii of yttrium and tetrahedral hydrogen is held constant, $R_Y : R_{\text{tet}} = 65 : 35$ (series III).

Figures 3 and 4 show the same information for series II and III respectively. For series II the yttrium radius decreases continuously with increasing hydrogen radii, which is consistent with a monotonic increase of E_F . The dominance of yttrium in determining the Fermi level of the system is marked by the $\Gamma_{2'}$ curve. All levels involving yttrium states follow the behaviour of the E_F curve, contrary to $\Gamma_{2'}$, which is a purely tetrahedral hydrogen anti-bonding level. Since for larger hydrogen ASA sphere radii the potentials of neighbouring tetrahedral atoms shade off into each other more and more, the anti-bonding level separation is indeed expected to decrease. It is seen that in this series the band overlap is almost constant and rather large.

While in the first two series four levels run approximately parallel to each other, in series III only three levels behave this way, namely Γ_1^{low} , $\Gamma_{25'}$ and Γ_{12} . These are the bonding level and the two metal d levels. They increase over the whole range, but faster for larger R_{oct} . The Γ_1^{high} level decreases slightly at first, but when R_{oct} is larger than approximately 0.65 Å, it starts to increase faster than the other levels. The $\Gamma_{2'}$ level, in contrast, is almost constant along the whole interval. First it decreases slightly, but when R_{oct} is bigger than 1 Å, it starts to increase. This happens more slowly than for the other levels. In this series the levels vary by an amount of the order of 0.15 Ryd, while in series I, with a constant R_Y , this variation is of the order of 0.10 Ryd. In the second series, characterized by a

predominant R_Y dependence, this variation is about 0.45 Ryd. Further, the gap remains negative but becomes small for choice 6, as already seen in series I (see figure 1).

We conclude that no gap shows up for YH_3 in the BiF_3 structure. The smallest band overlap value was obtained for choice 6, with a ratio of ASA radii $R_Y/R_{tet}/R_{oct} = 65/35/21.6$. It should be stressed that we ended up at that choice in searching for a gap. Regarding the behaviour of the total energy for the three series, shown in figure 5 as a function of R_{oct} , other choices, such as 3, 4, and 9, are to be preferred. A similar conclusion can be drawn by considering the overlaps of the different ASA spheres. For choice 6 volume overlaps of over 20% are found, while, according to a rule of thumb, all overlaps should be smaller than 15%.

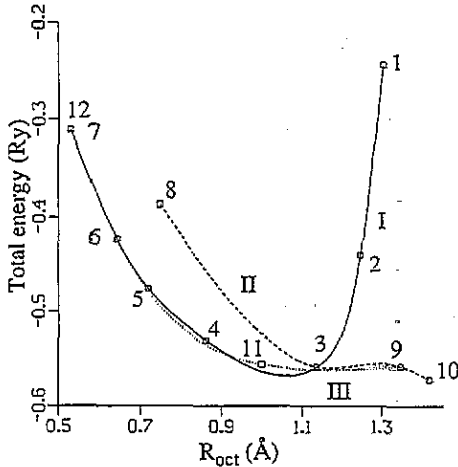


Figure 5. Total energies in the three series for YH_3 in the BiF_3 structure.

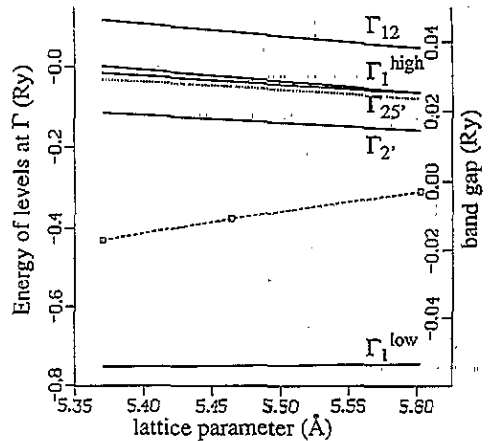


Figure 6. The energy of the levels at Γ when the lattice parameter is varied.

In order to be even more sure in our conclusion two additional types of test calculation were performed. For the sake of comparison the radii ratio of choice 6 was used in these tests. First the lattice parameter dependence of the results was calculated, because we have used a slightly too large lattice parameter in our series of calculations. In figure 6 the lattice parameter dependence of the gap value and the levels at Γ are shown. It is seen that the band overlap increases with decreasing lattice parameter, which result makes our conclusion even stronger.

Secondly, some runs were made for tetragonally distorted FCC lattices. Kulikov proposed such an effect in order to explain the semiconducting behaviour of LaH_3 . In $CeH_{2.75}$ a distortion of the c axis of 0.7% has been measured. Therefore we took lattices with a c/a ratio ranging from 0.97 to 1.05. A greater distortion seems unphysical. A compression of the c axis appeared to be in favour of a gap, because then the states around Γ mix in such a way that if one state is lowered in energy, say by 0.1 eV (e.g. by varying the ASA radii), a gap would open. An expansion, in contrast, induces a band which shows a large overlap at point M in the tetragonal Brillouin zone. But even a compression of 3% did not lead to a gap. Further, although the total energy did not change much, its variation pointed towards an expansion along the c axis. We conclude from these observations that a distortion cannot be regarded as a possible way out to induce a gap. At this point one restrictive remark could be made about our conclusion concerning a gap. Our calculations are based on the local density approximation for the exchange and correlation potentials,

which is known to underestimate a gap in apparently semiconducting crystals such as Si and Ge. However, this underestimation is of the order of 0.5 eV and at most 0.7 eV. So we believe that our conclusion, as far as YH_3 is concerned, remains valid. The small band overlap of 0.2 eV found for LaH_3 (see below) could be due to this effect. A calculation going beyond the local density approximation requires other tools than commonly available and implies a separate area of research.

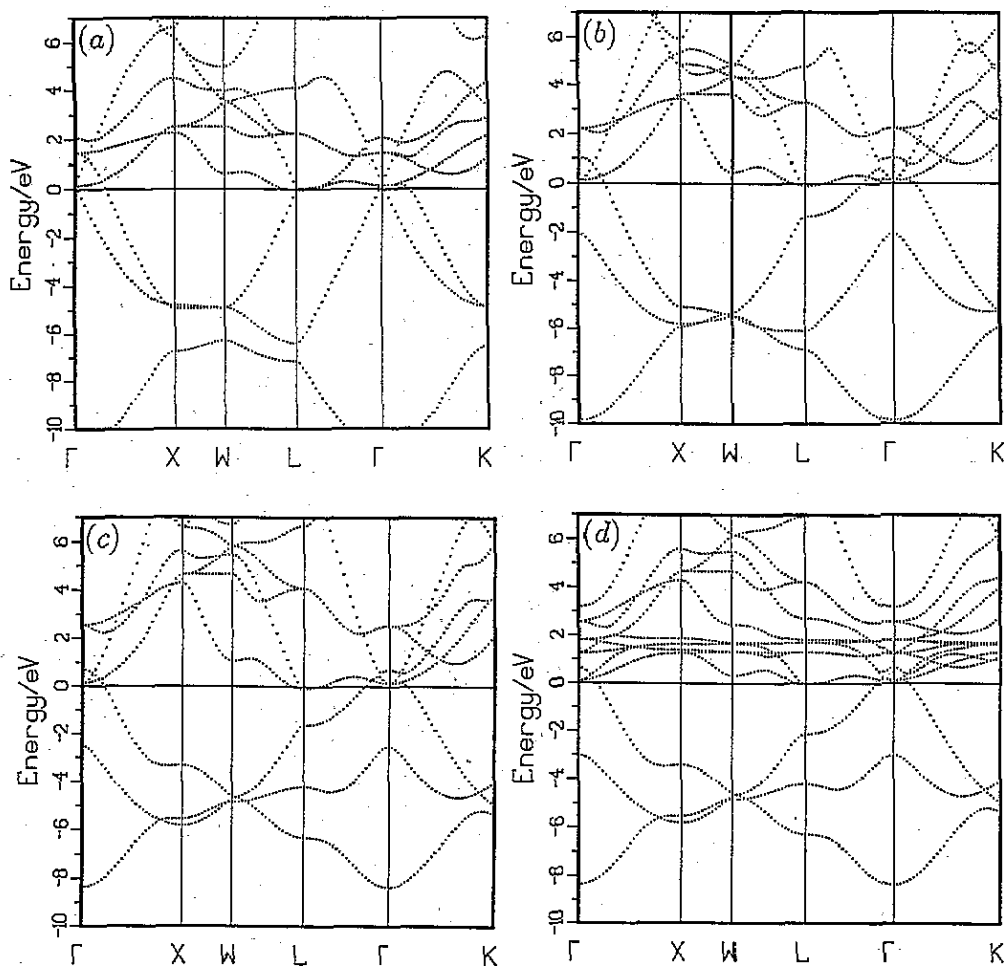


Figure 7. Band pictures of cubic group-IIIb trihydrides: (a) ScH_3 ($a = 4.9198 \text{ \AA}$); (b) YH_3 ($a = 5.3703 \text{ \AA}$); (c) LaH_3 ($a = 5.6021 \text{ \AA}$, $l_{\text{max}} = 2$); (d) LaH_3 ($a = 5.6021 \text{ \AA}$, $l_{\text{max}} = 3$). l_{max} is the maximum l value of the Hankel functions. If $l_{\text{max}} = 3$, f states are taken into account.

Finally, we would like to report in this section on a comparison of the electronic structure of the group-IIIb trihydrides, ScH_3 , YH_3 and LaH_3 , in the BiF_3 structure. The lattice parameters used were 4.9198 \AA , 5.3703 \AA and 5.6021 \AA respectively. The lattice parameter for the non-existing ScH_3 was derived using the ratio for La of lattice parameters between the pure metal and its trihydride. Guided by the behaviour of the total energy and the magnitude of the overlaps of ASA radii in YH_3 these calculations were performed for choice 9 in figure 1. The corresponding band pictures are shown in figure 7. The gap values are -1.5 , -1.0 and -0.2 eV respectively. Apparently, for the parameters chosen, even for

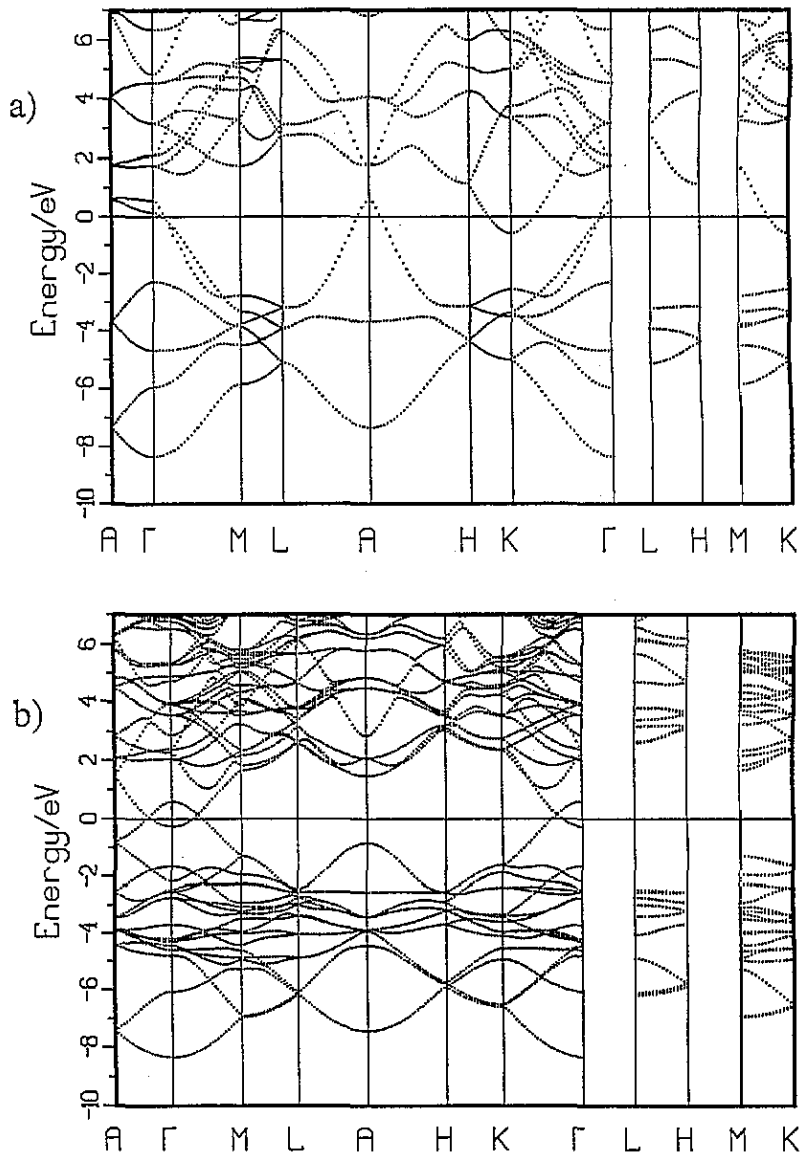


Figure 8. Band structures of YH_3 in two different crystal structures: (a) LaF_3 (12 electrons per unit cell); (b) HoD_3 (36 electrons per unit cell).

LaH_3 there is no gap. The pictures look similar, although the increasing lattice parameter implies narrowing of the bands, as usual.

5. The HCP-based structures

For the HCP and HoD_3 structures band overlap values of about 1.5 eV were found. The band structures for YH_3 in the LaF_3 and HoD_3 structures are shown in figure 8. For the LaF_3 structure the bands show up as neatly separated vertically, although indirectly there is still overlap. The picture for the HCP2 structure is very similar. For both structures indirect overlaps of about 1.0 eV exist between the points K and Γ and between K and

A. An interesting point about these structures is that the transmission of light through the compound, as measured by Huiberts *et al* (1992), can be explained. Light does not transfer momentum and so in the band picture electrons can only be excited vertically.

In the HoD_3 structure a density of states of 1.4 states Ryd^{-1}/YH_3 unit at the Fermi energy is found, which is very small compared with the metallic yttrium value of 26.9 states Ryd^{-1}/YH_3 unit. In the LaF_3 structure this quantity is 2.5 states Ryd^{-1}/YH_3 unit and therefore not as small as in the HoD_3 structure, but the bands are neatly separated, so that for optical transitions a vertical band gap of 1.5 eV is found. It is clear that the lattice structure dependence of the electronic structure is substantial.

Table 4. Relevant quantities for the different structures. The quantities shown are the total energy of the system per yttrium atom, the charges in the different ASA spheres, including the zirconium empty sphere Z, the lattice parameters and the ASA radii.

Quantity	FCC	HCP	HCP2	LaF_3	HoD_3
Total energy per YH_3 (Ryd)	-6766.571	-6766.531	-6766.618	-6766.552	-6766.610
Charges					
Y	2.181 73	2.198 85	2.318 25	2.473 66	2.295 13
H_{tet}	1.100 20	1.097 49	1.315 47	0.979 27	1.330 64
H_{oct}	1.617 87	1.606 17	—	—	1.104 92
H_{plane}	—	—	1.050 82	0.956 39	0.920 93
Z (empty sphere at octahedral position)	—	—	—	0.611 40	—
Lattice parameters; ASA radii					
a (Å)	5.370	3.673	3.673	3.673	6.362
c (Å)	—	6.628	6.628	6.628	6.628
R_Y (Å)	1.740	1.740	1.740	1.740	1.740
R_{tet} (Å)	0.937	0.937	1.166	0.883	1.166
R_{oct} (Å)	1.325	1.325	—	—	0.982
R_{plane} (Å)	—	—	0.930	0.883	0.803
R_Z (Å)	—	—	—	1.240	—

In table 4 the system total energy per YH_3 unit, the charges within the ASA spheres, the lattice parameters and the ASA sphere radii are given for the different lattice structures. For the sake of comparison the yttrium radius was given the same value in the different structures. In order to reduce the overlaps between the ASA spheres, the radii of the hydrogen atoms are different in the modified HCP-based structures, while for the LaF_3 structure an empty sphere was added at the octahedral site. Comparing the total energies it is seen that the HCP2 and HoD_3 structures are favoured structures. A test calculation for the HCP2 structure, in which an empty sphere was added, as in the LaF_3 structure, ended up with a total energy of -6766.549 Ryd, somewhat higher than the LaF_3 total energy. Putting the argument the other way round we are tempted to conclude that the LaF_3 structure belongs to the favoured structures as well. We expect that this conclusion can be made even stronger by searching for minimum energy parameters. This will be a subject for further research.

As for the charges it is seen that in the modified HCP-based structures the yttrium sphere attracts more electrons than in the FCC and HCP structures. In addition, the average charge per unit volume in the ASA spheres for those hydrogens that have been shifted into the yttrium plane (so in the HCP2, LaF_3 and HoD_3 structures) is increased strongly with respect to what is found for the octahedral hydrogens in the FCC and HCP structures. From the total energies in table 4 it thus seems that this increase of electronic charge density in the plane containing the yttrium and H_{plane} atoms stabilizes the compound with respect to the FCC and HCP structures.

6. Conclusions

In studying the lattice structure dependence of the electronic structure of YH_3 , particularly in the search for an energy gap in view of the measured semiconducting and optical absorption properties, an FCC structure and an unmodified HCP structure could be ruled out as realistic structures. The rather complicated HCP-based HoD_3 structure suggested by Mansmann and Wallace (1964) and the LaF_3 structure suggested by Wyckoff (1966), as well as a third modified HCP structure are more promising. Although for these structures no gap was found either, an interesting separation of bands showed up which allows for an explanation of the vertical gap measured by optical excitations. As described in section 2, these structures have in common the fact that the octahedral hydrogen atoms are vertically moved away from the octahedral positions. Comparable total energies have been found for them which are lower than the total energies for other structures. However, our calculations do not allow for a choice between these three related modified HCP structures. More detailed calculations for these structures, in which radii and even lattice parameters are varied, would be required for such a choice. This may be a subject for further research.

In conclusion, an all-electron self-consistent approach, such as the localized spherical wave method used in the present work, has been able to provide strong evidence concerning probable and very improbable lattice structures for YH_3 , considering the desire to find an energy gap or at least a separation of bands around the Fermi energy. However, calculations going beyond the local density approximation could be quite revealing for the trihydrides involved, because of the measured evidence of semiconducting properties.

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References

- Andersen O K and Jepsen O 1984 *Phys. Rev. Lett.* **53** 2571
Daou J N and Vajda P 1992 *Phys. Rev. B* **45** 10907
Griessen R P 1992 private communication
Gupta M and Burger J P 1980 *Phys. Rev. B* **22** 6074
Hahn Th (ed) 1987 *International Tables for Crystallography*, vol. A: *Space Group Symmetries* (Dordrecht: Reidel)
Hedin L and Lundqvist B I 1971 *J. Phys. C: Solid State Phys.* **4** 2064
Huiberts J N, Rector J, Goedkoop J, De Groot D G and Griessen R P 1992 *Int. Symp. on Metal-Hydrogen Systems* (Uppsala: Physics Department) p 1.32
Kulikov N I 1982 *J. Less-Common Met.* **88** 307
— 1985 *J. Less-Common Met.* **107** 111
Kulikov N I and Zvonkov A D 1979 *Z. Physiol. Chem. N. F.* **117** 113
Mansmann M and Wallace W E 1964 *J. Physique* **25** 454
Misemer D K and Harmon B N 1982 *Phys. Rev. B* **26** 5634
Moruzzi V L 1992 private communication
Mueller W M, Blackledge J P and Libowitz G G 1968 *Metal Hydrides* (New York: Academic)
Switendick A C 1970 *Solid State Commun.* **8** 1463
— 1971 *Int. J. Quantum Chem.* **5** 459
Van Leuken H, Lodder A, Czyzyk M T, Springelkamp F and De Groot R A 1990 *Phys. Rev. B* **41** 5613
Williams A R, Kübler J and Gelatt C D Jr 1979 *Phys. Rev. B* **19** 6094
Wyckoff R W G 1966 *Crystal Structures* vol 2 (New York: Interscience)