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Relaxation of internal stress field and hydrogen ordering on YH_x

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Abstract

Although there have been several theoretical efforts in the past to calculate both the best structure of H–H pairs in Y and the total energies as well as electronic structures, there exist no studies of the relation between hydrogen ordering and the shape of the Fermi surface. We use the FLAPW method, as implemented in the Wien2k code, focusing our research on the relation between chain ordering of H, the relaxation of internal coordinates and the electronic properties for hypothetical α-$YH_{1/3}$ and α-$YH_{2/3}$. In addition to the relaxed atomic positions in the cell, we obtain information on the negligible role of the H 1s state contribution near E_F and the shape of the Fermi surface.
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1. Introduction

Rare earths absorb hydrogen easily, forming phase diagrams with regions of solid solution and dihydrides as well as trihydrides. Among them, Sc, Y, and several hcp rare earths possess solid solutions where the hydrogens form second neighbor pairs on tetrahedral sites along the *c*-axis in a kind of quasi one-dimensional short range ordered chains. This phenomenon and the related effects upon various physical properties were described earlier (see, e.g. the review [1]) but, although there have been several theoretical efforts to understand it (e.g. [2] and [3]), the basic reasons for the existence of such a peculiar structure in these systems are not clear yet.

Some researchers [4] explained it through the picture of charge density waves while others [5] ascribed it to the formation of coherent stresses within the metal lattice; and it is not impossible that the two are secondary expressions of the same fundamental characteristic of the system such as the Fermi surface.

The purpose of this work is to investigate theoretically the ordering of hydrogen in yttrium focusing our research on the relation between chain ordering of H, the relaxation of internal coordinates, and the electronic properties for $YH_{1/3}$ and $YH_{2/3}$. For each concentration, we relax the internal positions of all atoms in the cell and study the density of states and the Fermi surface.

2. Method and computational details

The electronic calculations presented in this work were performed using the self-consistent, full potential linearized augmented plane wave (FLAPW) method as is implemented in the Wien2k package [6]. This uses the full-potential APW+lo method that makes no shape approximation to the potential or density. The generalized gradient approximation of Perdew et al. [7] was used for the correlation and exchange potentials. The atomic sphere radii, R_{MT}, selected for Y and H were 1.9 bohr and 0.8 bohr, respectively. Local orbital extensions were included for the $4s^2$ and $4p^6$ semicore states of Y. The basis set size $R_{MT}K_{max}$ (where R_{MT} are the smallest atomic sphere radii inside the cell and K_{max} is a cutoff for the basis function wave vector) were chosen, respectively, as 9 and 3.5 for pure Y and the Y–H systems studied in this work. The number of plane waves used in the basis set are

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719, 4100 and 2041 for Y-hcp, $YH_{1/3}$ and $YH_{2/3}$, respectively. The cut-off in the charge density Fourier expansion, $G_{\max}$, was selected as $20\,\mathrm{Ry}^{1/2}$. The maximum l values for partial waves inside the spheres and for the non-muffin-tin matrix elements were selected to be $l_{\max} = 12$ and $l_{\max} = 6$, respectively. A mesh of 240, 48 and 52 special k-points was taken in the irreducible wedge of the Brillouin zone to obtain the structural information in the Y-hcp, the Pmma and the P3m1 structure, respectively. A set of 120 special k-points was selected in the irreducible Brillouin zone for studying the Fermi Surface of the $YH_{1/3}$ system. The XcrysDen [8] package was used for that purpose. The iteration process is repeated until the calculated total energy converges to less than 0.1 mRyd/cell.

3. Results and discussion

3.1. Pure Y

Hcp Y ($P6_3$/mmc space group) was selected to begin with because it exhibits the same chain-like H ordering observed experimentally in some heavy hcp rare earths but without *f*-electrons and magnetic effects. In this way, we can limit our study to just the structural effects produced by the H ordering.

The structural results obtained for pure Y after the minimization of lattice parameters show excellent agreement between experiment and theory and are summarized in Table 1.

3.2. The Y–H systems

3.2.1. Structural information

As a first step in our research related to the origin of the chain structure in YH_x, two compositions were studied with chain-like H structure: $YH_{1/3}$ and $YH_{2/3}$ with Pmma and P3m1 space groups, respectively. We chose these compositions due to computational limitations, as they have small unit cells with, respectively, five and 10 non-equivalent atoms in the crystallographic base. Although the $YH_{2/3}$ structure has the $P6_3$/mmc symmetry, we selected a structural model with lower symmetry as is the P3m1. That choice allows more freedom to the atomic movements in order to see if the relaxation of atomic coordinates preserves the inversion symmetry consistent with the $P6_3$/mmc or the atoms in the cell relax independently in agreement with a lower symmetry space group. Due to computational limitations we chose a structural model with inversion symmetry for the composition $YH_{1/3}$ checking previously that the atoms relax according to the Pmma symmetry.

Table 1
Experimental [9] and computed lattice parameters for hcp Y

Y hcp	*a* (Å)	*c* (Å)	*c*/*a*
Experimental	3.648	5.732	1.571
Theoretical	3.651	5.696	1.560
Error (per million)	0.8	6	7

Table 2
Space groups and lattice parameters for $YH_{1/3}$ and $YH_{2/3}$

Composition	Space group	*a* (Å)	*b* (Å)	*c* (Å)	*c*/*b*
$YH_{1/3}$	Pmma	6.3923	3.6906	17.4935	4.7400
$YH_{2/3}$	P3m1	3.6817	3.6817	17.4710	4.7454

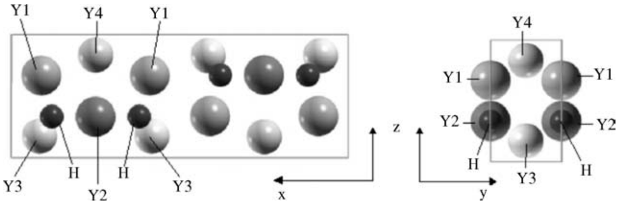

Fig. 1. Side view (left) and upper view (right) of the crystallographic cell for the composition $YH_{1/3}$. The cell contains 16 atoms and 5 non-equivalent atoms in its base.

The cell for the compositions $YH_{1/3}$ and $YH_{2/3}$ are shown in Figs. 1 and 2 respectively, with the nomenclature used for the different non-equivalent atoms.

Table 2 shows the structural information obtained after the minimization of the total energy was achieved. The minimization procedure includes the optimization as a function of the lattice parameter *a* and the *c*/*a* ratio, followed with the relaxation of the internal atomic coordinates in the optimized values of the lattice parameter. A necessary additional step includes checking for changes in the lattice parameter against atomic displacements, which could result in further minimization of the internal parameters. In our work, good agreement was found between the first and the second step in the minimization procedure. The expansions obtained in this work for both structures are in agreement with previous theoretical results [3].

We determined the atomic positions that minimize the forces with the limit that the maximum force must be smaller than 0.5 mRy/bohr. There is an energy gain per unit cell upon relaxation of 0.22 and 0.18 eV for $YH_{1/3}$ and $YH_{2/3}$, respectively.

Tables 3 and 4 summarize the results for $YH_{1/3}$ and $YH_{2/3}$ obtained before (unrelaxed state) and after (relaxed state) the geometrical optimization of the internal variables. They also show the displacement along the three axes for each non-equivalent atom. Tables 5 and 6 show the distances before and after the relaxation of internal coordinates for the group of atoms schematically represented in Fig. 3a and b for the compositions $YH_{1/3}$ and $YH_{2/3}$, respectively.

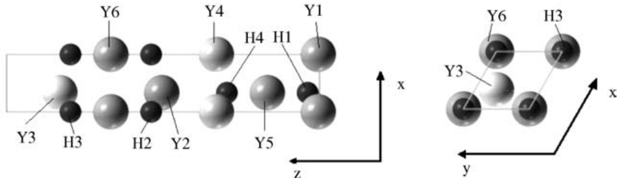

Fig. 2. Side view (left) and upper view (right) of the crystallographic cell for the composition $YH_{2/3}$. The cell contains 10 non-equivalent atoms in its base.

Table 3
Unrelaxed and relaxed positions of equivalent atoms for the $YH_{1/3}$ structure (Pmma space group) in units of lattice parameters (a, b, c) for (z, y, x) coordinates, respectively

$YH_{1/3}$	Unrelaxed			Relaxed			Δx	Δy	Δz
	x	y	z	x	y	z			
Y1 4i	0.08333	0	0.66666	0.08929	0	0.66421	0.00596	0	−0.00245
Y2 2e	0.25	0	0.33333	0.25	0	0.33036	0	0	−0.00297
Y3 4j	0.083333	1/2	0.16666	0.08353	1/2	0.17237	0.000197	0	0.00570
Y4 2f	0.25	1/2	0.83333	0.25	1/2	0.83209	0	0	−0.00124
H 4i	0.125	0	0.33333	0.12033	0	0.33228	−0.00467	0	−0.00105

Table 4
Unrelaxed and relaxed positions of equivalent atoms for the $YH_{2/3}$ structure (P3m1 space group) in units of lattice parameters (a, b, c) for (x, y, z) coordinates, respectively

$YH_{2/3}$	Unrelaxed			Relaxed			Δx	Δy	Δz
	x	y	z	x	y	z			
Y1 1a	0	0	0	0	0	0.00389	0	0	0.00389
Y2 1b	0.3333	0.6666	0.5	0.3333	0.6666	0.50389	0	0	0.00389
Y3 1b	0.3333	0.6666	0.83333	0.3333	0.6666	0.82944	0	0	−0.00389
Y4 1a	0	0	0.33333	0	0	0.32944	0	0	−0.00389
Y5 1b	0.3333	0.6666	0.16666	0.3333	0.6666	0.16666	0	0	0
Y6 1a	0	0	0.66666	0	0	0.66666	0	0	0
H 1b	0.3333	0.6666	0.04166	0.3333	0.6666	0.03775	0	0	−0.00392
H 1a	0	0	0.54166	0	0	0.53775	0	0	−0.00392
H 1a	0	0	0.79166	0	0	0.79558	0	0	0.00392
H 1b	0.3333	0.6666	0.29166	0.3333	0.6666	0.29558	0	0	0.00392

The magnitude of atomic movements found for $YH_{1/3}$ is less than 0.1 and 0.04 Å along the x- and the z-direction, respectively, which explains its non-observation by neutron scattering [4,5]. By symmetry, there is no displacement allowed in the y-direction where infinite H-chains have been formed in the structure. The relaxation due to H ordering has an appreciable effect up to the Y4 atoms. The hydrogen atoms move almost exclusively in the directions of the H-chain and the bridge forming atom Y2 moves only slightly from its initial position. The displacements of the remaining Y atoms depend on the distance to the neighboring H-chains. Fig. 3a and b schematizes the displacements found in our calculations for $YH_{1/3}$ and $YH_{2/3}$, respectively.

For $YH_{2/3}$, the atomic displacements are below 0.07 Å, relaxing only in the z-direction.

We observed that the relaxation of atomic coordinates for this composition preserves the inversion symmetry in agreement with the symmetries of the $P6_3/mmc$ space group.

4. Electronic structure information for the $YH_{1/3}$ system

4.1. DOS

A common feature observed for the total DOS, H- and Y-partial DOS, is that the peaks become smoother under the relaxation of atomic coordinates. However, no appreciable modification is observed near the Fermi level between pure Y DOS and Y1, Y2, Y3 and Y4 total DOS for $YH_{1/3}$. The

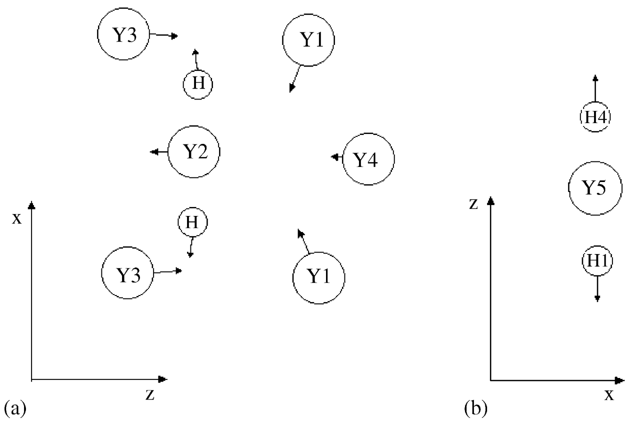

Fig. 3. Schematic representation (not to scale) for the atomic displacements obtained for: (a) $YH_{1/3}$ and (b) $YH_{2/3}$.

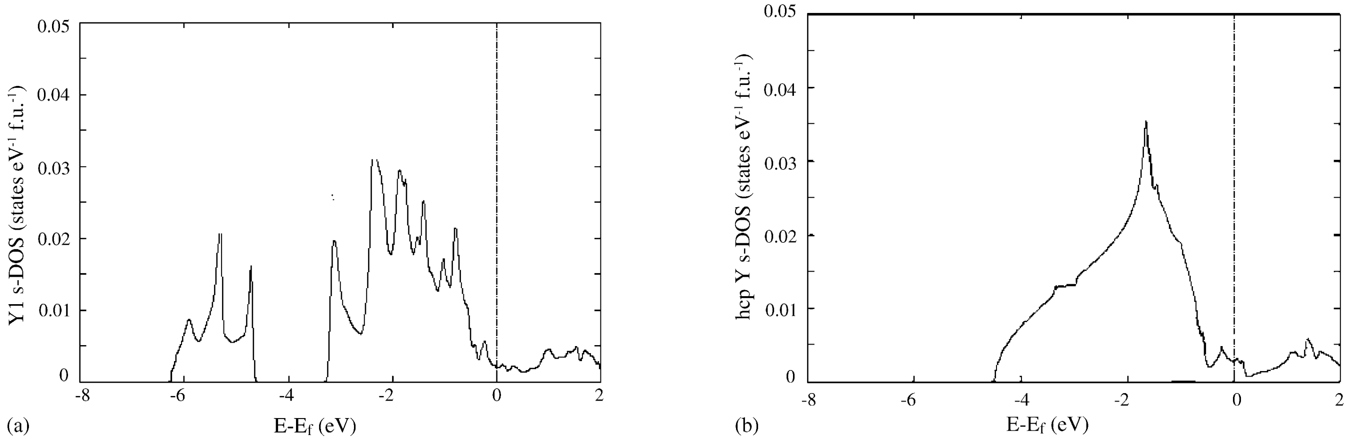

Fig. 4. s-DOS for pure hcp Y (left) and relaxed $YH_{1/3}$ (right). Similar DOS are obtained for Y2 and Y3. Y4 does not have the peaks around −5.5 eV.

Table 5
Distances between atoms (in Å) for $YH_{1/3}$ before and after relaxation of internal atomic coordinates for the group of atoms represented in Fig. 3a

Distances between atoms	Distances (Å)		Displacement (Å)
	Unrelaxed cell	Relaxed cell	
H-Y1	2.252	2.190	−0.062
H-Y2	2.187	2.268	+0.081
H-Y3	2.252	2.206	−0.046
H-Y4	4.290	4.331	+0.041
Y1-Y1	5.831	5.623	−0.208
Y1-Y2	3.611	3.529	−0.066

(Note that the Y1-Y1 distance in this table is not the shortest one in the cell).

most appreciable changes are the peaks around −5.5 eV due to s-states, which are not observed in pure Y where the s-states lie around −2 eV (Fig. 4). But, among the principal results found is the fact that the s-states from H contribute only negligibly near the Fermi level (see Figs. 4 and 5) and the main contribution to the DOS arises from the Y d-states, as in pure Y. As a consequence, we expect that the hydrogen will not have any appreciable contribution to the shape of Fermi surface.

4.2. Fermi surface

In order to compare the Fermi surface between pure Y and $YH_{1/3}$, it is preferable to perform the calculations in identical circumstances, i.e. in a structure corresponding to the Pmma space group. Although a direct comparison is not possible in the present work due to lack of space, the main geometrical features such as ring-like and planar-like shapes observed in Y are also present in $YH_{1/3}$ although the latter one is emphasized. For $YH_{2/3}$, only the ring-like shape is obtained.

Table 6
Distances between atoms (in Å) for the $YH_{2/3}$ before and after relaxation of internal atomic coordinates for the group of atoms represented in Fig. 3b

Distances between atoms	Distances (Å)		Displacement (Å)
	Unrelaxed cell	Relaxed cell	
H1-Y1	2.247	2.206	−0.041
H1-Y2	2.184	2.252	+0.068
Y1-Y2	3.605	3.550	−0.100

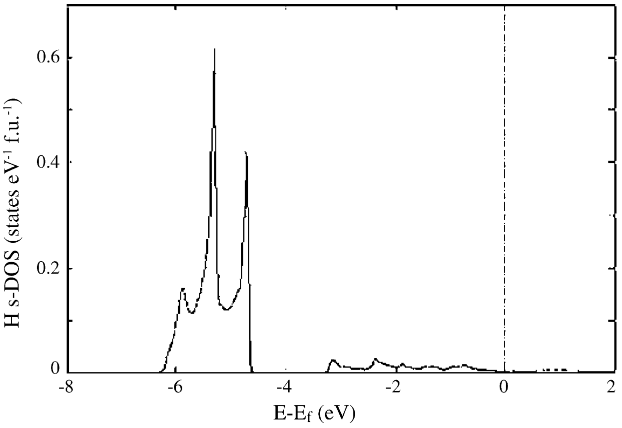

Fig. 5. H s-DOS for relaxed $YH_{1/3}$.

Our calculations show that the states at the Fermi level are predominantly of Y-4d character. There are no significant contributions coming from Y p- or s-state.

For pure Y, we observed 10 bands crossing the Fermi level although four of them have a small contribution. The remaining bands have ring-like and planar-like geometrical features mainly in the (x, y) plane of the real space.

For $YH_{1/3}$, the number of bands crossing the Fermi level is reduced to six. In most of them, the planar-like feature of the same plane as in pure Y is emphasized, reflecting the quasi-linear chain-like ordering of H along the z-direction.

5. Conclusions

In this work we study theoretical aspects related to hydrogen ordering in the hcp Y solid solution focusing on the relation between chain ordering of H, the relaxation of internal coordinates and the electronic properties for hypothetical α-$YH_{1/3}$ and α-$YH_{2/3}$. In addition to the relaxed atomic positions in the cell, we obtain information on the negligible role of the H 1s state contribution near E_F and on the shape of the Fermi surface.

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References

[1] P. Vajda, Hydrogen in rare earth metals, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 20, North-Holland, Amsterdam, 1995.

[2] B.J. Min, K.M. Ho, Phys. Rev. B 45 (1992) 12806.

[3] Y. Wang, M.Y. Chou, Phys. Rev B 49 (1993) 13357.

[4] M.W. McKergow, D.K. Ross, J.E. Bonnet, I.S. Anderson, O. Schaerpf, J. Phys. C 20 (1987).

[5] O. Blaschko, G. Krexner, J.N. Daou, P. Vajda, Phys. Rev. Lett. 55 (1985) 2876;
O. Blaschko, G. Krexner, J. Pleschiutschnig, G. Ernst, J.N. Daou, P. Vajda, Phys. Rev. B 39 (1989) 5605.

[6] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, J. Luitz, Wien2k, An Augmented Plane-Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universitat Wien, Austria), 2001. ISBN 3-9501031-1-2.

[7] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.

[8] A. Kokalj, XCrySDen—a new program for displaying crystalline structures and electron densities, J. Mol. Graphics Model. 17 (1999) 176–179 (code available from http://www.xcrysden.org/).

[9] B.J. Beaudry, K.A. Gschneidner, in: Handbook on the Physics and Chemistry of Rare Earths, vol. 1, North-Holland, Amsterdam (1978).