



First-principles study a superstoichiometric rare earth dihydride $GdH_{2.25}$

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Abstract— We have performed *ab initio* calculations of electronic structure and equilibrium properties for the rare earth superstoichiometric dihydride $GdH_{2.25}$ (with the space group $Pm-3m$ (No. 221)) using the full-potential linearized augmented plane wave method (FP-LAPW) approach within the density functional theory (DFT) in the generalized gradient approximation (GGA) and local density approximation (LDA) as implemented in the WIEN2k simulation code at 0K. The equilibrium properties have been determined, the density of states, electronic density and the energy band structures are studied in details. It was concluded that the GGA optimized lattice parameter agrees much better with the experimental findings than the LDA one. The non negligible electronic density of states at the Fermi level confirms that the $GdH_{2.25}$ has a metallic character. The Fermi energy E_F falls at a level where most of the states are rare-earth 5d-eg conduction states while negligible contributions of both interstitial (tetrahedral and octahedral) H s-states are observed near E_F . From electronic density, the bonding between Gd and tetrahedral H atoms is of prominent covalency, while is ionic between Gd and octahedral H atoms.

Keywords— rare-earth dihydrides, $GdH_{2.25}$, density functional theory, *ab initio* calculations, WIEN2k.

I. INTRODUCTION

Considering the shortage of fossil energies and because fossil fuels lead to polluting emissions, the hydrogen is an ideal substitute for fossil fuels. The important condition for hydrogen energy utilization is hydrogen storage, which requires a safe and low-cost material as a hydrogen carrier. Metallic and intermetallic hydrides can be used as hydrogen storage materials as they have several advantages over storage in gaseous or liquid forms. Electric charge on the hydrogen atom was created by charge transfer between the hydrogen atom and the transition metal. Authors found a relation between the minimum *H-H* internuclear distance and the stability of metal hydrides. Switendick [1] evaluated the minimum distance between adjacent hydrogen atoms to be about 2.1 Å for a stable hydride. Rare earths (R) are seen as promising materials owing to high hydrogen capacity per volume unit and an ability to absorb and store hydrogen under moderate conditions of temperature and pressure [2]. In the case of rare-earth hydrides, many research studies, both experimental and theoretical, have been performed to

investigate their interesting physical and chemical properties [3, 4]. General reviews of the properties of hydrogenated rare earths have been given by Vajda [5,6] and Schöllhammer [7]. On increasing hydrogen concentration, the crystal structure of heavy rare-earth hydrides changes generally from a metallic hcp (hexagonal close-packed) solid solution (α -phase), to a more metallic CaF_2 -type dihydride (β -phase), and then to an insulating or semimetallic HoD_3 -type trihydride (γ -phase) [8].

In this study we focus on the Gd-H system, whereas most of the other heavy rare-earths, the gadolinium dihydride keeps the fluorite (CaF_2) type structure, where the hydrogen atoms occupy only the tetrahedral (T) sites [8] to give the pure (stoichiometric) dihydride GdH_2 . By adding more hydrogen to the compound, octahedral (O) interstitial sites accommodate the additional x-hydrogen to give the superstoichiometric dihydride GdH_{2+x} up to $x_{\max}^{\beta} \approx 0.3$ when the insulating γ -phase starts precipitating [5]. The lattice parameters of GdH_{2+x} have been determined by X-ray diffractometry by Chiheb et al. (1993) [9]. In 1998, Ellner [10] investigated the unit cell parameters of the gadolinium dihydride $GdH_{2.25}$ by powder diffraction with space group $Fm-3m$.

Therefore, in this paper, we shall present complete results of a detailed electronic structure calculation of the stoichiometric $GdH_{2.25}$, which is based on *ab initio* calculations at 0K within density functional theory (DFT), using a full-potential linear augmented plane-wave (FP-LAPW) method as implemented in the WIEN2k code.

The outline of this paper is as follows: in Section 2, we give the calculation method. The results and discussion are presented in Section 3. Finally Section 4 concludes the paper.

II. COMPUTATIONAL METHOD

Our calculations are based on density functional theory (DFT) [11, 12]. In this work, the full potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2k package [13], which solves the Kohn-Sham equations self-consistently, was used for the calculations. The cutoff in the charge density Fourier expansion, G_{\max} , was taken to be $20 \text{ Ry}^{1/2}$.

Rare earths can be problematic for DFT calculations. We note that one can expect the existence of finite localized



magnetic moments on the $4f$ electrons. This magnetic aspect has not been considered in our calculations. It is known, indeed, that, in rare earths, the $4f$ electrons, being very close to the core, are expected to be chemically inert. This leads us to consider $4f$ electrons as atomic electrons, i.e. they cannot hybridize with the other valence s , p , and d electrons anymore and are perfectly localized [24]. For these reasons, the contribution of the $4f$ electrons are removed from the valence bands, and are treated as those of core electrons. It is known that in WIEN2k the core states feel only a spherical potential, are not split by crystal fields and do not contribute to it.

We used an energy of -8 Ry to separate core and valence states, and the Gd ($5s^2 5p^6 5d^1 6s^2$) and H ($1s^1$) orbitals were treated as valence states (we did not treat the f orbitals of Gd as valence electrons but as core electrons). Exchange and correlation effects were treated within the density functional with the generalized-gradient approximation of Perdew, Burke and Ernzerhof (GGA96) [14] and the local density approximation (LDA) [15]. The calculations were based on an optimized number of k-points of 1000, without considering the spin polarization. The self-consistent calculations are considered to be converged only when the calculated energy changes by less than 0.1 mRy.

III. RESULTS AND DISCUSSION

A. Equilibrium properties

The space group of $GdH_{2.25}$ is chosen to be $Pm-3m$ (No. 221), whose structure is plotted in Fig. 1 (by using XCrysden [16]).

The ground-state structural parameters have been obtained by fitting the total energy E versus volume V data to the non-linear Murnaghan equation of state [17]. We present the $E(V)$ relationship of the $GdH_{2.25}$ for both LDA and GGA approximations in Figs. 2(a) and 1(b) respectively. We extracted the lattice parameter, the value of the bulk modulus, and its first order pressure derivative. The results data are listed in Table 1 together with previous experimental findings. There are no experimental data for the bulk modulus available for this material and there is no direct *ab initio* theoretical information available for $GdH_{2.25}$ related to the effects of interstitial H atoms on their local atomic environment.

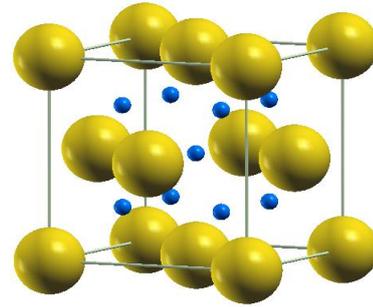


Fig. 1 The compound crystallises in the CaF_2 fluorite type structure: the large spheres represent rare earth atoms ($\times 4$) and small spheres hydrogen atoms occupying tetrahedral sites ($\times 8$) and the central octahedral site ($\times 1$) (figure plotted with XCrysden [16]).

The GGA equilibrium lattice parameter a_0 , from Table 1, slightly overestimates the experimental value by 0.28%, while the LDA value is clearly smaller than the experimental one by 2.6%. Conversely for the bulk modulus, it is the GGA value which is lower than that of the LDA by 22.2% as a result of an over-binding characteristic of LDA. Hence, GGA overestimates the lattice parameter whereas it underestimates bulk modulus B_0 in comparison with LDA, a feature also observed in several similar systems in other simulation works [18]. In addition, one can see a difference in the magnitude of the energy (see Table 1), which means it is sensitive to the approximations used in the calculation.

TABLE I
CALCULATED EQUILIBRIUM LATTICE CONSTANT a_0 (IN Å), BULK MODULUS B_0 (IN GPa), ITS FIRST ORDER PRESSURE DERIVATIVE B_0' , AND COHESIVE ENERGY E_c (IN eV) FOR GGA AND LDA COMPARED TO EXPERIMENTAL DATA.

	Method	a_0	B_0	B_0'	E_c
$GdH_{2.25}$	GGA	5.299	62.4385	3.0152	5.2859
	LDA	5.143	80.3544	3.1906	12.1737
$GdH_{2.26(6)}$	Exp.	5.284 ^a			
GdH_2	GGA	5.326 ^b	53.1873 ^b	4.0861 ^b	
$ErH_{1.95}$	Exp.		67 \pm 3 ^c	9 fixed ^c	
$ErH_{2.091}$	Exp.		73 \pm 4 ^c	8 fixed ^c	

^aRef. [10]-Expt.; ^bRef. [19]; ^cRef. [20]-Expt.

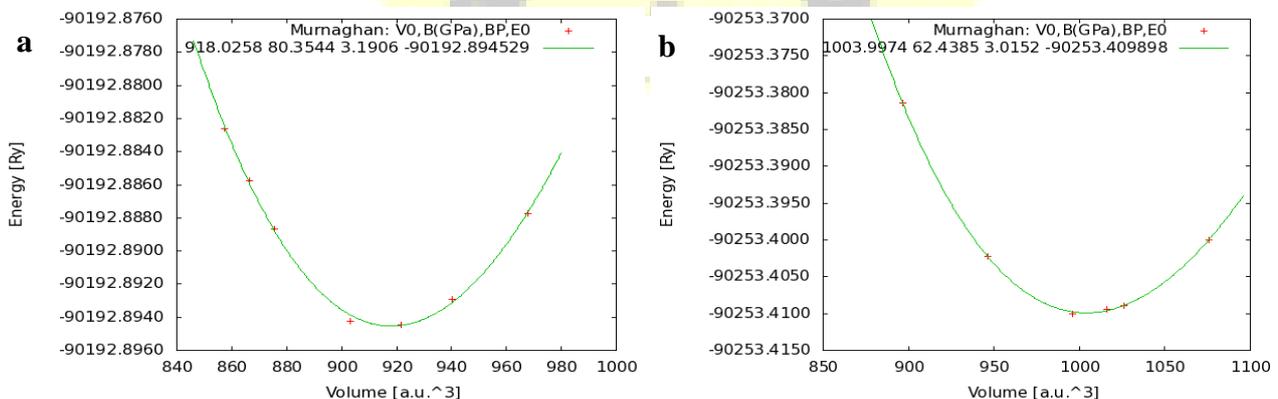


Fig. 2 Calculated total energy curves for $GdH_{2.25}$ as a function of cell volume in the (a) LDA and (b) GGA approximations.



B. Electronic properties

The calculated electronic band structures at the equilibrium lattice constant for different high-symmetry points in the Brillouin zone and the total density of states DOS (measured in one state per unit cell of two spins per electron-Volt) of $GdH_{2.25}$ in GGA and LDA at 0K are shown in Figs. 3 and 4 respectively, where the dashed line at zero eV indicates the Fermi energy.

Clearly, in both figures, several bands cross the Fermi level (E_F), confirming that $GdH_{2.25}$ possesses a metallic ground-state (the density of states on the Fermi level $N(E_F)$ doesn't negligible as seen in Table 2), in agreement with electrical resistivity measurement interpretations [5]. The LDA and GGA energy band structures are qualitatively similar. Indeed, the crossings of bands with the Fermi level are nearly the same in the two approximations, where the values of the Fermi energy is $0.46639 Ry$ in GGA and a higher $0.50542 Ry$ in LDA (as seen in Table 2). Another significant feature of the band structures in Figs. 3 and 4 is the different positions of the valence bands (at Γ), where, in the LDA, these shift towards the higher-energy region in the valence band top, and towards the lower energy region in the valence band bottom, and a clearer splitting between the valence bands, which indicates increase in the bandwidth, this is a consequence of the reduced the lattice parameter a [21].

The total DOS of $GdH_{2.25}$ has similar features in both GGA and LDA (see Fig. 5) especially at the Fermi level.

However, these figures show small but non negligible differences as the peaks in the GGA are fairly sharper and narrower than those of LDA, and the total DOS in LDA moves a little towards the lower energy region compared to GGA.

TABLE III

FERMI ENERGY (IN RY) AND DENSITY OF STATES AT THE FERMI LEVEL (IN STATES/Ry) FOR $GdH_{2.25}$ IN TWO APPROACHES GGA AND LDA.

	GGA	LDA
Fermi energy	0.46639	0.50542
$N(E_F)$	40.30	37.82
$N_s(E_F)$	0.00	0.00
$N_p(E_F)$	0.29	0.33
$N_d(E_F)$	2.97	3.02
$N_{d-eg}(E_F)$	2.69	2.71
$N_{d-t2g}(E_F)$	0.28	0.31
$N_{Htet-s}(E_F)$	0.06	0.05
$N_{Hoct-s}(E_F)$	0.12	0.10

In order to analyze the atomic interaction between a hydrogen atom and its different neighboring atoms, the total

DOS has been decomposed into its partial-wave (s , p , and d) components around the H.

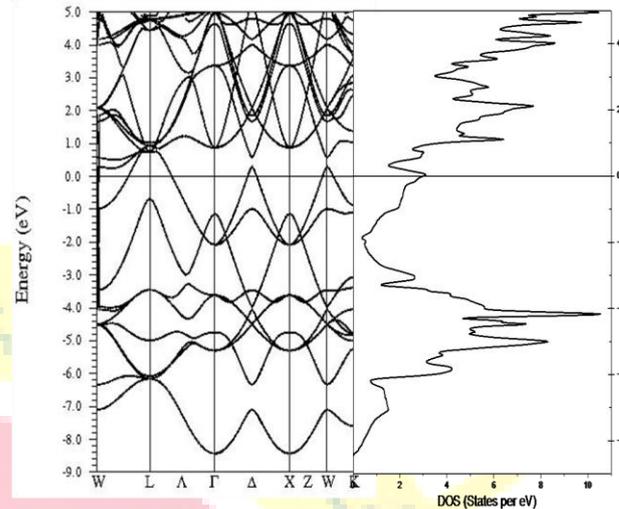


Fig. 3 Density of states (right panel) and electronic band structure along high-symmetry directions (left panel) of $GdH_{2.25}$ in the GGA, the Fermi energy being at 0 eV.

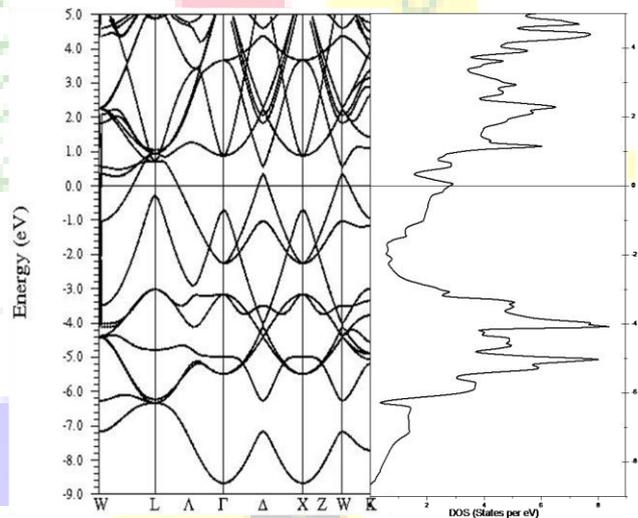


Fig. 4 Density of states (right panel) and electronic band structure along high-symmetry directions (left panel) of $GdH_{2.25}$ in the LDA, the Fermi energy being at 0 eV.

The total DOS decomposition into components according to the value of the angular momentum (s : $L=0$; p : $L=1$; d : $L=2$) inside the MT spheres of the metal and of the hydrogen as shown in Fig 5, where the left and the right columns correspond respectively to the GGA and LDA computations. It may be seen that in both cases the total DOS of $GdH_{2.25}$ is almost composed by that of Gd atoms, which itself is dominated by the $5d$ partial DOS. We can actually begin this analysis from the situation at the Fermi level. It can be seen

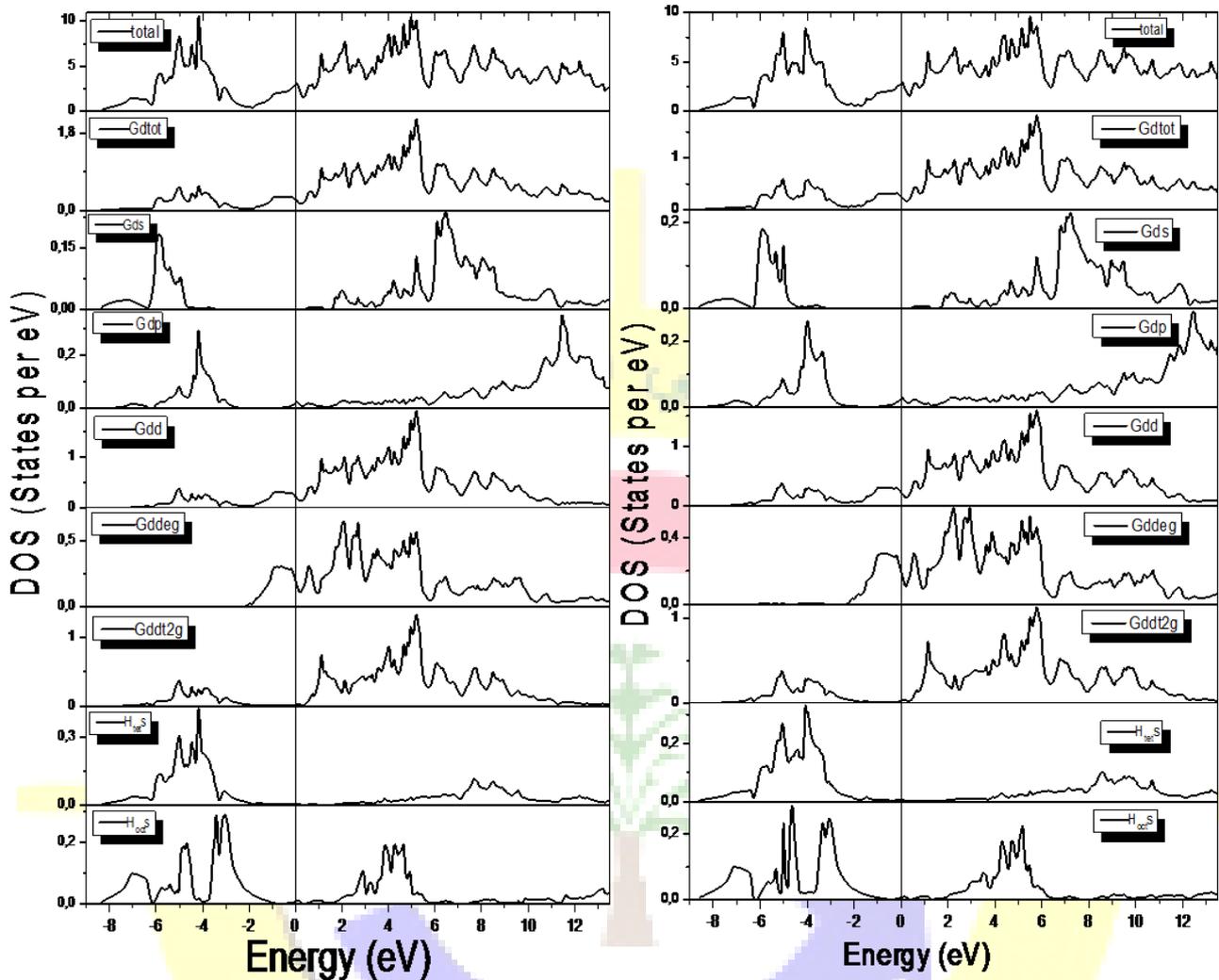


Fig. 5 The calculated total and partial density of states for $\text{GdH}_{2.25}$ in the LDA (right panel) and in the GGA (left panel), the Fermi energy being at 0 eV.

clearly in the Table 2 that the hydrogen in both interstitial sites (tetrahedral H_{tet} and octahedral H_{oct}), and both d - $t2g$ and p Gd, do not contribute significantly at the Fermi level, which means that they are essentially not involved in conduction properties. In contrast, the Gd d - eg electrons represent the majority contribution at E_F .

It is convenient to divide the DOS into regions: region I (-8.49533 to -1.47473 eV) of GGA and (-8.72703 to -1.54317 eV) of LDA with a major contribution of Gd d - $t2g$ states and both H $1s$ orbitals and much smaller contributions of Gd s and p ; region II (-1.47473 eV to E_F) of GGA and (-1.54317 eV to E_F) of LDA with Gd d - eg states and very few Gd p states; region III (above E_F in the lowest energy domain of the conduction band) with unoccupied s , p and d states from Gd and s from H in octahedral sites (H_{oct}).

It is interesting to note that a strong hybridization exists between Gd d - $t2g$ and H_{tet} atoms (in region I) as shown in Fig. 5, which leads to an appreciable covalent component in between Gd d - $t2g$ and H_{tet} atoms (in region I) as shown in Fig. 5, which leads to an appreciable covalent component in the Gd-H bond (in the direction [111]). On the other hand, hybridization between Gd and H_{oct} atoms is much weaker, indicating a degree of ionic character in this bond, which is mainly due to the longer Gd- H_{oct} distance (2.6495 Å of GGA and 2.5710 Å of LDA). The minimal atomic bonding distance (2.2945 Å of GGA and 2.2266 Å of LDA) exists between Gd and H_{tet} atoms. Therefore, the Gd-H bonds in $\text{GdH}_{2.25}$ have a mixed (covalent-ionic) character as is found in several metal hydrides [22, 23 and 24].



We now turn our attention to the analysis of valence electron-charge density. The charge-density in the (110) plane is displayed in Fig.6. It is observed that appreciable charge density exists in the outer regions of Gd and H_{tet} atoms with a slight deformation in the direction of these nearest-neighboring atoms. This feature indicates that the bonding between Gd and H_{tet} atoms is certainly covalent, a fact confirmed by the hybridization analysis. At the same time, it is clear that very little electronic charge is shared between Gd and H_{oct}, where most of the valence electrons of H_{oct} are tightly bound around their atoms and this implies that the bond has some ionic character (is much weaker). Another point of interest is the existence of a little charge in the interstitial regions away from the bonds which gives a metallic character to this compound, confirming therefore our DOS analysis.

We found that the total charge in each H_{tet} atom is around 0.64 e of GGA and 0.63 e of LDA and in each H_{oct} atom is around 0.55 e of GGA and 0.54 e of LDA, where the total interstitial charge in LDA is smaller than GGA by 8.04%.

IV. CONCLUSIONS

The work presented in this paper was aimed at establishing a clearer picture of the electronic structure and equilibrium properties for the superstoichiometric GdH_{2.25} compound. Calculations performed using an *ab initio* FP-LAPW method in the local density approximation (LDA); and the generalized gradient approximation (GGA) for the exchange correlation as implemented in the WIEN2k code at 0K. In the GGA the calculated lattice constant is 3% larger and bulk modulus 22.2% smaller, as compared to the LDA results. On other hand, the calculated lattice constant with the GGA agrees well with available experimental data. There are no bulk modulus data, to our best knowledge, for the considered material.

We have also calculated and presented the electronic band structure and density of states, which clearly show that GdH_{2.25} exhibits metallic behavior. The total DOS in GGA and LDA shows important differences in the vicinity of the valence band. Where, the GGA presents a tendency for underbinding in this material. In addition, the value of the DOS at the Fermi level $N(E_F)$ in GGA is larger than in LDA.

The DOS analysis shows that the Fermi energy (E_F) falls at a level where most of the electronic states are rare-earth 5*d*-*eg* conduction states, while negligible contribution of both interstitial H *s*-states is observed at E_F .

The *d* states of the Gd *d-t2g* atoms are the main contributors to bonding states in the valence bands, whereas *p* and *s* states have a smaller role. It is found that hybridization exists between the *s* electronic orbital of both interstitial H atoms and the *d-t2g* electronic orbitals of Gd. This hybridization implies that there is mixture of covalent (Gd-H_{tet}) and ionic (Gd-H_{oct}) bonds, which is confirmed by the charge density analysis.

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