



Ab initio investigations of the electronic and magnetic structures of CoH and CoH₂



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ABSTRACT

First principles investigation of the structural, electronic and magnetic properties study of cobalt and the hydrides CoH_x ($x = 1, 2$) show significant volume expansion effect versus Co–H bonding. As hydrogen is incorporated in the cobalt lattice, the density of states undergoes gradual modifications within the valence band and particularly near the Fermi level. A resulting strong reduction of magnetization characterizes the dihydride whereas the monohydride is revealed as a strong ferromagnet, like Co.

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1. Introduction

Hydrogen is by far the most abundant element in the universe. It forms alloys and compounds with many metals and is the smallest and the simplest impurity that can be implanted into a metal host. The study of hydrogen-metal systems is motivated by the scientific challenge it presents. There are many present and potential applications of the hydrogen-metal system in the energy related industry such as the interest in using it as the storage medium of hydrogen. For these purposes, the transition metal hydrides that are important in several fields of chemistry have been considered, specifically the transition metal polyhydrides have been studied both experimentally [1] and theoretically [2] due to the importance of the H-transition metal bond in catalysis [3–6].

Although many metals can exothermically dissolve considerable amount of hydrogen, cobalt seems to have peculiar chemical–physical properties that make it a highly attractive metal for hydrogen. It is known that the cobalt hydrides do not exist free in

nature [7]. Two phases are known for Co–H system, namely CoH and CoH₂ [8,9] with close packed hexagonal (hcp) phase and face centered cubic (fcc) structure for $x > 1$. Local density approximation band structure calculations have established the basic features of the electronic structure and bonding of the transition metal hydrides. The introduction of hydrogen into interstitial sites of the transition metal lattice lowers the interstitial crystal potential [10]. However, at the same time, each H atom introduces an additional electron into the crystal lattice. This electron, which enters at the Fermi energy, also makes a significant contribution to the bonding between Co and H. These extra electrons introduced by the addition of H atoms are then expected to enter predominantly the unoccupied minority spin 3d bands at the Fermi energy leading to a strong reduction in the moment. In this picture, the introduction of hydrogen atoms into cobalt forming CoH_x affects the magnetism of the crystal structure by the reduction in the spin moment due to the addition of electrons to the minority spin bands. One may anticipate that the reduction in the moment from Co to CoH could be larger. This is because as H is added, the exchange splitting of the 3d bands is likely to decrease. If this decrease is large enough, then the majority spin d bands may become partially unoccupied leading to a further reduction in the spin moment [10].

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In order to provide additional information about insertion of hydrogen atoms into cobalt pertaining to the magnetovolume versus bonding (spin pairing) effects, the structural, electronic and magnetic properties of CoH_x ($x = 1, 2$) are studied using ab initio calculations.

2. Method of calculation

At hydrogen pressure a cobalt hydride with $x \approx 1$ is formed on the basis of the high-temperature fcc cobalt modification [11]. Cubic CoH can be visualized as two interpenetrating fcc sublattices where one substructure is formed by Co-atoms and the other by H-atoms. In CoH_2 , Co forms a face centered cubic lattice within which tetrahedral voids are occupied by H. These structures are inscribed in the $Fm\bar{3}m$ (#225) space group, with the $4a$ (0, 0, 0) and $4b$ ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) Wyckoff positions for Co and H in CoH on one hand and $4a$ (0, 0, 0) and $8c$ ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) Wyckoff positions for Co and H in CoH_2 on the other hand.

Non-relativistic full potential (FP) linearized augmented plane waves (LAPW) calculations have been performed using the WIEN2k code [12]. For the exchange and correlation potential, we used the Generalized Gradient Approximation (GGA) with the parameterization of Perdew–Burke and Ernzerhof [13]. Basis functions, electron densities and potentials were expanded inside the muffin-tin spheres in combination with spherical harmonic functions with a cut-off $l_{\text{max}} = 10$, and in Fourier series in the interstitial region. We used a parameter which determines matrix size (convergence), $R_{\text{MT}} \cdot K_{\text{max}} = 8$, where K_{max} is the plane wave cut-off and R_{MT} is the smallest muffin tin (MT) radius of all atomic spheres. We chose the MT radii of Co, and H to be 1.9, 1.4 for CoH system and 1.85, 1.32 a.u. for CoH_2 system (1 a.u. = atomic unit = 0.529 Å).

In the calculations, we have distinguished the Co ($1s^2 2s^2 2p^6 3s^2$) inner-shell electrons from the valence electrons of Co ($3p^6, 3d^7, 4s^2$), H ($1s^1$) shells.

Parallel calculations for fcc Co were performed in order to enable comparison of the electronic structures of CoH , CoH_2 and host metal.

3. Calculations and results

3.1. Structural calculations

For the considered structures and at the two hydrogen x concentrations ($x = 1, 2$), the structural properties were obtained by a minimization of the total energy as a function of the volume for CoH and CoH_2 systems in the NaCl (rocksalt) and CaF_2 (calcium fluorite) structures.

As a first step, we calculated the equilibrium structural parameters of CoH_x in cubic symmetries for the extended cell by means of fitting the Murnaghan equation of state to the energy vs. deformation curves; this is the $x = 0$ case.

The next step was to introduce one hydrogen atoms into the cobalt lattice. This structure can be considered as ‘hydrogen

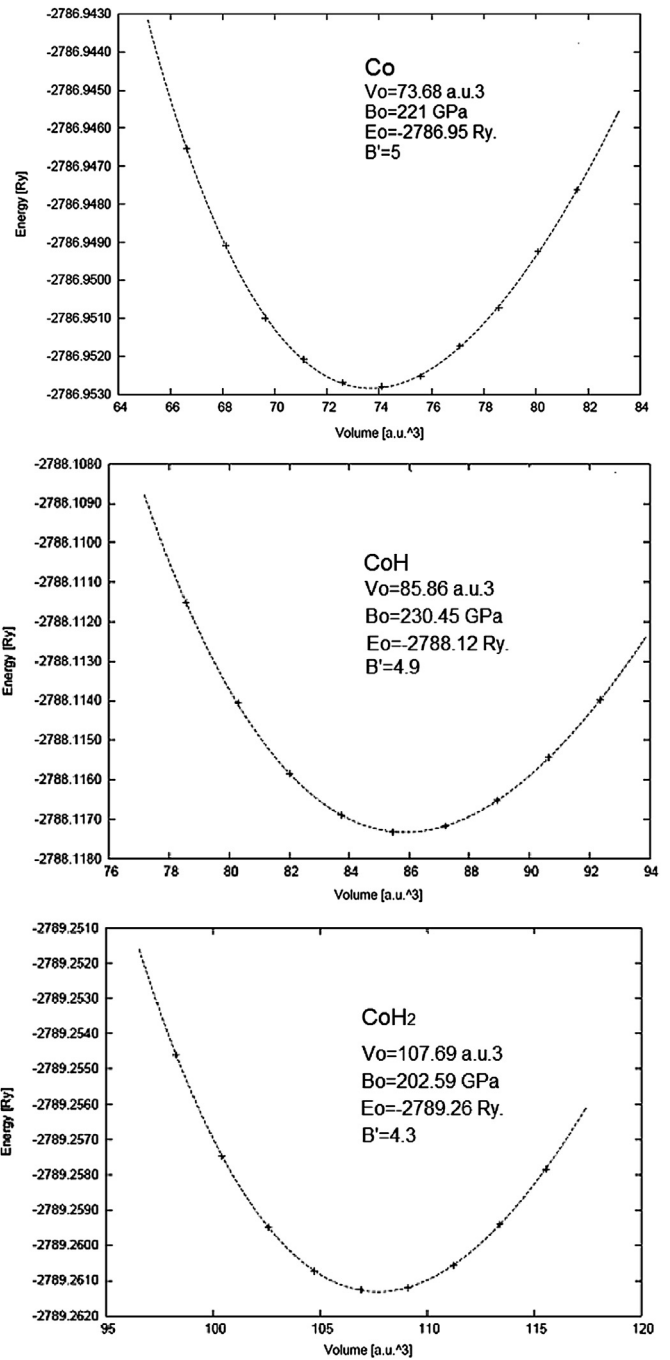


Fig. 1. Energy as function of volume for fcc Co (top), CoH (middle) and CoH_2 (bottom) in GGA DFT functional. Inserts show fit values from Murnaghan EOS.

Table 1

Lattice constants a , bulk modulus B_0 , and pressure derivative of bulk modulus B' for Co, CoH and CoH_2 solid solutions.

Material		This work GGA	Other theoretical studies	Experimental data
Co	a (Å)	3.52	3.53 [14], 3.50 [15]	3.54 [16], 3.55 [22]
	B_0 (GPa)	221.10	235 [17], 269 [18]	192 [19]
	B' (GPa)	5.03	—	—
CoH	a (Å)	3.70	3.735 [20]	3.7124 [21]
	B_0 (GPa)	230.46	200 [19]	—
	B' (GPa)	4.88	—	—
CoH_2	a (Å)	3.99	—	—
	B_0 (GPa)	202	—	—
	B' (GPa)	4.31	—	—

Table 2

Effect of the hydrogen concentration on the volume of cobalt hydrides CoH_x with x designating the composition.

x	This work		Other works		Experimental works	
	V (Å ³)	$(\Delta V/V_0)$ (%)	V (Å ³)	$(\Delta V/V_0)$ (%)	V (Å ³)	$(\Delta V/V_0)$ (%)
0	43.61	—	43.98 [14]	—	44.36 [16]	—
1	50.65	16.14	51.89 [20]	17.98	51.06 [21]	15.10
2	63.52	45.65	—	—	—	—

perturbed' cobalt lattice. The next step is generated by introducing two hydrogen atoms. In Table 1, we summarize the calculated equilibrium structural properties (lattice parameters, bulk modulus and their pressure derivatives) of Co, CoH and CoH₂ solid solutions

together with available theoretical [10,14,15,17–19,20] and experimental [8,16–19,21,22] data from the literature.

It needs to be mentioned that although the hcp structure for the hydrides appears only for $x < 1$ [11], we have calculated CoH in

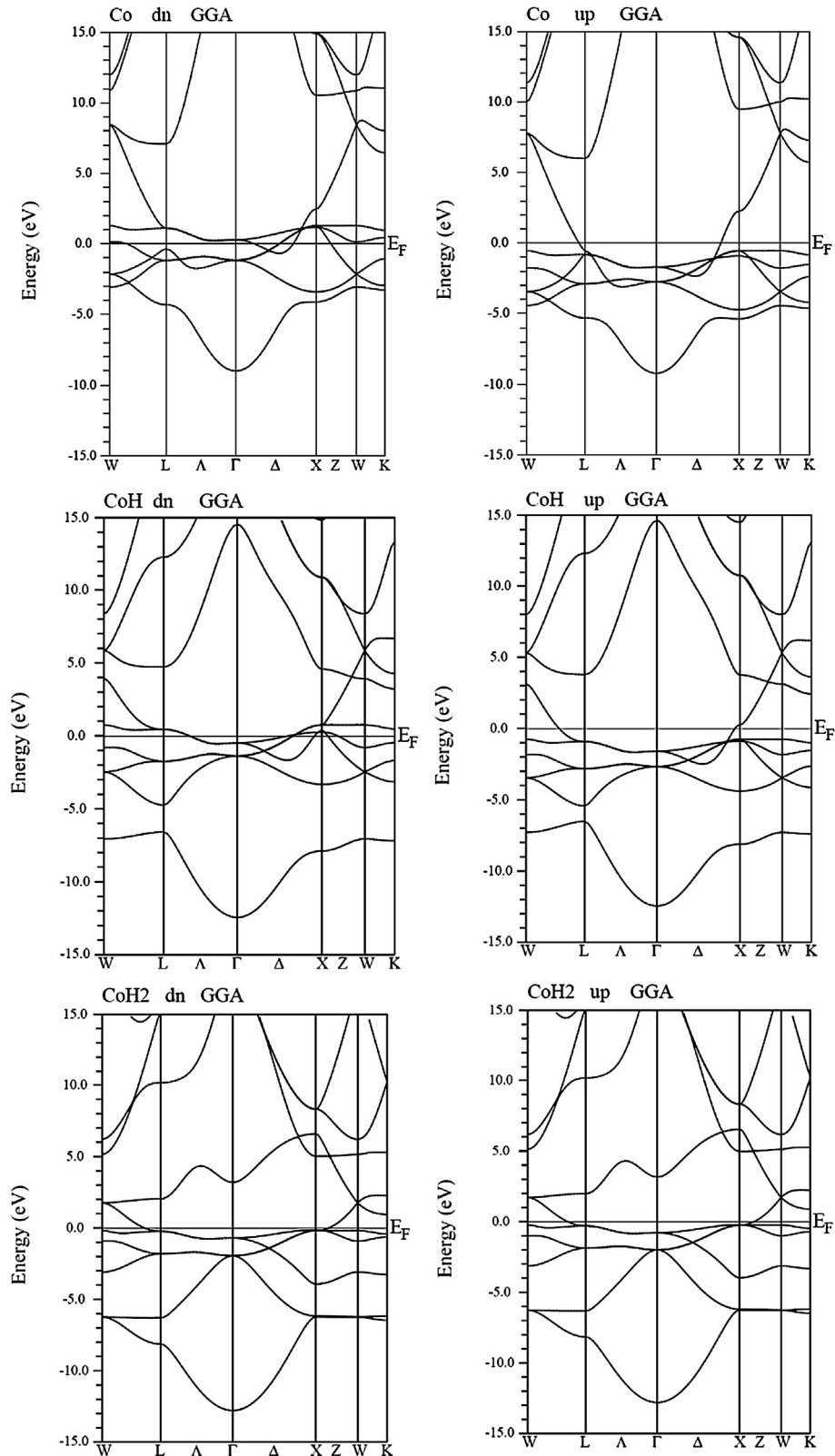


Fig. 2. Electronic band structures for minority spins (down) and majority spins (up) of fcc Co (top), CoH (middle) and CoH₂ (bottom).

hexagonal symmetry to compare the relative energy versus experimental fcc-CoH. The result is a large energy stabilization of cubic versus hexagonal CoH with ΔE (fcc-CoH – hcp-CoH) = -0.271 eV per formula unit.

For a better assessment of the results we derive the equilibrium zero pressure parameters from the energy-volume (E, V) equation of state (EOS) with (E, V) set of calculations around minima found from the calculations. The underlying physics of this procedure is that the calculated total energy corresponds to the cohesion within the crystal in as far as the solution of the Kohn–Sham DFT equations gives the energy with respect to infinitely separated electrons and nuclei. But the zero of energy depends on the choice of the potentials, then energy becomes arbitrary through its shifting, not scaling. However the energy derivatives as well as the EOS remain unaltered. For this reason one needs to establish EOS from which the fit parameters are extracted for an assessment of the equilibrium values. The resulting values are plotted in Fig. 1 for the three systems. They have a quadratic variation which can be fitted with an energy-volume Murnaghan EOS [26]. The fit values are given in the inserts of Fig. 1. E_0, V_0, B_0 and B' are the equilibrium energy, the volume, the bulk modulus and its pressure derivative, respectively. The corresponding zero pressure bulk modulus show an increase from fcc Co to CoH then a decrease for CoH₂. This can be interpreted as a hardening of the metal upon introducing one H through its bonding to Co, despite the volume increase. But upon introduction of extra hydrogen the cell expansion becomes too large ($\Delta V/V_0 \sim 46\%$, cf. Table 2) and the compound becomes largely compressible leading to a drop of B_0 .

3.2. Band structures

Calculations are all carried out considering two spin channels, majority spins \uparrow and minority spins \downarrow .

The calculated spin polarized band structures of CoH_x as well as fcc Co to enable comparisons, are shown in Fig. 2.

It is obvious that the majority of the d bands are entirely occupied at the same time in CoH and Co. A notable difference between the CoH and Co band structures is at the center of the Brillouin zone (Γ point) showing the broader valence band in the hydride. The topology of the band structures of Co, CoH and CoH₂ materials are almost the same for the two DFT exchange-correlation approximations used (GGA and LDA), which clearly exhibit a metal aspect, larger for minority spin bands. In the dihydride the two spin panels mirror each other, thus signaling vanishing energy shift between them, leading to absence of magnetization as shown below.

3.3. Density of states

The density of states (DOS) is an important information to understand the bonding and electronic properties of new compounds.

We have calculated the DOS at the two different hydrogen atoms concentrations. In Fig. 3 showing the total DOS the energy reference along the x-axis is with respect to the Fermi energy. Along the three panels, top, middle and bottom, there is a gradual transformation of the electronic structure as hydrogen is introduced in the cobalt matrix. The majority spin d bands are completely occupied in CoH, like in fcc-Co, leading to assign a strong ferromagnetic behavior for Co and the monohydride CoH. This is not the case for CoH₂ in which the spin moment is vanishingly small leading to the absence of energy shift between majority \uparrow and minority \downarrow spin DOS as shown in Fig. 3 bottom panel.

The effect of hydrogen in the upper portion of the valence band (-0.5 to -6 eV) is evident. In fact, the DOS for CoH is comparable to those of fcc Co. The difference between them is the formation of a narrow sub band in the lower energy part of the valence

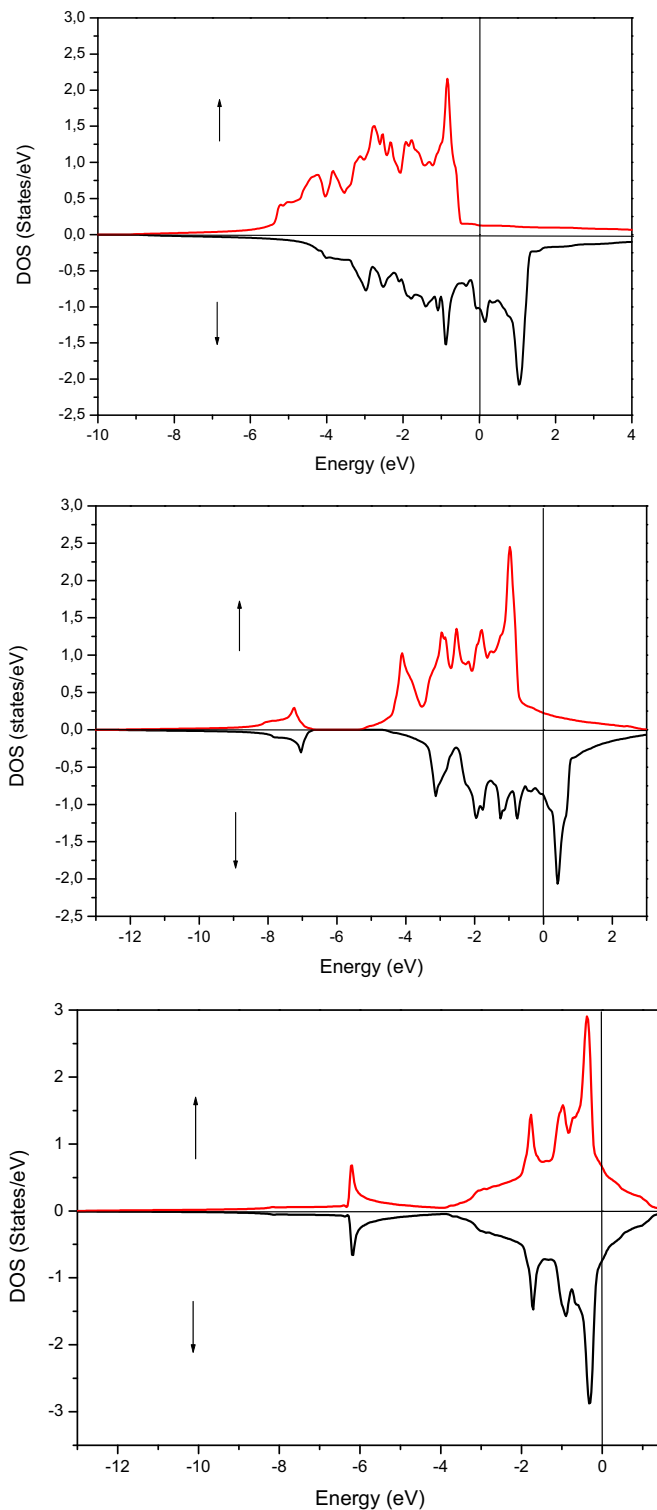


Fig. 3. Spin polarized total electronic density of states DOS of fcc-cobalt (top), CoH (middle) and CoH₂ (bottom).

band (around -6 eV) due to hydrogen. These states are also present in CoH₂.

As more hydrogen atoms are introduced in the Co matrix this band increases its importance and there is a significant energy shift for this sub band. The partial DOS reveals that this band is mainly due to H-1s states with small hybridization with Co-s, -p and -d

Table 3
Effect of the hydrogen concentration on the magnetic moment of cobalt hydrides.

Spin magnetic moment μ (μ_B) of cobalt hydrides system CoH_x			
Material	This work GGA	Other works	Experimental
Co	1.68	1.64 [23]	1.72 [22]
CoH	1.18	1.16 [10]	1.3 [8]
CoH ₂	-0.0041	–	–

states. For CoH this band is centered at -12.8 eV. The band moves to -13.1 eV for CoH₂.

3.4. Charge densities

We interpret this shift in terms of charge redistribution between Co and H, providing an indication of the degree of ionicity of Co–H bonding. This is made more quantitative from the charge density analysis using the AIM (atoms in molecules theory) approach [24]. Typically in chemical systems, the charge density reaches a minimum between atoms and this is a natural region to separate them from each other. Such an analysis does not constitute a tool for evaluating absolute ionizations but allows establishing trends between similarly chemical systems. For the two hydrides the average values (Q) are:

$$\begin{aligned} \text{CoH} : \quad Q(\text{Co}) &= +0.36 \quad Q(\text{H}) = -0.36 \\ \text{CoH}_2 : \quad Q(\text{Co}) &= +0.66 \quad Q(\text{H}) = -0.33 \end{aligned}$$

In both compounds the charge on hydrogen is rather covalent-like in as far as it is far below the closely fully anionic value (~ -1) of MgH₂ [25]. A slightly less covalent character is identified for the monohydride due to the larger Co–H separation as with respect to the fluorite structure, i.e. ~ 1.84 vs. ~ 1.73 Å. The effect of hydrogen in the upper portion of the valence band (-5 – 10 eV) is evident in Fig. 3 showing the total density of states (DOS).

3.5. Magnetic moments

The results show that the magnetic moment amounts to $1.68 \mu_B$, in fcc-Co and $1.18 \mu_B$ in CoH. These values are in good agreement with available experimental data [8,22] and theoretical [10,23] studies (Table 3). Our calculated spin moment for CoH is 9% smaller than the experimental moment, which contains an orbital component.

Thus, as stated above CoH is a strong ferromagnet, like Co.

Analysis of the distribution of the densities of spin in cobalt indicates that the magnetic moment of the material locates on the level of cobalt atom with $1.68 \mu_B$, the interstitial region presents a negative value of total magnetic moment $-0.06 \mu_B$. This situation is different in the case of CoH with a magnetic moment of $1.18 \mu_B$. The magnetic moment of hydrogen atom takes a small negative value of -0.020 as well as the interstitial region presents a negative value $-0.036 \mu_B$. Such negative signs of magnetization signal induced character due to Co–H bond.

For CoH₂ chemical system, a dramatic change occurs in the value of its spin magnetic moment since now this quantity has considerably reduced to the value of $-0.004 \mu_B$. This is directly related to the reduction of the d character.

The strong reduction in the magnetic moment is due to the extra electron introduced by the addition of H which is then expected to enter predominantly the unoccupied minority spin d bands at the Fermi level. Also significant amount of Co–H bonding is expected due to the smaller Co–H separation of 1.73 Å as with respect to the dihydride.

4. Conclusion

In this paper the magnetic and electronic structure of cobalt and CoH_x ($x = 1, 2$) have been studied by first principles calculations.

The equilibrium structures of cobalt and the binary compounds are obtained from DFT/GGA total energy minimizations. Our study shows that the:

Hydrogen insertion in cobalt leads to affect the structural, electronic and magnetic properties:

- Hydrogen insertion in cobalt causes an expansion of crystalline lattice (cell volume effect), the augmented cell volume for the hydride must entail higher H–H interactions since their distances increase as x increases;
- Our calculations reveal that the DOS undergo a gradual modification particularly near the Fermi level as hydrogen is incorporated in the cobalt lattice;
- Hydrogen insertion in cobalt causes a strong reduction in the magnetic moment (magnetic effect);
- CoH is revealed as a strong ferromagnet, like Co.

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