**Abstract**

We investigated the magnetic behavior of metal hydrides FeH$_x$, CoH$_x$ and NiH$_x$ for several concentrations of hydrogen ($x$) by using Density Functional Theory calculations. Several structural phases of the metallic host: bcc ($\alpha$), fcc ($\gamma$), hcp ($\varepsilon$), dhcp ($\varepsilon'$), tetragonal structure for FeH$_x$ and $\varepsilon$-$\gamma$ phases for CoH$_x$, were studied. We found that for CoH$_x$ and NiH$_x$ the magnetic moment ($m$) decreases regardless the concentration $x$. However, for FeH$_x$ systems, $m$ increases or decreases depending on the variation in $x$. In order to find a general trend for these changes of $m$ in magnetic metal hydrides, we compare our results with the Slater-Pauling curve for ferromagnetic metallic binary alloys. It is found that the $m$ of metal hydrides made of Fe, Co and Ni fits the shape of the Slater-Pauling curve as a function of $x$. Our results indicate that there are two main effects that determine the $m$ value due to hydrogenation: an increase of volume causes $m$ to increase, and the addition of an extra electron to the metal always causes it to decrease. We discuss these behaviors in detail.

**Keywords:** FeH$_x$, CoH$_x$, NiH$_x$, Ferromagnetic metal hydrides, Slater-Pauling curve, Metal hydrides alloys.

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**1. Introduction**

Magnetic hydrides (MH$_x$) based on 3d-metal alloys have been intensively studied for decades. They are of particular interest due to the different variations of the magnetic moment ($m$) of Fe, Ni and Co hydrides and their alloys as functions of the hydrogen concentration ($x$). There is a complete experimental study by Antonov et al. [1, 2, 3, 4, 5] describing in detail the magnetic properties and magnetic phase diagram at 7-8 GPa and temperatures around 700 K for Fe and Co hydrides, with an H:metal ratio close to 1 [1, 5].

Moreover, the FeH$_x$ systems are of particular interest from a geophysical point of view for processes in the Earth’s inner core. Related to this issue, recent works have reported synthesis of $\gamma$-FeH$_x$ at high pressures and temperatures with stoichiometric composition and low concentrations ($x < 1$) [6, 7]. Some reports explored the formation of new structures at higher concentrations ($x > 1$) as well [8]. Thus, new phase diagrams have been established at high temperatures from 0 to 1200 K and high pressures from 0-10 GPa [7] and 0-120 GPa [8]. Under these conditions, new structures based on FeH$_x$ ($x > 1$) that exhibit magnetic and non-magnetic orderings have been found [8].

On the other hand, the case of CoH$_x$ is of particular interest due to the study of single molecular magnets and anisotropy in magnetic molecular junctions for a high concentration ($x = 1, 2$) [9, 10].

Hence, the study of the magnetic moments of FeH$_x$ and CoH$_x$ as a function of the H concentration in ferromagnetic metals is a relevant issue. Indeed, several electronic structure calculations for FeH and CoH hydrides have been carried out previously, where the structural stabilities and magnetic properties have been studied [11, 12]. Concerning the limit of low concentration one can find studies on samples of FeH$_x$ for $x = 0.03$ and $x = 0.25, 0.5, 0.75$ [13, 14]. However, First-Principles-based studies on the magnetic moment in a wide range of concentrations, for both the previously-known and new phases of FeH$_x$ [8], have yet to be reported.

The magnetic properties of materials are strongly affected by their hydrogen absorption, normally leading to
a reduction in the $m$ of intermetallic compounds based on Co and Ni but to an increase in the $m$ of Fe. Indeed, experimental works on these metals and their alloys \cite{1 2 3 5} and Density Functional Theory (DFT) studies show these behaviors \cite{1 2 3 4 5}. This evident $x$ dependence on the magnetic properties of metal hydrides is accompanied by the increase of volume produced by the inclusion of H atoms within the metal. When $x$ increases, the volume also increases, which generates a localization of the electronic states, and, an increase in the value of $m$ is therefore expected. Additionally, the charge transference between the metal and the hydrogen can decrease or increase the magnetic moment, $m$, of the metal atom depending on whether or not the minority or majority spin band is full.

In order to study these effects, that modify the magnetic properties, we performed spin-dependent DFT calculations on the Fe and Co hydrides’ systems. We considered different structural phases such as α, γ, ε, and ε’ and tetragonal with a space group of $\text{I4/mmm}$ for FeH$_x$ systems, and ε and γ for the CoH$_x$ systems. The antiferromagnetic (AFM) phase of the ε-FeH$_x$ and γ-FeH$_x$ structures have also been studied in order to comprehend the stability between the AFM and ferromagnetic (FM) phases as a function of $x$. Additionally, the calculations of the new phase with the space group $Pm\text{-}3m$ at a high H concentration ($x = 3$) in Fe, reported in Ref. \cite{8}, have been reported in this study.

For comparison reasons, we superimpose our results on the Slater-Pauling (SP) curve \cite{16}. The SP curve shows the magnetic moment per atom of an alloy as a function of the number of valence electrons. It was constructed for binary metallic alloys, and the approach has also been extended to model the magnetic moment of a magnetic metal host with non-metallic interstitial impurities \cite{17 18}. In this work, we used the SP curve for the MH$_x$ system within the framework of the d-rigid band model \cite{2 5}.

2. COMPUTATIONAL DETAILS

In this study, the Vienna Ab Initio Simulation Package (VASP) \cite{19} is used, with the Generalized Gradient Approximation (GGA) along with the Perdew-Burke-Ernzerhof (PBE) \cite{20} prescription. As a result of the convergence tests, we used a kinetic energy cutoff of 360 eV for all the calculations, and Brillouin k-points grids of $8\times 8\times 8$ in α, $8\times 8\times 4$ in ε, $6\times 6\times 6$ in γ and $12\times 12\times 6$ in both the ε’ and tetragonal structures. The calculations were performed by considering spin-polarized configurations, FM and AFM, in order to obtain the magnetic configuration with the lowest energy. The relaxed structures were obtained when forces on each atom were less than 0.01 eV/Å.

3. CRYSTAL STRUCTURES

For the α and ε phases, we used a super cell of 16 Fe atoms, including 16 interstitial sites with tetrahedral ($\alpha$) and octahedral ($\varepsilon$) symmetry, which we filled with H in different concentrations. In the γ and ε’ structures of Fe, we used a super cell with 32 and 4 atoms with 32 and 4 interstitial sites with octahedral symmetry respectively. For Co, we used ε and γ super cell structures with 16 and 4 Co atoms, with 16 and 4 interstitial sites with octahedral symmetry, respectively.

The starting aspect ratios were $c/a = \sqrt{8/3}$ and $c/a = 2\times \sqrt{8/3}$ for the ε and the ε’ structures, respectively, while we used the unit cell reported in Ref. \cite{8} for the tetragonal phase of Fe. The unit cells for the obtained crystal structures are shown in Fig. 1.

![Figure 1: The different calculated crystal structures. Green spheres depict metal atoms coordinated with the H atoms filling the interstitial sites with tetrahedral and octahedral symmetry for the α, γ, ε, ε’ and tetragonal structures, as applicable. In the tetragonal structure H atoms fill sites with tetrahedral symmetry, but some H atoms are also connected with four metal atoms in the same plane.](image-url)
The calculated magnetic systems shown in Fig. 2a display two different remarkable behaviors. On one hand, there is always a steady decrease of $m$ when $x$ increases in systems based on Co and Ni. On the other hand, for the $\alpha$-FeH$_x$ phase, the $m$ value increases for $0 \leq x \leq 0.375$ towards a maximum, and, $m$ then decreases, as it does in the cases of Co and Ni. In the cases of $\gamma$, $\epsilon$- and $\epsilon'$-FeH$_x$ with $x > 0.25 (\gamma)$ and $x > 0.5 (\epsilon, \epsilon')$ respectively, the magnetic moment always decreases. For $I4/mmm$-FeH$_x$, with $x > 1$, the magnetic moment increases in the range of $1 \leq x \leq 1.5$ and decreases for $1.5 < x \leq 2$. Fitted curves of the magnetic moment for FeH$_x$, CoH$_x$ and NiH$_x$ as a function of $x$, are given in the Figs. 4-5 in [21].

As a general feature, when H atoms fill the interstitial places of a metal lattice, new electronic states are created at low energy with respect to the Fermi level, giving rise to a reordering of the electronic states of the metal, thus affecting the magnetic properties. Another
way to see this is to think of a Stoner-type of model\cite{15}, where the hybridization between the metal and H atoms changes the band energy (kinetic energy) and affects the magnetic energy, thus leading to a reduction or increase of the magnetic moment.

Besides, it is already known that H atoms inserted in the interstitial places of a metallic host, produce a volume increase. The volume expansion has the effect of localizing the electronic states, thus narrowing the bandwidth for both spins, which generally favors the stability of the ferromagnetic phase. To quantify the effect of the volume expansion, we performed our \textit{Ab Initio} calculations for pure metal systems incorporating the volume expansion produced by the H atoms. These results are shown in Fig. 3 with semi-filled symbols. A steady increase for \(m\) is clearly observed for the pure metal systems, indicating the effect of volume change on \(m\). In all cases, the expansion of metal produces a bigger \(m\) than that found in MH\(_x\) systems.

Moreover, if the volume in the MH\(_x\) systems is kept fixed to the value of the pure metal (empty symbols in Fig. 3), the \(m\) always diminishes due to the presence of H. These results indicate that there are two competing effects that determine the value of \(m\): solely increasing the volume always causes an increase of \(m\), but adding an extra electron to the metal always causes a decrease of \(m\).

Finally, we want to discuss our results for the magnetic moments shown in Fig. 2 for metallic hydrides in relationship to the SP curve. If we superpose our results, as explained below, with the SP curve, we obtain the curve shown in Fig. 4. This figure shows the \(m\) for MH\(_x\) as a function of the effective valence number per metal atom \((N)\). We used a \(d\)-band rigid model that has been used to explain the changes of \(m\) caused by H\cite{2,3}. In this model, \(N = N_M + \eta x\), where \(N_M\) is the number of valence electrons of the metallic host (Fe = 8, Co = 9 and Ni = 10), and \(\eta\) is the number of electrons that are transferred from H to the metal; these approximate values can be obtained from our \textit{Ab Initio} calculations \((\eta = 1 - Q_H\), where \(Q_H\) is the electronic charge of H inside a sphere with the Wigner Seitz radius at equilibrium volume). We found that \(\eta \approx 0.45\) for Fe, Co and Ni, for \(\alpha, \gamma, \epsilon, \epsilon'\) structures, and \(\eta = 0.39\) and 0.5 for Fe (I4/mmm and Pm-3m, respectively). These values are approximately half of the value of \(\eta\) for a substitutional impurity, where \(\eta = 1\).

As was previously mentioned, in the FeH\(_x\) system, it is possible to distinguish both an increasing and a decreasing behavior of the \(m\), obtaining a maximum value when \(N\) is about 8.2 electrons. Indeed, the elements that are located in the ascending part of the SP curve, such as Fe, have less than half-filled spin bands. Therefore, the behavior of their \(m\) requires a detailed analysis because the majority spin band is not full. Here, the Hund rules play a crucial role in the solid, the pairing energy (spin-up, spin-down pair) and the crystalline field splitting; all have to be computed in order to correctly fill the electronic levels.

From the FeH\(_x\) calculations in the \(\alpha\) structure in the region where \(m\) increases, we can see that the Fermi level lies near the minimum of the minority spin DOS, see Fig. 5(a) (pure Fe and FeH\(_{0.25}\)). This result is an indication of the system’s structural stability (similar to a filled electronic shell in an atom). In these cases, the filling of the bands occurs first in the majority spin bands (as shown in Fig. 5(a) for FeH\(_{0.25}\)), thus increasing the \(m\) of the system, as shown in Fig. 2 and also in Fig. 4 (for \(N = 8\) to \(N = 8.16\) blue circle symbols). After a certain H concentration, the minority spin band begins to be filled (see Fig. 5(b)), and the \(m\) begins to decrease. Nevertheless, the ferromagnetic materials located in the descending part of the SP curve, such as Co and Ni alloys, diminish their magnetic moment as the H concentration increases due to the filling of the minority band because the majority 3d band is already filled with 5 electrons.

Thus, in the case of \(\alpha\)-FeH\(_x\), \(m\) increases with \(N\) un-
for all the concentrations of H, thus decreasing the magnetic moment. Nevertheless, for $\alpha$-Fe, the band filling occurs first in the majority spin band for low concentration of H ($x \leq 0.375$), leading to an increase of the magnetic moment. For $x > 0.375$, the band filling occurs in the minority spin band causing $m$ to decrease, thus following the same rules for the band filling of the ferromagnetic metal alloys in the ascending and descending parts of the SP curve.

As a result of these two effects, the overall trend for the magnetic moment per metal atom as a function on the effective number of valence electrons follows the SP curve. The presented results and mechanisms for explaining them offer valuable insights for the study of magnetism in hydrated binary and tertiary transition metal alloys.

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