

Magnetic effects of interstitial hydrogen in nickel



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ABSTRACT

Hydrogen storage in materials is among the most relevant fields when thinking about energy conversion and storage. In this work we present a study that responds to a couple of questions concerning induced electronic changes that H produces in ferromagnetic nickel (Ni) host. We calculate and explain the change of magnetic properties of Ni with different concentrations of H. Density functional theory calculations (DFT) were performed for super-cells of fcc Ni with interstitial H in octahedral sites at different concentrations. In order to physically explain the effect of magnetization diminishing as the hydrogen concentration increases, we propose a simple Stoner type of model to describe the influence of the H impurity on the magnetic properties of Ni. The exchange splitting reduction, as shown in first principles calculations, is clearly explained within this physical model. Using a paramagnetic Ni fcc band with variable number of electrons and a Stoner model allow us to obtain the correct trend for the magnetic moment of the system as a function of the H concentration.

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1. Introduction

Metal hydrides is a subject which has long been studied and is still important due to its implications in energy issues like cell fuels and hydrogen storage. The thermodynamics of the processes at different temperatures and pressures is still a subject of interest [1–5]. From a more fundamental point of view, it is interesting because of its consequences in high temperature superconductivity, as hydrogen induces changes in the frequency of phonon modes, in the electronic density of states around the Fermi level and in the strength of the electron–phonon coupling [6–9]. If the conventional BCS theory is valid, there is no upper limit for the superconducting transition temperature, and solid hydrogen under pressure should be a superconductor, [10,11] as should many hydrides [12–14]. In recent years there have been many reports about the electronic structure of materials with hydrogen impurities or hydrides, regarding formation energies, enthalpies, charge transfer mechanisms, hybridization of hydrogen and metallic electronic states, and hydrogen–vacancy interactions

[15–21]. The magnetic changes induced by hydrogen in a ferromagnetic material has received less attention. The standard explanation is that hydrogen diminishes the magnetization of the bulk because of charge transfer from hydrogen to the nearest neighboring metallic atoms, mainly to the minority spin band [22]. Hydrogen also causes a volume increasing in almost all transition metals of about 2.8 Å³ for concentration up to 0.7 atomic percent [23].

In this paper we concentrate on the magnetic changes that occur when hydrogen atoms occupy interstitial sites in fcc Ni; we do this by taking the distortion of the lattice into consideration. It is found that hydrogen diminishes the exchange correlation splitting of the 3d bands in Nickel, and not simply filling the minority spin band. Measurements of the electronic specific heat corroborated this picture [24]. These results were obtained from first principles calculations of the electronic structure of interstitial hydrogen in fcc Nickel, which is allowed to relax. Moreover, we also explain the effect of volume expansion.

In the next section, we present the method used to calculate the system Ni fcc with interstitial hydrogen in octahedral interstitial positions. In the Results section, we summarize the main findings from the *ab initio* calculations. In the Discussion section, we comment on the results and present a Stoner model using the density of states (DOS) of paramagnetic Ni which is able to

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physically explain the exchange splitting reduction as the H concentration increases. Finally, we enumerate the main conclusions of this study.

2. Method

We performed DFT calculations on a Ni fcc super cell of $2 \times 2 \times 2$, where we have 32 Ni atoms, and therefore 32 interstitial sites with octahedral symmetry. To do this, we carried out first-principles calculations by using the Vienna *ab initio* simulation package (VASP) [25], with the Generalized Gradient Approximation (GGA) along the Perdew–Burke–Ernzerhof (PBE) [26] prescription, using a cutoff energy of 400 eV, and a Brillouin k -points mesh of $8 \times 8 \times 8$. Regarding pseudopotentials, we tested them for Ni, including 10 and 16 electrons in the valence band, finding that it is enough to use pseudopotentials with 10 electrons for the Ni atoms.

In the case of H, we used pseudopotentials that mimic 1.25 electrons per atom. We also tested pseudopotentials with 0.75 and 1.0 electrons per H atom, finding that the pseudopotential with 1.25 reproduces better the experimental magnetic moment changes as a function of H concentration, and the charge density profile around the proton. The calculations are done while relaxing the structure until the forces are less than 0.01 eV/Å and the pressure is less than 0.02 kbar. For a given concentration x of H atoms, there are many possibilities to fill the octahedral sites of the supercell (see Fig. 1); therefore, we explored all configurations, and calculated the deviations for a given property. This is particularly note-worthy when calculating the magnetic moments of the system. The energy difference between the system in a tetrahedral site and an octahedral site is of the order of 144 meV in favor of the octahedral site.

3. Results

The most important distinction between the DOS functions for the Ni hydrides and that of pure Ni is the appearance of structure due to new impurity states located below the Fermi level. These

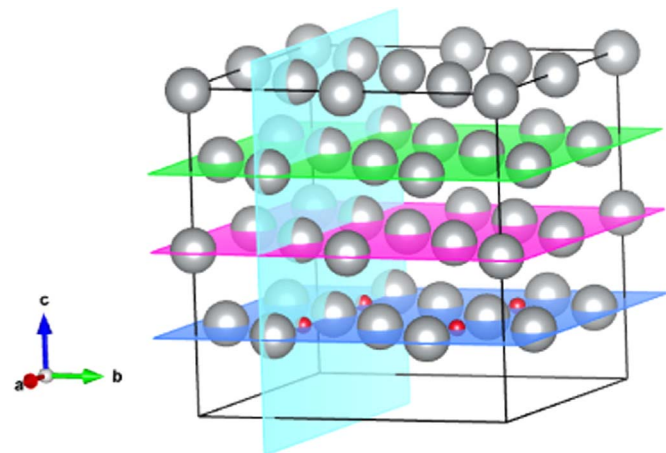


Fig. 1. One $2 \times 2 \times 2$ supercell of the NiH_x for $x=0.125$. Gray spheres depict Ni atoms and the red spheres the H atoms. In the blue plane we find H atoms as well as Ni atoms. In the magenta plane we find some Ni atoms that are nearest neighbors to the H atoms. In the green plane no Ni atoms are nearest neighbor to the H atoms. The cyan plane includes Ni atoms with both, nearest neighbors H atoms and no nearest neighbors H atoms. For a given concentration x there are many possibilities to fill the octahedral sites with H atoms; we explored all configurations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

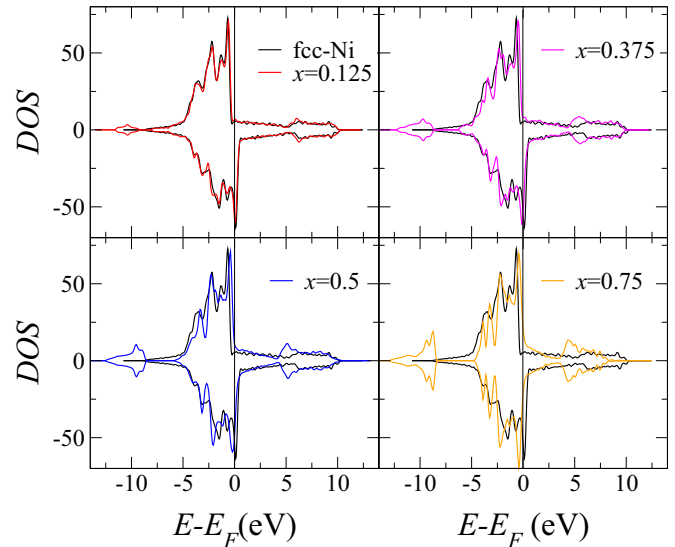


Fig. 2. Density of states [states/(eV \times unit cell)] of NiH_x for $x = 0.125, 0.375, 0.5$ and 0.75 . For direct comparison, the DOS of pure Ni is also included in black, in each figure.

states are mainly of s character and arise from the mixing of the Hydrogen $1s$ state with the electrons of the neighboring Ni atoms. These localized states are caused by the deepening of the effective potential seen by the electron due to the presence of a proton in the interstitial state. This new band with a width of about 4 eV is located at about 10 eV below the Fermi level in all NiH_x hydrides.

The Fig. 2 shows these effects on the DOS for different concentrations of H. In order to see the effect of the hybridization between the Ni electronic states and the s -states of H, the Fig. 3 shows partial s , p and d DOS for the Ni atoms that have none, one and two nearest neighbor H atoms.

The magnetic moment as a function of concentration, x , in NiH_x for the structural relaxed system is shown in the Fig. 4. The square symbols correspond to the experimental results [27], the triangles depict the results of early LMTO calculations [28], and the circles depict our results. Our results have a similar behavior as the experimental ones, especially around the values $0.5 < x < 0.7$ where the magnetic moment of the system is vanishing. Additionally, in Fig. 5 we show, for each Ni atom, the contribution to the average magnetic moment for a given concentration. There are Ni atoms that have from 0 to 6 nearest neighbor H atoms. As expected, for low H concentration there are many Ni atoms that have no nearest neighbor H atoms. This causes that the average magnetic moment to be close to the one of bulk Ni. We also clearly see that the magnetic moment of the Ni atoms, having nearest neighbor H atoms, is greatly diminished. The more neighbor H atoms the less the magnetic moment in the central Ni atom. The difference between two consecutive values is about $0.2 \mu_B$. From a concentration of $x=0.375$ and higher, every Ni atom has at least one nearest neighbor H atom. This implies an overall diminishing of the magnetic moment. The Ni atoms that have no H atoms as nearest neighbor show an increasing in their magnetization; this is the effect caused by the volume expansion, which localizes the $3d$ states.

We have also calculated the spin density of the system in each Ni atom and around each H. The magnetic moment of the H atom is negligible ($0.004 \mu_B$), but its sign is consistently the opposite to that of the Ni atoms. The average magnetic moment per Ni atom as a function of H concentration is shown in the Fig. 4. We see an overall good agreement with the experimental data [27].

We also found that the magnetization effects are very localized in this system. The Ni atoms that have no H atom as nearest

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