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Electronic structure of Ni–H from normal to superabundant vacancies

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Abstract

We present a theoretical study of the magnetic and electronic structure of two different Ni–H materials, the first one being synthesized under a few bar hydrogen pressure and the second one being stabilized under ultra high pressure. We used the KKR formalism with the coherent potential approximation (CPA) method for calculations related to the Ni–H system (normal hydride) obtained under moderate pressures. These calculations were made for different hydrogen contents since the materials exhibit atom disordering. In contrast, we used the full potential linear augmented plane waves (FLAPW) method for the material obtained under high pressure that exhibits metal vacancies at the highest hydrogen contents. As well as previous theoretical calculations, e.g. based on the linear muffin-tin orbital (LMTO) formalism, here we present in detail the density of states, the magnetic polarization and the charge transfer effect for Ni and H atoms. All the results will be discussed and compared to the experimental measurements undertaken elsewhere.

Keywords: KKR-coherent potential approximation (CPA); Full potential linear augmented plane waves (FLAPW); DOS; Fermi level; Charge density; Magnetism

1. Introduction

The solution of hydrogen in a metal lattice and the formation of a metal hydride considerably perturb the electronic distribution of the host metal. According to experimental studies, the hydrogen–metal interaction is not only of fundamental interest in understanding the formation of the hydride, but also sheds light on technologically important parameters such as the heat of formation, heat conductivity, and magnetic polarization. Recently there have been many studies carried out on this interaction due to substantial interest in using metals or alloys as a medium for storing gaseous hydrogen in fuel cell technology [1–3]. The activation energy calculations carried out by Haug et al. show that the H presence enhances the Ni atom mobility on the surface [4]. The present work will concentrate on more fundamental aspects. For the Ni–H_x hydride with various concentrations of hydrogen (x) we will use the coherent potential approximation (CPA) based on the formalism which mathematically takes into account the presence of the disordered H site for all concentrations. Other authors have studied this hydride by using the linear muffin-tin orbital (LMTO) formalism for $x=0.0$, 0.5, 0.75, 1.0, but this formalism does not integrate the disorder. To overcome this difficulty, the authors propose a numerical solution consisting of a super cell with an ordered hydrogen site to simulate the disorder in the hydride [5]. This model gives good results only for particular concentrations and it is not mathematically correct. Moreover, in contrast to the CPA method, the LMTO approach involving a super cell is not easy to employ at low concentrations because it requires a very large super cell with low symmetry for which the calculations are time consuming. In this paper we will reproduce the calculations for all concentrations with our CPA method for an x(H) concentration step equal to 0.1 in order to analyze the Ni physical properties. A comparison with previous published experimental and theoretical results will be reported here for this phase. In the second step we will calculate the state densities for the new Ni–H phase with vacancies by using the well adapted full potential linear augmented plane waves (FLAPW)

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method based on the full potential. The results will also be compared to the experimental.

2. Calculation methods

For the KKR-CPA method [6], we consider the Ni–H hydride as a lattice based on Ni and H atoms. We assume that the Ni site is perfectly ordered, but the H site is taken to be randomly occupied by a vacancy and H atom. The code proceeds with an effective potential assumed to be spherically symmetric giving non-overlapping muffin tin spheres around the atoms and constant potential in the interstitial region. The KKR-CPA code used is based on the DFT and the Green function where the exchange correlation effect and the local spin density are taken into account and evaluated consistently. For the ordered system with vacancies, we used a FLAPW method [7] which also performs DFT calculations using the local density approximation but with wave functions as a basis. The Kohn-Sham equation and energy functional are evaluated consistently using the full potential linearized augmented plane wave method. For this method, the space is divided into the interstitial and the non-overlapping muffin tin spheres centered on the atomic site. The employed basis function inside each atomic sphere is a linear expansion of the radial solution of a spherical potential multiplied by spherical harmonics. In the interstitial region the wave function is taken as an expansion of plane waves and no shape approximation for the potential is introduced in this region which is consistent with the full potential method. The core electrons are described by atomic wave functions which are solved relativistically using the current spherical part; the valence electrons are also treated relativistically in our case.

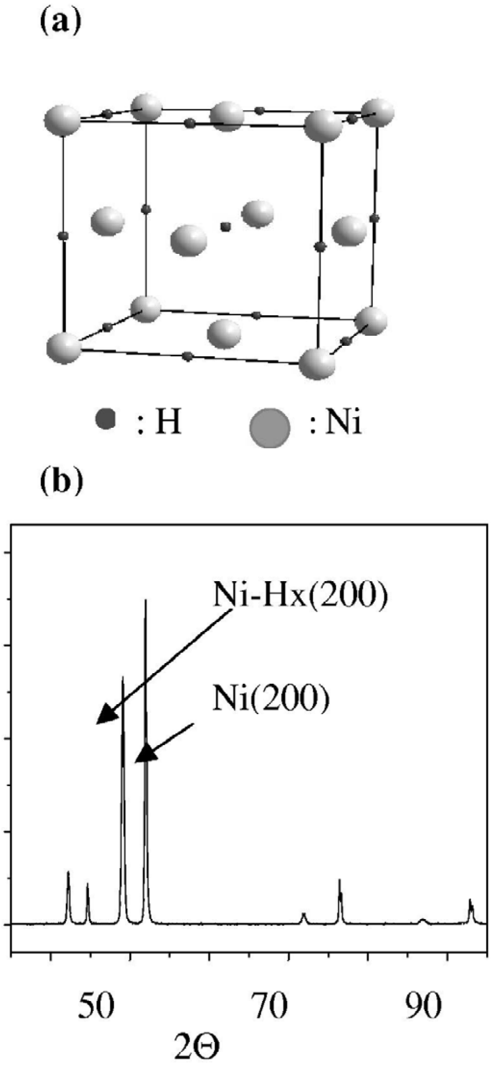

Fig. 1. Unit cell of the Ni–H sample (a) and its diffraction pattern (b).

3. Results and discussion

The subsequent results will be divided into two parts. In the first part special attention is paid to the non-stochiometric Ni–H_x hydride by using the well adapted KKR-CPA code. In the second part we will present the calculation results taking into account the hole presence in the hydride for which the FLAPW code is preferred. For the non-stochiometric Ni–H_x system we consider the disordered octahedral H site in the Ni f.c.c. lattice as shown in Fig. 1. Details of the band structure calculations led to the results shown in Fig. 2 for Ni–$H_{0.5}$. We notice first that the three Ni-like states 3d, 4p and 4s are affected by the presence of hydrogen in the lattice showing a modification in their shapes. The band width is reduced and the local DOS at the Fermi level is also reduced upon binding with hydrogen. But the most important change caused by the presence of the H states is the appearance of the new structure localized at 7.5 eV below the Fermi level with bandwidth equal to 4 eV. If we compare the DOS of hydrogen and those of the Ni 3d, 3p and 4s, we can conclude that the new additional states are mainly of s character and they are from the hybridization of the Ni states with those of H 1s. To understand the causes of the behavior changes observed upon H addition and those of the hydride formation, we analysed the variation of the Mulliken population for major spin and minor spin to evidence an eventual charge transfer. We find that the charge of s and p remain constant for both spins (minor and major). However the increase of the d minor spin charge is accompanied by a decrease of the d major spin, showing that the total charge of this band almost remains constant upon H content (Fig. 3). The spin polarized band structure calculations also give evidence for a magnetic moment localized on the Ni sites. This magnetization exhibits a continuous diminution versus the hydrogen content and disappears at x equal to or greater than 0.75 (Fig. 4). This decrease agrees with results from experimental measurements [1,8] and from the LMTO calculations

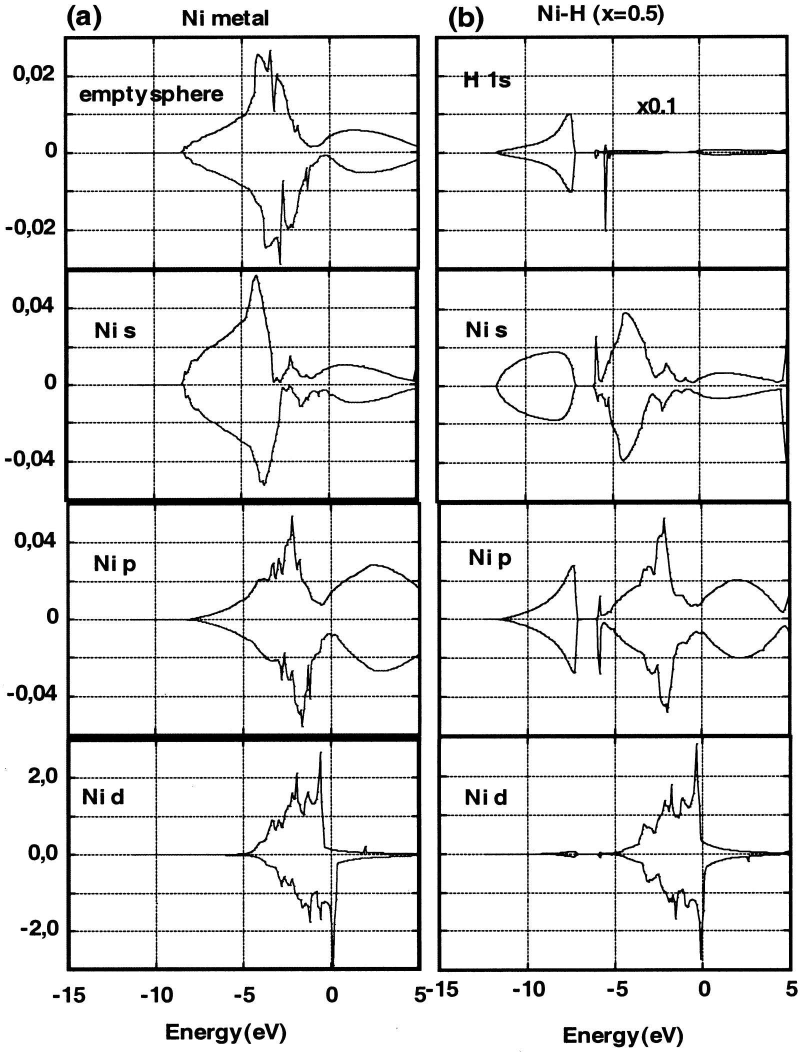

Fig. 2. DOS of the majority spin and the minority spin from KKR-CPA calculations: (a) starting Ni metal; (b) disordering Ni–H_x with $x=0.5$.

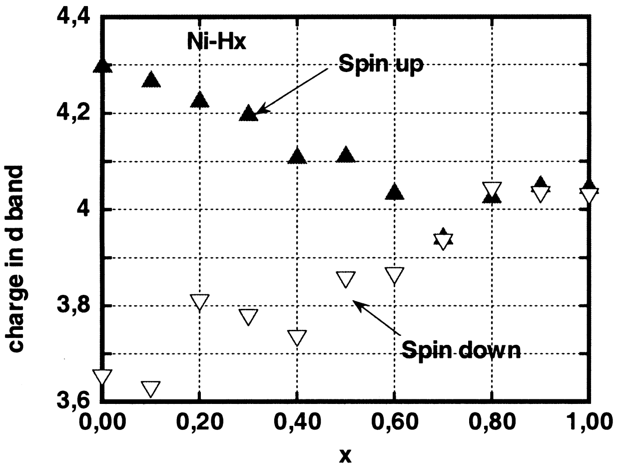

Fig. 3. The charge variation of the Ni d band for spin up and spin down.

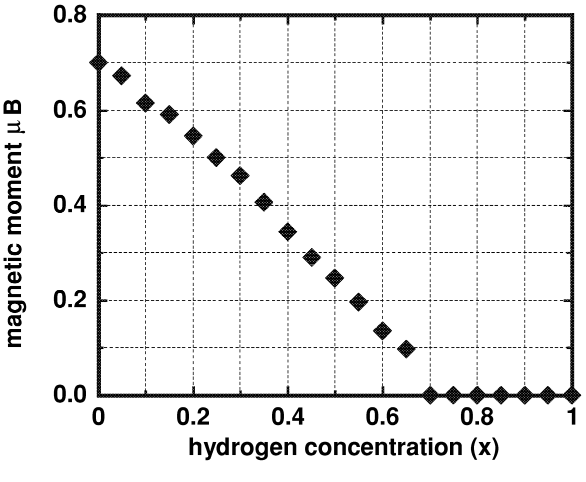

Fig. 4. Calculated magnetic moment for the non-stochiometric Ni–H_x hydride upon H content.

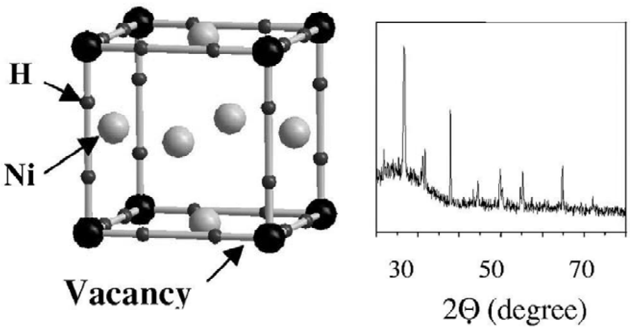

Fig. 5. Unit cell of Ni–H system with vacancies and its diffraction.

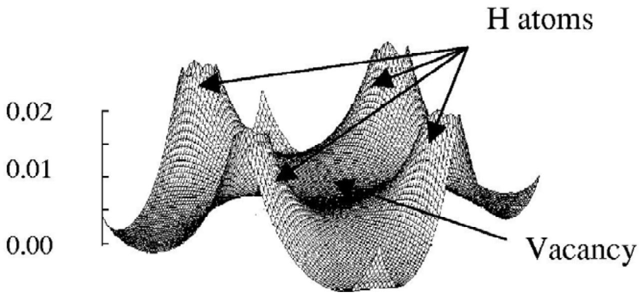

Fig. 7. The charge density distribution in the plane (2,2,2) showing a vacancy surrounded by three H atoms.

on the ordered H site with the super cell [5]. In addition our calculations show that the magnetization decrease is accompanied by a decrease of the DOS at the Fermi level due mainly to the diminution of the minor spin density in the d band at this level. More detailed analysis shows precisely that it is due not only to the filling of minority spin holes in this band, as reported, but also to the diminution of the occupied states in the majority d band. Therefore one can conclude that this moment decrease is a consequence of the rearrangement between both the population of the major spin and the minor spin in this band.

To understand the effects induced by the presence of vacancies in the new synthesized hydride (model shown in Fig. 5), we present in Fig. 6 the results of the calculations for Ni starting metal, the NiH hydride and the new hydride with vacancies. For nickel and its hydride the electronic density profiles, previously calculated by KKR-CPA and reported by other authors using other methods, are reproduced here from FLAPW calculations for comparison. From this comparison the results derived from DOS calculations for the superabundant hole system show more distinctive structures. The peak associated with hydrogen binding is present in the Ni-like states 4s, 4p and 3d. This new phase shows recovery of the DOS at the Fermi level. This increase results mainly from a strong d contribution. The Mulliken population of the various Ni-like states in this phase is comparable to that of the starting metal. The total DOS of the Ni also exhibits a shift between the band of the major spin and that of the minor spin evidencing a polarization of these bands. This polarization induces a magnetic moment localized on the Ni atom, of 0.2 μB. Fig. 7 shows the charge density distribution around the hole in the plane (2,2,2) where the charge density is more pronounced in the region between Ni and H resulting from Ni–H binding. In the region between the two H atoms the charge density is low or negligible showing no H–H binding.

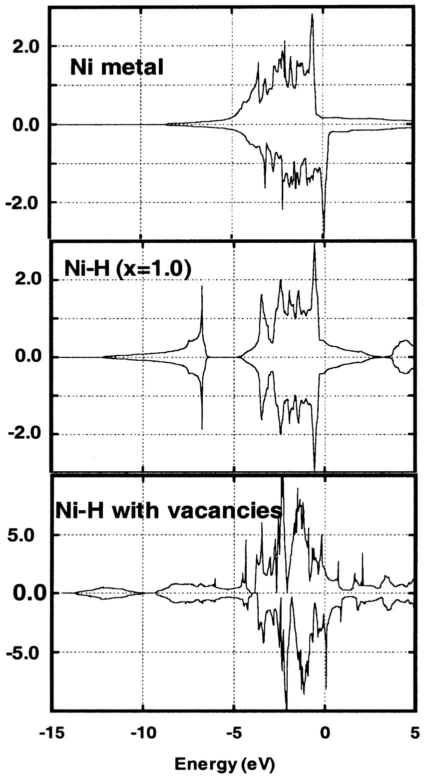

Fig. 6. Total DOS for Ni, Ni–H and Ni–H with vacancies from FLAPW calculations.

4. Conclusion

The presence of the hydrogen in the disordered interstitial site affects the Ni DOS. Indeed the three states 4s, 4p, and 3d of Ni exhibit a binding with the 1s-like state of the hydrogen without charge transfer. In addition, with the introduction of the hydrogen, the magnetisation is reduced and completely disappears when the H site occupation is almost complete. This is due essentially to the rearrangement between spin up and spin down populations in band. For the phase with the ordered vacancies we show that the Ni, even if its DOS shape shows more distinctive peaks similar to the molecular DOS, recovers its metal character because on the one hand the values of the charge in the various bands are comparable to those of the pure Ni and on the other hand a localised magnetisation appears on the Ni site.

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