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Calculation of the electronic and structural properties of cubic Mg_2NiH_4

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The electronic, structural, and stability properties of the cubic hydride Mg_2NiH_4 are analyzed based on *ab initio* total-energy calculations. We evaluate the electronic band structures, density of states, charge-density distributions, and bond character for different hydrogen configurations. The hydrogen distribution that minimizes the total energy corresponds to a tetrahedrally distorted square-planar coordination of the nickel atoms with a Ni-H bond length of 1.548 Å, in good agreement with neutron-diffraction experimental data. The evaluation of the relative stabilities of Mg_2NiH_4 and other hypothetical compounds of composition Mg_2NiH_δ ($\delta = 0,2,4,6$) agree with the observation that essentially stoichiometric Mg_2NiH_4 is the only phase present in the equilibrium phase diagram of the Mg-Ni-H system. [S0163-1829(99)13413-1]

I. INTRODUCTION

Metal hydrides based on intermetallic compounds are attractive candidates for hydrogen storage. In particular, the compound Mg_2Ni reacts readily with gaseous hydrogen to form the stable hydride Mg_2NiH_4 which, from the engineering point of view, is considered to be a very convenient material for storage purposes.[1] The reaction occurs by precipitation of Mg_2NiH_4 from the hexagonal intermetallic compound Mg_2Ni upon hydrogen absorption. Hexagonal Mg_2Ni is able to dissolve only a small amount of hydrogen, namely up to $Mg_2NiH_{0.3}$.[2,3]

The hydride Mg_2NiH_4 is the only stable ternary compound observed in the Mg-Ni-H system.[4] This compound shows a well-defined stoichiometry, essentially independent of temperature and hydrogen partial pressure.[5] Under the partial pressure of one atmosphere of hydrogen, Mg_2NiH_4 shows a structural phase transition at 510 K to a cubic high-temperature form (HT) where the metal atoms have an antifluorite-type structure.[6] The low-temperature form of Mg_2NiH_4 is monoclinic and represents a slightly distorted antifluorite lattice.[7]

An essential piece of information for the full characterization of any metal hydride is the description of the distribution of hydrogen atoms within the structure of the host. This information is relevant to the understanding and control of the hydrogen sorption properties. In this paper we concentrate on the hydrogen distribution in the cubic HT of Mg_2NiH_4. For this phase, hydrogen[8] atomic positions and temperature factors have been investigated experimentally by several authors using neutron-diffraction techniques.[2,9–11] In spite of these efforts, no final conclusion seems to have been reached on the interpretation, modeling, and structural refinement of these experimental data.[4]

In Fig. 1 we represent the antifluorite metal lattice of Mg_2NiH_4 and the whole set of hydrogen interstitial positions which have been considered by different authors in the interpretation of experimental data.[2,9–12] These positions are specified in terms of Wyckoff notation.[13] We first refer to those positions where the hydrogen atoms can be considered as associated to the metal atoms of the more easily hydride-forming element, Mg in this case. One possible distribution which has been proposed[9] corresponds to the H atoms forming a tetrahedral complex H_4 placed inside the Mg cube cage of the antifluorite structure. This tetrahedron is represented in Fig. 1(a) and in Wyckoff notation corresponds to positions 48*i*. Another possible distribution considered is the H atoms in positions 48*h*, forming a MgH_6-tilted octahedral complex as shown in Fig. 1(b).[2] These two possible modes of association of H to the Mg atoms have been discarded[2,12] because, in the former case, the fitting of the diffraction experimental data using the H_4 tetrahedron is not satisfactory[2] and, in the latter, an unusually short Mg-H distance is obtained from the fitting using the MgH_6 octahedral complex.[12]

Secondly, we refer to those interstitial positions where the H atoms are located in the neighborhood of the Ni atom and can be considered as forming a complex of nominal composition NiH_4. Within this view we would have a coordination complex rather than an interstitial metal hydride. Three possible H distributions around the Ni atom have been proposed in the literature in order to fit the neutron-diffraction data,[2,3,10,11] as follows: the partially occupied octahedral sites[3,10,11] determined by positions 24*e*, Fig. 1(c); the square planar and the distorted square-planar distributions[11] corresponding to positions 96*j*, Figs. 1(d) and 1(e), respectively; and the regular tetrahedral arrangement[10,11] corresponding also to positions 96*j*, Fig. 1(f). Positions 96*j* in Fig. 1(d) coincide with one of the square-planar arrangements determined by positions 24*e*, Fig. 1(c).

Structure factor calculations using the model defined by the 24*e* positions give a reasonably good agreement factor for the fitting to the diffraction data.[12] Attempts to improve this model by allowing for anisotropic thermal displacements of the H atoms give better results in terms of refinement.[11] Alternatively, similarly good results can be obtained by adopting the 96*j* positions shown in Fig. 1(e), which consist simply of small static displacements normal to the simple square-planar arrangement of Fig. 1(d).[11] The simple square-planar arrangement of H atoms shown in Fig. 1(d) has been assumed in order to explain some NMR measurements,[14] with this distribution of highly correlated H atoms rotating isotropically and fast around the Ni atom and in fact generating a statistically populated 24*e* sublattice as in Fig. 1(c). Regarding the regular tetrahedral arrangement of H atoms

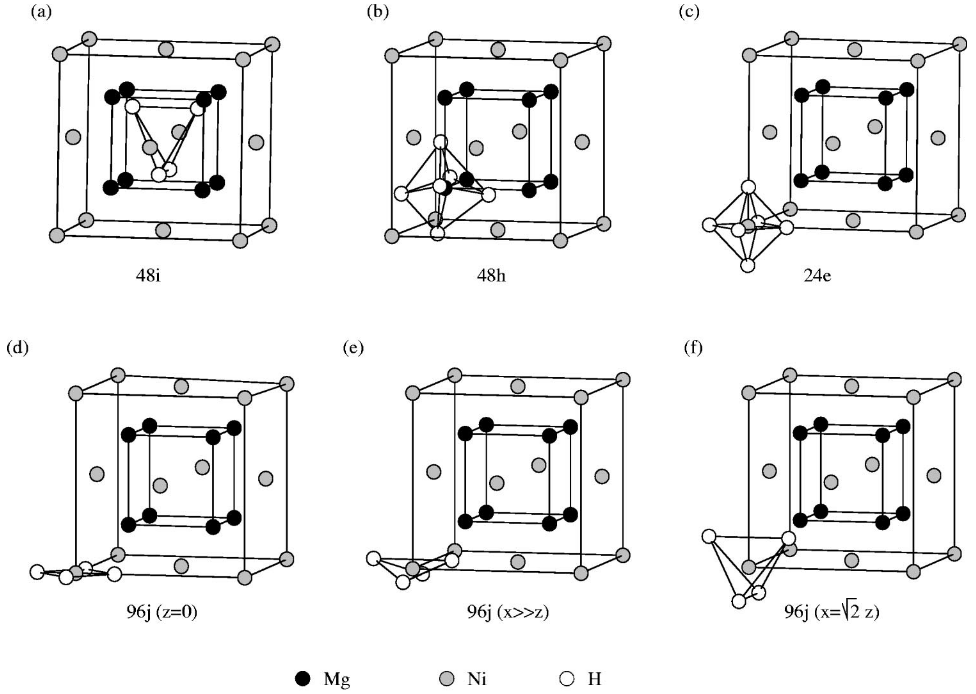


FIG. 1. Possible hydrogen atom sites in the antifluorite metal lattice structure of Mg_2NiH_4, as proposed by several authors (see text). These sites are indicated in terms of Wyckoff notation. Solid lines connecting hydrogen atoms do not intend to represent H-H bonds but are shown to guide the eye.

around the Ni atom,[10] Fig. 1(f), it has been concluded to be an inadequate model for structure refinement purposes even after allowing for thermal displacements.[11]

In spite of the ambiguity in choosing among the different distributions just described, a rather important feature common to all them is the relatively constant value obtained for the Ni-H distance, namely $d_{\text{Ni-H}} = 1.55$ Å.[11] This indicates the existence of a well-defined bonding length between the Ni and H atoms within the NiH_4 complex, independent of the particular relative positions taken by the hydrogen atoms. Summarizing, although the existence of a NiH_4 complex appears to be assured from the experimental point of view, the information obtained from neutron-diffraction data is ambiguous enough to hinder the determination of the detailed H configuration around the Ni atoms.[12]

The aforementioned experimental investigations of the H distribution in cubic Mg_2NiH_4 have been complemented by theoretical calculations of the electronic structure.[15–18] Gupta *et al.*[15,16] have calculated the electronic structure for two possible configurations of H atoms. These configurations correspond to the 48*h* and the statistically occupied 24*e* octahedral arrangement, using a Ni-H distance of 2.30 and 1.49 Å, respectively. Gupta *et al.* found that Mg_2NiH_4 should in both cases be a semiconductor, but the origin of the gap and the nature of the bonds turned out to be different in each case. Although no total-energy calculations have been performed by these authors they decided that the most stable H configuration is the 24*e* based on available experimental band-gap values.[15,16,19,20]

Lindberg *et al.*[17] calculated the structure of the NiH_4 complex by means of a schematic model which accounts for the ionic Mg lattice simply through its Coulomb field. The geometry of this complex was obtained by minimizing its total energy. Their conclusion is that the structure and bonding of the NiH_4 complex depend strongly on its total charge and therefore on the charge arbitrarily assigned to the Mg ions. They found that for Mg^{+1} (an uncommon oxidation state for Mg) the $[NiH_4]^{-2}$ complex would adopt the square-planar distribution. On the other hand, assuming Mg^{+2}, the $[NiH_4]^{-4}$ complex would take the regular tetrahedral configuration. In the first case the calculated Ni-H distance is close to the value obtained from experimental neutron-diffraction data, whereas in the second case the discrepancy between the calculated and measured values of this distance is significantly larger. More recently, Takahashi *et al.*[18] have analyzed theoretically the electronic structure of the hypothetical Mg_2NiH_6 compound, where positions 24*e* are considered fully filled with H atoms. These authors concluded that a strong Ni-H bonding exists, with $d_{\text{Ni-H}} = 1.49$ Å.

In conclusion, the experimental and theoretical results available on the H distribution in the cubic phase of Mg_2NiH_4 are not enough to establish completely the nature of this distribution. The present work aims to contribute to this problem by considering the energetics of specific, selected arrangements for the NiH_4 complex, using *ab initio* total-energy calculations. In particular, we study those H arrangements described by the 96*j* positions in the range between the square-planar configuration, Fig. 1(d), and the regular tetrahedron, Fig. 1(f). Judging from the available experimental information, the theoretical study of this particular set of configurations seems to be an adequate choice to analyze the equilibrium hydrogen arrangement in the cubic phase of Mg_2NiH_4.

This work is organized as follows. In Sec. II we present the *ab initio* total-energy calculation method. The results obtained for the calculated structural properties of the cubic hydride Mg_2NiH_4, electronic band structure, density of

TABLE I. Optimized values for the internal parameters x and z for different hydrogen configurations. The lattice constant used in our calculations is the experimental value $a=6.507$ Å (Refs. 10 and 11).

	Square planar $96j(z=0)$	Tetrahedrally distorted square planar $96j(x \gg z)$	Regular tetrahedral $96j(x=\sqrt{2}z)$	Experimental data [a]
x	0.2379	0.2208	0.1903	0.232
z	0.0	0.0883	0.1345	0.053
Energy (eV/formula unit) [b]	0.088	0.0	0.065	
d(Ni-H)(Å)	1.548	1.548	1.516	1.55
d(Mg-H)(Å)	2.302	1.948	1.833	2.07
d(H-H)(Å)	2.189	2.334	2.477	2.24
Bending angle (degrees)	0.0	21.8	35.3	12.9

[a] Reference 11.

[b] Total energy relative to the configuration of lowest energy.

states, and charge-density distribution are described in Sec. III. In Sec. IV we discuss the stability properties of Mg_2NiH_4 with reference to the Mg-Ni-H equilibrium phase diagram. The conclusions are given in Sec. V.

II. TOTAL-ENERGY CALCULATION METHOD

For our *ab initio* calculations of total energies we use the full-potential linearized augmented plane-wave method (FP-LAPW).[21] In brief, this is an implementation of density-functional theory with different possible approximations for the exchange and correlation potential, including the local-spin-density approximation (LSDA). The Kohn-Sham equations are solved using a basis of linearized augmented plane waves.[22] For the exchange and correlation potential we use the Perdew and Wang[23] parametrization of the Ceperley-Alder data in the LSDA case. Local orbital extensions to the LAPW basis[24] are used to describe the $3s$ and $3p$ orbitals of Mg, and the $3p$ orbitals of Ni. The wave functions are expanded up to $l=10$ within the muffin-tin spheres, and the potential and charge density are expanded up to $l=6$. We use a converged basis set of around 2000 plane waves and a sampling of the Brillouin zone (BZ) of 400 points, which in the irreducible wedge of the BZ correspond to 40 points for the case of the square-planar configuration and 58 for the tetrahedrally distorted square-planar and regular tetrahedral configurations. Muffin-tin radius of 1.8 Bohr for Mg and Ni, and 0.8 for H are used.

III. STRUCTURE OF Mg_2NiH_4

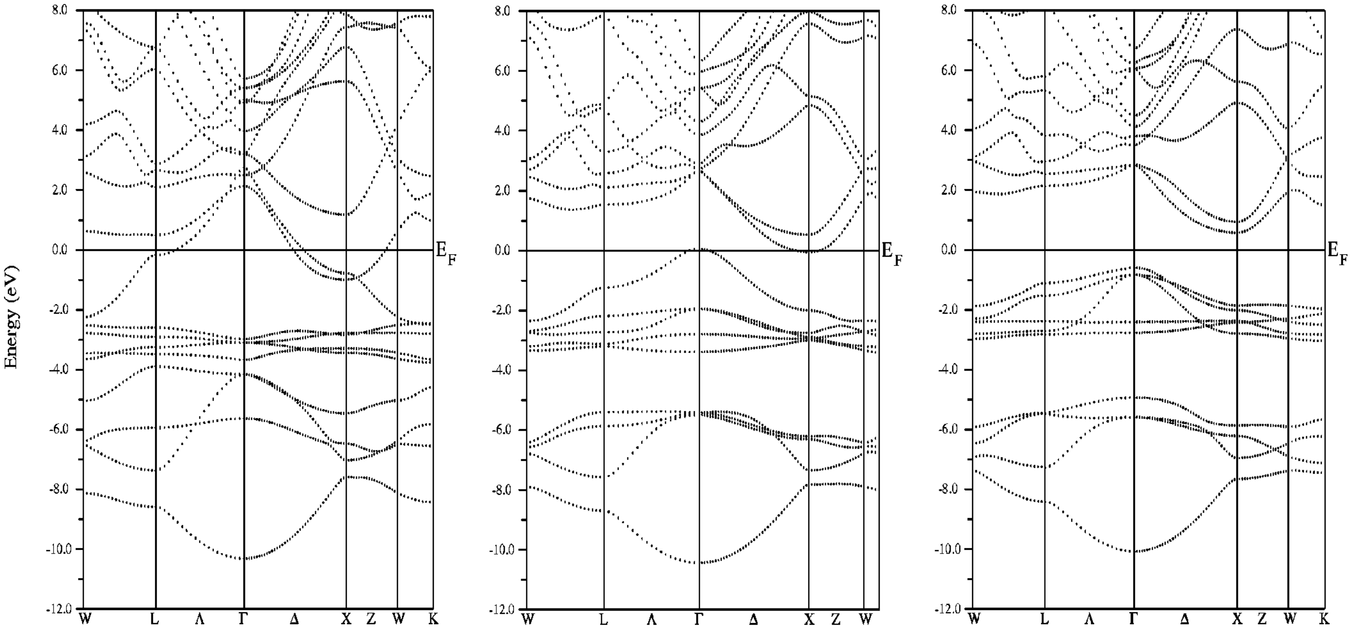
A. Structural model and total energy

We search for the hydrogen positions that minimize the total energy of the cubic hydride Mg_2NiH_4. The unit cell of this hydride corresponds to the cubic antifluorite structure (space group $Fm3m$) with Ni fully occupying the $4a$ sites and Mg the $8c$ sites.[13] The positions of Ni and Mg are fully determined by symmetry, without internal degrees of freedom. This is not the case of the hydrogen atoms and, as stated in the Introduction, we will explore the hydrogen arrangements that correspond to a complex NiH_4, with the four H atoms located at $(x,0,z)$, $(0,x,-z)$, $(-x,0,z)$, and $(0,-x,-z)$, in units of the lattice constant. These are only four of all the possible $96j$ sites available in the structure, which coincide with $24e$ sites when $z=0$, and form a regular tetrahedron around Ni when $x=\sqrt{2}z$. Tetrahedral distortions are characterized by the bending angle arctan(z/x). In our calculations we use the experimental lattice constant value of $a=6.507$ Å.[5,11] The number of valence electrons involved is 18 per formula unit Mg_2NiH_4.

We have minimized the total energy with respect to the internal parameters, x and z. The results obtained for the different configurations are summarized in Table I together with corresponding experimental values obtained by Noréus and Olson from neutron-diffraction data.[11] The tetrahedrally distorted square-planar configuration shows the smallest energy, with $x=0.2208$ and $z=0.0883$, in good agreement with the experimental values. The calculated Ni-H bond length is $d_{\text{Ni-H}}=1.548$ Å which compares well with the experimental value of 1.55 Å. The bending angle we obtain is 21.8 degrees, while the value deduced from experimental data is of 12.9 degrees. We think that this difference might be due to thermal-expansion effects and we are currently studying the dependence of the bending angle on volume changes.

B. Band structure

The hydrogen arrangement around the nickel atom has a noticeable impact on the band structure of the compound, mainly close to the Fermi level. In Fig. 2 we show the band structures calculated for each of the configurations of hydrogens atoms around nickel relevant to our discussion: the square planar, the tetrahedrally distorted square planar, and the regular tetrahedron. As can clearly be seen from the figure, the planar distribution would have a metallic behavior, the regular tetrahedron would be a semiconductor with an indirect gap, and the tetrahedrally distorted square-planar arrangement shows a pseudogap, a region around the Fermi level with a very low density of states. To understand these differences it is useful to have a general picture of the character of the bands of cubic Mg_2NiH_4. In the three cases shown in the figure, there is a separate set of four bands starting at around -10 eV. These are mainly hydrogen states corresponding to the four $1s$ hydrogen orbitals. Between this group of bands and the Fermi level there are five bands corresponding mainly to the nickel $3d$ orbitals. Above the Fermi level we found an empty magnesium $3s$ band and



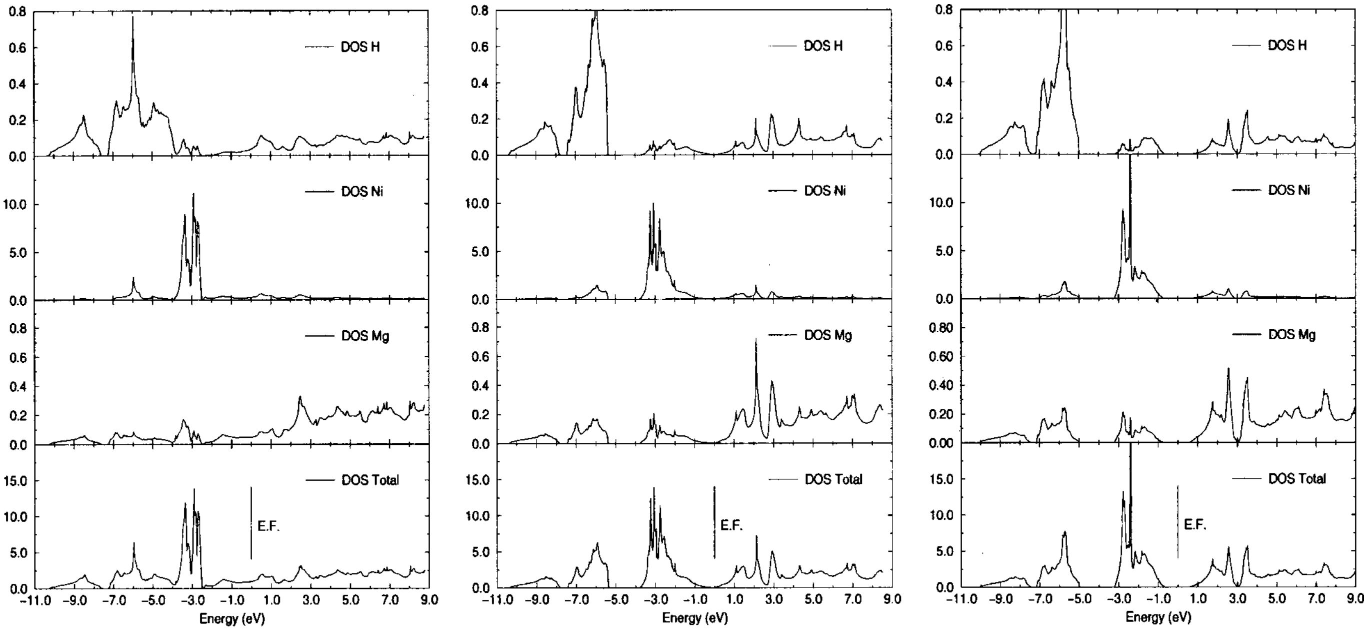
square planar tetrahedrally distorted square planar regular tetrahedral

FIG. 2. Electronic band structures for the three hydrogen configurations listed in Table I.

a nickel 4*s* band. As a result the magnesium is almost in a $+2$ state, transferring its two 3*s* electrons to the NiH_4 complex.

Four of the five 3*d* nickel bands are almost flat and the upper one, whose main character is $d_{x^2-y^2}$, is strongly dependent on the hydrogen arrangement around nickel. In the square-planar configuration this band is strongly hybridized with the hydrogen orbitals, mainly at the Γ point. Because of this hybridization the energy is higher and the band crosses the Fermi level. Since the $d_{x^2-y^2}$ orbital has its charge density mainly in the plane, by changing the bending angle the hybridization is reduced and the energy at the Γ point is lowered, thus opening a gap at some point. The minimum hybridization is obtained for the regular tetrahedral configuration where the band gap is a maximum.

The character of the different atomic states is shown in the density-of-state plots given in Fig. 3. In this figure the density of states for the three configurations considered is shown together with the partial density states corresponding to the magnesium, nickel, and hydrogen sites. For the mini-



square planar tetrahedrally distorted square planar regular tetrahedral

FIG. 3. Electron density of states for the three hydrogen configurations listed in Table I, in number of states per eV per cell.

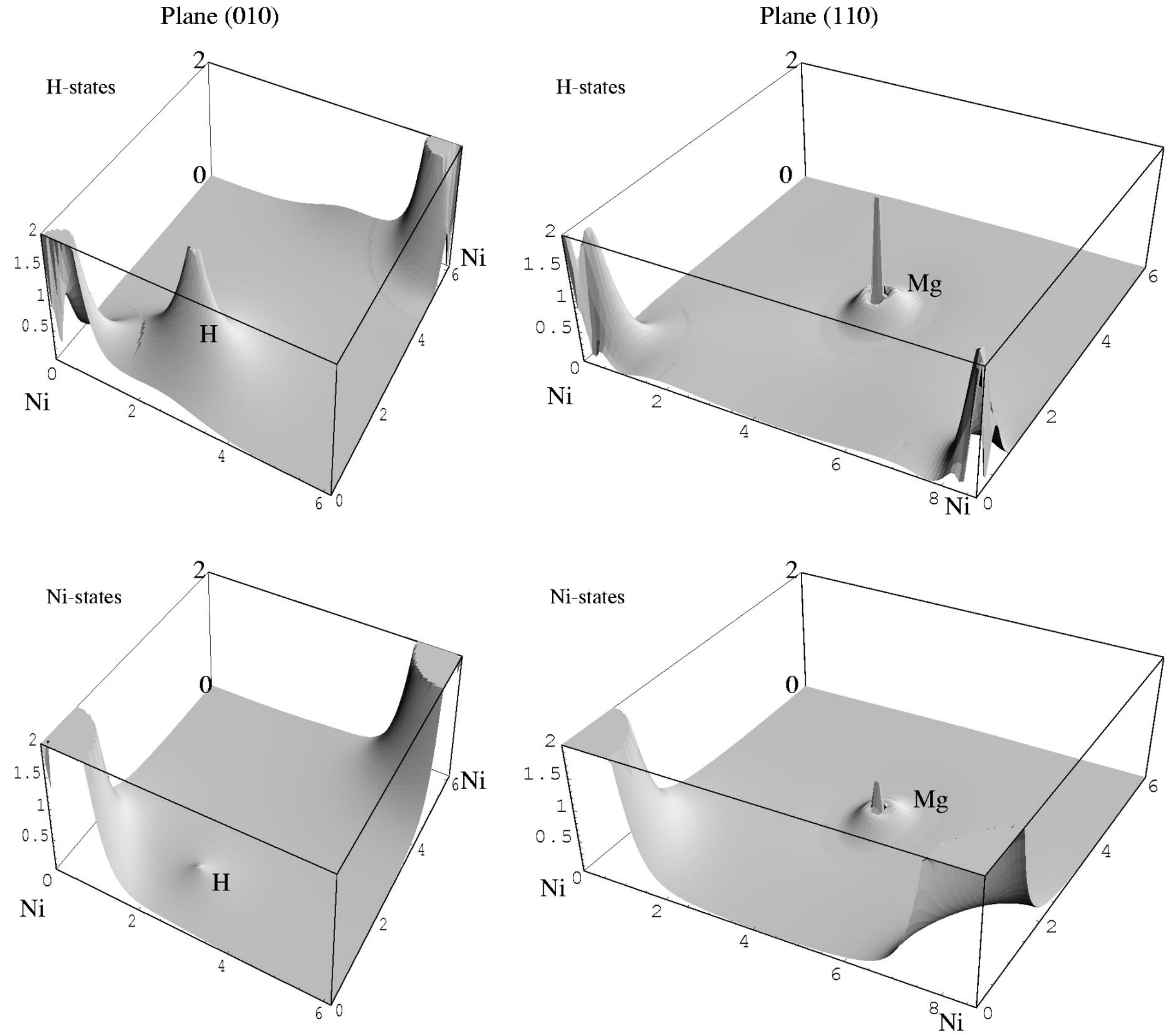


FIG. 4. Partial Ni *d* and H *s* charge densities along the (010) and (110) planes of the unit cell. The charge-density scale is shown from 0 to 2 electrons per Å^3.

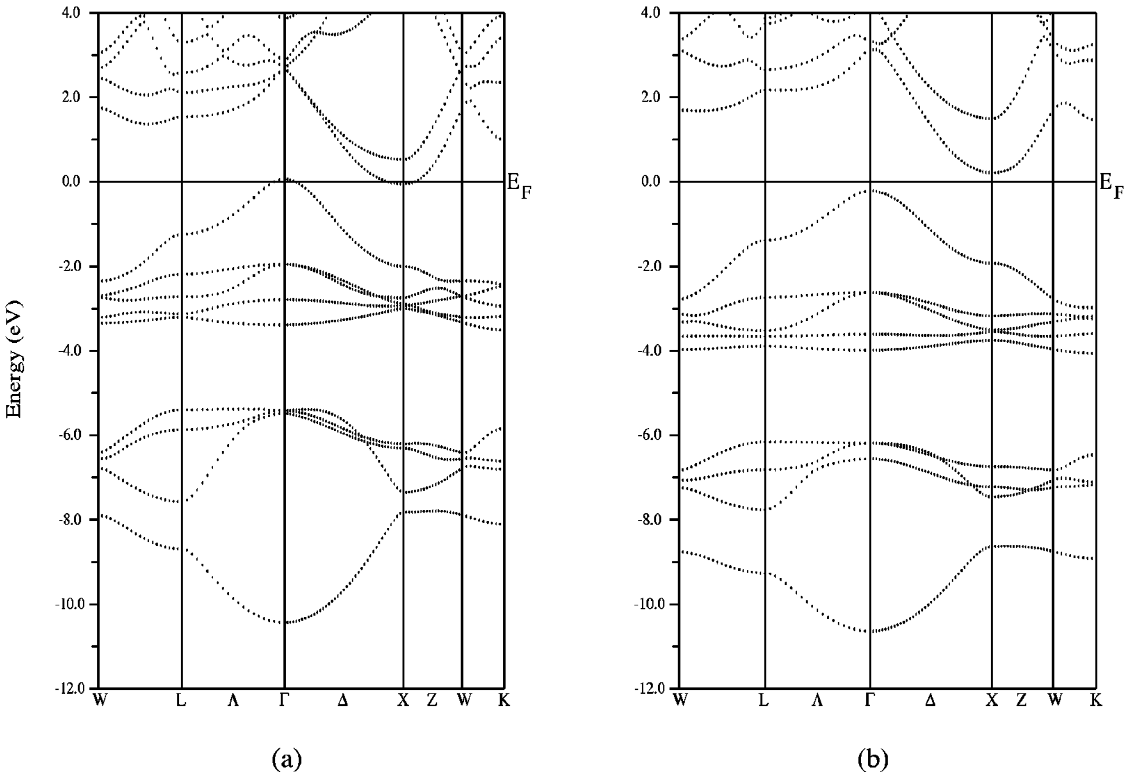
mum energy configuration, the tetrahedrically distorted square planar, we can clearly see a feature mentioned above, i.e., the pseudogap shows up as a very low density of states at the Fermi level. In this region there is a very highly dispersive band that touches the Fermi level from lower energies. The contribution of this band to the density of states is almost negligible compared to the contribution of the other *d* states of nickel.

In the literature of Mg_2NiH_4 it is usual to mention the 18-electron rule as a reason for its stability.[15] This picture is appealing through the comparison with the stable electronic structure of a novel gas atom where all *s*, *p*, and *d* shells are filled. Our band-structure results for Mg_2NiH_4 show that the 18 valence electrons occupy nine states of the NiH_4 complex. Of course, they are not states of an atom. The *s* subshell, for example, is formed by the symmetric combination of the four 1*s* hydrogen orbitals. The *p* subshell is also represented by the adequate combination of these states. The addition of more hydrogen atoms to Mg_2NiH_4 gives rise to new states of *d* symmetry and lower energies than those of the nickel 3*d* bands. These states interact producing bonding and antibonding combinations. Accordingly, the explanation to the fact that no more hydrogen can be incorporated to the structure of Mg_2NiH_4 is based not on a rigid-band-type model but on such interplay between the symmetry of the linear combination of hydrogen 1*s* orbitals and the nickel 3*d* states, with the resulting partial filling of the antibonding states.

C. Bonding and charge-density distribution

The charge-density distribution is obtained directly from the self-consistent calculation. The average valence charge density corresponds to 72 electrons per unit cell. We shall now discuss the nature of the nickel-hydrogen and magnesium-NiH_4 bonds looking at the distribution of charge within the unit cell.

Figure 4 shows the distributions of partial charge densities of the bands composed mainly of Ni *d* and H *s* orbitals along two planes of the unit cell, the (010) and (110). From the cut along the (010) plane we notice that the bands that are mainly H *s* in character will have some charge accumulation on the sites of Ni, and the bands that are mainly Ni *d* present some weight in the H region. This, together with the charge accumulation between both atoms, suggests a strong covalent character of the Ni-H bond.



(a)

(b)

FIG. 5. Electronic band structure for the stable hydrogen configuration of Mg_2NiH_4 (a) and for the hypothetical compound with the Mg^{2+} ions removed (b).

The cut along the (110) plane containing the Mg atoms shows that Mg has almost completely released its 3*s* electrons to the Ni-H bond. Thus, as already mentioned above, magnesium does not really participate in determining the valence states of the hydride. To further analyze the influence of magnesium, we have calculated the band structure of a hypothetical compound in which the atomic positions are those of Mg_2NiH_4, except for the Mg^{2+} ions, which have been removed. As shown in Fig. 5, the band structure of this hypothetical compound is remarkably similar to that of the real Mg_2NiH_4. In the same way as for the real hydride, the four states of hydrogen are placed below the five states of nickel and the bandwidth is very similar. These results show that the magnesium states do not really participate in the valence bands of the hydride.

IV. STABILITY PROPERTIES OF Mg_2NiH_4

The compound Mg_2NiH_4 is the only ternary phase present in the stable equilibrium phase diagram of the Mg-Ni-H system, where it shows a very restricted range of nonstoichiometry.[4] This indicates that the relative free energy of formation of this phase is definitely negative and quite sharp as a function of composition around the value Mg_2NiH_4. Since these stability properties are very important from the point of view of applications in hydrogen storage, in what follows we shall discuss them in terms of the cubic form of Mg_2NiH_4.

A. Stoichiometry

Although the stability properties of Mg_2NiH_4 are simple to state phenomenologically, their explanation in terms of electronic properties is an exceedingly complicated problem to solve since, in principle, all ternary compositions and all structures should be examined energetically. In our case we shall drastically restrict this examination to the antifluorite Mg_2NiH_δ structure as a function of hydrogen content, δ, with the hydrogens arranged around the Ni atoms. We have performed total-energy calculations for $\delta = 0,2,4,6$, evaluating the corresponding enthalpy of formations relative to the antifluorite compound Mg_2Ni ($\delta = 0$) and molecular H_2. Regarding the value $\delta = 6$, there is enough space in the crystal structure of Mg_2NiH_4 to incorporate two more hydrogen atoms per formula unit in an octahedral arrangement. The reason why Mg_2NiH_6 does not appear in the stable equilibrium phase diagram can be traced, as already mentioned, to the electronic structure of this compound. We have considered only even values of δ simply to avoid the computational effort involved in the calculation of structures without inversion symmetry.

In all cases we optimized the energy with respect to the volume and the Ni-H distance. The results obtained are listed in Table II and represented in Fig. 6.

Although our results are valid at 0 K, they nevertheless suggest that for $\delta \neq 4$ the antifluorite Mg_2NiH_δ structure is unstable, and will decompose into $Mg_2Ni + Mg_2NiH_4$ for $\delta < 4$, and into $Mg_2NiH_4 + H_2$ for $\delta > 4$. This decomposition behavior agrees with the experimental observation that the Mg_2NiH_4 has a well-defined stoichiometry and is the only phase observed in the stable equilibrium Mg-Ni-H ternary phase diagram.

B. Electron counting

Since we are mainly interested in its hydrogen content, the cubic phase Mg_2NiH_4 can be conceived as resulting from

TABLE II. Optimized lattice parameter and Ni-H distance for the antifluorite structure of Mg_2NiH_δ, as a function of δ. ΔH_f is the calculated enthalpy of formation relative to the antifluorite compound Mg_2Ni ($\delta=0$) and molecular H_2 (-2.3492 Ry).

δ	Lattice parameter (Å)	Ni-H distance (Å)	$\delta/(2+\delta)$ [a]	ΔH_f(kJ/mole)
0	6.000		0.0	0.0
2	6.151	1.524	0.50	-9.8
4	6.443	1.548	0.67	-14.6
6	6.267	1.636	0.75	7.7

[a] $\delta/(2+\delta)$ is the mole fraction of H_2.

the filling of the hydrogen sites starting from the metastable, hydrogen-free, antifluorite-type compound Mg_2Ni. Hydrogen can be thought of as being progressively incorporated to the antifluorite structure of Mg_2Ni until the composition NiH_4 is reached by the complex constituted by Ni plus the neighboring hydrogen atoms. In other words, upon hydrogen absorption the Ni atoms in cubic Mg_2Ni are finally substituted by the complex NiH_4, and the ternary Mg-Ni-H phase diagram demonstrates that at this specific hydrogen content the cubic Mg_2NiH_δ phase becomes abruptly stable as a function of δ.

According to this image, cubic Mg_2NiH_4 is a member of the Mg_2X family of compounds with the antifluorite structure where the Mg ions define the simple cubic sublattice. The consideration of this broader spectrum of materials might allow us to give a more global picture of the stability properties of Mg_2NiH_4. In fact, Hume-Rothery[25] pointed out the existence of well-defined antifluorite-type compounds of composition Mg_2IVB, where IVB represents an element of the Group IVB (Si, Ge, Sn, Pb). For these particular binary systems, and identical to the case of Mg_2NiH_4, the antifluorite phase Mg_2IVB is the only intermediate phase present in the respective stable equilibrium phase diagram, showing in all cases a negligible range of nonstoichiometry.[26] These Mg_2IVB compounds have been considered as typical examples of compounds where the electropositive Mg atoms transfer most of their valence electrons to the electronegative IVB elements.[25,27] In this way an essentially closed s-p electron shell results, and each IVB atom tends to complete its octet of valence electrons and so reach an electronic structure similar to that of the next inert gas element. This is essentially an ionic description, and the resulting stabilization of the now formally written $(Mg^{2+})_2$IVB^{4-} phase is very strong and very specific in composition. Thus, band gaps and nonmetallic behavior should, in principle, be expected in these compounds.[28,29] This qualitative bonding picture for the Mg_2IVB compounds is supported by recent calculations of their electronic structures[27,30] which reveal the following bonding situation: a weak Mg-Mg and IVB-IVB bonding, with a high degree of ionicity, and a predominantly ionic bonding between the Mg and IVB atoms. For example, these general bonding features are reflected in the electron-density map for the (110) plane of Mg_2Ge shown in Fig. 7(a), as calculated by us.

Consider now the antifluorite Mg_2NiH_4 compound, including for completeness its homologous Mg_2CoH_5 and

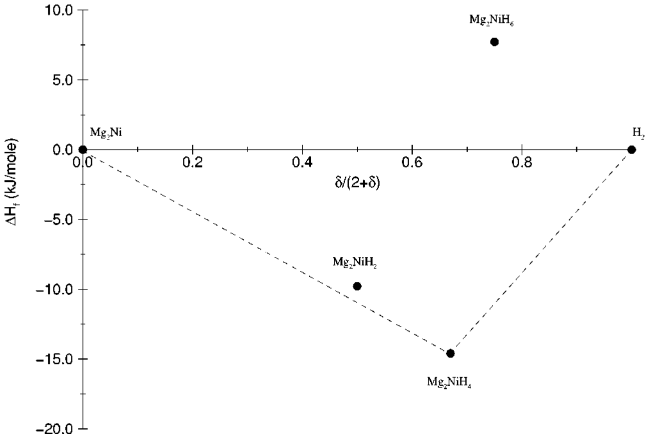
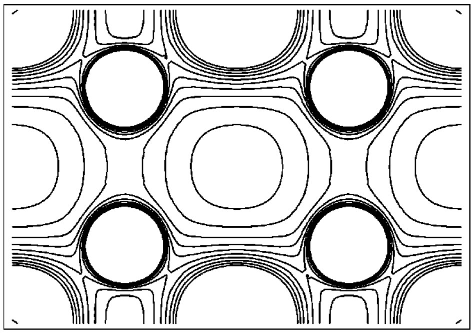
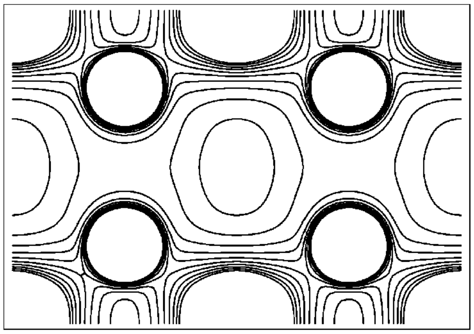


FIG. 6. Enthalpy of formation ΔH_f of the antifluorite Mg_2NiH_δ phase relative to Mg_2Ni ($\delta=0$) and molecular H_2, as a function of the mole fraction of H_2, $\delta/(2+\delta)$, see Table II.



(a) Mg_2Ge



(b) Mg_2NiH_4

FIG. 7. Electron density maps calculated in this work for Mg_2Ge (a) and Mg_2NiH_4 (b) along the plane (110) of the antifluorite unit cell. The contours are equally spaced between 0.005 and 0.3 electrons per Å^3. The lattice parameters used are the experimental values, 6.385 Å for Mg_2Ge (Ref. 31) and 6.507 Å for Mg_2NiH_4 (Refs. 10 and 11).

TABLE III. Room-temperature lattice parameters for antifluorite compounds Mg_2X.

Compound	Lattice parameter (Å)
Mg_2Si [a]	6.35
Mg_2Ge [a]	6.39
Mg_2FeH_6 [b]	6.43
Mg_2CoH_5 [c]	6.43
Mg_2NiH_4 [d]	6.48
Mg_2Sn [a]	6.76
Mg_2Pb [a]	6.81

[a] Reference 31.
[b] Reference 32.
[c] Reference 33.
[d] Reference 11.

Mg_2FeH_6. These hydrides fit in terms of lattice parameters within the series determined by the Mg_2IVB compounds. In Table III room-temperature lattice parameters are listed for the antifluorite-type compounds Mg_2X (X = Si, Ge, Sn, Pb, FeH_6, CoH_5, and NiH_4). The close values given for Mg_2Ge and Mg_2NiH_4, and Mg_2FeH_6 and Mg_2CoH_5, strongly suggest the existence of close similarities between their respective electric charge distributions; in particular, this points to an equivalence between the tetravalent entities Ge^{4-} and $[NiH_4]^{4-}$. In Fig. 7(b) we show our results for the electron density map on the (110) plane of cubic Mg_2NiH_4, calculated for the stable configuration of the complex NiH_4. The close similarity with the case of Mg_2Ge, Fig. 7(a), is remarkable. Hence, and in line with the octet filling picture advanced for Mg_2Ge, the tetravalent complexes $[NiH_4]^{4-}$, $[CoH_5]^{4-}$, and $[FeH_6]^{4-}$, could be described as different kinds of pseudo-Ge^{4-} anions. Alternatively, they could be considered as quite different valence state arrangements of 18 electrons in closed-shell configurations around the transition-metal atom. Both points of view go along with an inert gas formulation of the transition metal-hydrogen cluster, and in fact this formulation has its semiempirical counterpart in the well-known 18-valence electron rule.[34] The main difference between Ge^{4-} and $[NiH_4]^{4-}$, $[CoH_5]^{4-}$, and $[FeH_6]^{4-}$, is in the energy ordering of the nine occupied electron levels, which in each hydride depends essentially on the particular radial behavior of the electron wave functions centered in the transition-metal atom. Thus, the nature of the resulting energy band gap will eventually depend on each particular hydride. In this connection, it has already been remarked by Gupta *et al.*[16] that nine-band-filling effects appear to be a most important factor when considering the stability of the series of nonmetallic hydrides Mg_2NiH_4, Mg_2CoH_5, and Mg_2FeH_6. These authors remarked that the tetravalent complexes $[NiH_4]^{4-}$, $[CoH_5]^{4-}$, and $[FeH_6]^{4-}$, all satisfy the 18 valence electron rule. Even more generally, Gupta[15] has pointed out that Mg_2NiH_4 belongs to a family of antifluorite ternary metal hydrides $M_2\mathrm{TMH}_\epsilon$, where M is a divalent simple metal (M = Mg, Ca, Sr) and TM a transition metal (TM = Fe, Co, Ni, Rh, Ir, Ru, Os); in this family, the value of ϵ for a given TM is such that the 18 valence electron rule is always satisfied.

The fact that the Mg_2NiH_4 has a well-defined stoichiometry and is the only phase observed in the Mg-Ni-H ternary phase diagram can be also discussed in terms of the inert gas formulation mentioned above. In fact, it could be argued that the energy associated with the fragment $[NiH_\delta]^{\delta-}$ changes with δ in analogy with the variation of the free-atom total energy when moving horizontally in the Periodic Table towards and across the inert gas element. In the latter case a strong and positive discontinuity is observed in the energy derivative with respect to electron number at the inert gas value, related to a sudden change in the ionization energies. In the case of $[NiH_\delta]^{\delta-}$ there is a significant positive change in the energy rate of change with delta when crossing the value $\delta = 4$ associated either with the presence of a gap or, more generally, of a pseudogap in the electron density of states.

V. CONCLUSIONS

We have studied the energetics of the cubic hydride Mg_2NiH_4 for different hydrogen arrangements and obtained the hydrogen positions that minimize the total energy. This minimum-energy configuration corresponds to a tetrahedrally distorted square-planar distribution of hydrogen atoms around the nickel atom, which is in agreement with neutron-diffraction data. The calculated Ni-H bond length is $d_{\text{Ni-H}} = 1.548$ Å, while the experimental value is of 1.55 Å.[11] In turn, the optimized bending angle characterizing the tetrahedral distortion is of 21.8 degrees and the value obtained from fitting experimental diffraction data is of 12.9 degrees.[11] It is interesting to remark that the Ni-H equilibrium distance appears to be relatively independent of the bending angle, and therefore seems characteristic of the NiH_4 complex.

The electronic band structure of this compound close to the Fermi level is strongly dependent on the arrangement of the hydrogen atoms around the nickel atom. The character of the valence bands is given by the mixture of nickel $3d$ orbitals with a small component of the proper combination of the four hydrogen $1s$ orbitals. The hydrogen square-planar distribution results in a metallic compound with a highly dispersing band crossing the Fermi level. The tetrahedrally distorted square-planar distribution, i.e., the hydrogen configuration which minimizes the energy, generates a band structure showing a pseudogap at the Fermi level. Finally, the regular tetrahedral arrangement produces a semiconductor with an indirect gap of 1.17 eV.

From the calculated charge distribution we can infer the type of bonding in Mg_2NiH_4. Hydrogen is covalently bonded with nickel forming a complex $[NiH_4]^{4-}$ which in turn bonds ionically to the Mg^{2+} ions. The charge distribution in cubic Mg_2NiH_4 strongly resembles that of the family of compounds Mg_2IVB, confirming the idea of a $[NiH_4]^{4-}$ entity similar to the IVB^{4-} ions. Thus, Mg_2NiH_4 can be considered as a member of the Mg_2X family of compounds with antifluorite structure, including regularity in the lattice parameters, charge distributions, and the ionic bonding between the $[NiH_4]^{4-}$ cluster and the Mg^{2+} ions.

We have analyzed the stability properties of Mg_2NiH_4 and studied the energy of the antifluorite compounds

Mg_2NiH_δ with $\delta = 0,2,4,6$. Our results suggest that for $\delta\delta \neq 4$ the antifluorite Mg_2NiH_δ structure is unstable and will decompose into $Mg_2Ni + Mg_2NiH_4$ for $\delta < 4$, and into $Mg_2NiH_4 + H_2$ for $\delta > 4$. This decomposition behavior agrees with the experimental observation that the Mg_2NiH_4 has a well-defined stoichiometry and is the only phase observed in the equilibrium Mg-Ni-H phase diagram.

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