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On the possibility of metal hydride formation
Part II: Geometric considerations

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Abstract

A simple analysis based on crystal geometry is proposed as an aid in predicting the formation of hydrides from intermetallic compounds. It is derived from a slight variation Westlake's empirical geometric criterion that an interstitial site should have a radius ≥0.4 Å to be occupied by hydrogen. For comparison this criterion has been applied to a compound which hydrides ($LaNi_5$) and to a compound with a similar crystal structure ($MgNi_3B_2$) which does not. When applied to the $LaNi_5$–H system, this criterion predicts the occupation of the 6m and 12n sites in the P6/mmm α solid solution phase $LaNi_5H_{<1}$, the 6m and 12n (~6i) sites in the β hydride phase $LaNi_5H_3$, and 6m(6c), 6i(6c) and 4h(2b) sites of the γ hydride phase $LaNi_5H_{6-7}$ ($P6_3mc$). The compound $MgNi_3B_2$, on the other hand, has a densely packed crystal structure with almost no interstitial sites satisfying the Westlake criterion. Because of its relative simplicity, this type of analysis may prove to be a useful aid in the discovery and development of new intermetallic hydrides. © 1998 Elsevier Science S.A.

Keywords: Metal hydrides; Hydrogen absorption; Westlake Criterion; $LaNi_5$; $MgNi_3B_2$

1. Introduction

The future development of clean hydrogen energy would benefit greatly from the discovery of new hydride forming intermetallic compounds with weight, cost and hydriding properties vastly superior to the currently known metal hydrides. In the absence of practical methods for predicting which intermetallic compounds will form a hydride, we have had to rely on trial and error methods combined with some general empirical rules, as well as mere intuition in our search for new metal hydrides. Unfortunately, this often does not work. $MgNi_3B_2$ is a typical example of a compound which appeared to be a good candidate for hydrogen absorption. Its $CeCo_3B_2$ ($P6_222$) type crystal structure [1] is a variation of the $CaCu_5$ (P6/mmm) structure of $LaNi_5$ [2], and its elemental composition is characteristic of hydride forming compounds. However, testing showed that under moderate hydriding conditions this alloy does not absorb hydrogen [3].

A well known empirical geometric criterion for the interstitial occupation of hydrogen may provide some insight into the possibility of a compound to form a hydride. This criterion was formulated some years ago by Westlake [4–6]. It states that available interstitial sites must have a spherical volume with a radius ≥0.4 Å to be occupied by hydrogen. Using this criterion and the minimum allowable H–H distances determined by Switendick [7], Westlake was able to successfully account for the hydrogen content of $LaNi_5H_6$. We have employed a variation of this criterion to explain hydrogen occupancies in the α solid solution, and β and γ hydride phases of $LaNi_5$. As a counter example, we applied the same analysis to $MgNi_3B_2$ to see if it satisfactorily predicts the lack of hydrogen absorption by this compound.

Geometrical considerations are just one aspect of the atomic environment which dictates the conditions under which hydrogen will dissolve in the lattice and form a hydride. Electronic factors, diffusion kinetics and surface properties all contribute, to one degree or another, to an intermetallic compound's predilection for hydrogen absorption and hydride formation. On the other hand, the compactness of the geometric arrangement of atoms in a crystal lattice is an expression of the local electronic environment. Thus the geometry should reflect the electronic factors which also control the likelihood that hydrogen will occupy an interstitial site. The advantage of such a geometrical analysis lies in its simplicity. Knowing only the lattice parameters, a host of compounds possessing the same crystal structure can be rapidly evaluated.

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Such a geometric analysis may be a great aid in selecting only the most promising out of a multitude compounds, for synthesis and testing for hydrogen absorption.

2. Results and discussion

2.1. Interstitial site size calculations

There are two differences between Westlake's original work and the manner in which we have treated the concept of a minimum interstitial site size criterion. The first is that we did not use the 12-fold coordination radii for the metal atoms as Westlake did. Instead, the metal atom radii were determined directly from the special geometry of the compound's crystal structures. Metal atoms were assigned radii of spheres which touch but do not overlap. For the $LaNi_5$ crystal structure the atomic radii can be determined from a variation of the ideal packing geometry laid out by Magee et al. [8]. These are:

$$r(\mathrm{Ni}^{(2)}) = a/4\,, \tag{1}$$

$$r(\mathrm{Ni}^{(1)}) = (((a \tan 60°)^2 + c^2)^{1/2})/2 - r(\mathrm{Ni}^{(2)}), \text{ and} \tag{2}$$

$$r(\mathrm{La}) = (a \cos 30°)/2 - r(\mathrm{Ni}^{(1)}) \tag{3}$$

Thus for $LaNi_5$ (lattice parameters $a=5.017$ and $c=3.986$), the resulting metal radii are:

La(1a): $r = 1.687$ Å,

$Ni^{(1)}$(2c): $r = 1.210$ Å and

$Ni^{(2)}$(3g): $r = 1.254$ Å.

The second difference from Westlake's formulation is that we assume that site radii must be ≥ 0.4 Å before being occupied. Calculations were, therefore, made using the unhydrided compound's lattice parameters. In the case of multiple hydrides phases, the lattice parameters of the precursor phase were used.

Once the position and radii of the host metal atoms have been defined, the position and radius of the largest sphere that will fit into an interstitial site can then be determined. These radii were calculated for the tetrahedral, octahedral and trigonal sites as follows:

2.1.1. Tetrahedral sites

The size and position of a tetrahedral site is determined explicitly by the four coordinating atoms. If these four metal atoms are considered to be non-overlapping spheres, a fifth sphere can be created in-between them and expanding until it is in contact with all four metal atom spheres. These four non-coplanar points of contact define a unique sphere. This situation is depicted schematically in Fig. 1a. In addition, touching spheres contact tangentially. Thus, the distance between the center of the interstitial sphere and the center of any one of the metal atom spheres is just the sum of their two radii. This produces the following set of four independent equations from which can be solved for the four unknowns x, y, z, r:

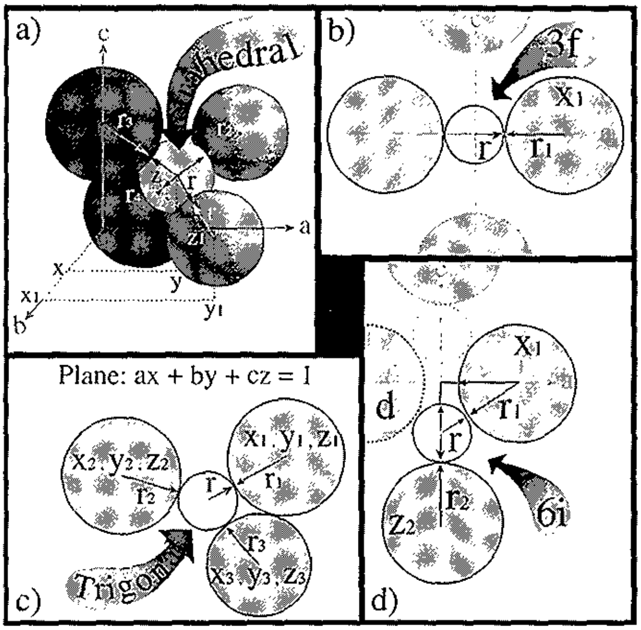

Fig. 1. Schematic representations of: (a) a tetrahedral site (general case), (b) an octahedral site ($3f-LaNi_5$), (c) a trigonal site (general case), and (d) a trigonal site (special case $6i-LaNi_5$).

$$(x-x_n)^2 + (y-y_n)^2 + (z-z_n)^2 = (r-r_n)^2 \tag{4}$$

Where x, y, z and r are the center coordinates and radius of the interstitial sphere and x_n, y_n, z_n and r_n ($n=1,2,3,4$) are the same for the coordinating host metal atoms. Note that, for the non-cubic compounds, atomic positions must be transformed into Cartesian coordinates. These equations are non-linear, however when rewritten as:

$$r^2 - x^2 - y^2 - z^2 + 2(xx_n + yy_n + zz_n + rr_n) = x_n^2 + y_n^2 + z_n^2 - r_n^2 \tag{5}$$

or:

$$2A \cdot u = H \cdot (1 + dh) \tag{6}$$

where

$A = [x_n, y_n, z_n, r_n]$,

$u = (x, y, z, r)$,

$H = (x_n^2 + y_n^2 + z_n^2 - r_n^2)$,

and dh is an iterative multiplier.

This set of equations can then be solved iteratively.

2.1.2. Octahedral sites

An octahedral site is found at the center of an octahedron formed by six metal atoms. The interstitial radius is simply given by the distance between the two closest atoms on one of the three center axis. An example is shown in Fig. 1b.

2.1.3. Trigonal sites

A trigonal site is located within the triangle formed between three metal atoms (Fig. 1c). Again Eqs. (4)–(6) apply for $n = 1$, 2 and 3. The fourth equation is the special condition that the centers of the metal atoms and the interstitial site are all confined to a plane:

$$ax + by + cz = 1 \tag{7}$$

Thus from Eq. (6): $A_4 = [a, b, c, 0]$, $H_4 = (1)$ and $dh = 0$ for the fourth equation.

For the special case of the 6i site of the P6/mmm symmetry (Fig. 1d), the problem reduces to an exact analytic solution:

$$x_1^2 + d^2 = (r + r_1)^2 \quad \text{and} \quad d = z_2 - r_2 - r, \tag{8}$$

Here d and r are the unknown position and radius of the interstitial sphere and x_1, r_1, and z_2, r_2 are the known coordinates and radii of the metal atoms. One can then solve exactly for r;

$$r = \frac{x_1^2 + (z_2 - r_2)^2 - r_1^2}{2(r_1 + z_2 - r_2)} \tag{9}$$

All of the above interstitial site radii are for the largest imaginary sphere which will fit between the metal atoms coordinating an interstitial site. In addition to these radii, the center position of these spheres can (and should) also be calculated. It is important to note, however, that the sphere center may not necessarily correspond to either the crystallographic coordinates of the associated site or the actual atomic positions of interstitial hydrogen. The spherical radius is simply a geometric means to evaluate the hypothetical space available between metal atoms. Calculating the sphere center position, on the other hand, ensures that the solution has converged to a sphere which is indeed centered within the interstitial site being evaluated. If this is not the case, the site size is determined by a different set of locally coordinating metal atoms.

2.2. Interstitial site calculations – $LaNi_5$

To verify this geometric criterion, we applied it to the hydrides of $LaNi_5$. The current view is that under the right conditions, $LaNi_5$ forms an α solid solution phase, and at least two separate hydride phases [9] and possibly more [10]. The two main hydride phases can be distinguished in the PCT diagrams at slightly elevated temperatures [11–13]. These have been referred to by Akiba et al. as the β (beta phase H/fu≈3) and the γ (gamma phase H/fu≈6). They examined all three phases (α, β and γ) using in-situ X-ray powder diffraction while desorbing $LaNi_5H_x$ from 6 to 0 H/fu at 64±5°C [11,14]. From these measurements, they determined the lattice parameters for each of the three phases as a function of hydrogen content. These are reproduced as linear fits to their data in Fig. 2.

Using these lattice parameters, we calculated the size of the main interstitial sites for each of the three phases. We began by using the most simple crystallographic model, i.e., assuming that the metal atoms maintain their original P6/mmm structure during hydriding. This is justified for the α and β phases [15,16]. It was also applied to the γ phase, as well as the currently accepted $P6_3mc$ structure, specifically to point out the effect that this structural change has on the size of the interstitial sites. The crystallographic positions of the main interstitial sites of the P6/mmm symmetry of α, β $LaNi_5H_x$ are given in Table 1. The corresponding interstitial sites for the $P6_3mc$ symmetry of γ $LaNi_5H_x$ are presented in Table 2.

The calculated radii of these sites are presented versus

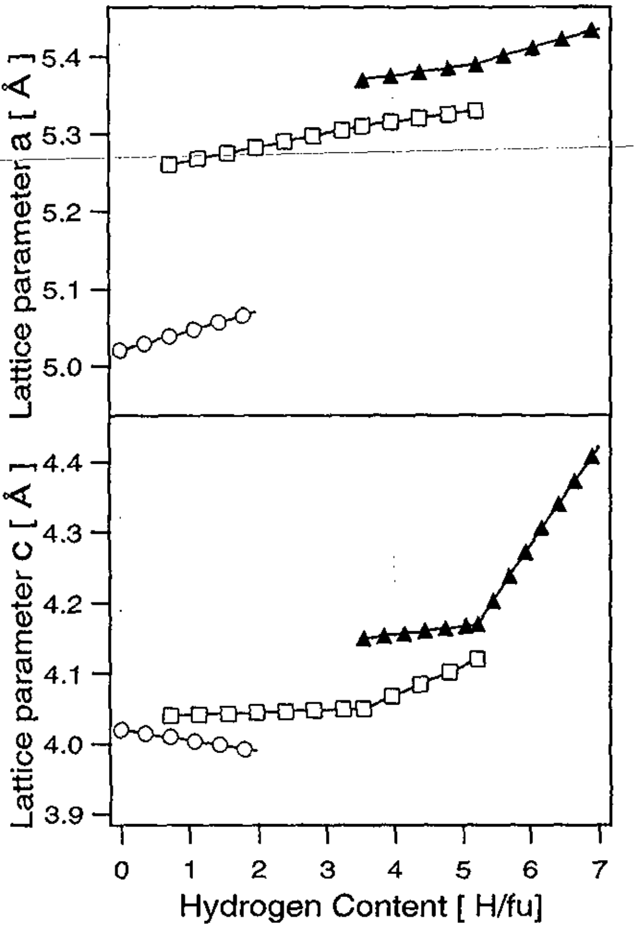

Fig. 2. Hexagonal lattice parameters a and c. Reproduced as linear fits to lattice parameter data determined by Akiba et al. from in-situ X-ray diffraction measurements made while desorbing $LaNi_5H_x$ from 6 to 0 H/fu at 64±5°C. (The lattice parameters of the γ phase have been extrapolated from 6 to 7 H/fu for the interstitial site calculations) [11,14].

Table 1
Metal atom positions and the most promising interstitial sites for hydrogen occupation in the P6/mmm symmetry of α and β $LaNi_5H_x$[a]

P6/mmmm			
Type	Site (Wyckoff)	Position (*x*, *y*, *z*)	Coordination
La	1a	0, 0, 0	
$Ni^{(1)}$	2c	1/3, 2/3, 0	
$Ni^{(2)}$	3g	1/2, 0, 1/2	
Octahedral	3f	1/2, 0, 0	2La, $2Ni^{(1)}$, $2Ni^{(2)}$
Trigonal	6i	1/2, 0, *z*	2La, $2Ni^{(1)}$, $1Ni^{(2)}$
Tetrahedral	12n	*x*, 0, *z*	1La, $2Ni^{(1)}$, $1Ni^{(2)}$
Tetrahedral	4h	1/3, 2/3, *z*	$1Ni^{(1)}$, $3Ni^{(2)}$
Tetrahedral	6m	*x*, 2*x*, 1/2	2La, $2Ni^{(2)}$
Tetrahedral	12o	*x*, 2*x*, *z*	1La, $1Ni^{(1)}$, $2Ni^{(2)}$

[a] The sites are labeled by their Wyckoff positions [31].

hydrogen content in Fig. 3a–f. Each plot has been labeled according to the Wyckoff notation of the interstitial sites associated with the P6/mmm symmetry. Westlake's criterion ($r=0.4$ Å) is also indicated in these plots. From these calculations, the following observations can be made for each of the three separate phases:

αphase: only the 6m sites meet the Westlake criterion. However the 12n sites are only just below the 0.4 Å limit. Experimental measurements by Fisher et al. and Furrer et al. located hydrogen on 3f or 12n sites [15,17]. Note that the 3f site is a subset of 12n sites. It is located at the common edge shared by four equivalent 12n tetrahedra. Thus, occupation of the 12n or 3f sites is in reasonable agreement with the Westlake criterion. However, the observation that the 6m sites are unoccupied is not supported by this geometric analysis. Other compounds need to be tested to determine to what extent this geometrical criterion can be successfully applied to hydrogen–metal solid solutions.

βphase: with the formation of the β hydride phase, a large lattice expansion occurs in the a direction and a moderate expansion in the c direction. There is a corresponding enlargement of all interstitial sites. Consequently the 6m, 12n and 12o sites now meet Westlake's criterion. The average nearest neighbor distances between these sites are: 6m–12n =2.13 Å, 6m–12o=1.18 Å and 12n–12o=1.31 Å. Thus only the neighboring 6m and 12n sites can be occupied and still maintain a distance greater than the minimum theoretical distance of 2.1 Å [7].

Hayakawa et al. performed a time of flight neutron diffraction study of $LaNi_5H_3$ [18]. They found that deuterium occupies the 6m and 6i sites. The 6i site is a subset of 12n, lying in the face shared by two 12n tetrahedra site (Table 1). Thus, even though the 6i site is slightly less that 0.4 Å, it is likely that a 12n hydrogen atom will take a position as close as possible to the 6i site. This allows it to coordinate with two lanthanum atoms, as well as, to distance itself, as much as possible from hydrogen in the 6m sites. Thus Westlake's criterion agrees reasonably well with the reported experimental results.

γphase: as a first approach we calculated the interstitial site radii of the γ phase using the P6/mmm structure (open triangles in Fig. 3a–f). Fig. 2 shows that, initially, there is an isotropic lattice expansion in the γ phase as the hydrogen content increases. At about 5.2 H/fu the lattice begins to expand rapidly in the c direction. This change in lattice expansion is likewise expressed in the calculated interstitial site radii. It can be seen that the sites 6m, 12n, 12o and now the 6i (at ≈5 H/fu) and 4h (at ≈6 H/fu) are all large enough for hydrogen occupation. Again, the 12o site is unlikely to be occupied due to short H–H distances. Likewise, occupation of the 6i site could be interpreted as the most energetically stable and, thus, the preferred subset of 12n sites.

In the past, such an interstitial site analysis was complicated by the fact that the crystal structure of $LaNi_5H_{\approx 6}$ was a source of great debate. Several structural models were proposed based on X-ray and neutron diffraction measurements. Four of these models are shown in Fig. 4 [19,20]. These are the two site P3lm [21–24] and P321 [25], five site P6/mmm [26,27], seven site $P6_3mc$ [28] and the five site $P6_3mc$ [29,30] models respectively. The difficulty has been that structural determination of $LaNi_5H_{\approx 6}$ by neutron diffraction was plagued by the inherent problems of anisotropic line broadening, as well as, the deuterium peaks being overwhelmed by the strong neutron scattering of nickel. This was resolved by Thomp-

Table 2
Metal atom positions and the most promising interstitial sites for hydrogen occupation in the $P6_3mc$ symmetry of γ $LaNi_5H_x$[a]

$P6_3mc$			
Type	Site (Wyckoff)	Position (*x*, *y*, *z*)	Coordination
La	2a	0, 0, *z*	
$Ni^{(1)}$	2b	1/3, 2/3, *z*	
$Ni^{(2)}$	2b	1/3, 2/3, *z*	
$Ni^{(3)}$	6cc	*x*, *y*, *z*	
Tetrahedral	D1 2b (4h)	0, 0, *z*	$1Ni^{(1)}$, $3Ni^{(3)}$
Tetrahedral	D2 2b (4h)	0, 0, *z*	$1Ni^{(1)}$, $3Ni^{(3)}$
Tetrahedral	D3 6c (6m)	*x*, 0, *z*	2La, $2Ni^{(3)}$
Tetrahedral	D4 6c (6m)	*x*, 0, *z*	2La, $2Ni^{(3)}$
Octahedral	D5 6c (6i)	*x*, 0, *z*	2La, $1Ni^{(1)}$, $1Ni^{(1)}$, $2Ni^{(3)}$

[a] The sites are labeled by their Wyckoff positions [31].

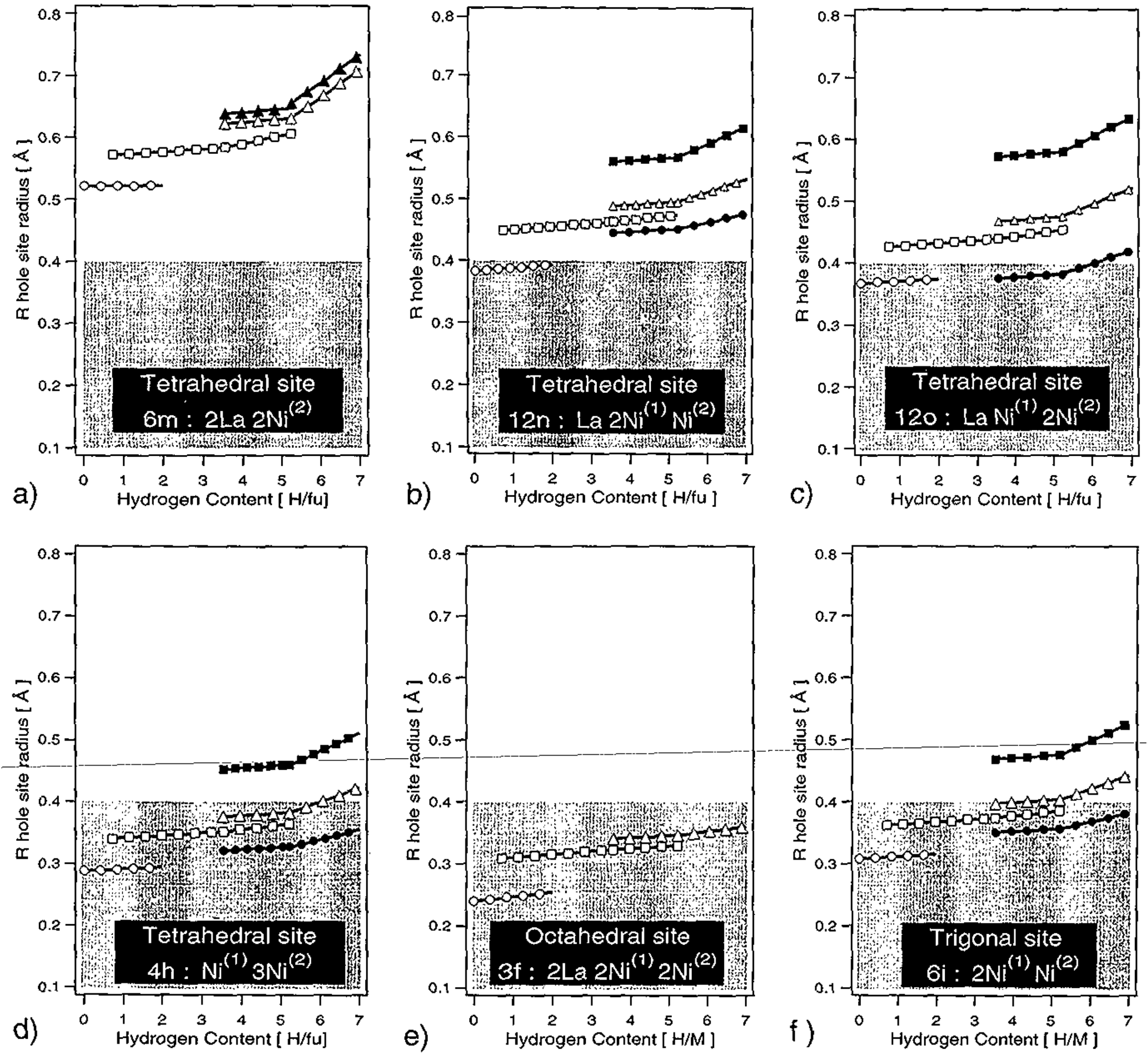

Fig. 3. The radii of spheres calculated for the most promising interstitial sites for hydrogen occupation in the α (—○—), β (—□—) and γ (—△—) phases of $LaNi_5H_x$. (P6/mmm-open symbols; $P6_3mc$ γ phases-closed symbols (—●—, —■—, —▲—).

son et al. by substituting nickel with an isotope which has a lower scattering cross-section (^{60}Ni). The crystal structure of the γ phase was eventually resolved independently by Thompson et al. and Percheron-Guégan et al., albeit determining somewhat different deuterium occupancies and metal atom positions [20]. Both groups identified the symmetry as $P6_3mc$ with deuterium occupying 2b and 6c sites. These correspond to the 4h, 6m and 6i sites in the P6/mmm symmetry (see Table 2).

The main difference between the P6/mmm and the $P6_3mc$ structures is that in the $P6_3mc$ structure the $Ni^{(2)}$ atoms have been shifted down out of the (x, y, 1/2) mid-plain by ≈0.4 Å causing a doubling of the unit cell in the c direction (Fig. 4). Because of this two sets of interstitial sites are formed for each of the corresponding sites in the P6/mmm structure (with the exception by symmetry of the 6m site).

We re-calculated the interstitial site radii for the γ phase using the reported $P6_3mc$ structure [29] (Fig. 3a–f). The interstitial volumes are identical for the two tetrahedral 6c sites (D3 and D4) which are related to the 6m site in the P6/mmm symmetry (Fig. 3a, closed triangles). These are slightly larger than the radii calculate for 6m site of the P6/mmm model. Because of the shift in the $Ni^{(2)}$ atoms, there are now two 6c sites corresponding to the 12n sites of the P6/mmm symmetry. Their radii are substantially different, but both are >0.4 Å. Again, for energetic reasons, hydrogen will probably prefer to take a position

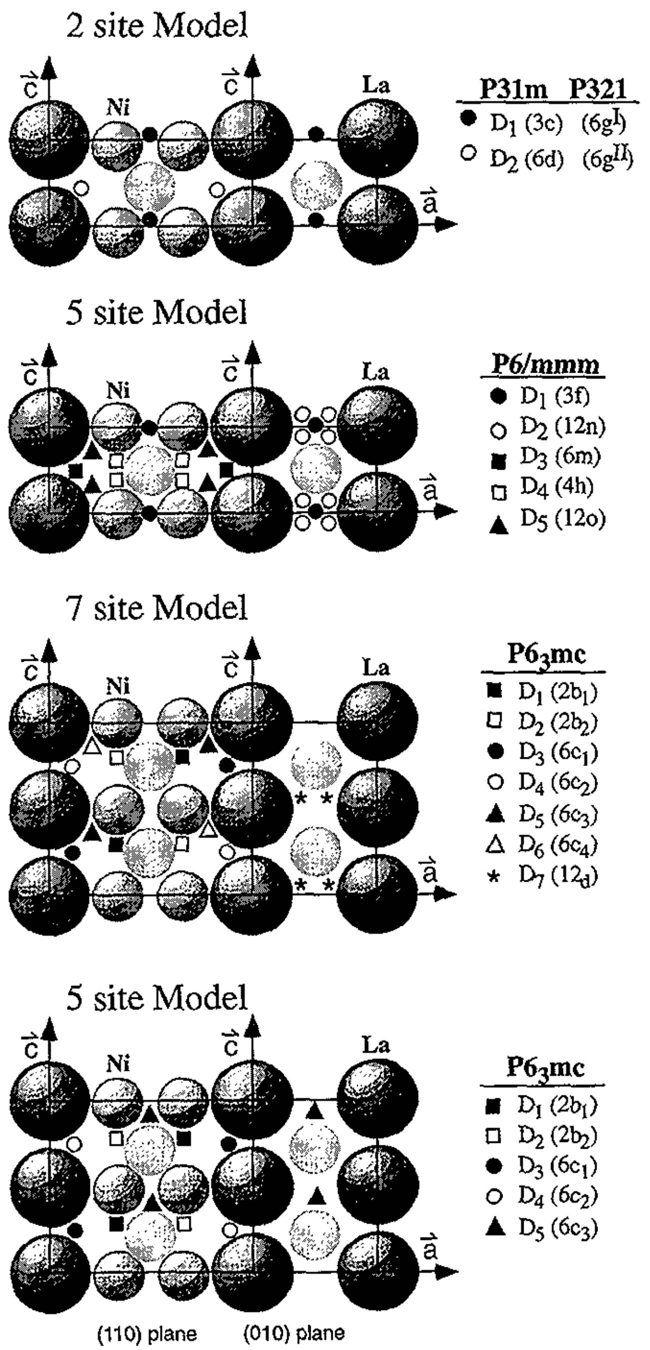

Fig. 4. Deuterium (Hydrogen) atomic sites and space group symmetries for four different structural models proposed for the γ $LaNi_5D_x$ phase (adapted from [19,28,20]). Wyckoff [31] positions are shown in parentheses.

within these tetrahedral sites which is equidistant between two La atoms. Thus the 12n hydrogen position will converge to a 6c site which is related to 6i in the P6/mmm symmetry. In this case, due to the shifting of the $Ni^{(2)}$ atom, only one of the 6i sites is large enough to be occupied by hydrogen (D5 of the five site model of Fig. 4). There are two sets of two 2b sites associated with the 4h site of the P6/mmm symmetry. In a manner analogous to the 6i sites, only one of these sets (D1 and D2 Fig. 4) have a radius >0.4 Å. The other set is <0.4 Å over the entire γ phase and is therefore unlikely to be occupied (Fig. 3d). Finally the 6c sites associated with the 12o sites have been modified as well, but are still assumed to be unoccupied due to short H–H distances. The 3f sites are identical and <0.4 Å in the two different crystal symmetries. This geometrical analysis suggests the occupation of the D1, D2, D3, D4 and D5 sites of the $P6_3mc$ γ phase $LaNi_5H_{6-7}$. This is consistent with the experimentally determined deuterium sites and is also in qualitative agreement with a similar interstitial site analysis done by Thompson et al. [29].

From these results, the following scenario for the formation of the hydrides of $LaNi_5$ can be proposed: the 6m sites are large enough to accept hydrogen from the very start of the α solid solution phase. 12n sites begin to fill and there is a transition to the β phase, in which both 6m and 12n sites are occupied. Hydrogen on 12n sites shift towards the 6i position. At the start of the gamma phase, hydrogen occupation of one set of the 6i sites, causes a displacement of $Ni^{(2)}$ {$Ni^{(3)}$ in the $P6_3mc$ structure} atoms. This opens up the upper set of 4h sites for hydrogen occupation (D1 and D2) and closes the lower ones (Fig. 4). Thus, in its final state, the γ phase consists of partial occupation of the original 6m {D3 and D4}, 6i {D5} and 4h {D1 and D2} sites of $LaNi_5$.

2.3. Interstitial site calculations – $MgNi_3B_2$

The same geometrical considerations has been applied to the alloy $MgNi_3B_2$. In part I of this investigation, we described the preparation and crystal structure determination of this compound [3]. Using powder X-ray diffraction, the sample was indexed in the space group ($P6_222$). This corresponds to the symmetry determined by Jung for the compound $Mg_2Ni_5B_4$, but with slightly different lattice constants [1]. A Rietveld refinement of the X-ray spectra produced fully occupied sites and no site substitution. Thus $MgNi_3B_2$ is a pseudo AB_5 compound with a crystal structure of the $CeCo_3B_2$ type which is a variation of the $CaCu_5$ structure of $LaNi_5$.

In contrast to $LaNi_5$, the more complex structure of $MgNi_3B_2$ creates, in turn, a larger variety of interstitial sites. The sites which are the most favorable for hydrogen occupation are represented schematically in Fig. 5. To calculate the radii of these interstitial sites, we used the crystal structure parameters that were determined from our X-ray refinement. The metal radii were again defined as touching spheres. The radius of Mg was determined from the shortest Mg–Mg distance, Ni(6f) from Mg–Ni(6f), Ni(3d) from Ni(6f)–Ni(3d) and B from Ni(6i)–B. The resulting metal radii were:

Mg(3a): $r = 1.464$ Å,

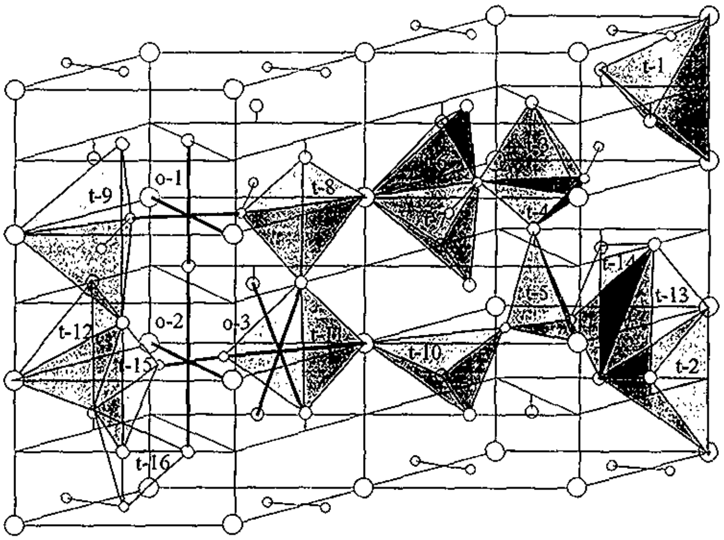

Fig. 5. Schematic representations of the most favorable sites for hydrogen occupation in the atomic crystal structures of $MgNi_3B_2$. Tetrahedral sites (t-) and octahedral (o-) are shown.

Ni(6f): $r=1.213$ Å,
Ni(3d): $r=1.254$ Å and
B(6i): $r=0.794$ Å.

Note incidentally, that the Ni radii are nearly identical to those determined for $Ni^{(1)}$ and $Ni^{(2)}$ of $LaNi_5$. It seems unlikely that this is coincidental.

The calculated radii of the interstitial sites are presented in Table 3 along with their counterparts for $LaNi_5$. Westlake's original calculations have also been included [6]. The sites marked with a † are tetrahedral sites for which the solution to Eq. (4) converged at a position located outside of the tetrahedra. In these cases the constraining trigonal or, in special circumstances, octahedral site have been indicated in the table.

All of the tetrahedral sites except t-12 are <0.4 Å and, therefore, do not meet the Westlake criterion for hydrogen occupation. The trigonal (t-12/12, t-12/14, t-10/11) and octahedral (o-3) sites which are >0.4 Å all share either a side, edge or corner with t-12 and all have smaller radii than t-12. They are, therefore, simply subsets of t-12.

Although not by a lot, the tetrahedral site t-12 is, nevertheless larger than Westlake's criterion. This can be somewhat reconciled by comparing this site with the one interstitial site of $LaNi_5$ which meets Westlake's criterion; the 6m site. Note that, by comparison:

- The 6m site is substantially larger than the t-12 site ($r=5.12$ and 4.17 Å respectively).
- t-12 sites are far less abundant than 6m sites. There are 1.33 (t-12) sites per formula unit in $MgNi_3B_2$ as compared to 6 (6m) sites per formula unit in $LaNi_5$.
- The interatomic distances between the t-12 sites of $MgNi_3B_2$ is far greater than for the 6m sites of $LaNi_5$. The 6m sites form a ring of six sites around La–La pairs (c axis). Each 6m site shares a face with two other 6m sites. The distance between the closest 6m sites in adjacent 6m rings is 3.987 Å in the c direction and 2.509 Å in the basal plane. The situation is not the same for the t-12 sites of $MgNi_3B_2$. Around each Mg–Mg pair (c axis) there are two sets of two t-12 sites, each sharing one a common face. These t-12 pairs appear only once per unit cell in the c-direction and twice per unit cell in the basal plain. The distance to the next nearest set of t-12 sites is 8.786 Å in the c-direction and 4.641 Å in the basal plane. Thus the jump distances for hydrogen diffusion between sites that meet Westlake's criterion are substantially greater in $MgNi_3B_2$ than $LaNi_5$.

These considerations combined with the small size of all the other interstitial sites of $MgNi_3B_2$ are consistent with the observed lack of hydrogen absorption by this compound [3].

3. Conclusion

This study was undertaken to test the correlation between the size of an intermetallic compound's interstitial sites and its ability to absorb hydrogen. An analysis based on a variation of Westlake's empirical geometric criterion for hydrogen occupation of interstitial sites was first tested on the intermetallic compound $LaNi_5$. It was successful in describing hydrogen occupancies of the α, β and γ phases of $LaNi_5H_x$.

The structure and composition of $MgNi_3B_2$ also made it a likely candidate for hydrogen absorption. However, this compound was not observed to absorb hydrogen under moderate hydriding conditions. When the same geometric

Table 3
A summary of the calculated radii of the interstitial sites for $LaNi_5$ (including Westlake's original calculations [4]) and $MgNi_3B_2$

Compound	$LaNi_5H_{6.5}$ Westlake [6]	$LaNi_5$ this work	$MgNi_3B_2$		
Structure	P6/mmm	P6/mmm	$P6_222$		
Lattice const.[a]	5.399	5.017	4.8799		
Lattice const.[c]	4.290	3.987	8.7858		
Atomic radii [Å]					
note	a,b	c	c		
A (1a)	La=1.877	La=1.687	Mg(3a)=1.464		
B^1 (2c)	$Ni^{(1)}=1.246$	$Ni^{(1)}=1.210$	B (6i)=0.794		
B^2 (3g)	$Ni^{(2)}=1.246$	$Ni^{(2)}=1.254$	Ni (6f)=1.213, Ni (3d)=1.254		
Interstitial Site radii [Å] (listed by related P6/mmm Wickoffpositions)					
Tetrahedral					
t 2A–2B (6m)	0.5548	0.512	(t-1) 0.371	(t-2) 0.390	
t A–3B (12n)	0.4482	0.379	(t-3) † o-1	(t-4) † o-1	(t-5) 0.395
t A–3B (12o)	0.4333	0.361	(t-6) 0.360	(t-7) 0.378	(t-8) 0.344
			(t-9) † t-5/5	(t-10) † t-10/11	(t-11) † t-10/11
			(t-12) 0.457	(t-13) † o-3	
t 4B (4h)	0.3927	0.280	(t-14) † o-3	(t-15) † t-12/14	(t-16) 0.311
Octahedral					
o 2A–4B (3f)	0.3126	0.283	(o-1) 0.000	(o-2) 0.167	(o-3) 0.431
Trigonal					
			(t-12/12) 0.439	(t-13/13) † o-3	(t-14/14) † o-3
			(t-12/14) 0.444	(t-13/16) † o-3	
			(t-5/5) 0.352	(t-10/11) 0.438	

[a], Westlake calculated the hole sizes for the hydride, using the Lattice parameters for $LaNi_5H_{6.5}$.

[b], Metal atomic radii for coordination number 12 were used [32].

[c], The metal atom radii were calculated from the assumption of touching spheres (see text).

†, The calculated solution converged outside of the tetrahedral (or trigonal) site, the interstitial radius is determined by the site indicated.

analysis was applied to this compound, it was found that most of the interstitial sites had a radius <0.4 Å and, therefore, did not meet the Westlake criterion for the formation of a hydride. One interstitial site was found to have a radius >0.4 Å, however, general considerations indicate that this site may also be unsuitable for hydrogen occupation. Employed prudently, Westlake's criterion may aid in the discovery and development of new hydride forming intermetallic compounds.

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