

## Theoretical studies of hydrogen storage in binary Ti-Ni, Ti-Cu, and Ti-Fe alloys

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Theoretical studies have been carried out to examine hydrogen storage in some binary transition metal alloys which include titanium as one of the alloying elements. Quantum mechanical calculations at the Extended Hückel level of approximation have been performed on numerous clusters of compositions  $\text{Ti}_{18}\text{Ni}_{18}$ ,  $\text{Ti}_{18}\text{Ni}_{18}\text{H}$ ,  $\text{Ti}_{18}\text{Ni}_{18}\text{H}_{12}$ ,  $\text{Ti}_{24}\text{Ni}_{12}$ ,  $\text{Ti}_{24}\text{Ni}_{12}\text{H}$ ,  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$ ,  $\text{Ti}_{16}\text{Cu}_{16}$ ,  $\text{Ti}_{16}\text{Cu}_{16}\text{H}$ ,  $\text{Ti}_{24}\text{Cu}_{12}$ ,  $\text{Ti}_{16}\text{Fe}_{16}$ ,  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_9$ , and  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$ , to yield information on energetics, densities of states, charge distributions, and the effects of hydrogenation on these properties. In addition, *ab initio* calculations at the split valence level of approximation have been performed on several smaller clusters. The hydrogens have been shown to acquire a partially anionic character in all cases. Another conclusion is that the preference of H for certain types of sites (for example the tetrahedral  $\text{Ti}_4$  sites in crystalline TiCu) is more likely to be related not to the intrinsically greater stability of a hydrogen atom located in such a site, but to more general topological and electronic considerations. Qualitative concepts related to the classification, spatial distribution, and sizes and shapes of "hole" sites which could become occupied by hydrogen atoms, have been shown to correlate with hydrogen storage capacity for crystalline materials. These qualitative concepts have been extended to amorphous materials and corroborate the observations that under optimized conditions amorphous alloys can be found with better reversible hydrogen storage properties than the crystalline or microcrystalline systems.

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Distorted tetrahedral and octahedral holes have been examined in detail, and parameters (volume, area, "tetrahedrality", and "octahedrality") have been introduced to describe their sizes and shapes. An algorithmic surveying technique has been introduced, and shown to provide useful information about the limiting amounts of hydrogen uptake.

**Key words:** Hydrogen storage — Binary alloys — Transition metals — Titanium — Extended Hückel — *ab initio* — Sites — Volume — Area — Tetrahedrality — Surveying technique — Split valence — Metal hydrides

## 1. Introduction

We have carried out theoretical studies in order to elucidate a theory related to the relationships and interactions of d band elements that take place in three-dimensional space in amorphous and disordered materials, particularly in their interactions with hydrogen in both dissociation and storage [1]. The general field of hydrogen storage and interaction has become an interdisciplinary research undertaken in various areas of science and engineering, and primarily motivated by the potential of hydrogen as a chemical and nuclear energy carrier [2]. The alloys of hydrogen and metals (metal hydrides) have been investigated by a large number of theoretical [3] and experimental [4] techniques, the materials development effort being mainly directed toward the development of materials useful for the reversible storage of hydrogen and its isotopes. However, in spite of this vast body of research, much remains to be discovered in terms of their structural and electronic properties, the various mechanistic processes involved, the thermodynamic and kinetic factors of significance, and how all these complex and often competing factors can best be balanced to prepare materials especially suitable for specific technological applications.

We report here the results of our work on hydrogen storage in some binary transition metal alloys which include titanium as one of the alloying elements. Although we have mainly concentrated on Ti-Ni alloys, we have also considered some Ti-Cu and Ti-Fe systems. *Ab initio* unrestricted Hartree-Fock calculations have been performed on small clusters of compositions  $Ti_4$ ,  $Ti_4H$ ,  $Ti_2Ni_2$ ,  $Ti_2Ni_2H$ ,  $Ni_4$  and  $Ni_4H$ . These calculations included all electrons and were carried out with minimal basis sets (with and without exponent optimization) and with split valence basis sets. Several different geometries were chosen to test the effects of the shape and the volume of the tetrahedral hole, as well as the composition of the cluster, on the binding of hydrogen.

Extended Hückel calculations [5] on the small metal clusters and their hydrides are in good qualitative agreement with the *ab initio* results. This serves to calibrate the Extended Hückel calculations on much larger clusters that are a better model of the bulk solid. Computations were performed on clusters of compositions  $Ti_{18}Ni_{18}$ ,  $Ti_{18}Ni_{18}H$ ,  $Ti_{18}Ni_{18}H_{12}$ ,  $Ti_{24}Ni_{12}$ ,  $Ti_{24}Ni_{12}H$ ,  $Ti_{24}Ni_{12}H_{12}$ ,  $Ti_{16}Cu_{16}$ ,  $Ti_{16}Cu_{16}H$ ,  $Ti_{24}Cu_{12}$ ,  $Ti_{16}Fe_{16}$ ,  $Ti_{16}Fe_{16}H_9$ , and  $Ti_{16}Fe_{16}H_{32}$ , to yield information on energetics, densities of states, charge distributions, and the effects of hydroge-

nation on these parameters, but its simplicity, which would otherwise be obtained interpreted.

Qualitative concepts, distribution, and sizes of hydrogen atoms, process. These sites depending on whether spaces contained substance, with in vertices may be met in some storage materials others (for example occupied, and they are determined by and kinetic factors and introduced parameters the same type of straightforward method

Consideration of the survey techniques, of selected structures hydrogen storage such as diffusion and but the insights obtained as well.

The theoretical principles concepts introduced basic conclusions take are indicated

## 2. Theoretical procedure

### *Ab initio calculations*

A series of non-empirical small metallic clusters systems. The core level (UHF) level with 11/780. Some of Tables 1 and 2.

Since our initial clusters with and

nation on these properties. Admittedly, the Extended Hückel method is approximate, but its simplicity and economy allow the performance of many calculations which would otherwise not be feasible. Valuable semi-quantitative information can be obtained if the results are appropriately calibrated and judiciously interpreted.

Qualitative concepts related to the classification into various types, spatial distribution, and sizes and shapes of "hole" sites which could become occupied by hydrogen atoms, have been shown to provide insight into the hydrogenation process. These sites are of distorted tetrahedral or distorted octahedral shape, depending on whether they are defined by four or six metallic atom vertices. The spaces contained within them generally span the entire interior of the storage substance, with incomplete (or "open") holes at the surfaces, where one or more vertices may be missing. The hydrogens are known to prefer the tetrahedral sites in some storage materials (for example, in  $\text{TiH}_2$ ) and the octahedral sites in some others (for example, in  $\text{NiH}$  and  $\text{PdH}$ ) [6]. The types of sites which become occupied, and the mobility of the hydrogens between the various possible sites, are determined by a delicate balance of geometric, electronic, thermodynamic, and kinetic factors [1]. We have examined the tetrahedral sites in greater detail, and introduced parameters to describe their sizes and shapes. The extension of the same type of analysis to describe octahedral sites can be carried out in a straightforward manner.

Consideration of the sizes and shapes and spatial distribution of hole sites using survey techniques, coupled with electronic structure calculations on large numbers of selected structures, is clearly seen to be a fruitful approach to the study of hydrogen storage in metal hydrides. Unfortunately, time-dependent processes such as diffusion are much more difficult to investigate by any of these techniques, but the insights obtained are likely to be valuable in approaching these problems as well.

The theoretical procedures and results are presented in Sect. 2, and the various concepts introduced and results obtained are discussed in Sect. 3. Some of our basic conclusions are summarized and future directions which the work might take are indicated in Sect. 4.

## 2. Theoretical procedures and results

### *Ab initio calculations*

A series of non-empirical, all electron SCF calculations was undertaken on a few small metallic clusters, to help calibrate the Extended Hückel results on larger systems. The computations were carried out at the Unrestricted Hartree-Fock (UHF) level with the Gaussian 80 series of programs [7] running on a VAX 11/780. Some of the results of nearly 300 h of CPU time are summarized in Tables 1 and 2.

Since our initial intention was to examine several tetrahedral and octahedral clusters with and without hydrogen, we began with a small minimal basis set

**Table 1.** Basis set effects in *ab initio* calculations on  $Ti_4$  and  $Ti_4H$  clusters<sup>a</sup>

Cluster	Basis set	Total energy (au)	$\bar{\Sigma}_H$ (eV)	$\overline{\Delta E}$ (eV)	$E_H$ (eV) <sup>b</sup>	$\bar{q}_H$
$Ti_4$	STO-3G (atomic exp.) <sup>c</sup>	-3359.1995				
$Ti_4H$	STO-3G (atomic exp.) <sup>c</sup>	-3359.6650	-0.03	2.54	-18.5, -16.7	-0.38
$Ti_4$	STO-3G (opt. exp.) <sup>d</sup>	-3359.2453				
$Ti_4H$	STO-3G (opt. exp.) <sup>d</sup>	-3359.7330	0.20	1.94	-17.5, -16.0	-1.03
$Ti_4$	Split Valence <sup>e</sup>	-3389.8605				
$Ti_4H$	Split Valence <sup>e</sup>	-3390.4237	-1.73	0.02	-20.1, -19.1	-0.71

<sup>a</sup> See Table 4 for notation;  $r(Ti-Ti) = 2.814 \text{ \AA}$

<sup>b</sup> The energies of the  $\alpha$  and  $\beta$  MO's with significant H contribution

<sup>c</sup>  $\zeta_{3d} = 2.68$ ,  $\zeta_{4sp} = 1.21$  for titanium [8];  $\zeta_{1s} = 1.0$  for hydrogen

<sup>d</sup>  $\zeta_{3d} = 2.77$ ,  $\zeta_{4sp} = 1.32$  for titanium optimized in  $Ti_4$ ; hydrogen exponent optimized in  $Ti_4H$  with Ti exponents fixed at their optimum values in  $Ti_4$ ,  $\zeta_{1s} = 0.85$

<sup>e</sup> Huzinaga basis set [12] for Ti, with a (2, 1) split of the 4s, and a (3, 1) split of the 3d shells; 311G for hydrogen [13]

(STO-3G, [8]). Atom-optimized exponents were felt to be more appropriate than ones optimized for organometallic complexes. Despite the use of minimal basis sets, the cluster calculations were characterized by SCF convergence difficulties. Atomic Ti is a  $3d^24s^2$  triplet at the UHF/STO-3G level. For tetrahedral  $Ti_4$  ( $r(Ti-Ti) = 2.814 \text{ \AA}$ ), the lowest energy state has a multiplicity of 9 and corresponds to an atomic configuration of  $3d^{1.8}4s^{1.3}4p^{0.9}$ . For  $Ti_4H$  (multiplicity = 10), the central hydrogen has a Mulliken population of 1.38 electrons, indicating substantial transfer of electron density from the metal to the hydrogen. Similar calculations on tetrahedral  $Ni_4$  ( $r(Ni-Ni) = 2.492 \text{ \AA}$ ) showed severe SCF convergence problems and yielded unrealistically high occupations of the 4p orbitals and large spin contaminations.

To test the appropriateness of the atomic exponents and to increase the flexibility of the minimal basis set calculations, we optimized the 3d and 4sp exponents in  $Ti_4$ . The optimized values ( $\zeta_{3d} = 2.77$ ,  $\zeta_{4sp} = 1.32$ ) are more like the atomic exponents (2.68, 1.21) than average values for organometallic complexes ( $\zeta_{3d} = 1.90$ ,  $\zeta_{4sp} = 1.70$ ). This justifies, to some extent, the choice of atomic exponents and the use of the Extended Hückel parameters of Lohr and Pyykkö [9] (see below) instead of the standard values used in organometallic calculations [10]. When the exponents optimized for  $Ti_4$  were used for  $Ti_4H$ ,  $\zeta_{1s} = 0.85$  was obtained for the optimum hydrogen 1s exponent. The Mulliken charge on hydrogen (2.03 electrons) is rather exaggerated because of the inadequacies of the minimal Ti basis set. Since exponent optimization had very little effect on the 4p populations in  $Ti_4$ , it is probable that optimization of the STO-3G exponents in  $Ni_4$  will not remedy the deficiencies in the  $Ni_4$  calculations.

It is generally recognized that at least two sets of d functions are required for the correct treatment of bonding in metal complexes [11]; however, double zeta

**Table 2.** Comparison of *ab initio* and Extended Hückel calculations on small metallic clusters and their hydrides<sup>a</sup>

Cluster	Symmetry	Bond distances (Å)	Ab initio		Extended Hückel	
			Total energy (au)	$\bar{\Sigma}_H$ (eV)	Total energy (eV)	$\bar{\Sigma}_H$ (eV)
$Ti_4$	$T_d$	$TiTi = 2.814$	-3389.8605		-197.27	
						Charges
						$\bar{q}_{Ti} = 0.0$

Table 2. Comparison of *ab initio* and Extended Hückel calculations on small metallic clusters and their hydrides<sup>a</sup>

Cluster	Symmetry	Bond distances (Å)	<i>Ab initio</i>			Extended Hückel		
			Total energy (au)	$\bar{\Sigma}_H$ (eV)	Charges	Total energy (eV)	$\bar{\Sigma}_H$ (eV)	Charges
Ti <sub>4</sub>	T <sub>d</sub>	TiTi = 2.814	-3389.8605	—	$\bar{q}_{Ti} = 0.0$	-197.27	—	$\bar{q}_{Ti} = 0.0$
	T <sub>d</sub>	TiTi = 2.814 TiH = 1.723	-3390.4238	-1.73	$\bar{q}_{Ti} = 0.18$ $\bar{q}_H = -0.72$	-215.23	-4.35	$\bar{q}_{Ti} = 0.02$ $\bar{q}_H = -0.06$
Ti <sub>2</sub> Ni <sub>2</sub>	C <sub>2v</sub> (regular tetrahedron)	TiTi = 2.814 TiNi = 2.814	-4705.5658	—	$\bar{q}_{Ti} = -0.10$ $\bar{q}_{Ni} = 0.10$	-474.18	—	$\bar{q}_{Ti} = 0.15$ $\bar{q}_{Ni} = -0.15$
		TiTi = 2.814 TiNi = 2.814	-4706.1338	-1.86	$\bar{q}_{Ti} = 0.26$ $\bar{q}_{Ni} = 0.10$ $\bar{q}_H = -0.71$	-492.08	-4.29	$\bar{q}_{Ti} = 0.27$ $\bar{q}_{Ni} = 0.19$ $\bar{q}_H = -0.16$
Ti <sub>2</sub> Ni <sub>2</sub> H	C <sub>2v</sub> (regular tetrahedron)	TiTi = 1.723 NiH = 1.723	-4705.5298	—	$\bar{q}_{Ti} = -0.15$ $\bar{q}_{Ni} = 0.15$	-473.32	—	$\bar{q}_{Ti} = 0.19$ $\bar{q}_{Ni} = -0.19$
		TiTi = 3.015 TiNi = 2.611 NiNi = 3.015	-4706.0881	-1.59	$\bar{q}_{Ti} = 0.20$ $\bar{q}_{Ni} = 0.13$ $\bar{q}_H = -0.67$	-491.33	-4.40	$\bar{q}_{Ti} = 0.33$ $\bar{q}_{Ni} = -0.24$ $\bar{q}_H = -0.18$
Ni <sub>4</sub>	T <sub>d</sub> T <sub>d</sub>	NiH = 1.685 NiNi = 2.814	-6021.1995	—	$\bar{q}_{Ni} = 0.0$	-758.35	—	$\bar{q}_{Ni} = 0.0$
		NiNi = 2.814 NiH = 1.723	-6021.6862	0.35	$\bar{q}_{Ni} = 0.19$ $\bar{q}_H = -0.77$	-773.26	-1.30	$\bar{q}_{Ni} = -0.05$ $\bar{q}_H = 0.18$
Ni <sub>4</sub> <sup>b</sup>	T <sub>d</sub> T <sub>d</sub>	NiNi = 2.492 NiNi = 2.492 NiH = 1.526	-6021.0837	—	$\bar{q}_{Ni} = 0.0$	-757.29	—	$\bar{q}_{Ni} = 0.0$
			-6021.5958	-0.34	$\bar{q}_{Ni} = 0.20$ $\bar{q}_H = -0.81$	-772.36	-1.46	$\bar{q}_{Ni} = -0.05$ $\bar{q}_H = 0.21$

<sup>a</sup> See Table 4 for notation<sup>b</sup> See also, the *ab initio* effective core potential SCF calculations of Basch H, Newton MD, Moskowitz JW (1980) J Chem Phys 73:4492 for the same geometry of Ni<sub>4</sub>

basis set calculations are considerably more costly and severely limit the number and size of clusters that can be examined. As a compromise, we have chosen a Huzinaga (4333/43/4) basis set [12] with a (2, 1) split of the 4s and (3, 1) split of the 3d. To ensure that electron distributions ranging from H to H<sup>-</sup> can be represented adequately, a triple zeta (311G) basis set [13] was chosen for hydrogen. SCF convergence was better than with the STO-3G basis set, but still quite slow (>100 cycles to reduce the average change in the density matrix to 10<sup>-5</sup>). The approximate electronic configuration of Ti<sub>4</sub>, 3d<sup>2.1</sup>4s<sup>1.9</sup> (multiplicity = 9), is much more realistic than with the STO-3G basis set and has relatively little contamination from higher spin states. Likewise, the binding energy of hydrogen, Σ<sub>H</sub>, and the charge on hydrogen, q<sub>H</sub>, are more reasonable than with the minimal basis set; therefore, the split valence basis sets were used for the remainder of the calculations.

Examination of a number of different spin states indicated that a multiplicity of 9 yielded the lowest energy for Ti<sub>4</sub> and Ni<sub>4</sub>, and a multiplicity of 10 for the metal cluster hydrides. In Ni<sub>4</sub> and Ni<sub>4</sub>H, the energy was lower for an electronic configuration on Ni of 3d<sup>8</sup>4s<sup>2</sup> than 3d<sup>9</sup>4s<sup>1</sup>; however, it is clear that there are numerous states of similar energy, and that the addition of electron correlation could easily change the order of the states. To be consistent and so that structural effects on hydrogen binding would not be obscured, we chose a multiplicity of 9 for all of the *ab initio* calculations on the clusters involving four metals, and a multiplicity of 10 for the corresponding hydrides.

The results of *ab initio* calculations on several small metallic clusters and their hydrides are given in Table 2. These are compared with Extended Hückel calculations which are outlined in the next section. Three of the clusters (Ti<sub>4</sub>, Ti<sub>2</sub>Ni<sub>2</sub> and Ni<sub>4</sub>), and their hydrides, are regular tetrahedra with the same metal-metal distance (2.814 Å). These clusters illustrate the role of composition in hydride binding. The effect of distortion can be seen in the Ti<sub>2</sub>Ni<sub>2</sub> and Ti<sub>2</sub>Ni<sub>2</sub>H clusters in which the Ti-Ti and Ni-Ni distances have been increased by 0.201 Å relative to the regular tetrahedral clusters, and the Ti-Ni distance decreased by 0.203 Å. The effect of size can be judged by comparing the large (Ni-Ni = 2.814 Å) and small (Ni-Ni = 2.492 Å) Ni<sub>4</sub> clusters and their hydrides.

As might be expected at the Hartree-Fock level, Ti<sub>4</sub>, Ti<sub>2</sub>Ni<sub>2</sub> and Ni<sub>4</sub> are not bound relative to the free atoms. In Ti<sub>4</sub>H, Ti<sub>2</sub>Ni<sub>2</sub>H and the smaller Ni<sub>4</sub>H, the hydrogen is bound relative to the cluster plus H atom, but not relative to the cluster plus 1/2H<sub>2</sub>. On the other hand, the Extended Hückel results yield much more reasonable binding energies for the H atom relative to 1/2H<sub>2</sub>; however, the trends in binding energies are quite similar. In both the *ab initio* and the Extended Hückel calculations, the hydrogen atom is much more strongly bound in the Ti<sub>4</sub>H and Ti<sub>2</sub>Ni<sub>2</sub>H clusters than in the Ni<sub>4</sub>H clusters. The two levels of calculations also agree on the fact that decreasing the size of the Ni<sub>4</sub> cluster increases the binding energy for hydrogen, although this effect is smaller in the Extended Hückel calculation. The only disagreement in the trends is the effect of distorting the Ti<sub>2</sub>Ni<sub>2</sub> cluster on H binding.

In each of the hydrides, the binding energy attributes to the hydrogen atom are calculated using the atomic orbitals on H. The use of a more flexible than the minimal basis set Mulliken population analysis to solve the problems, as well as the fact that the results cannot be compared with the important trend can be seen in the results. The results agree that, relative to the hydrogen cluster, the binding energy of nickel is almost un-

Figure 1 shows the one-electron energy levels for the Hartree-Fock level of Ti<sub>4</sub>, Ti<sub>4</sub>H, Ni<sub>4</sub> and Ni<sub>4</sub>H. The energy levels are dominated by the metal d-orbitals derived from the metal atoms. This is reflected in the fact that the highest orbital lies above the energy of the appropriate symmetry of the metal d-orbitals. The mixing with the low energy orbitals is also found in the STO-3G

#### Extended Hückel calculations

Extended Hückel calculations were performed using the software package [10]. The results of the calculations described in Table 2 are

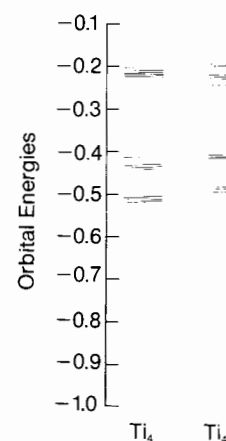


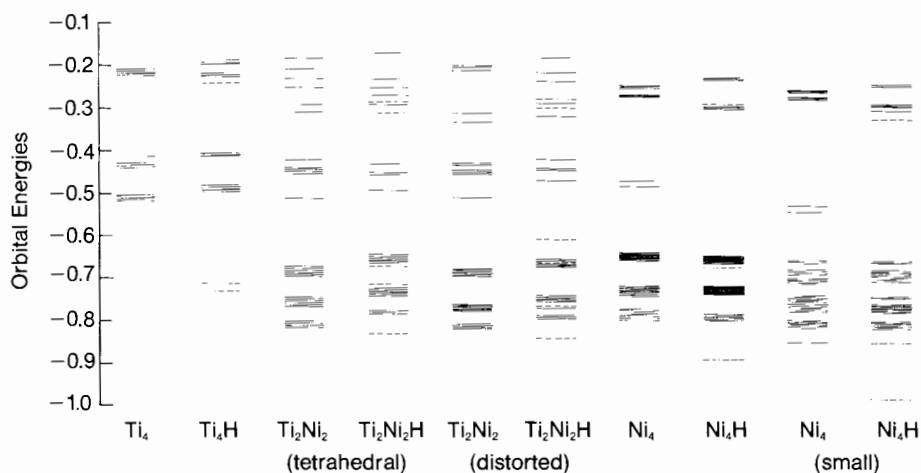
Fig. 1. One-electron energy levels for the Hartree-Fock level of Ti<sub>4</sub>, Ti<sub>4</sub>H, Ni<sub>4</sub> and Ni<sub>4</sub>H. The energy levels are dominated by the metal d-orbitals derived from the metal atoms. This is reflected in the fact that the highest orbital lies above the energy of the appropriate symmetry of the metal d-orbitals. The mixing with the low energy orbitals is also found in the STO-3G

In each of the hydrides, the Mulliken population analysis in the *ab initio* calculations attributes too much negative charge to the hydrogen due to the diffuse functions on H. Likewise, the basis functions on Ti are more spread out and more flexible than those on Ni. Therefore, when Ti and Ni are bonded, the Mulliken population analysis makes the Ti atom too negative. Because of these problems, as well as the differences in spin states, the *ab initio* Mulliken charges cannot be compared *directly* with the Extended Hückel results. Nevertheless, one important trend can still be discerned. Both the *ab initio* and the Extended Hückel results agree that, in the  $Ti_2Ni_2H$  clusters, most of the electron density transferred to the hydrogen comes from the titanium atoms, while the Mulliken charge on nickel is almost unchanged.

Figure 1 shows the *ab initio* molecular orbital energies obtained at the unrestricted Hartree-Fock level. The lowest-lying totally symmetric *ab initio* valence orbitals of  $Ti_4$ ,  $Ti_4H$ ,  $Ni_4$  and  $Ni_4H$  are displayed in Fig. 2. In  $Ti_4H$ , the molecular orbital dominated by the hydrogen 1s atomic orbital lies lower in energy than those derived from the metal 3d and 4s atomic orbitals, and thus is doubly occupied. This is reflected in the large negative charge on H. In  $Ni_4H$ , the hydrogen 1s orbital lies above the metal 3d but below the 4s, and mixes strongly with the appropriate symmetry adapted combinations of the 3d and the 4s orbitals. Strong mixing with the lowest energy (totally symmetric) combinations of the 3d orbitals is also found in SCF- $X\alpha$ -SW calculations on  $Ni_4H$  [3y].

#### Extended Hückel calculations

Extended Hückel [5] calculations were carried out with the FORTICON8 software package [10] on an IBM 3033U computer. The largest of the cluster calculations described below took just under 11 min of CPU time.



**Fig. 1.** One-electron energies of the occupied orbitals (alpha and beta) in au. Details of the structures are given in Table 2. Orbitals of predominantly hydrogen character are *dashed*

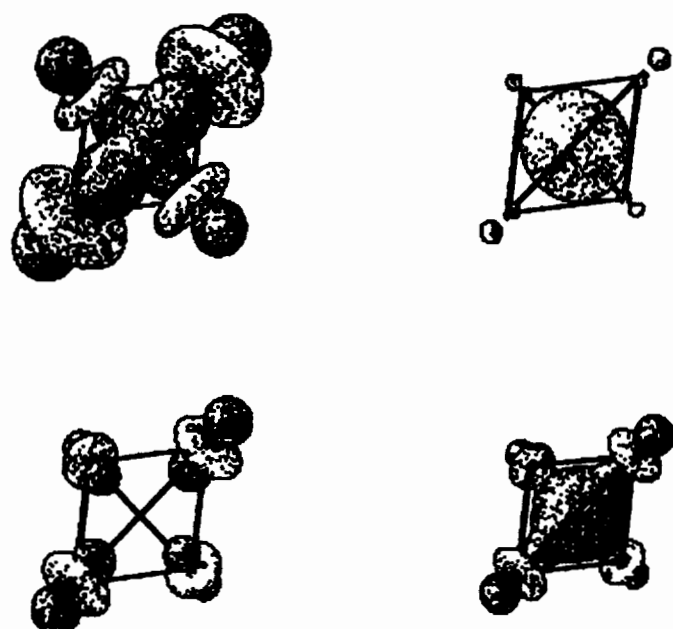


Fig. 2. Lowest-lying totally symmetric *ab initio* valence orbitals of  $Ti_4$ ,  $Ti_4H$ ,  $Ni_4$  and  $Ni_4H$

The orbital exponents and Coulomb integrals used are listed in Table 3. Since no semi-empirical parameterization designed specifically for describing the properties of metal hydride systems is available, the values for the Coulomb integrals were chosen from the non-relativistic parameterization [9] of Desclaux' atomic Dirac-Fock calculations [14]. Although there are certain drawbacks of this set of values (for example, the depth of the 3d levels of Ni is overestimated),

Table 3. Orbital exponents and coulomb integrals<sup>a</sup>

Atom	s orbitals			p orbitals			d orbitals					
	<i>n</i>	exp	coul	<i>n</i>	exp	coul	<i>n</i>	exp <i>d</i> <sub>1</sub>	exp <i>d</i> <sub>2</sub>	coul	<i>c</i> <sub>1</sub>	<i>c</i> <sub>2</sub>
H	1	1.0	-13.606	—	—	—	—	—	—	—	—	—
Ti <sup>b</sup>	4	1.075	-6.039	4	0.675	-3.863	3	4.55	1.4	-11.04	0.42061	0.78391
Ni <sup>b</sup>	4	1.825	-7.532	4	1.125	-4.284	3	5.75	2.0	-18.97	0.5683	0.6292
Cu <sup>b</sup>	4	1.95	-6.49	4	1.2	-3.359	3	5.95	2.1	-13.37	0.57696	0.61675
Fe <sup>b</sup>	4	1.575	-7.079	4	0.975	-4.183	3	5.35	1.8	-16.54	0.53659	0.66779
Ti <sup>c</sup>	4	1.195	-6.039	4	0.998	-3.863	3	2.353	—	-11.04	—	—
Ni <sup>c</sup>	4	1.473	-7.532	4	1.203	-4.284	3	3.62	—	-18.97	—	—

<sup>a</sup> *n* denotes the principal quantum number, exp the orbital exponent, and coul the coulomb integral. For the double zeta *d* orbitals, *c*<sub>1</sub> and *c*<sub>2</sub> denote the contraction coefficients of the two *d* orbitals with exponents exp *d*<sub>1</sub> and exp *d*<sub>2</sub>, respectively

<sup>b</sup> Double zeta *d* orbitals

<sup>c</sup> Single zeta *d* orbitals, used in some additional calculations for comparison (see text)

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its use provides a theoretically consistent way of treating these systems, without introducing any semi-empirical parameters. (See Sect. 3 for more detailed discussion of this point.)

The densities of states of these metallic clusters can only be calculated in a satisfactory manner if each set of  $d$  orbitals is treated by contracted  $d$  orbitals which are linear combinations of two  $d$ -type Slater functions. If only one  $d$  orbital exponent is used per atom, the bands become unrealistically narrow and sharp due to the inflexibility of such a basis set. Thus, all calculations were carried out using contracted  $d$  orbitals on each transition metal atom, the exponents and contraction coefficients being chosen as the values suggested by the program documentation [10, 15]. The atomic orbital exponent value of 1.0 was found to describe the  $1s$  orbital of H much better than the value 1.3 usually used in calculations on molecules where H forms a normal chemical bond, such as most organic compounds. Here, just as the double zeta representation allows the transition metal  $d$  orbitals to interact better with one another, the exponent value of 1.0 allows the hydrogen, which acts as an alloying element with four or six near neighbors, to utilize its  $1s$  orbital much more effectively, to expand and to form stronger links to its transition metal neighbors.

Even when an exponent value of 1.0 is used for H, the effect of its introduction is still somewhat underestimated, as will be shown below when the energetics are discussed. This is because the contracted pairs of  $d$  orbitals used for the metals allow stronger bonding for these atoms than the single  $1s$  orbitals can allow for H. Since it was not practical to use a contracted  $1s$  orbital for H, a few calculations were carried out on the Ti-Ni-H systems by representing the Ti and Ni  $3d$  orbitals by a single exponent each (last two rows of Table 3) [9, 14]. This enabled us to assess the amount of underestimation of the energetic effect of H on these clusters, by treating all atoms at an equal level of flexibility.

Relativistic effects [16] can also be expected to produce a small effect on the densities of states. For example, Desclaux' atomic relativistic Dirac-Fock calculations [14] show that the  $3d$  levels of Ni split into two sets separated by 0.277 eV, due to spin-orbit effects. These effects could be much more significant for heavier elements such as the lanthanides, actinides, and the elements on the sixth row of the periodic table. However, they can be justifiably neglected for fourth row elements such as Ti, Ni, Cu and Fe, and were therefore not considered in this work.

The sizes of the clusters to be utilized in the electronic structure calculations was considered next. This depends on the properties or processes under consideration. For example, proper treatment of the problem of hydrogen embrittlement [17] in metals might require calculations on clusters of several hundred atoms followed by finite-element calculations to deal with the macroscopic propagation of cracks [17a], or alternatively, embedded atom techniques [17b]. Another study [18], which applied the spin density functional formalism to the study of a hydrogen impurity within the context of a "jellium" cluster model, showed that a large cluster size (about 100 atoms) was needed to obtain an accurate description of some electronic properties of the impurity, although a partial cancellation of

**Table 4.** Energetics and average atomic charges for  $\text{Ti}_{18}\text{Ni}_{18}$ ,  $\text{Ti}_{18}\text{Ni}_{18}\text{H}_{12}$ ,  $\text{Ti}_{24}\text{Ni}_{12}$ ,  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$ ,  $\text{Ti}_{10}\text{Cu}_{16}$ ,  $\text{Ti}_{24}\text{Cu}_{12}$ ,  $\text{Ti}_{16}\text{Fe}_{16}$ ,  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_9$ , and  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$  clusters<sup>a,b</sup>

Quantity	Cluster		$\text{Ti}_{18}\text{Ni}_{18}$		$\text{Ti}_{18}\text{Ni}_{18}\text{H}_{12}$		$\text{Ti}_{24}\text{Ni}_{12}$		$\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$		$\text{Ti}_{10}\text{Cu}_{16}$		$\text{Ti}_{24}\text{Cu}_{12}$		$\text{Ti}_{16}\text{Fe}_{16}$		$\text{Ti}_{16}\text{Fe}_{16}\text{H}_9$		$\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$	
	$E_{\text{LUMO}}$	$E_{\text{F}}$	$E_{\text{G}}$	$E_{\text{HT}}$	$E_{\text{HB}}$	$E_{\text{MT}}$	$E_{\text{MB}}$	$\delta_{\text{Ti}}$	$\delta_{\text{H}}$	$\delta_{\text{M}}$	$\Delta_{\text{TiH}}$	$\Delta_{\text{HM}}$	$\Delta_{\text{TiM}}$	$\Sigma$	$\bar{\Sigma}_{\text{H}}$	$\Delta\bar{E}$	$CE$	$\bar{q}_{\text{Ti}}$	$\bar{q}_{\text{M}}$	$\bar{q}_{\text{H}}$
	-11.139	-11.110	-11.239	-11.171	-11.192	-10.5657	-10.806	-11.508	-11.552	-11.708										
	-11.228	-11.160	-11.244	-11.183	-11.221	-10.5660	-10.890	-11.551	-11.579 <sup>e</sup>	-11.761										
	-13.407	-13.068	-13.917	-13.161	-13.180	-12.838	-13.191	-12.879	-12.451	f										
	—	-13.095	—	-13.789	-14.038	—	—	—	-12.519	f										
	—	-17.893	—	-17.359	-18.172	—	—	—	-15.220	f										
	-18.174	-18.255	-18.334	-18.419	-18.419	-12.863	-13.206	-15.236	-15.433	f										
	-19.911	-20.305	-19.952	-20.512	-20.742	-14.400	-14.404	-18.090	-19.109	f										
	2.179	1.908	2.673	1.978	1.959	2.272	2.301	1.328	0.872	f										
	—	4.798	—	3.570	4.134	—	—	—	2.701	f										
	1.737	2.050	1.618	2.093	2.323	1.537	1.198	2.854	3.676	f										
	—	0.027	—	0.628	0.858	—	—	—	0.068	f										
	—	0.362	—	1.060	0.247	—	—	—	0.213	f										
	4.767	5.187	4.417	5.258	5.239	0.025	0.015	2.357	2.982	f										
	-4290.486	-4506.241	-3460.434	-3673.968	-3674.941	-3107.624	-2942.275	-3061.792	-3216.440	-3616.251										
	—	-4.374	—	-4.189	-4.270	—	—	—	-3.577	-3.721										
	—	0.0005	—	0.186	0.105	—	—	—	0.797	0.653										
	4.022	—	6.024	—	—	9.296	9.937	13.551	—	—										
	0.166	0.286	0.1235	0.195	0.190	-1.091	-0.594	1.706	1.856	2.102										
	-0.166	-0.179	-0.247	-0.234	-0.222	1.091	1.188	-1.706	-1.798	-1.741										
	—	-0.161	—	-0.155	-0.157	—	—	—	-0.105	-0.180										

<sup>a</sup> The notation is as follows:

$E_{\text{LUMO}}$  = Energy of the lowest unoccupied molecular orbital (MO) for the cluster;

$E_{\text{F}}$  = Fermi Energy, i.e., the energy of the highest occupied MO;

$E_{\text{G}}$  = Lowest with predominantly Ti contributions;

$E_{\text{HT}}$  = Highest with predominantly H contributions;

$E_{\text{HB}}$  = Lowest with predominantly H contributions;

$E_{\text{MT}}$  = Highest with predominantly M contributions (M = Ni, Cu or Fe);

$E_{\text{MB}}$  = Lowest with predominantly M contributions;

<sup>a</sup> The notation is as follows:

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$E_{HT}$  = Highest with predominantly H contributions;

$E_{HB}$  = Lowest with predominantly H contributions;

$E_{MT}$  = Highest with predominantly M contributions (M = Ni, Cu or Fe);

$E_{MB}$  = Lowest with predominantly M contributions;

$\delta_{Ti} = E_F - E_G$ ;

$\delta_H = E_{HT} - E_{HB}$ ;

$\delta_M = E_{MT} - E_{MB}$ ;

$\Delta_{TiH} = E_G - E_{HT}$ ;

$\Delta_{HM} = E_{HB} - E_{MT}$ ;

$\Delta_{TiM} = E_G - E_{MT}$ ;

$\Sigma$  = Total energy, i.e., the sum of the energies of all occupied one-electron levels;

$\bar{\Sigma}_H = 1/n[\Sigma(Ti_i M_m H_n) - \Sigma(Ti_i M_m) - n\Sigma(H)]$ ;

$\bar{\Delta E} = 1/n[\Sigma(Ti_i M_m H_n) - \Sigma(Ti_i M_m) - 0.5n\Sigma(H_2)]$ ;

$CE$  = Cohesive energy (see text for definition);

$\bar{q}_{Ti}$ ,  $\bar{q}_M$ , and  $\bar{q}_H$  = The average net charge on the Ti, M, and H atoms in the cluster, obtained by a Mulliken Population Analysis.

<sup>b</sup> All energies are in electron volts

<sup>c,d</sup> These two  $Ti_{24}Ni_{12}H_{12}$  clusters have the same  $Ti_{24}Ni_{12}$  framework, but different H locations (see text for description)

<sup>e</sup> The highest occupied MO is only singly occupied in  $Ti_{16}Fe_6H_6$ , which has an odd number of electrons

<sup>f,d</sup> It was impossible to classify the levels for  $Ti_{16}Fe_6H_{32}$  meaningfully into groups of Ti, H, and Fe levels

errors could be achieved by comparing the results of calculations with and without the impurity. Fortunately, for the types of properties of interest to us (such as densities of states, the positions of the energy levels, changes per hydrogen of the total energy upon hydrogenation, and Mulliken charge distributions), convergence to the bulk properties is very rapid. For example, it has recently been shown that a  $\text{Be}_{22}$  cluster can already adequately represent many aspects of the chemisorption of atomic hydrogen on the (0001) surface of beryllium, while a  $\text{Be}_{36}$  cluster is very close to the bulk limit [19]. Our own preliminary calculations on small clusters of various sizes supported this result, and showed that for the properties mentioned above the convergence with increasing lattice size was very rapid. Consequently, we carried out our calculations on clusters containing 32 or 36 transition metal atoms, whichever was more convenient for a crystal structure of a given symmetry.

The coordinates of the  $\text{Ti}_{18}\text{Ni}_{18}$ ,  $\text{Ti}_{24}\text{Ni}_{12}$ ,  $\text{Ti}_{16}\text{Cu}_{16}$ ,  $\text{Ti}_{24}\text{Cu}_{12}$ ,  $\text{Ti}_{16}\text{Fe}_{16}$ , and  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$  clusters were obtained from the appropriate experimental structural data [20]. The unit cell had to be repeated several times to obtain the  $\text{Ti}_{18}\text{Ni}_{18}$ ,  $\text{Ti}_{16}\text{Cu}_{16}$ ,  $\text{Ti}_{24}\text{Cu}_{12}$  and  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$  clusters. Since the  $\text{Ti}_2\text{Ni}$  phase contains 96 atoms in its unit cell, the reverse procedure was applied and only a central portion of the unit cell was kept to obtain the  $\text{Ti}_{24}\text{Ni}_{12}$  cluster. The TiFe and the TiNi phases have the same type of crystal lattice ( $\text{B}_2$ ). However, since the so-called  $\gamma$ -phase  $\text{FeTiH}_2$  required the use of only 32 transition metal atoms to get a reasonably shaped cluster, four atoms were eliminated from the 36 atom cluster for the  $\text{B}_2$  structures to give the coordinates of  $\text{Ti}_{16}\text{Fe}_{16}$ .

The coordinates of  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_9$  were obtained from those of  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$  by eliminating all the hydrogens located on "open" sites at the surface, not fully surrounded by a distorted octahedron of Ti and Fe atoms. The coordinates of  $\text{Ti}_{18}\text{Ni}_{18}\text{H}_{12}$  were obtained by assuming that the lattice expands to give a lattice parameter of 3.072 Å for  $\text{Ti}_{18}\text{Ni}_{18}\text{H}_{12}$  (consistent with lattice parameters of 3.015 Å for the TiNi and 3.10 Å for the TiNiH phases) [21], and using a method, to be described below, to distribute twelve hydrogens among the tetrahedral holes, which have been examined in the past by other authors, in studies of the relationship of thermodynamic properties to interstitial hole sizes [22]. It has been shown experimentally [21] that the hydrogen atoms are distributed statistically in the tetrahedral holes of the TiNi lattice in the TiNiH phase. The  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  clusters were obtained by using the experimentally known lattice parameter value (11.60 Å) [21] for the  $\text{Ti}_2\text{NiH}$  phase, rather than 11.3193 Å as in the  $\text{Ti}_2\text{Ni}$  phase, and using the same method to distribute twelve hydrogens between available tetrahedral sites in two different ways. The  $\text{Ti}_{16}\text{Cu}_{16}\text{H}$ ,  $\text{Ti}_{18}\text{Ni}_{18}\text{H}$  and  $\text{Ti}_{24}\text{Ni}_{12}\text{H}$  clusters were obtained by taking the parent (unhydrogenated) cluster, finding the sites of various types of interest, and placing one H, in turn, into the most deeply embedded (farthest away from the surfaces) site of each type.

The energetics and average atomic charges for the  $\text{Ti}_{18}\text{Ni}_{18}$ ,  $\text{Ti}_{18}\text{Ni}_{18}\text{H}_{12}$ ,  $\text{Ti}_{24}\text{Ni}_{12}$ ,  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$ ,  $\text{Ti}_{16}\text{Cu}_{16}$ ,  $\text{Ti}_{24}\text{Cu}_{12}$ ,  $\text{Ti}_{16}\text{Fe}_{16}$ ,  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_9$ , and  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$  clusters are listed in Table 4. In this table,  $E_{\text{LUMO}}$  refers to the energy of the lowest unoccupied molecular orbital (MO), and  $E_{\text{F}}$  is the Fermi energy, that is, the

energy of the highest occupied molecular orbital with predominant  $d$  character,  $E_{\text{MT}}$  is the energy of the lowest  $H$ ,  $E_{\text{MT}}$  is the energy of the highest  $M$  band width,  $E_{\text{MT}} - E_{\text{MB}}$ . The energy difference  $\Delta_{\text{HM}} = E_{\text{HB}} - E_{\text{MT}}$  is the energy of all occupied orbitals. The total energy, per atom, is  $E_{\text{tot}} = E_{\text{Ti}_m\text{M}_m} + 1/2nH_2$  and  $H$  atoms in the cluster are represented by  $\bar{q}_{\text{Ti}}$ ,  $\bar{q}_{\text{M}}$  and  $\bar{q}_{\text{H}}$ .

The cohesive energy

$$CE(\text{bulk}) = [C(\text{bulk}) - C(\text{cluster})] / \bar{C}(\text{bulk})$$

where  $\bar{C}(\text{bulk})$  is the average coordination number of the atoms in the bulk, and  $C(\text{cluster})$  is the energy of the cluster.

$$CE(\text{cluster}) = [E_{\text{tot}}(\text{cluster}) - E_{\text{tot}}(\text{bulk})] / \bar{C}(\text{cluster})$$

where  $E_j$  is the free energy of the  $j$ th atom in the cluster relative to the bulk. The factor  $\bar{C}(\text{bulk})/\bar{C}(\text{cluster})$  (Table 4) to take into account the pairwise "bonding" of the atoms in the bulk. For the alloys for which the  $\bar{C}(\text{cluster})$  is not known,  $\bar{C}(\text{cluster})$  is taken as  $\bar{C}(\text{Ti}_2\text{Ni}(7.444, 13))$ , and the atomic energies are taken as  $E_{\text{Ti}}$  and  $E_{\text{Ni}}$  while the cluster energy is taken as  $E_{\text{Ti}_2\text{Ni}}$  of the  $\Sigma(\text{H})$  and  $\Sigma(\text{M})$  respectively  $-13.60$  eV, and  $13.60$  eV by an Extended Hückel method for the bond distances.

Figures 3–6 depict the electronic properties have been calculated for discrete molecular orbitals of the clusters falling into the energy interval was plotted in pairs to emphasize the differences of states of  $\text{Ti}_{18}\text{Ni}_{18}$ ,  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  cluster and  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$ .

energy of the highest occupied MO.  $E_G$  is the energy of the lowest-lying MO with predominantly Ti contributions,  $E_{HT}$  highest with predominantly H,  $E_{HB}$  lowest H,  $E_{MT}$  highest M (M = Ni, Cu, or Fe), and  $E_{MB}$  lowest M. The Ti, H, and M band widths are given by  $\delta_{Ti} = E_F - E_G$ ,  $\delta_H = E_{HT} - E_{HB}$ , and  $\delta_M = E_{MT} - E_{MB}$ . The distances between various band edges are:  $\Delta_{TiH} = E_G - E_{HT}$ ,  $\Delta_{HM} = E_{HB} - E_{MT}$ , and  $\Delta_{TiM} = E_G - E_{MT}$ . The total energy  $\Sigma$  is the sum of the energies of all occupied one-electron levels.  $\bar{\Sigma}_H$  and  $\overline{\Delta E}$  are the changes in the total energy, per hydrogen atom, in the reactions  $Ti_1M_m + nH \rightleftharpoons Ti_1M_mH_n$  and  $Ti_1M_m + 1/2nH_2 \rightleftharpoons Ti_1M_mH_n$ , respectively. The average net charges on the Ti, M and H atoms in the cluster, obtained by a Mulliken population analysis, are given by  $\bar{q}_{Ti}$ ,  $\bar{q}_M$  and  $\bar{q}_H$ , respectively.

The cohesive energy ( $CE$ ) is defined as follows:

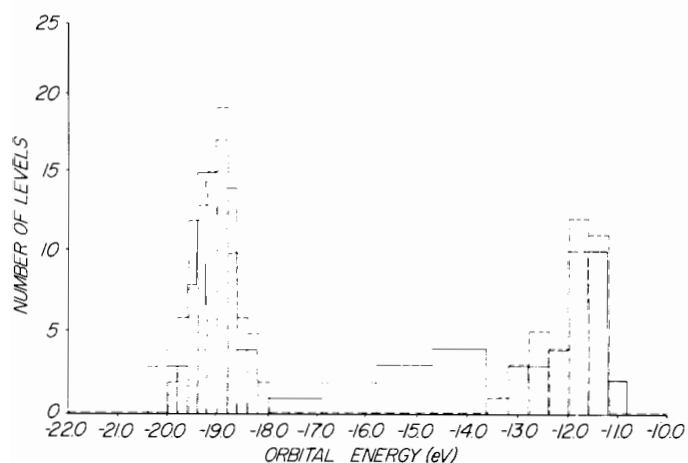
$$CE(\text{bulk}) = [CE(\text{cluster} \times \bar{C}(\text{bulk}))] / \bar{C}(\text{cluster})$$

where  $\bar{C}(\text{bulk})$  and  $\bar{C}(\text{cluster})$  refer, respectively, to the average coordination number of the atoms in the solid and in the finite-sized cluster, and the cohesive energy of the cluster is defined as:

$$CE(\text{cluster}) = \left[ \sum_{j=1}^m (n_j E_j) - E(\text{cluster}) \right] / \left( \sum_{k=1}^m n_k \right),$$

where  $E_j$  is the free atom energy of atom type  $j$ , and  $\sum_{j=1}^m n_j$  is the total number of atoms in the cluster. Thus,  $CE(\text{cluster})$  is just the stabilization energy of the cluster relative to an equal number of free atoms, per atom in the cluster. The factor  $\bar{C}(\text{bulk})/\bar{C}(\text{cluster})$  is included in the calculation of  $CE(\text{bulk})$  (or  $CE$  in Table 4) to take into account the fact that the cluster contains a smaller number of the pairwise "bonding" interactions per atom than does the solid. For example, for the alloys for which we have attempted to calculate the cohesive energies, the  $[\bar{C}(\text{cluster}), \bar{C}(\text{bulk})]$  pairs have the following values: TiNi(7.833, 14), Ti<sub>2</sub>Ni(7.444, 13), TiCu(7.437, 14), Ti<sub>2</sub>Cu(7.833, 14), and TiFe(7.688, 14). The atomic energies are: Ti(-44.16), Ni(-189.70), Cu(-140.19), and Fe(-132.32), while the cluster energies are given by the  $\Sigma$  values in Table 4. Finally, the values of the  $\Sigma(H)$  and  $\Sigma(H_2)$  quantities used in the calculation of  $\bar{\Sigma}_H$  and  $\overline{\Delta E}$ , are respectively -13.606 eV and -35.960 eV, where the value for H<sub>2</sub> has been obtained by an Extended Hückel calculation assuming the experimental value of 0.74611 Å for the bond distance [23].

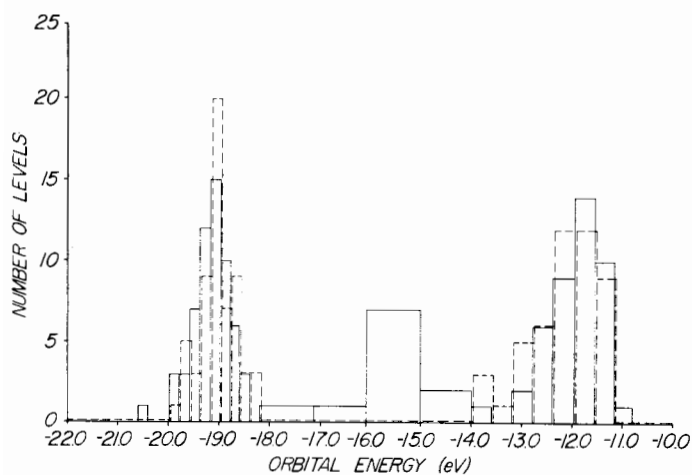
Figures 3-6 depict the densities of states obtained for some of the clusters whose properties have been listed in Table 4. Since the clusters were all finite, sets of discrete molecular orbital energy levels were obtained. These were then listed in groups falling into given energy intervals, and the number of levels in each interval was plotted in the form of a histogram. The histograms were plotted in pairs to emphasize their similarities and differences. Figure 3 depicts the densities of states of Ti<sub>18</sub>Ni<sub>18</sub> and Ti<sub>18</sub>Ni<sub>18</sub>H<sub>12</sub>, Fig. 4 of Ti<sub>24</sub>Ni<sub>12</sub> and the first of the two Ti<sub>24</sub>Ni<sub>12</sub>H<sub>12</sub> clusters, Fig. 5 of Ti<sub>16</sub>Cu<sub>16</sub> and Ti<sub>24</sub>Cu<sub>12</sub>, and Fig. 6 of Ti<sub>16</sub>Fe<sub>16</sub> and Ti<sub>16</sub>Fe<sub>16</sub>H<sub>32</sub>.



**Fig. 3.** Histograms depicting the occupied molecular orbital energy levels of  $Ti_{18}Ni_{18}$  (dashed lines) and  $Ti_{18}Ni_{18}H_{12}$  (solid lines). (Note that different histogram widths have been used at different portions of the plot, so that the number of electronic states is *not* simply proportional to the area under the histogram.)

### The concept of tetrahedrality

Table 5 lists the tetrahedral hole types and their parameters, for all the binary alloys mentioned above, as well as for TiCo [20a] and the monoclinic phase of TiNi [20e]. The volume, area, and “tetrahedrality” parameters can be defined as follows: Let four points A, B, C, and D form a substructure in three dimensions, as shown in Fig. 7. Then, the total surface area of this substructure is equal to



**Fig. 4.** Histograms depicting the occupied molecular orbital energy levels of  $Ti_{24}Ni_{12}$  (dashed lines) and the first of the two  $Ti_{24}Ni_{12}H_{12}$  clusters considered (solid lines). (Note that different histogram widths have been used at different portions of the plot, so that the number of electronic states is *not* simply proportional to the area under the histogram.)

**Fig. 5.** Histograms depicting the occupied molecular orbital energy levels of  $Ti_{24}Cu_{12}$  (solid lines) and  $Ti_{24}Cu_{12}H_{12}$  (dashed lines).

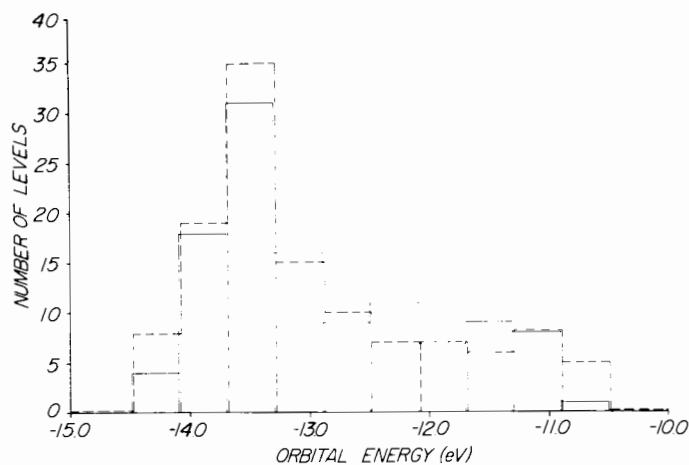
the sum of the areas of the four triangles:

$$\text{Area} = \text{Area}(ABC) + \text{Area}(BCD) + \text{Area}(CDA) + \text{Area}(DAB)$$

(If the four points A, B, C, and D are in a plane, the area of the projection of the substructure on the plane is zero.)

infinitesimal thickness  $h$ .

**Fig. 6.** Histograms depicting the occupied molecular orbital energy levels of  $Ti_{16}Fe_{16}H_{32}$  (solid lines) and  $Ti_{16}Fe_{16}$  (dashed lines). (Note that different histogram widths have been used at different portions of the plot, so that the number of electronic states is *not* simply proportional to the area under the histogram.)

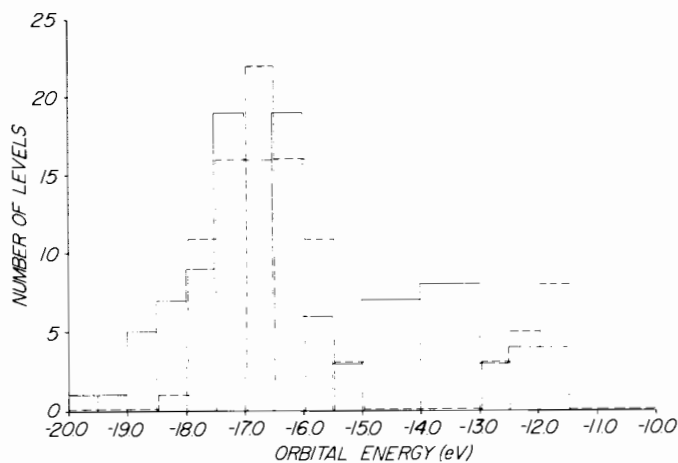


**Fig. 5.** Histograms depicting the occupied molecular orbital energy levels of  $\text{Ti}_{16}\text{Cu}_{16}$  (*dashed lines*) and  $\text{Ti}_{24}\text{Cu}_{12}$  (*solid lines*)

the sum of the areas of its four triangular faces:

$$\text{Area} = \text{Area}(\text{ABC}) + \text{Area}(\text{ABD}) + \text{Area}(\text{ACD}) + \text{Area}(\text{BCD}).$$

(If the four points lie on the same plane, then this definition reduces to twice the area of the plane, i.e., it treats the plane like a three-dimensional solid of infinitesimal thickness.)



**Fig. 6.** Histograms depicting the occupied molecular orbital energy levels of  $\text{Ti}_{16}\text{Fe}_{16}$  (*dashed lines*) and  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$  (*solid lines*). (Note that different histogram widths have been used at different portions of the plot, so that the number of electronic states is *not* simply proportional to the area under the histogram.)

**Table 5.** Tetrahedral hole types and their parameters<sup>a</sup>

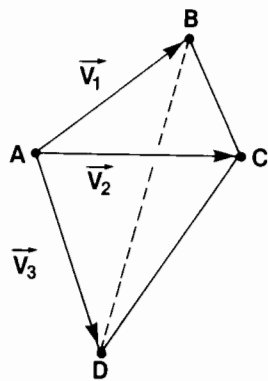
Phase	Hole type	Volume	Area	Tetrahedrality
TiNi(B <sub>2</sub> )	Ti <sub>2</sub> Ni <sub>2</sub>	2.2839	12.8555	0.9532
TiCo(B <sub>2</sub> )	Ti <sub>2</sub> Co <sub>2</sub>	2.2298	12.6517	0.9532
TiFe(B <sub>2</sub> )	Ti <sub>2</sub> Fe <sub>2</sub>	2.1964	12.5251	0.9532
TiNi	Ti(1) <sub>2</sub> Ni(3)Ni(4)	2.2761	12.7231	0.9650
(monoclinic)	Ti(2) <sub>2</sub> Ni(3)Ni(4)	1.5174	10.1382	0.8970
	Ti(1)Ti(2)Ni(3) <sub>2</sub>	2.2761	12.5637	0.9866
	Ti(1)Ti(2)Ni(4) <sub>2</sub>	3.0348	15.2585	0.9824
Ti <sub>2</sub> Ni	Ti(f) <sub>3</sub> Ni <sup>b</sup>	2.6779	14.0068	0.9864
	Ti(f) <sub>3</sub> Ni	2.5644	13.6228	0.9843
	Ti(f) <sub>2</sub> Ti(c)Ni	2.5189	13.4513	0.9858
	Ti(f)Ti(c)Ni <sub>2</sub>	2.3717	12.9360	0.9841
	Ti(c)Ni <sub>3</sub>	2.1489	12.0767	0.9888
	Ni <sub>4</sub>	2.6356	13.7485	1.0
TiCu	Ti <sub>4</sub>	2.8814	14.7504	0.9815
	Ti <sub>3</sub> Cu	2.6413	14.2254	0.9463
	Ti <sub>2</sub> Cu <sub>2</sub>	2.4012	13.4182	0.9383
	TiCu <sub>3</sub>	2.1610	12.2869	0.9657
	Cu <sub>4</sub>	1.9209	12.2206	0.8574
Ti <sub>2</sub> Cu	Ti <sub>4</sub>	2.7730	14.2434	0.9974
	Ti <sub>3</sub> Cu	2.6406	14.5228	0.9116
	Ti <sub>2</sub> Cu <sub>2</sub>	2.5082	13.4027	0.9871
	Ti <sub>2</sub> Cu <sub>2</sub>	2.5082	13.9309	0.9238

<sup>a</sup> The volume and area parameters have been obtained using the lattice parameters of the unexpanded unit cells. The number or letter in parentheses after some of the atom names, such as Ni(3) or Ti(f), refers to sites of different symmetry type for that atom

<sup>b</sup> This is the most common hole type for the Ti<sub>2</sub>Ni phase

The area of each triangle can be obtained readily from vector analysis. For example, if we define  $V_1 = B - A$ ,  $V_2 = C - A$ , and  $V_3 = D - A$ , where  $A$ ,  $B$ ,  $C$ , and  $D$  are vectors drawn from the origin of the coordinate system to the points A, B, C, and D, respectively, then:

$$\text{Area}(ABC) = 1/2 |V_1 \times V_2|.$$

**Fig. 7.** A distorted tetrahedron

$$\text{Volume} = 1/6$$

The volume is of a tetrahedron, with the volume reduce to  $\sqrt{3} r^2 a$

The "tetrahedrality"

$$\text{Tetrahedrality} =$$

where  $\prod_{i=1}^6 r_i$  is the product of the bond lengths B, C and D. The tetrahedrality, as a measure of overall size, depends on the approach to a regular tetrahedron. The tetrahedrality approaches a regular tetrahedron as a plane (the most common) of how closely the

Of the two Ti<sub>24</sub>Ni<sub>12</sub>H<sub>2</sub> hydrogens in the Ti<sub>24</sub>Ni<sub>12</sub>H<sub>2</sub> cluster. The second Ti<sub>24</sub>Ni<sub>12</sub>H<sub>2</sub> sites, two in Ti(f).

Table 6 lists the Ti<sub>16</sub>Cu<sub>16</sub>H<sub>2</sub> cluster. The Ti<sub>24</sub>Ni<sub>12</sub>H<sub>2</sub> calculation. Ti(f)<sub>2</sub>Ti(c)Ni and

Table 7 presents the two Ti<sub>24</sub>Ni<sub>12</sub>H<sub>2</sub> clusters. (A) values extra hydrogen; (C) values and the difference details.

*The surveying technique*

It is well known [1] that non-bonded hydrogens to the very strong "Criterion") [3e, f] sites located further



The volume of the distorted tetrahedron formed by the four points is given by:

$$\text{Volume} = 1/6 |(\mathbf{V}_1 \times \mathbf{V}_2) \cdot \mathbf{V}_3|.$$

The volume is clearly zero if the four points lie on a plane. For a perfect tetrahedron, with all six side lengths equal to  $r$ , the total surface area and volume reduce to  $\sqrt{3} r^2$  and  $r^3/6\sqrt{2}$  respectively.

The "tetrahedrality" is defined as follows:

$$\text{Tetrahedrality} = \frac{6\sqrt{6} \text{Volume}}{\left[ \prod_{i=1}^6 r_i \right]^{1/6} \text{Area}}$$

where  $\prod_{i=1}^6 r_i$  is the product of the lengths of the six sides between the points A, B, C and D. The sixth root of this quantity is included in the definition. The tetrahedrality, as defined above, is clearly dimensionless and independent of overall size, dependent only on how closely the figure formed by the four points approaches a regular tetrahedron in shape, acquiring its maximum value (1.0) for a regular tetrahedron, and its minimum value (0.0) for four points falling on a plane (the most non-tetrahedral shape possible). Thus, it is a valid indicator of how closely the shape of a site approaches that of a regular tetrahedron.

Of the two  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  clusters mentioned in Table 4, the first one contains eleven hydrogens in the more common type of  $\text{Ti}(f)_3\text{Ni}$  sites and one in a  $\text{Ti}(c)\text{Ni}_3$  site. The second  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  cluster contains six hydrogens in the same type of  $\text{Ti}(f)_3\text{Ni}$  sites, two in  $\text{Ti}(f)_2\text{Ti}(c)\text{Ni}$  sites, three in  $\text{Ti}(f)\text{Ti}(c)\text{Ni}_2$  sites, and one in a  $\text{Ni}_4$  site.

Table 6 lists the results of some calculations on the  $\text{Ti}_{18}\text{Ni}_{18}\text{H}$ ,  $\text{Ti}_{24}\text{Ni}_{12}\text{H}$ , and  $\text{Ti}_{16}\text{Cu}_{16}\text{H}$  clusters whose coordinates were obtained as described above. In the  $\text{Ti}_{24}\text{Ni}_{12}\text{H}$  calculations, the two  $\text{Ti}_3\text{Ni}$  sites hydrogenated are, respectively, of the  $\text{Ti}(f)_2\text{Ti}(c)\text{Ni}$  and the more common  $\text{Ti}(f)_3\text{Ni}$  types.

Table 7 presents a comparison of  $\overline{\Delta E}$  values obtained for the  $\text{Ti}_{18}\text{Ni}_{18}\text{H}_{12}$  and the two  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  clusters by three different methods: (A) values listed in Table 2; (B) values extrapolated from the calculations on the clusters with only a single hydrogen; (C) values obtained using a single zeta d orbital for each metal atom; and the differences (A-B) and (A-C). See the footnotes to this table, for more details.

#### *The surveying technique*

It is well known [2, 6b] that distances of less than about 2.0 Å or 2.1 Å between non-bonded hydrogens are unfavorable due to energetic considerations related to the very strong anti-bonding H-H interactions involved (the "Switendick Criterion") [3e, f]. Assume that we are interested in finding a set of tetrahedral sites located further away from one another by at least a distance of  $r_c$  and that

**Table 6.** Calculations on  $\text{Ti}_{18}\text{Ni}_{18}\text{H}$ ,  $\text{Ti}_{24}\text{Ni}_{12}\text{H}$ , and  $\text{Ti}_{16}\text{Cu}_{16}\text{H}$  Clusters<sup>a</sup>

Cluster	Hydrogenated hole type	$\Sigma$	$\Sigma_{\text{H}}^{\text{b}}$	$\Delta E^{\text{b}}$	$E_{\text{H}}^{\text{c}}$	$q_{\text{H}}^{\text{b}}$
$\text{Ti}_{18}\text{Ni}_{18}\text{H}$	$\text{Ti}_2\text{Ni}_2$	-4308.812	-4.720	-0.346	-14.828	-0.185
	$\text{Ti}_4\text{Ni}_2^{\text{d}}$	-4308.399	-4.306	+0.068	-14.783	-0.135
	$\text{Ti}_2\text{Ni}_4^{\text{d}}$	-4309.190	-5.098	-0.724	-14.948	-0.230
$\text{Ti}_{24}\text{Ni}_{12}\text{H}$	$\text{Ni}_4$	-3478.460	-4.420	-0.045	-14.567	-0.167
	$\text{TiNi}_3$	-3478.609	-4.569	-0.195	-14.784	-0.178
	$\text{Ti}_2\text{Ni}_2$	-3478.856	-4.815	-0.441	-15.115	-0.173
	$\text{Ti}_3\text{Ni}^{\text{e}}$	-3478.891	-4.851	-0.477	-15.159	-0.183
	$\text{Ti}_3\text{Ni}^{\text{e}}$	-3478.678	-4.638	-0.264	-15.601	-0.173
$\text{Ti}_{16}\text{Cu}_{16}\text{H}$	$\text{Cu}_4$	-3126.166	-4.936	-0.562	-16.663	-0.310
	$\text{TiCu}_3$	-3126.168	-4.938	-0.564	-16.405	-0.332
	$\text{Ti}_2\text{Cu}_2$	-3126.364	-5.135	-0.760	-16.516	-0.289
	$\text{Ti}_3\text{Cu}$	-3125.929	-4.700	-0.326	-16.472	-0.242
	$\text{Ti}_4$	-3125.743	-4.514	-0.140	-16.408	-0.206

<sup>a</sup> All energies are in electron volts<sup>b</sup> These quantities do not have a bar (—) above them, since there is only one H in the clusters, and therefore no need to take an average<sup>c</sup> The energy of the MO with predominantly H contribution<sup>d</sup> A distorted octahedral (rather than tetrahedral) hole<sup>e</sup> One of two different types of  $\text{Ti}_3\text{Ni}$  holes hydrogenated (see text)

two lattice atoms are considered to be bonded to each other if they are not further away from one another than a distance of  $r_B$ . A tetrahedral site is formed by four lattice atoms which are all within at most a distance of  $r_B$  from one another. Assume that such a group of four atoms has been found, and that the coordinates of the tetrahedral site are simply given by the average of the coordinates of these vertices of the distorted tetrahedron. Then, when a second potential tetrahedral site is found, only keep it if it is not closer than  $r_c$  to the first one. After  $(n-1)$

**Table 7.** Comparison of  $\Delta E$  values obtained by different methods

Cluster	$\Delta E$	Calculations			Differences	
		A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	(A-B)	(A-C)
$\text{Ti}_{18}\text{Ni}_{18}\text{H}_{12}$		0.0005	-0.346	-0.565	0.3465	0.5655
$\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}^{\text{d}}$		0.186	-0.258	-0.347	0.444	0.533
$\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}^{\text{d}}$		0.105	-0.326	-0.367	0.431	0.472

<sup>a</sup> Values listed in Table 4<sup>b</sup> Values extrapolated by the formula  $\overline{\Delta E} = 1/n \sum_{j=1}^k (m_j \Delta E_j)$  where  $n$  is the total number of hydrogens (here 12), the summation is over the  $k$  distinct types of holes occupied,  $m_j$  is the number of occupied holes of type  $j$  ( $\sum_{j=1}^k m_j = n$ ), and  $\Delta E_j$  is the  $\Delta E$  value for hole type  $j$  (from values listed in Table 6)<sup>c</sup> Values obtained by carrying out the calculations on the  $\text{Ti}_{18}\text{Ni}_{18}$ ,  $\text{Ti}_{18}\text{Ni}_{18}\text{H}_{12}$ ,  $\text{Ti}_{24}\text{Ni}_{12}$ , and  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  clusters using a single zeta d orbital (rather than double zeta) for each metal atom<sup>d</sup> One of the two different  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  clusters considered (see text)

such sites, all at a keep the next potential kept  $(n-1)$  sites.

Clearly, the specific distribution according to the atoms are listed in the calculation, unless the phases considered two  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  clusters generating 12 of the mechanical calculation was obtained by listing all the Ni's increase indefinitely into the computer sequentially drawn with 1000 atoms, identification number reorder the atom statistical limits and of lattice points.

Such considerations uptake. For example if a cutoff value of to one per Ti or consistently with hydrogenated up  $\text{Ti}_{48}\text{Ni}_{48}\text{H}_{48}$ . If  $r_c$  it is impossible to tions. For the mu unit cells of the T  $r_c = 2.0 \text{ \AA}$ , 111 sites atoms in each unit 1.23) is very close most heavily hydrogenated the  $\text{Ti}_2\text{Ni}$  phase, put in. Thus, it is further away from making the  $\text{Ti}_2\text{Ni}$  are now on the border

If the algorithm is by the atomic arrangement holes, then all the this.) The statistics of how the atoms

such sites, all at a distance of no less than  $r_c$  from one another, have been found, keep the next potential site only if it is not closer than  $r_c$  to any of the previously kept  $(n - 1)$  sites.

Clearly, the specific holes which are kept, as well as their total number and distribution according to types, will depend to some extent on the order in which the atoms are listed in the input to the computer algorithm which carries out the calculation, unless the tetrahedral holes are all of the same type, as in the  $B_2$  phases considered. The coordinates for the hydrogens in the  $\text{Ti}_{18}\text{Ni}_{18}\text{H}_{12}$  and the two  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  clusters were obtained by using this algorithm and just hydrogenating 12 of the sites kept by the algorithm, in carrying out the quantum mechanical calculation. The first of the two  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  hydrogen coordinate sets was obtained by listing all the Ti's first, while the second set was obtained by listing all the Ni's first. If the numbers of atoms in the clusters are allowed to increase indefinitely, and the order in which the lattice atom coordinates are fed into the computer is chosen by a completely random process (for example, by sequentially drawing cards numbered 1 through 1000 from a hat, for a cluster with 1000 atoms, and feeding in the coordinates belonging to the atom whose identification number was drawn; or by using a random number generator to reorder the atoms, which is a much more efficient randomization process), statistical limits are obtained, both for the ratio of holes kept to the total number of lattice points, and for the statistical distributions of holes of different types.

Such considerations can give fundamental insight into the amount of hydrogen uptake. For example, for the extremely simple  $B_2$  lattices such as that in  $\text{TiNi}(B_2)$ , if a cutoff value of  $r_c = 2.1 \text{ \AA}$  is chosen, the number of holes kept rapidly converges to one per Ti or Ni. That is, for a  $\text{Ti}_{48}\text{Ni}_{48}$  cluster, 47 hydrogen sites are kept, consistently with the experimental fact [21] that the  $\text{TiNi}$  phase can only be hydrogenated up to a stoichiometry of  $\text{TiNiH}$ , i.e.,  $\text{Ti}_{48}\text{Ni}_{48}$  to a limit of  $\text{Ti}_{48}\text{Ni}_{48}\text{H}_{48}$ . If  $r_c$  is decreased to  $2.0 \text{ \AA}$ , still only 47 sites are kept, indicating that it is impossible to force more hydrogens in without creating unfavorable interactions. For the much more complicated  $\text{Ti}_{128}\text{Ni}_{64}$  cluster corresponding to two unit cells of the  $\text{Ti}_2\text{Ni}$  phase, convergence is much slower. For a calculation with  $r_c = 2.0 \text{ \AA}$ , 111 sites are kept; while for  $r_c = 2.1 \text{ \AA}$ , 90 sites are kept, when the Ti atoms in each unit cell have all been listed first in the input. The ratio  $(111/90 = 1.23)$  is very close to  $2.5/2.0 = 1.25$ , where  $\text{Ti}_2\text{NiH}_{2.5}$  and  $\text{Ti}_2\text{NiH}_2$  are the two most heavily hydrogenated limiting stoichiometric compositions obtainable from the  $\text{Ti}_2\text{Ni}$  phase, with the last half unit of hydrogen being the most difficult to put in. Thus, it is conceivable that in  $\text{Ti}_2\text{NiH}_2$  the hydrogens occupy sites all further away from one another by at least  $2.1 \text{ \AA}$ , while the relative difficulty of making the  $\text{Ti}_2\text{NiH}_{2.5}$  stoichiometry is due to the fact that many H-H distances are now on the borderline ( $2.0 \text{ \AA} - 2.1 \text{ \AA}$ ) of being unfavorably close to one another.

If the algorithm is carried out with  $r_c < r_T$ , where  $r_T$  is the closest distance allowed by the atomic arrangement in the cluster between the centers of the tetrahedral holes, then *all* the holes are kept. (Setting  $r_c = 0.0$  would obviously accomplish this.) The statistical distribution of hole types is then obtained directly, regardless of how the atoms are numbered, provided that the cluster is truly representative

of the material, and large enough for it to contain a statistically significant number of each type of hole; however, in order to obtain smaller subsets of holes suitable for simultaneous occupancy by hydrogens, calculations with reasonable  $r_c$  values would still have to be carried out.

#### Octahedral sites

Clearly, the generalization of our algorithmic surveying procedure to include distorted octahedral sites, which could be defined and characterized by parameters in a manner similar to that used for tetrahedral sites, is fairly straightforward. For example, the "octahedrality" of a substructure formed by six distinct points in three dimensions, as illustrated in Fig. 8, can be defined in direct analogy with tetrahedrality:

$$\text{Octahedrality} = \frac{3\sqrt{6} \text{ Volume}}{\left[ \prod_{i=1}^{12} r_i \right]^{1/12} \text{ Area}}$$

Here, Volume is the volume of the distorted octahedron, Area is the sum of the areas of its eight triangular faces,  $r_i (i = 1, 2, \dots, 12)$  are the lengths of its twelve sides, and the twelfth root of the product  $\prod_{i=1}^{12} r_i$  is included to make octahedrality dimensionless and scale-independent. The volume of the distorted octahedron illustrated in Fig. 8, is the sum of the volumes of the four distorted tetrahedra ABCF, ACDF, ADEF, and ABEF which span it.

For a perfect octahedron, with all side lengths equal to  $r$ , the total surface area and volume are  $2\sqrt{3}r^2$  and  $\sqrt{2}r^3/3$  respectively, giving the maximum possible octahedrality value of 1.0. The octahedrality acquires its minimum value of 0.0 for all six points falling on a plane (the most non-octahedral shape possible).

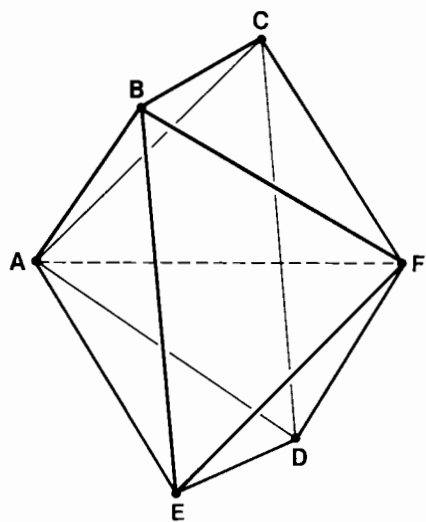


Fig. 8. A distorted octahedron

The octahedrality of TiFe [20a]) is always high, indicating that the holes are not too distorted.

In this connection, the octahedrality of the holes in both special cases is quantified. The octahedrality quantifies how close the vertices approximating

### 3. Discussion

#### Comparison of atomic

The results of the calculations for the metallic clusters show that there is good quantitative agreement between the two methods. Both methods overestimate the distortion of the cluster. Distortion causes a slight increase in the volume. The calculations agree with the results of the above. In  $\text{Ti}_2\text{Ni}_2$ , the distortion of the charges; however, in the hydride, the charge is on the nickel.

While the agreement is not quantitative, the results reproduced qualitatively. Both computational methods

#### Extended Hückel

The Extended Hückel method is a scheme which converts a single matrix diagonalization of the pairs, into the matrix of contributions to the integrals closest to the valence electrons. The energy is lower than that of the parameterization of the electron distribution. The parameters are not [25] where "hybridization" of the covalent bond and hydride system is directional. The

The octahedrality of the octahedral holes in  $B_2$  phases (such as TiNi, TiCo, and TiFe [20a]) is always equal to 0.9532, just like the tetrahedrality of their tetrahedral holes.

In this connection, it should be noted that tetrahedrality and octahedrality are both special cases of the more general concept of “sphericity” [24], which quantifies how closely the shape of a polyhedron with any random number of vertices approximates a perfect sphere, which has a sphericity of 1.0.

### 3. Discussion

#### *Comparison of ab initio and Extended Hückel calculations on small clusters*

The results of the *ab initio* and Extended Hückel calculations on several small metallic clusters and their hydrides are compared in Table 2. For the most part, there is good qualitative agreement between the *ab initio* and Extended Hückel results. Both methods show better hydride binding when titanium is included in the cluster. Distortion of the shape of the  $Ti_2Ni_2$  cluster has a relatively small effect on the hydride binding energy, while decreasing the size of the  $Ni_4$  cluster causes a slight increase in the binding energy. Both *ab initio* and Extended Hückel calculations agree that the hydrogen is negatively charged, but the former method overestimates the charge considerably because of the basis set effects discussed above. In  $Ti_2Ni_2$ , *ab initio* and Extended Hückel calculations disagree in the sign of the charges; however, the two methods agree that in the formation of the hydride, the charge on the titanium changes much more than the charge on the nickel.

While the agreement between the *ab initio* and Extended Hückel calculations is not quantitative, it is clear that the most important features and trends are reproduced qualitatively. Because of the complexity of even the small clusters, *both* computational methods must be interpreted cautiously.

#### *Extended Hückel results*

The Extended Hückel method consists of a non-iterative (i.e., non-self-consistent) scheme which computes the eigenvalues and eigenvectors of the Hamiltonian by a single matrix diagonalization step. The valence electrons are then placed, in pairs, into the molecular orbitals (MO's) of lowest energy. The predominant contributions to each MO come from atomic orbitals (AO's) which have Coulomb integrals closest to the energy of that MO. For example, for the Ni atom, the ten valence electrons all go into the 3d levels, since their Coulomb integral is much lower than that of the 4s level ( $-18.97$  eV versus  $-7.532$  eV in the particular parameterization we used [9] as listed in Table 3). Although the effects of this electron distribution scheme and the numerical values chosen for the orbital parameters are much less pronounced in organic and organometallic systems [25] where “hybridization” is forced upon the AO's by the directional nature of the covalent bonding, they are more obvious for the binary transition metal alloy and hydride systems considered here, where the bonding is metallic and non-directional. The “charge iteration” options available in the program [10] for

crudely taking electron correlation into account, make very little improvement in the results, while increasing the computational times by about an order of magnitude, since the matrix diagonalization step now has to be repeated at each iteration. Therefore, the densities of states reported here are for the total electron density, not broken down into s and d contributions. In spite of these limitations, when the results are interpreted with full awareness of the method's strengths and weaknesses, valuable insight and semi-quantitative information can be obtained on properties such as relative energy levels, exothermicities, and charge distributions. Furthermore, by requiring only a minimal amount of computer time, the method allows large numbers of detailed calculations to be performed, as well as extensions to much larger systems than are practical for most other methods.

With these limitations in mind, the results in Table 4 and Figs. 3–6 can be analyzed as follows:

(1) The Ti–Ni and Ti–Ni–H systems are the ones for which the limitations of the computational scheme manifest themselves least. The following observations can be made about the Ti–Ni systems:

(i) The expected double peak density of states is obtained for  $\text{Ti}_{18}\text{Ni}_{18}$  and  $\text{Ti}_{24}\text{Ni}_{12}$ , as shown in Figs. 3 and 4. The large gap between the bottom of the Ti levels and the top of the Ni levels is consistent with the large difference in the 3d Coulomb integrals used for Ti and Ni, although it is exaggerated when compared to band structure calculations [31, m]. As mentioned previously, this gap could be reduced by selecting a different set of parameters where the 3d Coulomb integrals of Ti and Ni are closer to each other, but the current values have been chosen to provide an internally consistent, non-empirical set. For example, if we choose the parameters given in [25], where the Coulomb integrals of Ti and Ni are taken to be  $-10.81$  and  $-14.20$  eV respectively, the Ti–Ni peak-to-peak splitting for  $\text{Ti}_{18}\text{Ni}_{18}$  decreases to 2.75 eV, which is much closer to the band structure calculations [31, m]. On the other hand, the cohesive energy of TiNi with this set of parameters is equal to 8.784 eV/atom, which is too large by approximately a factor of two (see paragraph (iv)), and the effects of the inclusion of H on the total energy and on the charge distributions are correspondingly underestimated.

(ii) The widths of the Ti and Ni portions of the density of states are reasonable. For example, metallic Ti has been shown, by ultra high vacuum photoemission measurements, to possess narrow occupied d bands of width 1.7 eV [26]. We calculate *total* Ti band widths of 2.179 and 2.673 eV for  $\text{Ti}_{18}\text{Ni}_{18}$  and  $\text{Ti}_{24}\text{Ni}_{12}$  respectively. These are wider than the d band width of metallic Ti since they are total band widths, with four valence electrons per Ti, rather than two. They are not *much* wider, though, since there are many fewer Ti–Ti interactions in Ti–Ni alloys than in metallic Ti. It is these strong interactions between atomic orbitals of identical energy which give the major portion of the band broadening, rather than the much weaker Ti–Ni interactions between Ti and Ni orbitals of very different energies. The widening of the Ti band in going from  $\text{Ti}_{18}\text{Ni}_{18}$  to  $\text{Ti}_{24}\text{Ni}_{12}$ , which has more near neighbor Ti–Ti interactions per Ti atom, is consistent with

this analysis. Sim  
 $\text{Ti}_{18}\text{Ni}_{18}$  and  $\text{Ti}_{24}$   
the latter alloy, w  
(iii) The  $\text{Ti}_{18}\text{Ni}_{18}$   
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for  $\text{TiH}_2$  [26].  
(iii) The  $E_{\text{LUMO}}$  a  
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this analysis. Similarly, the band widths of the Ni levels (1.737 and 1.618 eV for  $\text{Ti}_{18}\text{Ni}_{18}$  and  $\text{Ti}_{24}\text{Ni}_{12}$ , respectively), as well as the narrowing of the Ni band in the latter alloy, which has few near neighbor Ni–Ni interactions, are as expected.

(iii) The  $\text{Ti}_{18}\text{Ni}_{18}$  and  $\text{Ti}_{24}\text{Ni}_{12}$  densities of states shown in Figs. 3 and 4 are very similar, except for the differences in the band widths, and in the total electron densities in the Ti and Ni portions of the diagrams, both of these differences being a direct consequence of the different Ti/Ni ratios of the two alloys.

(iv) The  $E_{\text{LUMO}}$ ,  $E_{\text{F}}$ ,  $E_{\text{G}}$ ,  $E_{\text{MT}}$ , and  $E_{\text{MB}}$  values are all slightly lower in  $\text{Ti}_{24}\text{Ni}_{12}$  than in  $\text{Ti}_{18}\text{Ni}_{18}$ , indicating stronger bonding in the  $\text{Ti}_2\text{Ni}$  phase than in the TiNi phase. The cohesive energy ( $CE$ ) values of  $\text{Ti}_{18}\text{Ni}_{18}$  (4.022 eV/atom) and  $\text{Ti}_{24}\text{Ni}_{12}$  (6.024 eV/atom) also support the idea that the  $\text{Ti}_2\text{Ni}$  phase is more strongly bonded. The cohesive energies of metallic Ti and metallic Ni are 4.85 eV/atom and 4.44 eV/atom, respectively [27]. Thus, it should be expected that  $\text{Ti}_{24}\text{Ni}_{12}$  will give a slightly larger  $CE$  than  $\text{Ti}_{18}\text{Ni}_{18}$ ; however, this difference is somewhat overestimated here, due to the positive and negative deviations of the  $CE$  values for  $\text{Ti}_{24}\text{Ni}_{12}$  and  $\text{Ti}_{18}\text{Ni}_{18}$ , respectively, from the values that would be predicted by applying Vegard's law, i.e., taking a linear interpolation in concentration between  $CE$  values of the pure components. This is not surprising, since the cohesive energy is one of the most difficult properties to calculate using a cluster model, even when *ab initio* techniques are used [28].

(v) Consistently with the slightly greater Pauling electronegativity of Ni relative to Ti (1.91 versus 1.54) [29], the Ni atoms acquire a small average negative charge and the Ti atoms acquire a small average positive charge, in the Mulliken population analysis. Since this average charge is distributed over more Ti and fewer Ni atoms in  $\text{Ti}_{24}\text{Ni}_{12}$ ,  $|\bar{q}_{\text{Ti}}|$  is slightly lower and  $|\bar{q}_{\text{Ni}}|$  is slightly higher in this cluster. However, the average  $|\bar{q}|$  value over all the atoms is almost identical for the two clusters (0.166 for  $\text{Ti}_{18}\text{Ni}_{18}$  and 0.165 for  $\text{Ti}_{24}\text{Ni}_{12}$ ).

(2) The following changes take place upon inclusion of the hydrogens:

(i) A set of energy levels with predominantly hydrogen contributions appears in Figs. 3 and 4, in the gap between  $E_{\text{G}}$  and  $E_{\text{MT}}$ . For both  $\text{Ti}_{18}\text{Ni}_{18}\text{H}_{12}$  and  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$ , these levels are more heavily located on the Ti side than on the Ni side, consistently with the smaller separation between the Ti(3d) and H(1s) Coulomb integrals than between the H(1s) and Ni(3d) Coulomb integrals. The density of states for the second  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  cluster is very similar to the first, and has not been shown. (The fact that these two  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  clusters give such similar densities of states in spite of the rather different site occupancy schemes, is an interesting observation on its own right.)

(ii) The medians of the Ti and H portions of the diagrams (Figs. 3, 4) are separated by 2.929 eV for  $\text{Ti}_{18}\text{Ni}_{18}\text{H}_{12}$ , and 3.326 and 3.206 eV for the two  $\text{Ti}_{24}\text{Ni}_{12}\text{H}_{12}$  clusters. This is consistent with the observation [26] that the peak of the H band in metallic Ti is about 5 eV below the peak of the Ti band. The  $\delta_{\text{H}}$  values listed in Table 4 are very similar to the H band width of about 4 eV found for  $\text{TiH}_2$  [26].

(iii) The  $E_{\text{LUMO}}$  and  $E_{\text{F}}$  values get pushed up slightly relative to the unhydrogenated clusters, due to some anti-bonding hydrogen admixture in what were

previously just bonding Ti levels. The  $E_G$  values go up even more. However, the lowest Ti levels have considerable H contributions, and the highest H levels have considerable Ti contributions, and this increase in  $E_G$  is partially an artifact of our artificially grouping the MO's as Ti or H levels. Thus,  $\delta_{Ti}$  becomes smaller upon hydrogenation.

(iv)  $E_{MT}$  becomes a little more negative upon hydrogenation. However, the most pronounced effect at the Ni end of the diagrams is that a number of MO's, equal to the number of hydrogens in the cluster, become detached from the low end of the Ni levels, and become a tail, with a very considerable decrease in  $E_{MB}$  and increase in  $\delta_M$ . This effect has been found in calculations on clusters of various sizes, as well as different numbers of hydrogens. For example, the inclusion of 1, 2, 4, 6 or 12 hydrogens in the cluster leads, respectively, to a "tail" consisting of 1, 2, 4, 6 or 12 MO levels at the low end of the Ni levels.

(v) The  $\bar{\Sigma}_H$  and  $\bar{\Delta E}$  values are the total energy changes in the cluster, per hydrogen atom included, if the source of hydrogen is atomic H or molecular  $H_2$ , respectively. These values are consistently underestimated by about 0.5 eV/hydrogen, for the reasons (related to basis set flexibility) discussed in Sect. 2. For example, the experimental value of  $\bar{\Delta H}^0$ , i.e., the enthalpy of hydrogenation defined in the same way as  $\bar{\Delta E}$ , is -0.436 eV/hydrogen atom obtained by breaking up  $H_2$ , for the formation of the TiNiH phase at 373°K [30]. (It should, of course, be remembered that  $\bar{\Delta H}^0$  is a temperature-dependent quantity, while  $\bar{\Delta E}$  is calculated at 0°K.) Our calculated value is  $\bar{\Delta E} = +0.0005$  eV for the  $Ti_{18}Ni_{18}H_{12}$  cluster. This subject will be discussed again later, in connection with TiFeH<sub>2</sub> phase calculations, as well as in relation to Table 7.

(vi) The  $\bar{q}$  values show that H acquires an average net negative charge of about -0.16. Ni atoms become slightly more negative in  $Ti_{18}Ni_{18}H_{12}$ , and slightly more positive in  $Ti_{24}Ni_{12}H_{12}$ . In all cases, the Ti atoms lose electrons and become more positive. These results suggest the validity of a model with partially anionic hydrogens, most of the charge transfer taking place from Ti to H, to give the average partial negative charge of H.

(vii) At this point, it is instructive to compare our densities of states for the hydrides of TiNi and  $Ti_2Ni$  with the results of more accurate calculations on simpler systems such as NiH [3i] and PdH [3o]. The most significant similarities of the results are that the metallic *d*-band manifold is narrower after hydrogenation, and that there is an upward shift in the Fermi energy, and a considerable reduction of the density of states at the Fermi level, caused by this upward shift. The most significant difference is the fact that the levels with primarily H contributions lie below the metal *d* levels in the NiH and PdH calculations, while in our calculations there is both a group of hydrogen-dominated levels between the Ti and Ni levels, and a "tail" at the low energy end containing a number of levels equal to the number of hydrogen atoms in the cluster. This is again a direct consequence of the numerical value chosen, for reasons discussed above, for the 3d Coulomb integral of Ni. The choice of -14.20 eV [25] would have improved the agreement.

(3) The Ti-Cu and Ti-Fe calculations also provide very interesting results, although the deficiency of the computational scheme is somewhat more

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calculations:

(i) The  $E_{LUMO}$ ,  $E_{MB}$ ,  $E_G$  and  $E_{MT}$  for  $Ti_{16}Cu_{16}$ , and the  $\delta_{Ti}$  and  $\delta_M$  with the tighter b  
Ti atoms (the  $C_{2v}$  and  $C_{3v}$  respectively [27]).

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pronounced for these calculations. For example, since the 4s orbital of Cu lies above the 3d orbital of Ti, Cu loses its 4s electron to levels of primarily Ti(3d) admixture, as can be seen from the  $\bar{q}$  values. Similarly, Fe acquires a  $\bar{q}$  value which is far too negative, because almost two electrons “fall” from Ti levels into the lower-lying Fe levels. We can make the following observations on these five calculations:

(i) The  $E_{\text{LUMO}}$ ,  $E_{\text{F}}$ ,  $E_{\text{G}}$ ,  $E_{\text{MT}}$  and  $E_{\text{MB}}$  values are all lower for  $\text{Ti}_{24}\text{Cu}_{12}$  than for  $\text{Ti}_{16}\text{Cu}_{16}$ , and the  $CE$  is a little larger for  $\text{Ti}_{24}\text{Cu}_{12}$ . These results are all consistent with the tighter binding expected for the cluster containing a larger fraction of Ti atoms (the  $CE$  values of metallic Ti and Cu are 4.85 and 3.49 eV/atom, respectively [27]), but the  $CE$  is again too large. It is also overestimated for  $\text{Ti}_{16}\text{Fe}_{16}$  ( $CE$  (metallic Fe) = 4.28 eV/atom [27]).

(ii)  $\delta_{\text{Ti}}$  has values very similar to those in the Ti-Ni phases for  $\text{Ti}_{16}\text{Cu}_{16}$  and  $\text{Ti}_{24}\text{Cu}_{12}$ . The reason for its being very small for  $\text{Ti}_{16}\text{Fe}_{16}$  is that each Ti has lost close to two electrons, so that the Ti portion of the density of states diagram is very narrow and has few electrons.

(iii) As shown in Fig. 5, because of the closeness of the 3d eigenvalues of Ti and Cu, and because of the much larger number of electrons at the Cu end, there is no obvious double peak structure. The  $\text{Ti}_{16}\text{Cu}_{16}$  and  $\text{Ti}_{24}\text{Cu}_{12}$  energy level structures are very similar, the main difference being in the relative numbers of levels occupied at each end.

(iv) The  $\text{Ti}_{16}\text{Fe}_{16}$ ,  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_9$  (not shown) and  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$  calculations all give a pair of peaks for Ti and Fe, although their separation is not as great as that between the Ti and Ni peaks (see Fig. 6). The reason for the very small number of electrons at the Ti end, is again the depletion of the Ti levels. The hydrogens provide levels between the Ti and Fe bands, as well as enriching the Ti band. They also again have the effect of creating a “tail” at the low end of the energy scale and lowering  $E_{\text{MB}}$  drastically. It should be noted, however, that the partitioning of levels into Ti, H and Fe levels is far less straightforward than it was for the Ti-Ni-H alloys, since there is a much more gradual progression in relative amounts of Ti, H and Fe contributions to the MOs because the Coulomb integrals for Ti(3d) and Fe(3d) are much closer than those for Ti(3d) and Ni(3d). In fact, for the  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$  cluster, it was found to be very difficult to classify the levels in a meaningful manner, although the lower energy portion has predominantly Fe contributions, and the higher energy portion has predominantly Ti contributions.

(v) The  $\overline{\Delta E}$  values for  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_9$  (0.797 eV/atom) and  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$  (0.653 eV/atom) are again underestimated, and should really be slightly negative. (For example, for the FeTiH system,  $\overline{\Delta H}^0 = -0.145$  eV/atom [30].) See the further discussion in relation to Table 7.

(vi) It is clear from the  $\bar{q}_{\text{H}}$  values ( $-0.105$  for  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_9$  and  $-0.180$  for  $\text{Ti}_{16}\text{Fe}_{16}\text{H}_{32}$ ) that an anionic model with a slightly negative average partial charge on the hydrogens is favored again.

(vii) If the results presented here are compared with Gupta’s work<sup>3j,k</sup> on  $\beta$ -FeTiH, which used the augmented plane wave method and a non-self-consistent potential, and provided the first calculation of the electronic structure of an intermetallic

hydride, both certain similarities and certain differences can be seen. For example, while our calculations give a set of low-lying “tail” states with strong Fe and H bonding contributions, and equal in number to the number of hydrogens in the cluster, Gupta’s calculations give an even lower-lying group of states which is “detached” from the two-peak structure characteristic of the metal states. Both our results and Gupta’s results show that the lower energy portion of the metal bands has predominantly Fe contributions, and the higher energy portion has predominantly Ti contributions. On the other hand, while Gupta finds that the number of states at  $E_F$  increases substantially from FeTi to FeTiH, we find that the number of states at  $E_F$  (i.e., at the high-energy end of the histograms depicted in Fig. 6) decreases in going from the  $Ti_{16}Fe_{16}$  cluster to the  $Ti_{16}Fe_{16}H_{32}$  cluster. Although these comparisons are quite instructive, nevertheless, they are not conclusive since both sets of calculations used non-self-consistent computational techniques, and furthermore applied them on different hydrogenated phases of TiFe (Gupta on  $\beta$ -TiFeH and the present authors on  $\gamma$ -TiFeH<sub>2</sub>).

(4) Finally, Table 4 shows that  $CE(Ti_{18}Ni_{18}) < CE(Ti_{24}Ni_{12}) < CE(Ti_{16}Fe_{16})$ , and  $\overline{\Delta E}(Ti_{18}Ni_{18}H_{12}) < \overline{\Delta E}(Ti_{24}Ni_{12}H_{12}) < \overline{\Delta E}(Ti_{16}Fe_{16}H_n, n=9 \text{ or } 32)$ . In other words, the more stable the original binary alloy, the weaker is the tendency to form a hydride, that is, a less exothermic  $\overline{\Delta E}$  value is calculated, in agreement with Miedema’s model and the rule of reversed stability [31].

#### *Hole distribution and its relation to amount of hydrogen uptake*

Table 5 lists the hole types and their parameters, as discussed in Sect. 2. It should be noted that the approach outlined in the present work is more general than the method introduced in [22], since, when used in connection with the computer algorithm also described in Sect. 2, it provides a list of *all* the types of tetrahedral holes in the system, their statistical distributions, parameters, locations, and abundances as a function of adjustable cutoff distance  $r_c$ . All that is needed is the specification of the coordinates of the atoms constituting the cluster. No analytic work is involved, the procedure is completely automatic, takes a negligible amount of computer time, and *does not depend upon or require any type of crystalline symmetry*. The sizes of the lattice atoms automatically get considered, since they are among the determining factors of the atomic coordinates in any real or model structure. If desired, considerations of hole size in terms of volume, area or radius can be more explicitly included, by eliminating all holes smaller than specified cutoff values for these parameters.

For structures analogous to those examined in [22], the volume and area parameters provide a similar ordering in terms of size as the radii of the tetrahedral holes (compare the results for  $TiNi(B_2)$ ,  $TiCo(B_2)$ ) and a similar correlation between the stabilities of the metal hydrides and the sizes of the tetrahedral holes, while the “tetrahedrality” provides information about the amount of deviation of the hole shapes from that of a regular tetrahedron. The approach described here can also be compared with Westlake’s discussion (in an excellent recent review article) [6b] of numerous other attempts to correlate the observed

stabilities, stoichiometric compounds. It is pointed out in Westlake’s paper that he uses only a minimum of information to develop a ratio of stabilities for different compounds, and

It has been shown that the phases as a function of composition information about the system when the basic lattice undergoes a volume change and TiNi have a stoichiometric composition can undergo a change of composition in the smaller in TiFe, hydrogen by under different hydrogen positions among the sites a

#### *Amorphous materials*

Amorphous materials, their distribution around several centers on how irregular the crystalline  $Ti_2Ni$  rather than the theoretical addition, find a distribution of  $Ti_4$  sites at all.

Thus, under favorable conditions hydrogen into an amorphous phase as shown by Ovsyannikov may attribute this to (i) Amorphous materials analogous crystalline structures sizes larger, and to (ii) In addition, the amorphous phase found to be further (iii) Completely random for  $Ti_2Ni$ . (iii) Especially in being favorable

stabilities, stoichiometries and preferred hydrogen sites in hydrides of intermetallic compounds. In this review, several factors influencing stability are discussed, and it is pointed out that no single factor plays the dominant role in all systems. Westlake's paper also proposes a geometric model similar to ours in spirit that uses only a minimum hole radius (0.40 Å) and a minimum H-H distance (2.10 Å) to develop a rationale for the observed stoichiometries in hydrides of intermetallic compounds, and illustrates the model by using  $\text{LaNi}_5\text{H}_{6.5}$  as an example.

It has been shown, in an analysis of the hole densities in the TiNi and  $\text{Ti}_2\text{Ni}$  phases as a function of  $r_c$ , how this type of analysis can provide valuable information about the amount of hydrogen uptake by the material, especially when the basic lattice type does not change upon hydrogenation, but merely undergoes a volume expansion. The situation is less simple for materials which undergo a change of lattice type. For example, although the  $B_2$  phases of TiFe and TiNi have the same limiting hydrogen absorption capacity (up to stoichiometric compositions of TiFeH and TiNiH) for  $r_c = 2.0$  Å, the Ti-Fe system can undergo a change of lattice type and absorb H up to a limiting stoichiometry of  $\text{TiFeH}_2$ . In this case, although the holes in the original  $B_2$ -type lattice were smaller in TiFe, the material becomes capable of absorbing twice as much hydrogen by undergoing a transition and acquiring a new lattice type with definite hydrogen positions [20c], rather than a statistical distribution of the hydrogens among the sites available in the original lattice.

#### *Amorphous materials*

Amorphous materials are also amenable to this type of analysis [1]. For amorphous materials, since the atoms are not located at periodic lattice points, there will be distributions of types of tetrahedral holes, with parameter values centered around several central values and having standard deviations whose sizes depend on how irregular their structure is. For example, for an amorphous analog of the crystalline  $\text{Ti}_2\text{Ni}$  phase, we could expect to find a distribution of  $\text{Ti}_3\text{Ni}$  sites, rather than the three discrete types of  $\text{Ti}_3\text{Ni}$  sites listed in Table III. We may, in addition, find a distribution of  $\text{Ti}_4$  sites, while the crystalline  $\text{Ti}_2\text{Ni}$  phase has no  $\text{Ti}_4$  sites at all.

Thus, under favorable experimental conditions, it is possible to force more hydrogen into an amorphous material than into an analogous crystalline material, as shown by Ovshinsky et al. [32]. Following the analysis described above, we may attribute this improved performance in part to the following:

- (i) Amorphous materials generally have lower density and greater volume than analogous crystalline materials. This volume expansion makes their average hole sizes larger, and therefore the sites become more accommodating on the average. In addition, the average intersite distances increase, and thus more sites may be found to be further than a given value of  $r_c$  from one another.
- (ii) Completely new types of sites will appear, for example, possibly  $\text{Ti}_4$  sites for  $\text{Ti}_2\text{Ni}$ .
- (iii) Especially in cases where groups of holes are just below the threshold of being favorable for accommodating a hydrogen (either because of intersite

distance, size, or shape considerations), many more holes may become favorable for occupancy due to the statistical distribution putting some of these sites, all of which were just below the threshold of acceptability, among sites which can accommodate hydrogen [33].

(iv) By definition, amorphous materials are metastable states, which are not absolute minima on the potential surface. When there is a crystalline analog, this analog would be the true minimum. Therefore, if the rule of reversed stability [31] holds, it would be predicted that the amorphous material, which is less stable, will have a stronger tendency to absorb hydrogen.

For the recently discussed case of TiCu [4f], a combination of these factors may be responsible for the fact that the limiting composition is TiCuH for crystalline TiCu and TiCuH<sub>1.4</sub> for amorphous TiCu. This is consistent with the view that the lack of a periodic lattice structure in amorphous materials should be considered as an extra degree of freedom which can be manipulated to give "tailor-made" synthetic materials with desired properties, rather than as a shortcoming [34]. It is likely that when the preparation conditions are optimized, many amorphous alloys will be found with better reversible hydrogen storage properties than the best known crystalline or microcrystalline systems. Most of these might not even have a crystalline analog [35].

#### Exothermicities

Another problem that had to be addressed was whether the preference of H for certain types of sites (for example the tetrahedral Ti<sub>4</sub> sites in crystalline TiCu) was related to the intrinsically greater stability of a hydrogen located in such a site, or to more general geometric and electronic considerations. To gain some insight into this problem, calculations were carried out on several Ti<sub>18</sub>Ni<sub>18</sub>H, Ti<sub>24</sub>Ni<sub>12</sub>H, and Ti<sub>16</sub>Cu<sub>16</sub>H clusters, and some of the results are presented in Table 6. Note, from the  $\Delta E$  column, that there is *no* correlation between the stability of a single hydrogen in a given type of hole, and the site preference of the hydrogens when a large number of them is present. Two of the most striking examples are provided by the Ti<sub>18</sub>Ni<sub>18</sub>H and the Ti<sub>16</sub>Cu<sub>16</sub>H calculations. For the former,  $\Delta E(\text{Ti}_2\text{Ni}_4 \text{ site}) \ll \Delta E(\text{Ti}_2\text{Ni}_2)$ , while the tetrahedral Ti<sub>2</sub>Ni<sub>2</sub> site is known to be preferred in TiNiH. For the latter,  $\Delta E(\text{Ti}_2\text{Cu}_2) < (\Delta E(\text{TiCu}_3) \leq \Delta E(\text{Cu}_4)) < \Delta E(\text{Ti}_3\text{Cu}) < \Delta E(\text{Ti}_4)$ , i.e.,  $\Delta E$  is *least* negative for the Ti<sub>4</sub> site which is favored in TiCuH. Similarly, for the Ti<sub>24</sub>Ni<sub>12</sub>H clusters,  $\Delta E$  is generally less negative if more Ti atoms are at the vertices of the tetrahedron.

Although these results may appear surprising at first sight, they are not unexpected at all if we remember that the gas-phase diatomic bond strengths of Ti-H, Ni-H, and Cu-H bonds are 38, 69 and 67 kcal/mol respectively [36]. In other words, the best exothermic hydrogen absorber among these three transition metals, titanium, which can reach a stoichiometry of TiH<sub>2</sub>, when faced with an H atom on a one-to-one basis, bonds far more weakly to H than either nickel which can only form a limiting stoichiometry of NiH in the bulk, or copper which does not even absorb hydrogen exothermically! In our clusters, when only one hydrogen is placed in a tetrahedral or octahedral hole, its interaction with its nearest

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neighbors dominates, making the actual M-H bond energies an important factor. This is, however, tempered by the presence of the rest of the lattice, and in particular by the sizes and shapes of the holes involved, so that, for example, the tiny and misshaped Cu<sub>4</sub> hole (see the parameter values in Table 5) gives a less negative  $\Delta E$  than the Ti<sub>2</sub>Cu<sub>2</sub> hole, although the Cu-H bond energy is much greater than the Ti-H bond energy. However, as more hydrogens are added, hydrogen starts acting more and more like an alloying element, and H-H interactions also become increasingly important. Thus, the spatial distribution of allowed sites of different types, the H-H interactions created by these spatial distributions, and the electronic interactions which result, are of extreme importance in determining the favored types of holes. These long-range distribution effects seem to be the true reason why in general larger holes are favored, rather than their intrinsically greater stability on accommodating an individual hydrogen.

Table 6 also lists the atomic charge acquired by hydrogen ( $q_H$ ), which is again negative for all 13 calculations, in accordance with a model where the hydrogens become partially anionic. Furthermore, the actual  $q_H$  and  $\bar{q}_H$  values should be even more negative than those listed in Tables 4 and 6, because of the aforementioned underestimation of the effect of hydrogens in our Extended Hückel calculations. In fact, the following simple considerations suggest that the hydrogens are likely to be partially anionic on the average in *all* transition metal hydrides: for all transition metals, the  $ns$  ( $n = 4, 5, \text{ or } 6$ ) valence shell atomic orbital lies above the singly occupied H(1s) orbital. Thus, even for those transition metal atoms whose Pauling electronegativity [29] is at least equal to that of H (such as Pd), there will be low-lying MO's with predominantly H contributions, to which some net electron density will inevitably flow. This will result in a negative  $q_H$  in the Mulliken Population Analysis, although individual sites might be found where a hydrogen would have a slightly positive net charge. Furthermore, if a protonic model were to hold, the anti-bonding H-H interactions would not become important limiters of the amount of hydrogen uptake as rapidly as they do [3e], and at least some transition metal hydrides with much higher hydrogen storage densities and  $r_c \ll 2.0 \text{ \AA}$  would have been possible.

Table 7 presents a comparison of  $\overline{\Delta E}$  values obtained by three different methods, as described in the footnotes. The (A-B) column shows that when a large number of hydrogens is present, the energy gain per hydrogen becomes less. Thus, the Ti<sub>18</sub>Ni<sub>18</sub>H<sub>12</sub> and Ti<sub>24</sub>Ni<sub>12</sub>H<sub>12</sub> calculations give  $\overline{\Delta E}$  values which are less negative by 0.35 to 0.45 eV/hydrogen than those which would be obtained by filling a set of non-interacting sites, each assumed to contribute the amount given in Table 6 to the total energy. This result is consistent with the fact that as more hydrogens are added to a system, it gradually becomes more difficult and less energetically favored to add additional hydrogens, until a limiting amount is reached. This result is also consistent with the observation that in removing the hydrogens, it gradually becomes more difficult to remove any additional hydrogens, especially the last few remaining ones.

The (A-C) column shows the effect of underestimating the exothermicity of hydrogen absorption due to the fact that the basis set allows two contracted

orbitals for the description of the transition metal 3d orbital, while only one for H(1s). When a single orbital exponent is used for all orbitals, the reactions consistently become more exothermic by about 0.5 eV/hydrogen.

#### 4. Conclusions

Consideration of the sizes and shapes and spatial distribution of hole sites using survey techniques, coupled with approximate electronic structure calculations on large numbers of selected structures, is clearly a fruitful approach to the study of hydrogen storage in metal hydrides. One obvious generalization would be to implement the same type of algorithmic surveying procedure for distorted octahedral sites which can be defined and characterized by parameters in a manner similar to that used for tetrahedral sites. Unfortunately, time-dependent processes such as diffusion are much more difficult to investigate by any of these techniques, but the insights obtained are likely to be valuable in approaching these problems as well.

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