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Band structure and chemical bonding in the hydrogen solid solution of Ti_3P

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Abstract

Band structure calculations have been made for the Ti_3P–H solid solution system using the LMTO-ASA method. Hydrogen was placed in eight different tetrahedral sites in the Ti_3P structure and the differences in stability and chemical bonding for the sites were deduced from calculated total energies and electronic densities of states. A major factor influencing the stabilities of the tetrahedral sites are the Ti–H distances: hydrogen prefer those tetrahedral sites surrounded by a metal atoms at shorter distances, i.e. those sites surrounded by metal atoms with stronger metal–metal bonds.

Keywords: Ti_3P; Hydrogen; Band structure; Chemical bonding

1. Introduction

Numerous compounds between transition metals and non-metals can accommodate hydrogen atoms in interstitial solid solutions or form hydride phases. The crystal structures of these phases are often complex and there are several types of interstice that might conceivably accommodate hydrogen atoms. The distribution of hydrogen atoms on interstitial sites in the structures appears to be mainly governed by the size and shape of the surrounding metal atom polyhedron, as well as distances to the nearest non-metal and hydrogen neighbours: it has been found that the hydrogen atoms are always more than 2 Å apart and that sites occupied by hydrogen are those most distant from the p-element [1–3].

Hydrogen solubility measurements have shown that Ti_3P dissolves appreciable amounts of hydrogen. Ti_3P has an extensive region of solid solution up to 1.2 hydrogen per formula unit and forms a hydride phase with 2.2–2.4 hydrogens per formula unit [4–6]. Ti_3P crystallizes in a tetragonal structure [7] with various tetrahedral interstices between the titanium atoms. In a neutron diffraction investigation of the solid solution of deuterium in Ti_3P the deuterium atoms were located in two types of tetrahedral interstice [8] with different occupancies. Qualitatively, this condition has been explained by considering that the size of the tetrahedron accommodating the higher amount of deuterium is somewhat larger than the other, and that the deuterium atoms occupying the smaller tetrahedron have a larger number of phosphorus neighbours in their near surroundings. Previously, the band structures and total energies have been calculated for the solid solution of hydrogen in Ti_3P [9] with hydrogen atoms in the two tetrahedral sites found experimentally. In addition to the tetrahedral holes already mentioned, there are 36 tetrahedral interstices per unit cell. These correspond to six crystallographically non-equivalent positions, for which no hydrogen occupation has been reported. The present investigation was started in order to obtain a quantitative understanding of the ability of hydrogen to occupy different tetrahedral sites in this system. In this work all tetrahedral sites have been investigated and the precision of the calculations has been increased. An investigation of the Ti_3P–H hydride system [10] is in progress.

2. Calculations

The computational method used for the band structure calculations was the linear muffin tin orbital–atomic sphere approximation (LMTO–ASA) method [11] in the scalar-relativistic formulation. The calculations were performed self-consistently and the com-

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bined correction terms were included. The computer programs used were modified versions of these developed by Skriver [12]. Band structures and total energies were calculated for pure Ti_3P and eight different solid solutions in which one crystallographic position at a time was completely filled with hydrogen. In addition, calculations were performed with the most preferable position (H1) half-filled and for the combination of site H1 with one of the seven sites filled at a time. The same host Ti_3P structure [7] was used in all calculations. The unit cell dimensions for all structures were varied uniformly and the theoretical sizes of the unit cells were obtained from the minimum in the total valence electron energies. The coordinates for the hydrogen atoms were chosen so that the Ti–H distances were equal, except for H1 and H5a where the coordinates found experimentally were used [8].

An important assumption in the atomic sphere approximation is that the wavefunctions are independent of the radius ratios between the various atoms. In practice, the wavefunctions and the total energy are weakly dependent on the chosen radius ratio. To reduce these effects the total energy of Ti_3P was minimized by varying the radius ratio. Close to the minimum the total energy is independent of this quantity. The value of the radius ratio r_{Ti}/r_P at the energy minimum was found to be 1.11 and was subsequently used in all calculations. This value resulted in almost neutral atomic spheres (0.04–0.08 excess electrons on titanium) in Ti_3P. A similar procedure was applied to find the radius ratio r_H/r_P for the solid solutions. In these cases the total energy was always slightly decreasing with increasing r_H/r_P ratio. However, the total energy decrease per hydrogen atom was almost identical for all solid solutions. Energy differences between solid solutions are therefore independent of r_H/r_P ratio, though the values of the total energies and corresponding heats of formations are dependent on the actual ratio. A value of 0.525 for r_H/r_P was chosen because this results in essentially identical volumes for titanium and phosphorus atoms in Ti_3P and in the solid solutions, which simplifies the comparison between various calculated quantities. The value chosen results in about 0.8 electrons in the hydrogen spheres due to charge transfer to the surrounding titanium atoms. The calculations were carried out for 63 *k*-points in 1/16 of the Brillouin zone and orbitals of *s*, *p*, and *d* character were considered. The crystallographic parameters for the Ti_3P–H system are summarized in Table 1. Enthalpies of formation from $Ti_3P(s)$ and $H_2(g)$ have been calculated using a value of 432 kJ mol^{-1} [13] for the dissociation of $H_2(g)$.

Table 1
Structural parameters used in calculations

Atom	Position	*x*	*y*	*z*
Ti1	8g	0.1661	0.6428	0.7153
Ti2	8g	0.1101	0.2785	0.5295
Ti3	8g	0.0696	0.5334	0.2407
P	8g	0.0440	0.2919	0.0354
H1	4e	3/4	1/4	0.0340
H2	8g	0.0100	0.5941	0.5594
H3a	8g	0.6620	0.3191	0.4144
H3b	8g	0.6670	0.3151	0.1484
H4a	2a	1/4	1/4	1/4
H4b	2b	1/4	1/4	3/4
H5a	8g	0.0620	0.7730	0.5140
H5b	8g	0.0713	0.6962	0.4167

Space group $P4_2/n$ (No. 86), origin at $\bar{1}$.
Unit cell dimensions for Ti_3P: $a = 9.9592$, $c = 4.9869$ Å.

The ASA model with its focus on the local description of the wavefunctions within atomic spheres and the frozen core approximation [14] makes it possible to express the total valence energy E_{tot} as a sum of the partial energy contributions E_i from atoms of type *i* and a Madelung term E_{Mad}:

$$E_{tot} = \sum n_i E_i + E_{Mad}$$

where

$$E_i = \int N_i \cdot E \, dE + E_i^c$$

with n_i the number of atoms of type *i* and N_i the partial electronic densities of state of atoms of type *i*. E_i^c comprises the exchange and correlation terms and was obtained using the parameterisation of von Barth and Hedin [15]. The electronic densities of state were calculated using the tetrahedron method [16]. In the following the partial atomic energies are used for a discussion of the chemical bonding and the stability of the solid solutions.

3. Results and discussion

A projection of the Ti_3P structure along the *c*-axis is shown in Fig. 1. Figs. 2 and 3 show the total densities of states for pure Ti_3P and the eight hydrogen sites. In Fig. 4 the partial electronic densities of states for the titanium and phosphorus atoms in Ti_3P are shown.

The energy levels for the valence electrons in Ti_3P can be separated into three main regions, see Figs. 2–4. At −0.8 Ryd below the Fermi level there is a narrow band which consists of orbitals of phosphorus *s* character to 70%. This low-lying band is insensitive to the formation of the hydrogen solutions and is not considered further. In the energy range −0.43 to −0.20 Ryd the densities of states mainly correspond to Ti–P bonding. This band consists of phosphorus *p*-like orbitals and approximately equal amounts of the *s*-, *p*-, and *d*-like orbitals of titanium. Below the Fermi

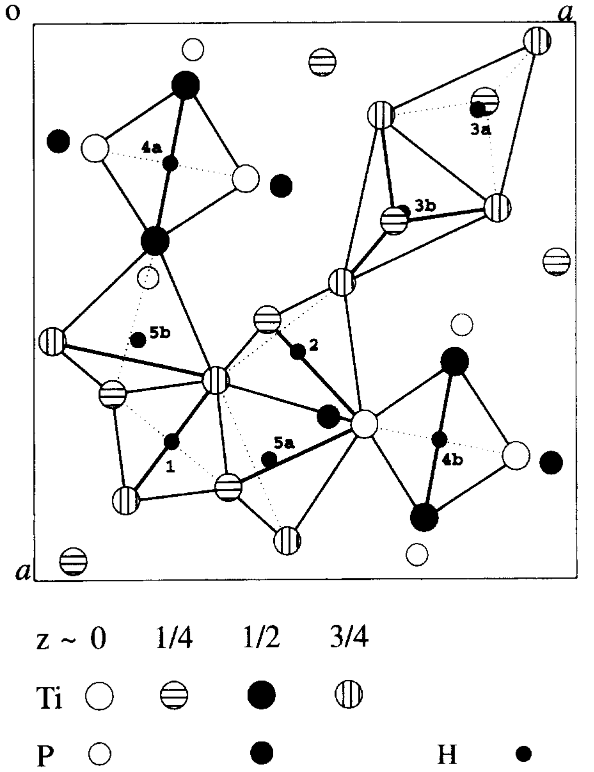

Fig. 1. Projection of the Ti_3P structure along the c-axis showing the eight different hydrogen sites and their surroundings.

level the titanium d character dominates and comprises the Ti–Ti bonding. The solution of hydrogen gives rise to an additional band below the Ti–P bonding band, consisting of hydrogen s-like orbitals overlapping with orbitals of s-, p-, and d-character of titanium and orbitals of p-character of phosphorus. The most important aspect for the bonding of hydrogen is the overlap of state densities in the H–Ti–P band and the changes in state densities in the other energy intervals caused by the formation of this new band. Values of integrated number of states of all atomic positions and orbital characters are listed in Table 2 for pure Ti_3P together with changes in these quantities on formation of the hydrogen solid solutions.

3.1. Ti_3P

The number of titanium and phosphorus neighbours is different for the three titanium positions. All Ti–P bond distances are within the range 2.49 to 2.63 Å, but Ti1 has two, Ti2 four and Ti3 three phosphorus neighbours (Table 3). The Ti–Ti distances vary over a wide range and the number of titanium neighbours within 3.4 Å is 12 for Ti1, 8 for Ti2 and 10 for Ti3. The metal–non-metal interaction increases in the series Ti1 to Ti3 to Ti2, while the metal–metal interaction varies in the opposite direction. This results in an increase in the partial densities of states and the integrated number of states for titanium atoms in the Ti–P bonding interval and a corresponding decrease in the metal–metal bonding band on going from Ti1 to Ti3 to Ti2. In this sequence the densities of states are shifted towards lower energies, resulting in a decrease in partial energies of the titanium atoms, see Table 4. The electrons on the Ti2 atoms are thus more effectively involved in bonding than those on Ti1. Ti3 takes an intermediate position. The influence of these conditions on the stability of the various solid solutions is discussed in the following section.

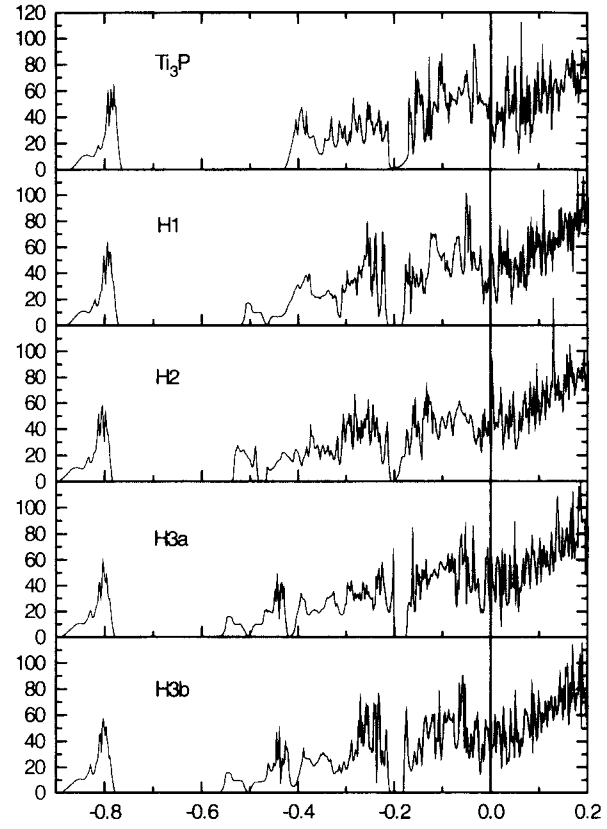

Fig. 2. Total densities of states (DOS) for Ti_3P and the four solid solutions H1 to H3b. The Fermi level has been shifted to zero and the energy unit is Rydberg. The DOS is given in units of number of states per formula unit and Rydberg.

3.2. Ti_3P–H

3.2.1. General changes in the DOS

The formation of the bonding to hydrogen can be described as a transfer of titanium electrons from orbitals of higher energy to those of lower energy. The changes in state densities depend on the character of the orbital. The major component in the bonding to hydrogen is s-like titanium orbitals which move from the Ti–P band to the H–Ti–P band. Titanium p-like orbitals are shifted from the Ti–Ti band to both the H–Ti–P and the Ti–P band. Finally, there is a transfer

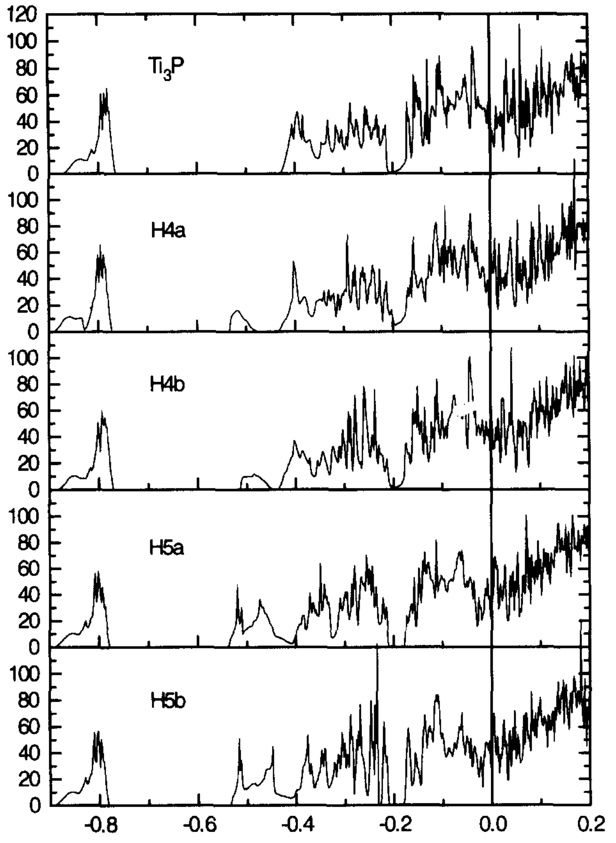

Fig. 3. Total densities of states (DOS) for Ti_3P and the four solid solutions H4a to H5b. The Fermi level has been shifted to zero and the energy unit is Rydberg. The DOS is given in units of number of states per formula unit and Rydberg.

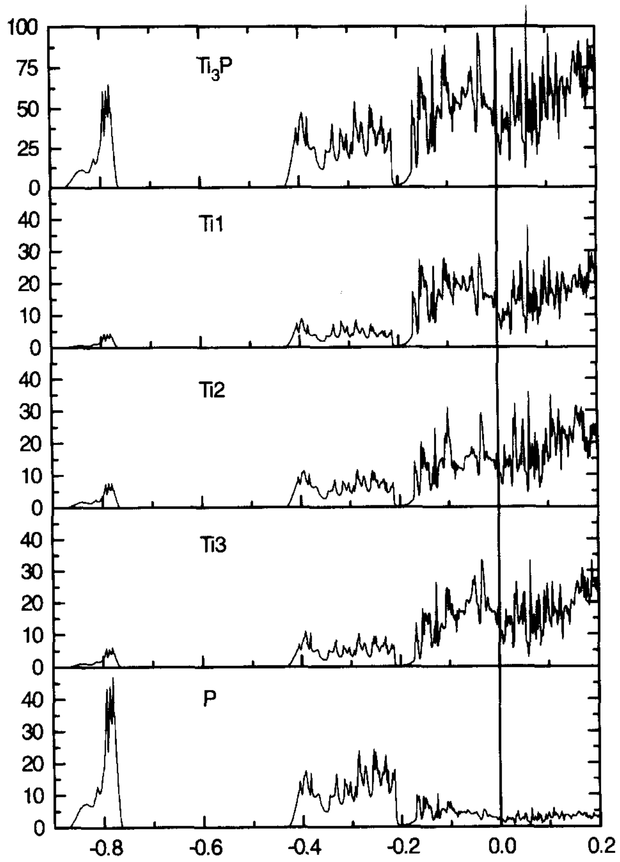

Fig. 4. Total and atomic densities of states (DOS) for Ti_3P. The Fermi level has been shifted to zero and the energy unit is Rydberg. The DOS is given in units of number of states per formula unit and Rydberg.

of titanium *d*-like electrons from the Ti–Ti band to the Ti–P band and some minor transfer to the H–Ti–P band. In all, this means that the number of electrons in the Ti–Ti band is decreased. The formation of bonds to hydrogen takes place at the expense of a weakening of metal–metal bonds. A shift of phosphorus *p*-like orbitals from the Ti–Ti band to the H–Ti–P band can also be noted. These types of change occur for all eight sites, although different atoms are affected differently, see Table 2. The Fermi level is shifted to higher energies as a result of the charge transfer from the hydrogen to the titanium atoms, see Table 4.

3.2.2. *Size of the metal polyhedra*

The change in total energy on hydrogen insertion into the Ti_3P structure can be separated into three different contributions. Namely, (i) the energy of the hydrogen atoms themselves contribute with an energy close to −1 Ryd per atom, (ii) charge transfer from the hydrogen atoms to the nearest titanium atoms (iii) the Madelung energy caused by the charge transfers between the different atoms. These changes in partial atomic energy are given in Table 4. For Ti–H bond distances around 1.85 Å the energy per bond can be identified as approximately 60 mRyd. For bond distances close to 2.0 Å the bond energy decreases to 40 mRyd. Atoms not closest neighbour to hydrogen have energy changes close to zero. The bond energy thus increases with decreasing bond length, but obviously there must be a maximum bond energy at some distance. The shortest Ti–H bond distances in these structures are 1.80 Å and there are no tetrahedral interstices with titanium atoms at shorter distances.

3.2.3. *The H–P distance*

The most stable site, H1, has the longest H–P distances while the least stable site, H4a, has the shortest. All other sites are intermediate in stability as well as H–P distance, Tables 3 and 4. By comparing the stability for the sites H2, H3a, H3b, H4a, H4b, H5a and H5b, it appears that the stability is not a simple function of H–P distance. H2 and H3a, for instance, have almost the same H–P distance but H2 is the second most stable site while H3a is much less stable. On comparing sites having the same surrounding atoms, H3a with H3b, H4a with H4b, and H5a with H5b, the stabilities seem to be a function of H–P distance, however, H5a and H5b have almost the same

Table 2
The number of states (NOS) in Ti_3P (top) corresponding to the four bonding intervals discussed in the text and the changes in NOS (Ps band omitted) on forming the solid solutions

Ti_3P		Ps	H	Ti–P	Ti–Ti
Ti1	s	0.05	0.00	0.35	0.16
	p	0.05	0.00	0.26	0.50
	d	0.04	0.00	0.31	2.31
Ti2	s	0.09	0.00	0.34	0.11
	p	0.10	0.00	0.38	0.35
	d	0.08	0.00	0.66	2.00
Ti3	s	0.06	0.00	0.34	0.16
	p	0.07	0.00	0.31	0.46
	d	0.06	0.00	0.48	2.15
P	s	1.40	0.00	0.04	0.01
	p	0.00	0.00	2.51	0.48
	d	0.00	0.00	0.03	0.31

		H	Ti–P	Ti–Ti	H	Ti–P	Ti–Ti	H	Ti–P	Ti–Ti	H	Ti–P	Ti–Ti
Ti_3PH_x		H1			H2			H3a			H3b		
Ti1	s	0.23	−0.20	−0.06	0.18	−0.18	−0.02	0.26	−0.23	−0.07	0.26	−0.24	−0.07
	p	0.12	0.07	−0.12	0.09	−0.01	−0.04	0.21	0.04	−0.17	0.21	0.06	−0.18
	d	0.10	0.25	−0.23	0.10	0.11	−0.18	0.23	0.30	−0.38	0.24	0.33	−0.38
Ti2	s	0.05	−0.05	−0.01	0.20	−0.19	−0.04	0.08	−0.08	−0.02	0.09	−0.08	−0.01
	p	0.02	−0.01	−0.01	0.11	−0.01	−0.08	0.05	−0.02	−0.04	0.05	−0.03	−0.03
	d	0.03	−0.02	0.00	0.14	0.07	−0.14	0.06	0.02	−0.06	0.06	−0.02	−0.02
Ti3	s	0.05	−0.05	−0.01	0.20	−0.17	−0.09	0.16	−0.16	−0.02	0.17	−0.17	−0.02
	p	0.03	−0.03	0.00	0.15	0.04	−0.14	0.08	−0.02	−0.04	0.08	0.00	−0.05
	d	0.03	−0.04	0.00	0.19	0.21	−0.25	0.09	0.08	−0.12	0.10	0.07	−0.11
P	s	0.02	−0.01	0.00	0.04	−0.02	0.00	0.04	−0.01	0.00	0.04	−0.01	0.00
	p	0.16	−0.09	−0.08	0.38	−0.38	−0.07	0.29	−0.17	−0.15	0.31	−0.22	−0.13
	d	0.00	0.00	−0.01	0.01	0.02	−0.02	0.01	0.01	−0.03	0.01	0.01	−0.03
H	s	0.18	0.17	0.00	0.40	0.29	0.03	0.44	0.23	0.05	0.41	0.27	0.00
	p	0.00	0.00	0.02	0.00	0.01	0.04	0.00	0.01	0.05	0.00	0.01	0.03
	d	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00

		H4a			H4b			H5a			H5b		
Ti1	s	0.02	−0.01	−0.01	0.02	−0.01	−0.01	0.23	−0.22	−0.04	0.23	−0.22	−0.05
	p	0.01	0.01	−0.02	0.01	0.00	−0.01	0.16	0.04	−0.14	0.16	0.06	−0.17
	d	0.01	0.02	−0.03	0.01	−0.01	0.00	0.15	0.20	−0.22	0.16	0.20	−0.24
Ti2	s	0.04	−0.05	0.00	0.09	−0.10	−0.01	0.16	−0.15	−0.04	0.17	−0.16	−0.04
	p	0.05	−0.02	−0.02	0.07	0.01	−0.07	0.10	0.01	−0.09	0.10	0.00	−0.09
	d	0.07	0.07	−0.09	0.09	0.14	−0.15	0.12	0.10	−0.15	0.12	0.10	−0.15
Ti3	s	0.02	0.00	−0.02	0.01	−0.01	0.00	0.15	−0.15	−0.02	0.17	−0.17	−0.03
	p	0.01	0.00	0.00	0.01	0.00	−0.01	0.09	−0.03	−0.05	0.09	0.00	−0.08
	d	0.01	0.00	−0.01	0.01	0.00	−0.01	0.10	0.07	−0.11	0.11	0.04	−0.08
P	s	0.03	0.00	0.00	0.01	−0.01	0.00	0.04	−0.02	0.00	0.04	−0.02	0.00
	p	0.11	−0.14	0.03	0.08	−0.10	0.01	0.26	−0.14	−0.15	0.29	−0.20	−0.13
	d	0.01	0.01	−0.02	0.00	0.01	−0.01	0.01	0.01	−0.03	0.01	0.01	−0.02
H	s	0.11	0.04	0.01	0.11	0.06	0.01	0.46	0.24	0.00	0.43	0.26	0.04
	p	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.01	0.04	0.00	0.01	0.05
	d	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01

distance and stability, H3a and H3b have different H–P distances, longer for H3b which is the most stable, and H4a and H4b have very different distances, H4a the shortest and H4b is the most stable. When the local arrangement is the same the distances to neighbouring phosphorus atoms may decide which site is the most stable one, but when comparing sites with different surrounding atoms the stabilities are not a function of H–P distances alone. Therefore, it seems appropriate to say that it is the local metal surrounding that will decide the stability order for the different sites rather than distances to phosphorus which however, may play a secondary role in determining the stabilities. An increasing H–P distance also indirectly leads to increasing Ti–P distances for the nearest titanium neighbours. There is no clear dependence between Ti–H bond energy and Ti–P distance: for the series H5a to H5b to H2 the Ti–H bond energy increases as the Ti–P distances decrease, while on going from H3b to H3a the bond energy decreases.

Table 3
Interatomic distances shorter than 3.4 Å for titanium and phosphorus in Ti_3P and shorter than 3.0 Å for the solid solutions

Ti1–P	2.52	P–Ti3	2.49	H4A–4Ti2	2.00
P	2.57	Ti1	2.52	4P	2.36
Ti1	2.71	Ti2	2.55		
Ti3	2.78	Ti2	2.55	H4B–4Ti2	1.80
Ti3	2.94	Ti2	2.55	4P	2.54
Ti3	3.00	Ti1	2.57		
Ti2	3.04	Ti3	2.60	H5a–Ti1	1.82
Ti3	3.08	Ti2	2.61	Ti2	1.82
Ti2	3.11	Ti3	2.63	Ti1	1.96
4Ti1	3.15			Ti3	1.97
Ti3	3.16	H1–2Ti1	1.85	P	2.59
		2Ti1	1.86	Ti3	2.78
Ti2–P	2.55	2H1	2.51		
P	2.55	2P	2.97	H5b–Ti1	1.86
P	2.55			Ti1	1.86
P	2.61	H2–Ti3	1.82	Ti3	1.86
Ti3	2.83	Ti2	1.82	Ti2	1.86
Ti2	2.84	Ti3	1.82	P	2.56
Ti3	2.86	Ti1	1.82	Ti3	2.89
Ti3	2.95	H2	2.00	P	3.00
2Ti2	2.98	P	2.40		
Ti1	3.04				
Ti1	3.11	H3a–Ti3	1.88		
		Ti1	1.88		
Ti3–P	2.49	Ti1	1.89		
P	2.60	Ti1	1.89		
P	2.63	H3a	2.25		
Ti1	2.78	P	2.39		
Ti2	2.83	Ti2	2.97		
Ti3	2.85	4H3a	2.98		
Ti2	2.86				
Ti1	2.94	H3b–Ti1	1.86		
Ti2	2.95	Ti3	1.86		
Ti1	3.00	Ti1	1.86		
Ti3	3.01	Ti1	1.86		
Ti1	3.08	H3b	2.12		
Ti1	3.16	P	2.45		
		4H3b	2.93		

3.2.4. The H–H distance

The effect of the H–H distance has been investigated in two different ways. In the first, site H1 was half-filled in the second, site H1 was combined with each of the other seven sites, one at a time.

The partial densities of states for Ti1 and H1 with H1 half-filled and fully occupied are shown in Fig. 5. The state densities are quite different for these atoms in the two structures but result in the same change in total energy per hydrogen atom. The H1–H1 distances are 2.5 and 5.0 Å for the fully occupied and half-filled sites respectively. The H–H distance does not affect the energy per hydrogen atom when the distances are large.

All combinations of H1 with other sites are stable with respect to Ti_3P and $H_2(g)$, but the combinations H1 + H3a and H1 + H3b produce a considerable in-

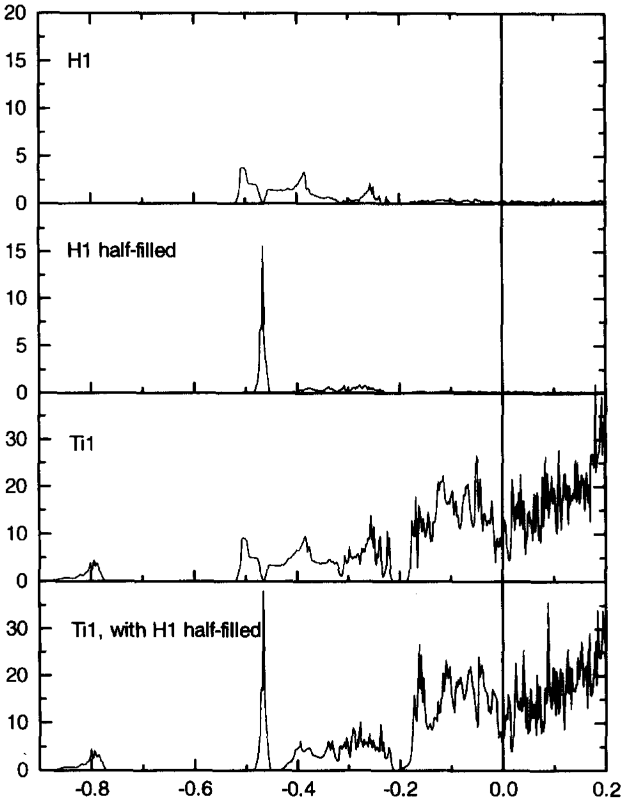

Fig. 5. Atomic densities of state (DOS) for Ti1 and H1 in the two structures $Ti_3PH1_{0.5}$ and $Ti_3PH1_{0.25}$. The Fermi level has been shifted to zero and the energy unit is Rydberg. The DOS is given in units of number of states per formula unit and Rydberg.

Table 4
Partial atomic energies in Ti_3P and differences in energy for the atoms on forming the solid solutions. The energies are given per atom and the energy unit is mRydberg. The three columns to the right give the Fermi level and total energies per formula unit (in Rydberg) and the calculated heat of formation per hydrogen (in kilojoules per mole)

Site	Ti1	Ti2	Ti3	P	H	Fermi level	E_{tot}	ΔH_f
O	−7875	−7954	−7902	−13186	–	0.6973	−36.9344	–
H1	−134	10	−1	−7	−951	0.7242	−37.5638	−122
H2	−87	−56	−137	−2	−928	0.7506	−38.1923	−121
H3a	−173	19	−75	−16	−948	0.7460	−38.1697	−90
H3b	−182	17	−78	−14	−946	0.7448	−38.1828	−108
H4a	−2	−41	−5	−1	−924	0.7182	−37.2210	26
H4b	−1	−67	−5	2	−912	0.7154	−37.2474	−113
H5a	−126	−72	−38	−25	−948	0.7502	−38.1795	−104
H5b	−132	−51	−63	−21	−944	0.7505	−38.1834	−109

Table 5
The table has been constructed by taking the differences in partial energy for the calculations of two sites filled and the sum of energies of the calculations in which only one site was filled (e.g. H(1 + 2) − (H1 + H2)). The energies are given per atom and the energy unit is mRydberg. The three columns to the right give the Fermi level and total energies per formula unit (in Rydberg) and the calculated heat of formation per hydrogen (in kilojoules per mole)

Site	Ti1	Ti2	Ti3	P	H1	H	Fermi level	E_{tot}	ΔH_f
H1 + 2	23	79	38	6	3	−7	0.7623	−38.8158	−116
H1 + 3a	50	71	28	16	23	14	0.7833	−38.7573	−65
H1 + 3b	51	70	31	19	21	11	0.7877	−38.7687	−75
H1 + 4a	−8	79	36	14	11	7	0.7374	−37.8510	−74
H1 + 4b	−2	79	37	14	9	−2	0.7365	−37.8726	−111
H1 + 5a	21	83	39	9	6	0	0.7660	−38.8005	−102
H1 + 5b	33	79	36	7	3	−1	0.7676	−38.8025	−104

crease in energy compared with the sum of the cases in which one site is occupied, see Table 5. The distances H1–H3a and H1–H3b are 1.28 and 1.21 Å respectively, which are obviously unrealistically short. The other H1–H distances are 2.93, 1.93 and 1.90 Å to H2, H5a and H5b respectively, and the distances to H4a and H4b are well over 5 Å in both cases. It can be concluded that H–H distances down to 1.90 Å do not affect the stability in any drastic way.

From the minimum in total electron energy a volume expansion of 1.9 Å^3 per hydrogen atom was calculated for all sites. This is close to the experimental value of 1.7–1.8 Å^3 per hydrogen (deuterium) [8].

4. Conclusions

The effect on stability for different hydrogen sites in Ti_3P has been discussed from the point of view of size of interstitial sites, H–P, Ti–H and H–H distances. No single factor determining which site is preferred by hydrogen has been found. Instead, the whole system is quite complex with several different factors influencing the final distribution between the sites.

A general trend, however, is noted. By comparing the densities of states corresponding to the eight solid solution structures the following observations can be made. A major effect is the change in densities of state from higher to lower energies. The shift towards lower energy is largest in the case of H1 and smallest for H4a. For H1, all four of the surrounding titanium atoms are less strongly bound to neighbouring phosphorus atoms than the four titanium atoms surrounding H4a, i.e. the titanium atoms surrounding H1 have stronger metal–metal bonds. The other six sites take intermediate positions in stability as well as in distance to neighbouring phosphorus atoms. This means that hydrogen will prefer those tetrahedral sites surrounded by metal atoms at shorter distances, i.e. those sites surrounded by metal atoms with stronger metal–metal bonds. In general, this is equivalent to those sites most distant from the non-metallic element, in agreement with experimental results.

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