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Application of a geometric model to the hydrides of FeTi

D. G. WESTLAKE
Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

Criteria of hole size and hydrogen–hydrogen distance have been used to develop rationales for the observed stoichiometries and preferred hydrogen sites in the α-, β_1-, β_2- and γ-phases of the FeTi–H system. For these four phases of $FeTiH_n$, the respective values of n approximate 0, 1, 1.4 and 2. Structures and position vectors for the metal atoms were obtained from the literature for use in calculating the radii of the various interstices and the intersite distances in each phase. The model does not allow one to predict the nature of the structural transformations that occur in this system with increasing hydrogen concentrations, but knowing the metal atom positions in each phase does allow one to predict the preferred sites for hydrogen atoms. Most of the occupied interstices are octahedral sites coordinated by four titantium atoms and two iron atoms, but the reported occupation of a pseudo-octahedral site in FeTiD is explained within the framework of the model by allowing a deuterium atom to occupy a hexahedral interstice coordinated by three titanium atoms and two iron atoms. For $n \simeq 2$, i.e. for the γ phase, geometric considerations allow the correct prediction of some hydrogen atoms situated in octahedral interstices coordinated by four iron atoms and two titanium atoms. Occupation of such a site could not have been predicted by considering the relative affinities of the metals titanium and iron for hydrogen.

1. Introduction

One of the most promising of the intermetallic compounds that have been considered as potential storage media for hydrogen is FeTi [1]. Hydride phases $FeTiH_n$ have been reported for the following approximate values of n: 1, 1.4 and 2. For each of these phases and for the α-phase, there are neutron diffraction results that have been interpreted [2–7] to mean that hydrogen (deuterium) atoms occupy octahedral interstices. Thompson *et al.* [3] reported that, in FeTiD, the deuterium atoms prefer sites in which their nearest neighbours are iron atoms, a fact they considered surprising because elemental iron does not form a hydride.

Recently, we have developed a geometric model that allows the rationalization of preferred hydrogen sites and stoichiometries for a variety of metals and intermetallic compounds [8–12]. Two criteria used in the model are that an interstice in a stable hydride cannot be occupied unless it can accommodate a sphere of radius 0.040 nm, and that two interstices cannot be occupied simultaneously unless they are at least 0.210 nm apart. In the present work, we have applied the same model to FeTi and its hydrides (deuterides) in an attempt to understand the reported stoichiometries and their respective site occupancies.

2. Calculations

In the geometric model, the hole radius, r_h, is taken to be the radius of the largest sphere that can be accommodated in a given interstice. For tetrahedral holes, we solve a set of four equations that, together, state that the sphere is tangent to the spherical surfaces of all four coordinating metal atoms. The four unknowns are the radius of the sphere and the position parameters for the

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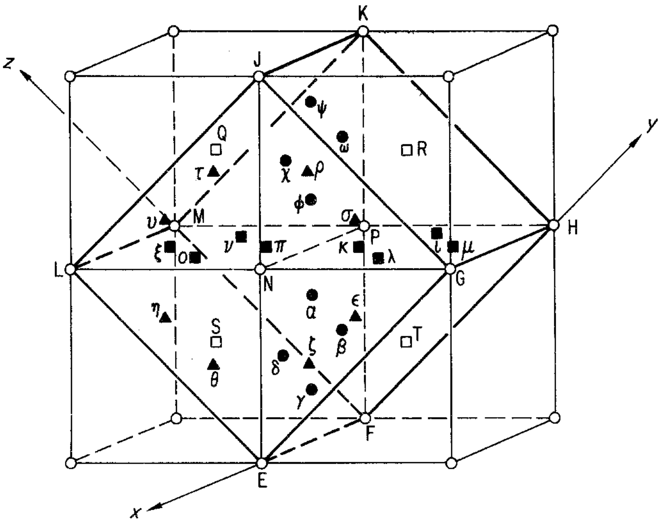

Figure 1 Four unit cells of α-phase FeTi. ○, iron; □, titanium. Solid symbols represent tetrahedral (t) interstices: ●, in the plane FEJK; ■, in the plane GHML; ▲, in the plane EGJL. Heavy lines show how the orthorhombic structure of β-phase $FeTiD_n$ is generated.

centre of the sphere. The distances between sites are taken as the distances between centres of the respective tangential spheres. Regardless of hydrogen (deuterium) concentration, the atomic radii of iron and titanium were taken to be 0.1274 and 0.1462 nm, respectively, as reported in a compilation [13] of metallic radii for coordination number 12. The position parameters for the metal atoms and the lattice parameters of the several phases have been reported by other researchers and these are specified below.

2.1. α-phase FeTi

The intermetallic compound FeTi has a CsCl structure with $a_0 = 0.297\,63$ nm [14]. Four unit cells are shown in Fig. 1. We designate the octahedral (o) hole between titanium atoms Q and S by the symbol QS. It has $r_h = 0.002\,62$ nm, and obviously cannot be occupied by hydrogen. The octahedral hole NP has $r_h = 0.021\,42$ nm and the tetrahedral (t) holes surrounding it have $r_h = 0.030\,66$ nm (Fig. 2). An example of a (t) site coordinated by atoms at N, P, Q and R is designated ϕ in Fig. 1. The centres of this (t) site and site NP are 0.053 25 nm apart. According to the size criterion, none of these sites should be occupied by hydrogen atoms – not even in solid solution [8]. Thompson *et al.* [2] have reported that solute deuterium atoms occupy the (o) site between two iron atoms in α-phase FeTiD with $a_0 = 0.2979$ nm. If that is true (and we have no evidence to contradict this), and, if there is a minimum hole radius approaching 0.040 nm, then the introduction of deuterium atoms in solid solution must introduce a local tetragonal distortion by causing the two iron atoms to separate by approximately an additional 10%. It is a little wonder, then, that the solubility of H(D) in the cubic phase of FeTi is very low. From the work of Wenzl and Lebsanft [15], we make a very rough approximation that n is of the order of 10^{-3} for $FeTiH_n$ at the room-temperature solubility limit. Reilly *et al.* [16] agree that the terminal solubility is very low: "at the phase boundary . . . the composition of the bulk material is $FeTiH_{\approx 0.007}$".

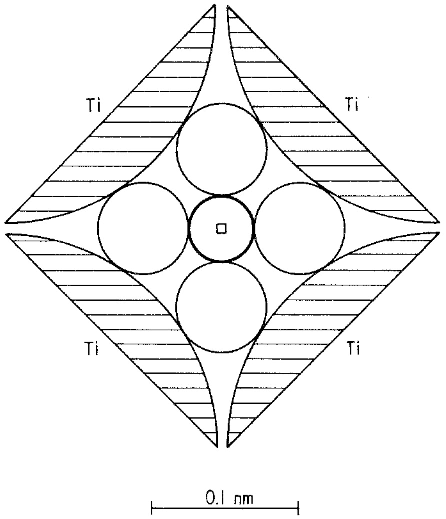

Figure 2 Scale diagram of an octahedral (o) hole coordinated by four titanium atoms and two iron atoms in α-phase FeTi. The heavy circle shows the radius of the (o) site as determined by the two iron atoms which lie above and below the plane of the page. The four surrounding circles show the radii of tetrahedral interstices that are each coordinated by two titanium atoms and two iron atoms.

In a survey of intermetallic compounds, we found that the increment of volume produced by addition of one hydrogen atom to the lattice seems always to lie between 0.002 and 0.003 nm^3 [8]. Here, we choose the value 0.0025 nm^3 per hydrogen atom in an attempt to ascertain whether one should expect FeTi to form a cubic hydride. We calculate that cubic FeTiH would have $a_0 =$ 0.306 75 nm and hole radii of 0.025 98 and 0.035 72 nm for the (o) and (t) interstices, respectively. On the basis of r_h, we conclude that a cubic hydride FeTiH should not be formed. The lattice parameter of cubic $FeTiH_2$ would be 0.315 37 nm, and the respective values of r_h for (o) and (t) sites would be 0.030 29 and 0.040 51 nm. Thus, the (t) holes would barely meet the size criterion.

Had the geometric model been applied to FeTi prior to any experiments, one would have had to conclude that FeTi *might* be able to form a cubic hydride $FeTiH_2$ with hydrogen atoms occupying tetrahedral holes, but hydrides of lower stoichiometry could not exist unless there was a distortion of the cubic lattice that made at least some of the interstices larger. Now, of course, it is known that such a transformation does occur.

2.2. β-hydride (deuteride) of FeTi

Several research groups [3, 4, 14–19] have reported on pressure–composition–temperature (PCT) equilibria and/or structure determinations from which phase diagrams have been inferred for the FeTi–H(D) system. There is no general consensus concerning the β-phase. One interpretation is that the β-phase exists over a composition range with $1.0 < \text{D/FeTi} < 1.4$, while another interpretation is that there are two orthorhombic phases: β_1 at the low end of the range and β_2 at the high end. Reidinger *et al.* [14] believe that sample history determines which of the two phases will be present in $FeTiH_n$ at a given value of n. If there are two distinct β-phases, their structures are very similar; only small differences in lattice parameters and in position parameters for the metal atoms are reported.

The β-phase with composition FeTiD is orthorhombic [3, 4, 14], and, for the purpose of our calculations, we have chosen to use the following parameters [3]: $a = 0.2956$ nm, $b = 0.4543$ nm and $c = 0.4388$ nm. In space group $P222_1$, there are iron atoms in 2c sites (Wyckoff notation) at 0, 0.206, 0.25 and 0, 0.794, 0.75 and Ti atoms in 2d sites at 0.5, 0.25, 0.75 and 0.5, 0.75, 0.25. The orthorhombic cell arising from the distortion of the originally cubic unit cells is shown in Fig. 1, where the origin has been shifted 0, 0.206, 0.25 to the iron atom designated F. The distortion of the cubic unit cells that accompanies the $\alpha \rightarrow \beta$ transformation is ignored in the drawing in order to show, clearly, the simple relationship between the two structures.

Midway between an iron atom and each of its nearest iron atoms are (o) sites which must be considered for potential occupancy by hydrogen (deuterium) atoms. One of these is between iron atoms N and P. This pair and the pair of titanium atoms R and T form the tetrahedron that has been designated κ in Fig. 1. The (o) site NP is surrounded by the four (t) sites α, κ, π, and ϕ. All 24 (t) sites in the unit cell have been given Greek letter designations, and their calculated radii are given in Table I. Each face of an original cubic cell has the centres of four (t) sites associated with it. In the following discussion, sites designated by primed Greek letters have $x > 1$.

In Table I, we see that the largest sites are tetrahedral sites β, δ, ν and o, followed closely by ζ, η, θ and υ. We note, further, that the set β', δ, θ, ζ surrounds the (o) site NE and the set ν', o, υ, η surrounds the (o) site NL. These two (o) sites are much larger than any of the other sets of (o) sites.

In Fig. 3, we show a diagram of the relative sizes and positions of the interstices in the plane that lies midway between iron atoms N and E. There is a large overlap of nearest neighbour (t) sites such as δ and θ and the trigonal saddle point between the sites has a radius of 0.046 99 nm. This is reminiscent of the situation in V_2H [11] and also in the hydrides of A_6B_{23} compounds [10, 12]. For the latter compounds, it was pointed out that the site between two tetrahedral interstices is actually a hexahedral site, coordinated by five metal atoms. For the present case, the hexahedral site midway between δ and θ is coordinated by iron atoms N and E and Ti atoms S, S′ and T (Fig. 1). The distances from the centre of the hexahedral site to the centres of atoms S and T are 0.193 319 and 0.218 88 nm, respectively. Because the hexahedral sites are only very slightly smaller than the (t) sites and offer coordination by an additional Ti atom, we would predict that H(D) atoms might prefer the hexahedral sites, which are 4e sites. The site ($\delta\theta$) between δ and θ is a member of the $4e_7$ set having $x = 0.0538$, $y = 0.5236$ and $z = 0.0297$, where these are position parameters for the space

TABLE I Hole radii, r_h for the tetrahedral, octahedral and hexahedral sites in FeTiD and $FeTiD_{1.37}$. Double-primed symbols lie at $x = 0$ in Fig. 1

Type	Wyckoff notation	Site	r_h (nm)	
			β_1	β_2
(t)	$4e_1$	β, δ, ν, o	0.048 67	0.051 45
	$4e_2$	$\zeta, \eta, \theta, \upsilon$	0.048 32	0.051 37
	$4e_3$	α, γ, ξ, π	0.039 26	0.043 09
	$4e_4$	κ, μ, ϕ, ψ	0.032 48	0.035 44
	$4e_5$	$\iota, \lambda, \chi, \omega$	0.031 40	0.031 34
	$4e_6$	$\epsilon, \rho, \sigma, \tau$	0.029 79	0.030 86
(o)	2d	EF, NP	0.020 40	0.027 00
	$2a_1$	GN, JN	0.016 80	0.013 89
	$2b_1$	NE, NL	0.045 44	0.048 00
	$2a_2$	RT, QR	0.011 70	0.011 25
	$2b_2$	ST, QS	0.011 70	0.011 25
	2c	QQ′, SS′	0.001 60	0.008 20
hex.	$4e_7$	$\delta\theta, \upsilon''\nu, \eta''\nu$	0.046 99	0.049 73
	$4e_8$	$o\upsilon, o\eta, \theta'', \beta, \zeta''\beta$	0.046 99	0.049 73

group $P222_1$ with origin at 212_1. Other members of the $4e_7$ set are $\delta\zeta$, $\nu'\upsilon$ and $\nu'\eta$. The members of the $4e_8$ set are $o\upsilon$, $o\eta$, $\beta'\theta$ and $\beta'\zeta$, which have $x = 0.9462$, $y = 0.4764$ and $z = 0.5297$.

These two sets of hexahedral interstices ($4e_7$ and $4e_8$) in each unit cell give a total of eight hexahedral sites of this size ($r_h = 0.046\,99$ nm). As shown in Fig. 3, however, the centres of such sites in each cluster of four are separated by far less than 0.210 nm, so no more than one H(D) atom can occupy a cluster.

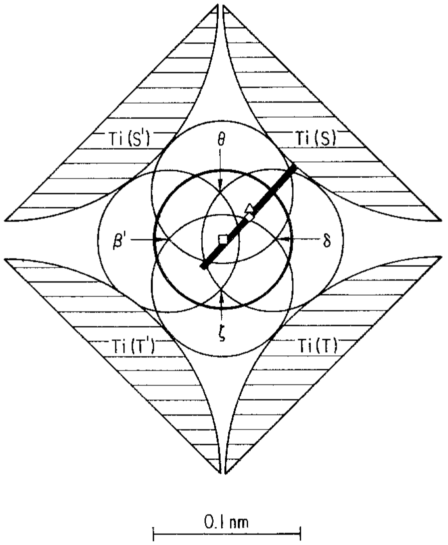

Figure 3 Octahedral, tetrahedral and hexahedral interstices in β_1-phase FeTiD. Letters refer to atoms and interstices in Fig. 1. Tips of arrows indicate centres of respective tetrahedra. Bar shows the diameter of a hexahedral site. □, centre of octahedral interstice NE; ◇, calculated centre of a hexahedral interstice, △, observed [3] location of deuterium atom.

The distances between individual hexahedral sites in the clusters centred around octahedral sites NL and NE (Fig. 2) are given in Table II. Here, we observe that, if either $o\upsilon$ or $\nu'\upsilon$ is occupied, any one of the hexahedral sites around NE is available for occupancy because they are all at distances greater than 0.210 nm. Accordingly, for $FeTiH_x$, the maximum value of n with only hexahedral $4e_7$ and $4e_8$ sites occupied would be 1.0. On the other hand, when either $o\eta$ or $\nu'\eta$ is occupied, only one of the two sites, $\delta\zeta$ and $\beta'\zeta$, is available for occupancy. The sites $\delta\theta$ and $\beta'\theta$ are both too close to sites $o\eta$ and $\nu'\eta$ for simultaneous occupation. Obviously, then, some degree of short-range order is required in order for n to approach 1.0 when only hexahedral $4e_7$ and $4e_8$ sites are occupied.

TABLE II Intersite distances for $4e_7$ and $4e_8$ hexahedral interstices in β_1 FeTiD

Site	Distance (nm)			
	$\delta\theta$ ($4e_7$)	$\delta\zeta$ ($4e_7$)	$\beta'\theta$ ($4e_8$)	$\beta'\zeta$ ($4e_8$)
$o\upsilon$ ($4e_8$)	0.220 44	0.245 48	0.222 73	0.247 53
$o\eta$ ($4e_8$)	0.193 32	0.220 44	0.195 92	0.222 73
$\nu'\upsilon$ ($4e_7$)	0.222 73	0.247 53	0.220 44	0.245 48
$\nu'\eta$ ($4e_7$)	0.195 92	0.222 73	0.193 32	0.220 44

TABLE III Intersite distances for (t) sites of type $4e_3$ and hexahedral sites for types $4e_7$ and $4e_8$ in β_1 FeTiD

Site	Distance (nm)							
	$\delta\theta$	$\delta\zeta$	$\beta'\theta$	$\beta'\zeta$	$o\upsilon$	$o\eta$	$\nu'\upsilon$	$\nu'\eta$
α	0.163 61	0.165 90	0.190 18	0.192 16	0.216 86	0.205 25	0.237 55	0.227 00
π	0.205 25	0.216 86	0.227 00	0.237 55	0.165 90	0.163 61	0.192 16	0.190 18

In three different PCT studies of FeTi–H [4, 15, 19], the phase in equilibrium with α in the plateau region appears to have the composition FeTiH, the same as we have just attributed to 25% occupation of hexahedral sites neighbouring the largest octahedral interstices. Whereas most authors have referred to the occupied site as "octahedral", Thompson *et al.* [3] state, "From these tests we can deduce with a high degree of certainty that the deuterium atom does not occupy the position $0\frac{1}{2}0$, proper". Instead, they reported 0.061, 0.537, 0.025, which lies 0.0270 nm away from the centre of the $0\frac{1}{2}0$ octahedral hole, but only 0.0066 nm away from our calculated centre of a hexahedral hole (Fig. 3).

Tetrahedral sites α, π, γ and ξ have $r_h = 0.039\,26$ nm, which, for a number of other systems [8], appears to be large enough for solute hydrogen atoms. From this, the β-phase might be expected to have observable solubility for hydrogen, and it does [14, 15]. Taken in pairs, these (t) sites form 2d hexahedral interstices that have $x = 1/2$, $y = 0.3520$ and $z = 1/4$ in the orthorhombic space group 222_1. In Fig. 1, site $\alpha\pi$ is located at $x = 1/2$, $y = 0.442$ and $z = 1/2$. For these hexahedral sites, however, r_h is only 0.034 60 nm. We question the validity of the position parameters given by Thompson *et al.* [3] for the second occupied site in FeTiD. They report $x = 1/2$, $y = 1/4$ and $z = 1/4$, from which we calculate r_h would be only 0.021 75 nm. We would predict, therefore, that (t) sites α, γ, ξ and π would be preferred by solute hydrogen atoms. In order to ascertain how many of these sites might be occupied, we must consider their distances from the partially occupied hexahedral sites of types $4e_7$ and $4e_8$. These calculated distances are shown in Table III.

Taking into account the symmetry of the cell, we can deduce from the results in Table III that occupation of any of the hexahedral sites centred on NL (Fig. 1) blocks both ξ and π, and occupation of any of the hexahedral sites centred on NE blocks both α and γ. For a stable hydride phase, therefore, the distance criterion tells us that these (t) sites of type $4e_3$ could be occupied only to the extent that the hexahedral sites of type $4e_7$ and $4e_8$ were emptied. We recall, however, that we are not dealing with a stable hydride at the moment; instead we are trying to ascertain whether the $4e_3$ sites can accept hydrogen atoms into solution in FeTiH. In view of the fact that, in the cluster of hexahedral sites nearest to α, there are two $4e_8$ sites at distances greater than 0.19 nm from the α site (Table III), it is not inconceivable that an increase in hydrogen pressure over FeTiH could simultaneously force hydrogen atoms into the α site and into either the $\beta'\theta$ or $\beta'\zeta$ site. Seemingly, however, the solubility would be quite limited and very significant additional absorption would probably require a transformation.

As mentioned above, the nature of the β-phase (or phases) is not completely understood. Careful scrutiny of only the PCT plots of Wenzl and Lebsanft [15] can lead one to believe that there is actually a $\beta_1 \rightarrow \beta_2$ first-order phase transformation. In Fig. 4, we see that their absorption plateau for 298 K appears to end at $n = 1$ for FeTiH_n. The terminal solubility for hydrogen in this β_1-phase seems to occur at about $n = 1.2$, and the β_1-phase at this composition is in equilibrium with β_2 ($n \simeq 1.4$). The β_2-phase also can accept hydrogen in solution, and the saturated phase ($n \simeq 1.8$) is in equilibrium with the γ-phase ($n \simeq 1.9$). The apparent terminal solubilities in the β_1- and β_2-

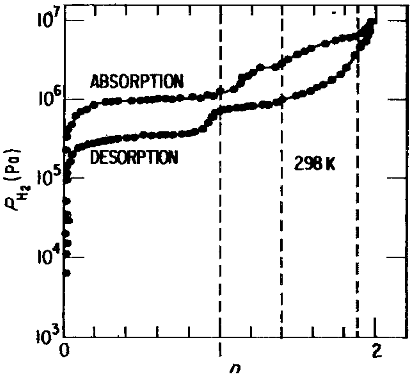

Figure 4 Pressure–composition plots of the FeTi–H system at room temperature. Data points are from Wenzl and Lebsanft [15].

TABLE IV Intersite distances for $4e_7$ and $4e_8$ hexahedral interstices in β_2 $FeTiD_{1.37}$

Site	Distance (nm)			
	$\delta\theta$ ($4e_7$)	$\delta\zeta$ ($4e_7$)	$\beta'\theta$ ($4e_8$)	$\beta'\zeta$ ($4e_8$)
$o\upsilon$ ($4e_8$)	0.220 65	0.246 96	0.223 37	0.249 39
$o\eta$ ($4e_8$)	0.192 14	0.220 65	0.195 25	0.223 37
$\nu'\upsilon$ ($4e_7$)	0.223 37	0.249 39	0.220 65	0.246 96
$\nu'\eta$ ($4e_7$)	0.195 25	0.223 37	0.192 14	0.220 65

phases are higher than they would be if there were no mechanical constraint to the formation of the β_2- and γ-phases, respectively [20, 21].

Upon desorption of hydrogen (Fig. 4), the γ-phase is retained down to a value of $n \simeq 1.5$, probably because of mechanical constraint to formation of the β_2-phase. For $1.4 < n < 1.5$, β_2 and γ would coexist; for $1.35 < n < 1.4$, there would be only β_2; for $1 < n < 1.35$, β_1 and β_2 would coexist; for $0.8 < n < 1$, only β_1 would exist; and at lower values of n, α and β_1 would coexist. The β_1-phase continues to exist at a lower value of n than during absorption, because of the mechanical constraint to the precipitation of the α-phase during desorption. We shall try to develop a rationale, based on the foregoing scenario, for the observed occupancies of sites in β_2-$FeTiD_n$.

For our calculations we have used the following lattice and position parameters [4]: $a_0 = 0.3088$ nm, $b_0 = 0.4515$ nm, $c_0 = 0.4391$ nm; two iron atoms in 2c positions with $y = 0.197$, and two titanium atoms in 2d positions with $y = 0.750$. These position parameters are for orthorhombic space group $P222_1$ with the origin at 212_1. In order to facilitate the use of Fig. 1 for the discussion that follows, the origin has been shifted by the vector 0, 0.197, 0.250 to the iron atom designated F.

In Table I, one can see that the $4e_1$ and $4e_2$ tetrahedral sites are largest, but are closely followed by the $4e_7$ and $4e_8$ hexahedral sites. The $2b_1$ octahedral sites are only slightly smaller. Thus, a diagram of r_h for the clusters of sites in $FeTiD_{1.37}$ would appear very much like that in Fig. 3. Again, we would predict that hydrogen (deuterium) atoms might prefer the hexahedral sites. For type $4e_7$, our calculated position parameters are $x = 0.0562$, $y = 0.5244$ and $z = 0.0312$; for type $4e_8$, $x = 0.9438$, $y = 0.4756$ and $z = 0.5312$.

By comparing Tables II and IV, we can see that, with respect to the 0.210 nm criterion, there is no difference between the β_1- and β_2-phases so far as mutual blocking of hexahedral $4e_7$ and $4e_8$ sites is concerned. The maximum number of hydrogen atoms in these hexahedral sites, therefore, is still one per formula unit of FeTi.

The value of r_h approximates 0.043 nm for the $4e_3$ tetrahedral sites (Table I). According to the size criterion, therefore, the sites α, π, γ and ξ should be capable of accommodating hydrogen atoms in a stable hydride phase. We have calculated the distances between these (t) sites and the partially occupied $4e_7$ and $4e_8$ hexahedral sites, however, and find, again, that $\delta\theta$ and $\delta\zeta$ are considerably less than 0.210 nm from the α site, and $\beta'\theta$ and $\beta'\zeta$ are slightly less than 0.210 nm from the α site (Table V). In strict accord with the distance criterion, occupation of α, π, γ or ξ tetrahedral sites in $FeTiH(D)_{1.37}$ would be an unstable condition.

None of the other tetrahedral sites is large enough (Table I) to accommodate hydrogen atoms, even in solid solution. The same can be said of the octahedral hole NP, contrary to the reported [4] occupancy of that site. We have calculated r_h and position parameters for the 2d hexahedral sites such as $\alpha\pi$ and find the following: $r_h = 0.039\,67$ nm; $y = 0.6617$ in the orthorhombic space group $P222_1$ with the origin at 212_1. In Fig. 1, therefore, $\alpha\pi$ has coordinates $\frac{1}{2}$, 0.4647, $\frac{1}{2}$. Because the value of r_h is virtually the same as the criterion value of 0.040 nm, the 2d hexahedral sites are suitable candidates for occupancy in a stable hydride, according to the geometric model.

Intersite distances between the hexahedral, 2d $\alpha\pi$ site and the hexahedral $4e_7$ and $4e_8$ sites are shown in Table V. Careful scrutiny of this table

TABLE V Separations of the sites α and $\alpha\pi$ from $4e_7$ and $4e_8$ sites in β_2 $FeTiD_{1.37}$

Site	Distance (nm)							
	$\delta\theta$	$\delta\zeta$	$\beta'\theta$	$\beta'\zeta$	$o\upsilon$	$o\eta$	$\nu'\upsilon$	$\nu'\eta$
α	0.172 26	0.174 87	0.200 99	0.203 23	0.218 17	0.207 15	0.241 50	0.231 60
$\alpha\pi$	0.187 25	0.194 60	0.213 98	0.220 44	0.194 60	0.187 25	0.220 44	0.213 98

leads us to the conclusion that, with a degree of long-range ordering, half of the hexahedral 2d sites can be occupied. The scheme is as follows: in the unit cell shown in Fig. 1, if we fill $o\upsilon$, then either $\delta\theta$ or $\delta\zeta$ can also be filled (Table IV). On the other hand, if we fill $o\eta$, then only $\delta\zeta$ could be filled. Likewise, if we fill $\upsilon''\nu$, then either $\theta''\beta$ or $\zeta''\beta$ could also be filled, but if we fill $\eta''\nu$, then only $\zeta''\beta$ could be filled. For the double-primed symbols, $x = 0$. In any case, it is possible to put four hydrogen (deuterium) atoms into the $4e_7$ and $4e_8$ interstices of this unit cell. For the unit cell with $1 \leqslant x \leqslant 2$, however, the sites $\nu'\upsilon$, $\nu'\eta$, $\beta'\theta$ and $\beta'\zeta$ would have to be empty. Thus, in this second unit cell, we can fill the site $\alpha\pi$ and the other hexahedral 2d site and leave all $4e_7$ and $4e_8$ sites empty. By alternating these two types of unit cell, therefore, we can achieve the stoichiometry $FeTiH(D)_{1.5}$, where one-fourth of the $4e_7$ sites, one-fourth of the $4e_8$ sites and one-half of the hexahedral 2d sites are occupied. Without this long-range order, the value of n for β_2 $FeTiH(D)_n$ in equilibrium with the β_1-phase should be expected to be somewhat less than 1.5, and it is (Fig. 4). According to the geometric model, absorption of hydrogen or deuterium atoms for values of $n > 1.5$ would require some kind of transformation that enlarges interstices as yet unoccupied, or that increases the distances between those sites for which r_h is already greater than 0.040 nm.

2.3. γ-hydride (deuteride) of FeTi

The transformation to the γ-hydride phase, which is monoclinic [4–7, 14] and belongs to space group $P2/m$, causes some of the interstices to undergo remarkable changes. There is good agreement among the several researchers on the structure of γ-$FeTiD_{1.9}$, so we have averaged the results of [4, 6, 7] to obtain the parameters we used in our calculations: $a_0 = 0.470\,61$ nm, $b_0 = 0.283\,33$ nm, $c_0 = 0.469\,95$ nm and $\beta = 96.98°$; iron in 2m sites with $x = 0.201$ and $z = 0.728$, and titanium in 2n sites with $x = 0.282$ and $z = 0.226$.

Fig. 5 has the (t) sites denoted the same as in Fig. 1, but, for this monoclinic structure of the γ-phase, the coordinate system has been changed. We have used the unique axis b with origin at $(2/m)$, but, in Fig. 5, we have translated the origin through 0.201, 0, 0.728, to the iron atom designated E. The monoclinic distortion has been omitted in order to show, more clearly, the relationship between the γ- and α-phases.

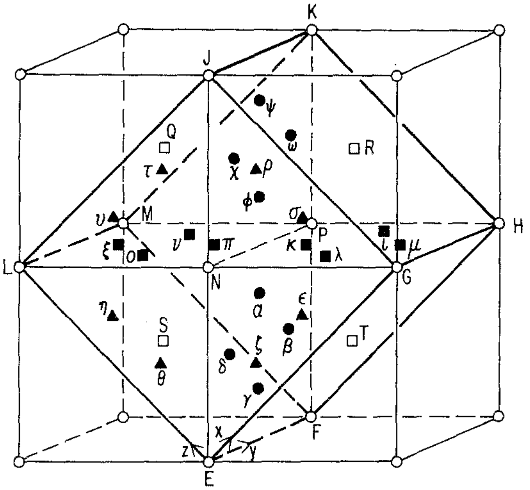

Figure 5 Generation of the monoclinic γ-phase $FeTiD_{1.9}$ from four unit cells of α-phase FeTi. Atoms and interstices are designated the same as in Fig. 1, but the origin and axes are different.

The (t) sites split into many varieties in the γ-phase. Table VI shows the calculated position parameters and hole sizes for all 24 of these tetrahedral interstices and for all 12 of the octahedral interstices. The largest of these are represented in Fig. 6. Obviously, the 2l and $2m_3$ tetrahedral interstices are virtually indistinguishable from each other or from the 1g octahedral site at the centre. We would expect, therefore, that all of the 1g octahedral sites in $FeTiD_{1.9}$ should be occupied, and this is consistent with the reported experiments [4, 6].

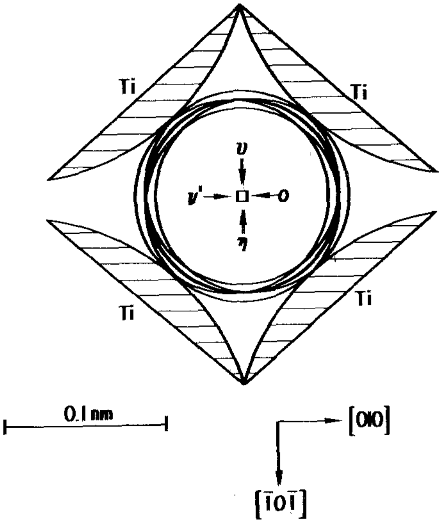

Figure 6 Scale diagram of the octahedral interstice NL (Fig. 5) in γ-phase $FeTiD_{1.9}$. □, centre of site NL. Tips of arrows indicate the centres of the surrounding tetrahedral interstices. Circles show r_h for the various sites.

TABLE VI Hole radii r_h and position parameters for the tetrahedral and octahedral interstices in $FeTiD_{1.9}$

Atom or site	Wyckoff notation	Designation in Fig. 5	Position parameters (Space group $P2/m$, unique axis b)			r_h (nm)
			x	y	z	
Fe	2m	E	0.201	0	0.728	
Ti	2n	S	0.718	0.5	0.774	
(t)	2i	ι	0	0.8694	0	0.044 64
		λ	0	0.1306	0	0.044 64
(t)	2j	β	0.5	0.9295	0	0.051 95
		δ	0.5	0.0705	0	0.051 95
(t)	2k	χ	0	0.4159	0.5	0.051 07
		ω	0	0.5841	0.5	0.051 07
(t)	2l	ν	0.5	0.9796	0.5	0.059 63
		o	0.5	0.0204	0.5	0.059 63
(t)	$2m_1$	ϵ	0.9415	0	0.9537	0.043 81
		σ	0.0585	0	0.0463	0.043 81
(t)	$2m_2$	ζ	0.5241	0	0.9727	0.051 76
		θ	0.4759	0	0.0273	0.051 76
(t)	$2m_3$	η	0.4925	0	0.4907	0.059 61
		υ	0.5075	0	0.5093	0.059 61
(t)	$2m_4$	ρ	0.1332	0	0.3863	0.032 49
		τ	0.8668	0	0.6137	0.032 49
(t)	$2n_1$	α	0.6547	0.5	0.1508	0.036 88
		γ	0.3453	0.5	0.8492	0.036 88
(t)	$2n_2$	κ	0.8946	0.5	0.1404	0.035 67
		μ	0.1054	0.5	0.8596	0.035 67
(t)	$2n_3$	ξ	0.3376	0.5	0.6216	0.038 37
		π	0.6624	0.5	0.3784	0.038 37
(t)	$2n_4$	ϕ	0.9600	0.5	0.4590	0.051 24
		ψ	0.0400	0.5	0.5410	0.051 24
(o)	1g	NL	0.5	0	0.5	0.059 54
(o)	1d	NE	0.5	0	0	0.050 84
(o)	1a	NG	0	0	0	0.040 61
(o)	2n	NP	0.7990	0.5	0.2720	0.014 27
		EF	0.2010	0.5	0.7280	0.014 27
(o)	1c	NJ	0	0	0.5	0.006 63
(o)	1f	QR	0	0.5	0.5	0.049 62
(o)	1n	RT	0	0.5	0	0.013 38
(o)	1h	QS	0.5	0.5	0.5	0.011 25
(o)	1e	ST	0.5	0.5	0	0.010 18
(o)	2m	TT′	0.7180	0	0.7740	0
		RR′	0.2820	0	0.2260	0

The second largest set of sites (Table VI) consists of the 1*d* octahedral site NE and the 2j and $2m_2$ tetrahedral sites surrounding it. We note in Fig. 7 that there is considerably more overlap of the (t) sites and the (o) site than the same configuration has in β_1, FeTiD (Fig. 3). Thus, a neutron diffraction experiment might be expected to find deuterium atoms located in the 1d octahedral sites rather than in the nearly indistinguishable hexahedral sites. This, too, is consistent with published results [4, 6].

The separation of the 1d and 1g site is 0.234 98 nm, so these can be filled simultaneously. We note that these two octahedral sites correspond to the $2b_1$ sites (Table I), which are the largest octahedral sites in both β_1 and β_2. The third largest set of interstices in the γ-phase, however, played no role at all in either β_1 or β_2.

The 1f octahedral site QR in γ-$FeTiD_{1.9}$ (Fig. 5) has $r_h = 0.049\,62$ nm compared with 0.011 25 nm in β_2-$FeTiD_{1.37}$. Furthermore, it is surrounded by (t) sites ϕ, χ, ψ and ω having $r_h \simeq 0.051$ nm compared with $r \leqslant 0.035$ nm for the analogous sites in the β_2-phase. The large overlap of the 1f octahedral site and the 2k and $2n_4$ tetrahedral sites is shown in Fig. 8. For this configuration, also, the hexahedral sites between pairs of tetrahedral sites are roughly the same size as the octa-

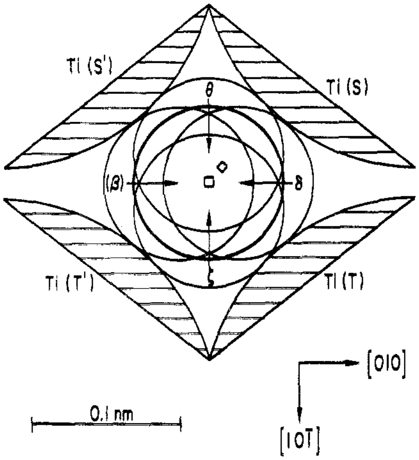

Figure 7 Scale diagram of the octahedral interstice NE (Fig. 5) in γ-phase FeTiD$_{1.9}$. □, centre of site NE. Tips of arrows indicate the centres of the surrounding tetrahedral interstices. Circles show r_h for the various sites. ◇, centre of a hexahedral site coordinated by three titanium atoms and two iron atoms.

hedral and tetrahedral sites, and the locus of the centres of all three types of sites has a radius of only about $0.08b_0$. Titanium metal has a much stronger affinity for hydrogen than iron metal has, and if that fact plays any role in site occupation, then there may be less likelihood for hexahedral occupation in the configuration depicted in Fig. 8 than in that depicted in Fig. 3. This is because the shift from a tetrahedral site to a hexahedral site allows an extra Ti–H(D) bond in Fig. 3, but an extra Fe–H(D) bond in Fig. 8. In the present case, the Ti–H(D) distance would be minimized and the Fe–H(D) distance would be maximized if the 1f octahedral site was occupied. The distance between the 1f site and the 1g site is 0.274 66 nm and the 1f–1d distance is even greater, so the occupied 1g and 1d sites should not block any 1f sites.

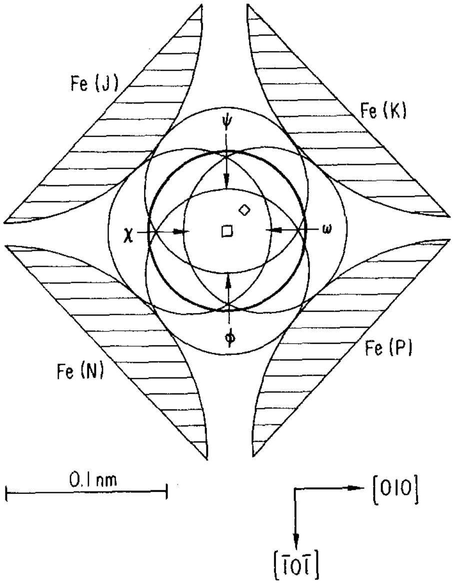

Figure 8 Scale diagram of the octahedral interstice QR (Fig. 5) in γ-phase FeTiD$_{1.9}$. □, centre of site QR. Tips of arrows locate the centres of the surrounding interstices. Circles show r_h for the various sites. ◇, centre of a hexahedral site coordinated by two titanium atoms and three iron atoms.

If the 1f site is occupied, there must be a diffusion path for hydrogen atoms to reach the site. In earlier applications of the geometric model, we have found it useful to assume that diffusion of hydrogen atoms occurs by jumps through trigonal saddle points between nearest-neighbour interstices. In Fig. 5, we note that diffusion between the occupied octahedral sites NL and NE could occur through tetrahedral sites η and θ. For diffusion between NL and QR, there is a path $o \rightarrow \pi \rightarrow \phi$, in which the smallest tetrahedral site, π, has $r_h = 0.038\,37$ nm, a value that is adequate for acceptance of hydrogen atoms in solid solution. The saddle points between θ and η, between o and π and between π and ϕ have respective radii of 0.022 55, 0.027 67 and 0.029 61 nm. These approximate the value of 0.025 93 nm for vanadium metal in which the high diffusion rate of hydrogen is well known. Thus, there seems to be no problem of access to the octahedral 1f site QR, from the standpoint of available intermediate sites. As an aside, however, on the basis of jump distance one might expect the diffusion coefficient to be relatively low. The respective jump distances of 0.216 96, 0.169 23 and 0.140 56 nm are much longer than the jump distance of 0.107 02 nm in vanadium metal.

While the geometric model leads us to predict full occupation of the 1f site, this site was taken to be only 85% occupied in the refinements [4, 6] of neutron diffraction results on FeTiD$_{1.9}$. In both of those studies, however, the agreement factor was higher than the researchers would have liked, so something close to full occupancy of the 1f site may still be a possibility.

The only other sites listed in Table VI that have $r_h \geqslant 0.040$ nm are the 1a octahedral site NG and the 2m$_1$ (σ and ϵ) and 2i (ι and λ) tetrahedral sites surrounding it. In Fig. 9, we show that configuration, and we note the similarity with Fig. 3. It

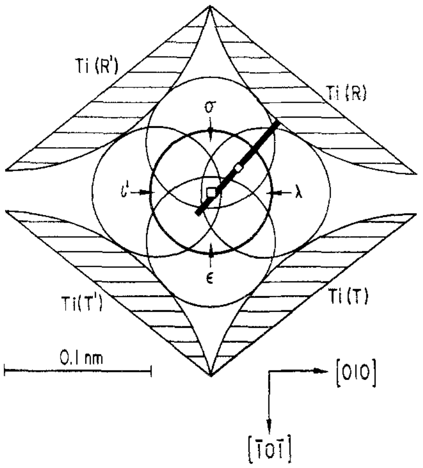

Figure 9 Scale diagram of the octahedral interstice NG (Fig. 5) in γ-phase FeTiD$_{1.9}$. □, centre of site NG. Tips of arrows locate the centres of the surrounding tetrahedral interstices. Circles show r_h for the various sites. Bar shows diameter of hexahedral site σλ, which is centred at ◇.

seems highly likely, therefore, that hydrogen (deuterium) atoms might prefer the hexahedral sites between pairs of tetrahedral sites rather than situating themselves in either the somewhat smaller octahedral site or the slightly larger tetrahedral site. Possibly, such a refinement could help to improve the agreement factor in the neutron diffraction experiments [4, 6] in which the octahedral site was taken to be occupied. The hexahedral sites in question are interstices of the 4*o* type and have $x = 0.0329, y = 0.080$ and $z = 0.0260$ in the space group *P*2/m. They have $r_h = 0.04242$ nm.

The distance between hexahedral site σλ and octahedral site QR is greater than 0.25 nm, and the distance between hexahedral site ελ and octahedral site NE is greater than 0.22 nm. The distance between octahedral site NL and either σλ or ελ far exceeds the criterion value of 0.210 nm. Thus, none of these hexahedral sites should be blocked by previously occupied sites. Of course, only one-fourth of the hexahedral sites surrounding NL could be occupied because of their proximity to each other. Thus, one hydrogen (deuterium) atom per unit cell could be accommodated in hexahedral sites of type 4*o*.

From the foregoing analysis of γ-FeTiD$_{1.9}$, we conclude that the maximum number of hydrogen (deuterium) atoms in the γ-phase is 4.0 per unit cell, i.e. 2.0 per formula unit. All other interstices are less than 0.210 nm from those sites that we have predicted to be occupied in the discussion above, and, therefore, must remain empty.

3. Conclusions

1. The low solubility that has been reported by other researchers for hydrogen in α-phase FeTi can be rationalized. The tetrahedral interstices and both types of octahedral interstices are too small for the accommodation of significant numbers of hydrogen atoms.

2. The exact nature of the β-phase (or phases) cannot be ascertained from available experimental results. If one accepts that there are four distinct phases, α, β_1, β_2 and γ, then one can develop a rationale for β_1-phase FeTiH(D) with 25% occupation of hexahedral $4e_7$ and $4e_8$ interstices surrounding the two largest octahedral interstices.

3. The existence of β_2-phase FeTiH$_n$, with *n* approaching 1.5, can be explained by the somewhat ordered occupation of up to 50% of the hexahedral 2d sites neighbouring the 2d octahedral interstices.

4. According to the geometric model, in γ-phase FeTiH$_{1.9}$ there would be full occupation of the octahedral 1g, 1d and 1f interstices, and the remainder of the hydrogen atoms would occupy the hexahedral sites of type 4*o* surrounding the octahedral interstice of type 1a.

5. In γ-phase FeTiH$_n$, *n* cannot exceed 2.0.

6. For the hydrides of FeTi, the predictions of the geometric model are in very good agreement with experimental observations, and the minor discrepancies may even suggest possible refinements to be tried in analysing neutron diffraction results.

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