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Self-trapped hydrogen states in metals determined from quantum mechanical calculations using potentials based on *ab initio* data: II. Hydrogen isotopes in Fe

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Abstract. An auxiliary short-ranged Fe–H pair potential is constructed on the basis of *ab initio* pseudopotential calculations for hydrogen in α -Fe. This pair potential is used in self-consistent quantum mechanical calculations of hydrogen states and lattice displacements which have been performed in order to investigate the relative stability of self-trapped states formed at tetrahedral (T) or octahedral (O) sites as a function of the isotopic mass. It is found that for the light hydrogen isotopes μ^+ and π^+ the total energy is lower at the O site whereas it is lower at the T site for the heavy isotopes p, d and t. The site with higher energy is found to be unstable. The physical origin of the stabilization of O sites for the lighter particles is the lower vibrational energy at the O site whereas the isotope effect in the lattice displacements is of minor importance in this respect.

1. Introduction

In the preceding paper, which we refer to as part I† (Krimmel *et al* 1994), we described a procedure by which a pair potential representing the particle–host interaction of hydrogen introduced in a metal (applicable to high as well as to low hydrogen concentrations) can be constructed with the help of *ab initio* data obtained from calculations on relatively small supercells. In part I the method was applied to the calculation of vibrational states of isolated hydrogen isotopes in Pd in order to discuss energetics, site assignment, excitation spectra, and the Jahn–Teller effect of excited vibrational states. A detailed account was given of the effects due to lattice relaxation, in particular of those which are the result of the dependence of the latter on the extension of the particle wavefunction which in turn depends on the isotopic mass and on the excitation state.

The computational method which was used in order to carry out these calculations is described in I.2. In the present paper, part II, the same method is applied to hydrogen in α -Fe. The aim of the investigation is to determine the sites at which a hydrogen isotope, dependent on its mass, will form stable (or metastable) self-localized states. Calculations with empirical pair potentials on other BCC metals (Nb, Ta) predicted that the heavier hydrogen isotopes (p, d, t) occupy tetrahedral (T) sites whereas the light isotope (π^+ , μ^+) should occupy octahedral (O) sites (Sugimoto and Fukai 1980, 1981 Klamt and Teichler 1986a, 1986b). The investigation of whether such an isotope effect in the site occupation also exists in α -Fe is highly desirable for reasons discussed below. From μ^+ SR experiments

† Sections of part I will be referred to as I.1 etc, and equations as (I.1) etc.

(Fritzsche *et al* 1990, Seeger and Schimmele 1992) it is known that μ^+ occupy O sites in α -Fe. From channelling experiments the same conclusion for the π^+ site at low temperatures was drawn (Staiger *et al* 1990). However, because the experimental data are not at hand, due to, for example, the low hydrogen solubility in α -Fe, no calculations based on empirical pair potentials are available.

Unfortunately, the only calculation for hydrogen in α -Fe based on the quasi-atom method (Puska and Nieminen 1984), which is probably not very reliable, gives only the site for the proton (O site) but not that for other isotopes, in particular not that for the light isotopes π^+ and μ^+ . There is also no experimental information on the site occupied by the hydrogen isotopes p, d and t in α -Fe. In contrast, for Nb and Ta it is known from experiment that p, d and t occupy T sites but the site occupied by μ^+ is unknown. Therefore the theoretical predictions concerning the isotope effect in the site occupation could not really be tested. To a certain extent this can be done by combining theoretical and experimental results on Nb, Ta on the one hand and Fe on the other. To know whether the heavier isotopes p, d and t, like the μ^+ and π^+ , occupy the O site in α -Fe or the T site as they do in Nb and Ta would be very welcome also because this affects the conclusions that can be drawn from the diffusivities of p, d measured in α -Fe (Hayashi *et al* 1989) in combination with the μ^+ hopping rates as deduced from μ^+ experiments (Herlach *et al* 1989, Seeger and Schimmele 1992).

Details on the construction of the pair potential are given in the next section. In contrast to hydrogen in Pd for which *ab initio* data for many different supercell sizes and different lattice parameters were available, the Fe–hydrogen pair potential is based on data obtained for just one supercell (FeH). For this reason no direct *ab initio* forces are available but only the averaged information on forces contained in the volume expansion. Because of the resulting uncertainties in the forces on the nearest and next-nearest Fe atoms of the T or O site the calculations presented in the following have been performed with three pair potentials resulting in quite different values in these forces. It will turn out that the basic results are fairly insensitive to the particular choice of the potential.

2. Construction of the pair potential

In order to determine the parameters in the *ansatz* for the hydrogen–iron pair potential the same route as described in I.3 for the hydrogen–Pd interaction is followed. Some modifications come in because the database in the case of Fe is smaller than in the case of Pd.

The pair potential has to fit the energy versus displacement curves which have been determined by *ab initio* pseudopotential calculations in local-density approximation along the directions shown in figure 1 (Elsässer *et al* 1994a). In contrast to Pd, only calculations in one supercell geometry (body-centred FeH) have been performed. However, from calculations on FeH, in which each host atom is surrounded by several nearby hydrogen atoms, forces on individual neighbour atoms due to a single hydrogen impurity cannot be determined. In particular, this is the case if hydrogen is located at the exceptionally important high symmetry sites where the total forces vanish due to symmetry. On the other hand, as mentioned in I.2 and I.3, information on these forces can be obtained from the double-force tensor P , if the interaction potential may be assumed to be short-ranged. The interstices with the highest point symmetry, i.e. the octahedral and tetrahedral interstices, are the most likely candidates for being equilibrium positions of a hydrogen isotope in BCC metals. In the BCC structure both interstices possess tetragonal symmetry and both exist in three different subclasses each characterized by the orientation of the tetragonal axis which may be along

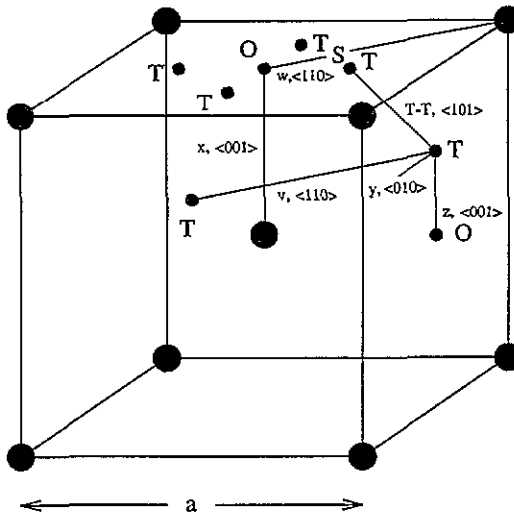


Figure 1. The elementary unit cell of body-centred Fe with the lines along which the energy versus displacement curves have been calculated *ab initio*.

any one of the three different $\langle 001 \rangle$ directions. The double-force tensor of a defect having tetragonal point symmetry is given by (Leibfried and Breuer 1978, Peisl 1978)

$$P = \begin{pmatrix} B & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & A \end{pmatrix} \quad (1)$$

where the z axis of the cubic coordinate system is parallel to the tetragonal axis. No experimental information is available on P in α -Fe for the hydrogen isotopes p , d and t . The only experimental information on P which we have is on the anisotropy $A - B$ for μ^+ . From μ^+ SR experiments on α -Fe it was found that μ^+ occupies O sites and that $A - B \simeq +2$ eV (see Fritzsche *et al* 1990, Seeger and Schimmele 1992). This information is not used in constructing the pair potential. However, $A - B \simeq 2$ eV is nearly reproduced by the calculations presented in the following. Instead of dealing with experimental information, one can use, as mentioned already in I.2 and I.3, the volume change of the crystal due to hydrogen loading, which can be determined from *ab initio* supercell calculations. From the volume expansion per hydrogen atom, the trace of the double-force tensor may be determined via equation (I.12). The volume expansion per hydrogen atom was determined from the *ab initio* calculations on FeH. Of course, this is not quite the situation for which equation (I.12) is devised, because the validity of equation (I.12) is restricted to low defect concentrations. Nevertheless, it can be expected that such an extrapolation leads to a reasonable estimate for $\text{tr}P$. From the *ab initio* calculations in which hydrogen has been placed at the T site $\text{tr}P = 10.7$ is obtained. In the following, three different H-Fe pair potentials are used, all three cut off by the same smooth cut-off function. The parameters in the pair potentials are determined such that the *ab initio* energy versus displacement curves are reproduced well and that at the same time a certain value of $\text{tr}P$ is reproduced. The different potentials are characterized by the different values of $\text{tr}P$ to which they give rise. One of the potentials gives a $\text{tr}P$ which is close to the *ab initio* estimate of 10.7 eV, the other two lead to smaller values of $\text{tr}P$. Calculations with three pair potentials are performed in order to check the sensitivity of the final results to the size of the forces on nearest-neighbour and the next-nearest-neighbour atoms which cannot be determined unequivocally from just

$\text{tr}P$ (additional information is contained, however, in $A - B$). The three potentials used below are

$$V(r)/\text{eV} = 4621.20417 \exp[-r/(0.05477a)] f(r) \quad (2)$$

$$V(r)/\text{eV} = \{5392.95509 \exp[-r/(0.05264a)] + 8.43593 \exp[-r/(0.19301a)]\} f(r) \quad (3)$$

$$V(r)/\text{eV} = \{10025.76685 \exp[-r/(0.04840a)] + 11.44028 \exp[-r/(0.21287a)]\} f(r). \quad (4)$$

The cut-off function $f(r)$ is the one given by (I.3.2) with a cut-off radius of one lattice constant ($a = 2.96 \text{ \AA}$). For t located at a T site the potentials (2), (3) and (4) give $\text{tr}P = 4.0$, 7.0 and 9.1 eV. The triton is the hydrogen isotope with the best localized wavefunction and should therefore be used when comparing with *ab initio* data which are obtained treating hydrogen as a classical particle (effectively as having an infinite mass). A simultaneous fit to the energy versus displacement curves and to $\text{tr}P$ could not be achieved with a simple exponential if higher values of $\text{tr}P$ are demanded (see potentials (3) and (4)).

The three pair potentials are shown in figure 2. All three pair potentials reproduce the energy versus displacement curves almost equally well. The transferability of such pair potentials seems to be quite reasonable since adiabatic potentials for face-centred cubic FeH constructed with the three pair potentials reproduce quite well the adiabatic potential calculated very recently *ab initio* (Elsässer et al 1994 a). The curves obtained from potential (4) for body-centred cubic FeH are shown in figure 3 in comparison with the *ab initio* results.

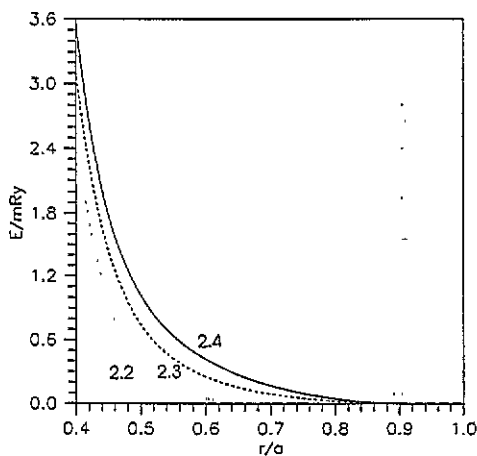


Figure 2. The three Fe-H pair potentials (2), (3), (4).

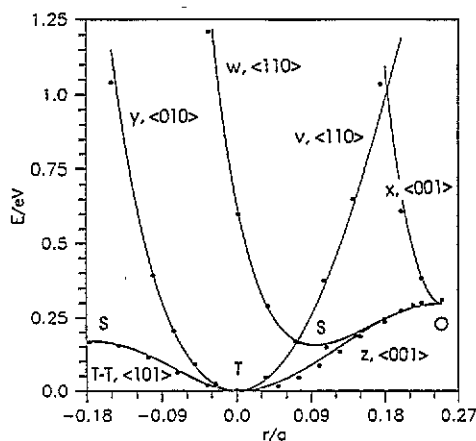


Figure 3. The pair-potential description of the *ab initio* calculated energy versus displacement curves (dots) for Fe along the various paths depicted in figure 1 and for the pair potential (4).

3. Self-localized states

3.1. States localized at T sites

Figure 3 shows that the potential energy surface of a classical particle determined from *ab initio* calculations at the undistorted host-lattice configuration has minima at T sites.

Therefore it is obvious to investigate self-localized T states. The boundary condition imposed on the particle wavefunction is that it has to vanish at the surface of a sphere of sufficient size around the T site. The calculation of the wavefunctions was performed on a grid of mesh width 0.0467 Å. The reference configuration to which the local lattice distortions are referred is the undistorted Fe lattice with the lattice constant $a = 2.80$ Å which is obtained from the *ab initio* calculations. In computing the local lattice distortions the lattice Green function given by MacGillivray and Sholl (1983) has been used. Table 1 gives the ground-state vibrational energy E^{vib} , the energy E^{min} of the bottom of the potential well, the deformation energy E^{def} as well as the total energy E^{tot} (the sum of the three energy terms mentioned) for various hydrogen isotopes self-localized at the T site and for the three potentials introduced in section 2. Furthermore, trace and anisotropy of the double-force tensor and the displacements of the nearest-neighbour atoms in units of a ($= 2.80$ Å) are given. The quite different absolute values of E^{min} and therefore of E^{tot} obtained within the three different pair potentials have of course no significance. Significant are only differences in the variations in E^{min} as a function of the isotope mass obtained with different pair potentials and in particular the energy differences between the E^{tot} values for T-site occupation and the corresponding values for O-site occupation which are discussed in section 3.2. It is obvious from table 1 that the results for the vibrational energies from the present calculation (using the pair potential (4)), which takes into account the local relaxation of the Fe atoms surrounding the particle, agree very well with the data obtained by *ab initio* calculations for a classical particle occupying the T site in undistorted FeH at the equilibrium lattice constant of FeH. The volume relaxation of Fe upon loading with particles up to the composition FeH which is included in the *ab initio* calculations accounts for most of the effect of local relaxations around an isolated particle located at the T site in Fe. It should be noted that for Pd the effect of local relaxations around an isolated particle is essentially accounted for by the volume relaxation upon loading with hydrogen up to Pd₄H (instead of PdH). Obviously, both for Fe and Pd an appropriate homogeneous volume relaxation may simulate the influence of local lattice relaxations on the vibrational properties of isolated particles, but it is of course not clear *a priori* to which hydrogen concentrations different materials must be loaded to obtain the required volume expansion. In the BCC structure this situation is specific to the T site (the situation is completely different for the O site, see below). In the case of the T site the four nearest neighbours are shifted by an equal amount. The symmetry of the immediate neighbourhood is thus preserved just as it is in the case for an isotropic expansion of the lattice.

The particle potential corresponding to the lattice configurations of the self-trapped state is shown in figure 4. The difference in the potentials as obtained for the proton and the triton is just a constant energy shift (difference in E^{min} for p and t, see table 1); the shape of the potential shows no isotope effect.

3.2. The octahedral site

In the *ab initio* calculations performed for the undistorted BCC lattice the O site comes out to be a saddle point. Nevertheless, a self-localized state centred at O sites may exist as a result of local lattice relaxation. In order to investigate such a state the wavefunction is again required to vanish at the surface of a sphere around the O site. The sphere is chosen large enough so that it includes the four surrounding T sites in addition to the O site (see figure 1). In this way the possible formation of a four-T-ring state can be investigated by the same procedure. In all cases investigated here the wavefunctions are almost zero already at some distance from the surface of the sphere. This means that no errors come in through

Table 1. Quantities characterizing the self-trapped ground state of various hydrogen isotopes at a T site in Fe obtained from the three different pair potentials ((2) first, (3) second and (4) third line). Ground-state vibrational energy E^{vib} , the energy E^{min} of the bottom of the potential well, deformation energy E^{def} , total energy E^{tot} , trace and anisotropy $A - B$ of the double-force tensor, and displacements of nearest-neighbour atoms in per cent of the Fe lattice constant ($a = 2.80 \text{ \AA}$). In brackets the *ab initio* results for periodic FeH (Elsässer et al 1994) at the equilibrium lattice constant ($a = 2.96 \text{ \AA}$).

	E^{vib} (meV)	E^{min} (meV)	E^{def} (meV)	E^{tot} (meV)	trP (eV)	$A - B$ (eV)	$(\Delta l/a)_{\text{NN}}$ (%)
μ^+	728	510	113	1350	5.5	-1.2	2.5
	693	1519	233	2445	8.4	-1.4	3.6
	675 (676)	2250	335	3260	10.4	-1.5	4.1
π^+	639	517	106	1261	5.2	-1.2	2.4
	605	1528	225	2357	8.1	-1.4	3.5
	587 (586)	2259	327	3173	10.2	-1.5	4.1
p	254	558	72	884	4.2	-0.9	1.9
	236	1572	187	1994	7.2	-1.3	3.1
	226 (225)	2302	289	2817	9.3	-1.4	3.8
d	180	567	66	812	4.1	-0.9	1.8
	166	1582	179	1927	7.1	-1.2	3.0
	160 (163)	2311	281	2752	9.1	-1.4	3.8
t	147	571	63	781	4.0	-0.8	1.8
	136	1586	176	1897	7.0	-1.2	3.0
	129 (137)	2315	278	2722	9.1	-1.4	3.8

the boundary condition at the surface of the sphere. In the calculation of wavefunctions and lattice relaxation the same procedure was followed as in the calculations performed for the tetrahedral state (section 3.1). In particular, the same mesh width, reference lattice, and lattice Green function has been used. The energies characterizing the O state (in section 3.3 we will compare them with the corresponding energies for the T state) are shown in table 2 together with trace and anisotropy of the double-force tensor and displacements of the two nearest neighbours. The displacements of the four next-nearest neighbours is smaller by an order of magnitude and the formation of the local potential well at the O site due to lattice relaxation can therefore by no means be simulated by an homogeneous and isotropic lattice expansion.

The particle potentials corresponding to the lattice configurations of the self-trapped O states as obtained from pair potential (4) are shown in figure 4 for (μ^+ , π^+) and (p, t). It is seen that a wide flat potential well is created due to self-trapping around the O site. The isotopè dependence of the potential consists, as in the case of the T state, in a shift in energy (cf. the variations in E^{min} as a function of the isotopic mass which is given in table 2) whereas the potential shape is nearly unaffected. In order to make the very small isotope effect in the potential shape explicit the shifts of E^{min} have been suppressed in figure 4 by taking the respective potential minima as energy zero. In all cases the wavefunction has one maximum at the O site. The situation is different for pair potential (2), which gives rise to weaker forces on the neighbouring Fe atoms. In this case the particle potential corresponding to the lattice configuration of the self-trapped state shows a marked isotope dependence not

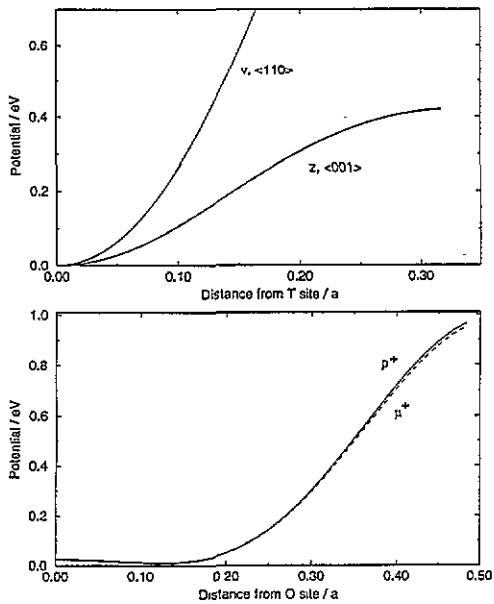


Figure 4. Top: the energy versus displacement curves for the hydrogen isotopes (p, d and t) in α -Fe corresponding to the lattice configuration associated with the self-trapped (ground) state of the T site. Curves are given for two directions (see figure 1). The calculations have been performed with pair potential (4). Bottom: energy versus displacement curves for the lattice configuration of the self-trapped O states as calculated with pair potential (4) for the heavy isotopes p, d and t (solid curve) and the light isotopes π^+ , μ^+ (dashed curve). In both drawings (top and bottom) constant relative energy shifts of the curves obtained for the different isotopes as expressed by the isotope dependence of E^{\min} (see tables 1 and 2) are suppressed.

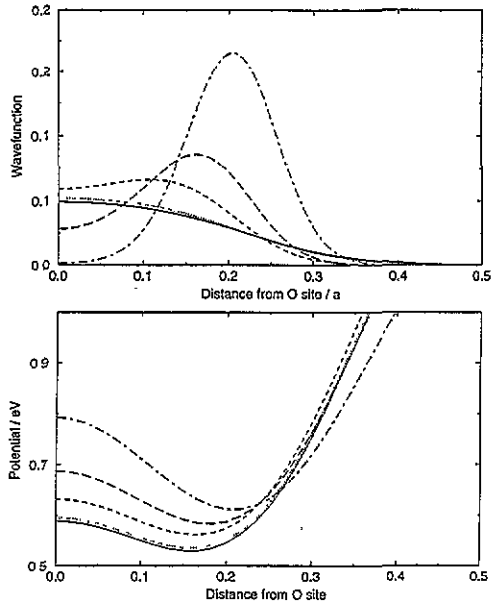


Figure 5. Top: the particle wavefunction along the z path of figure 1 for the self-trapped state of the O site in Fe (calculated by use of potential (2)). From bottom to top at the ordinate axis: t, d, μ^+ , π^+ , p. Bottom: the energy versus displacement curves for Fe (calculated by use of potential (2)) along the z path of figure 1 of a particle in the lattice configuration which corresponds to the self-trapped state of the particle at the O site. From bottom to top at the ordinate axis: μ^+ , π^+ , p, d and t.

only in the energetic position but also in its shape (see figure 5). In particular, remainders of the minima at the T sites are found. These minima are deeper for the heavier particles. Correspondingly, the wavefunctions for the heavier particles show pronounced peaks near the T sites. These states are therefore better classified as 4-T-ring states (the situation is like the one found by Sugimoto and Fukai 1980 for Nb, less pronounced 4-T-sites were found by Puska and Nieminen 1984 for d in Nb). For the lighter particles, including the proton, a real O state with main occupation probability in the vicinity of the O site develops (see figure 5). It should be noted that pair potential (2) gives rise to a rather small $\text{tr}P = 4.0$ eV which is much smaller than the value $\text{tr}P = 10.7$ eV deduced from the volume expansion of FeH. It seems to be extremely unlikely that the larger part of this difference can be attributed to long-range forces beyond the second-neighbour shell of the T site. Very recent *ab initio* results on forces in another BCC metal (Nb, Elsässer *et al* 1994 b) give only very small forces at distances beyond the second-neighbour shell. From these calculations there exists no indication of an unusually large contribution of the second-neighbour shell of an

Table 2. Quantities characterizing the lowest self-trapped state at O sites in Fe (see caption of table 1). The bottom of the potential well, which is characterized by E^{\min} , is not necessarily located at an O site but four equivalent minima may occur shifted from the O towards the four neighbouring T sites (see figure 5).

	E^{vib} (meV)	E^{\min} (meV)	E^{def} (meV)	E^{tot} (meV)	TrP (eV)	$A - B$ (eV)	$(\Delta l/a)_{\text{NN}}$ (%)
μ^+	631	529	133	1293	5.1	2.3	4.3
	586	1575	241	2402	8.2	2.4	5.4
	561	2339	335	3235	10.5	2.3	6.1
π^+	545	534	128	1207	4.9	2.3	4.3
	503	1581	236	2320	8.1	2.4	5.4
	480	2346	329	3155	10.3	2.3	6.0
p	215	561	105	881	4.1	2.2	3.9
	182	1605	216	2003	7.3	2.5	5.3
	170	2371	308	2849	9.7	2.4	6.0
d	168	583	85	835	4.1	1.8	3.4
	128	1610	213	1951	7.2	2.5	5.3
	118	2374	305	2797	9.6	2.4	5.9
t	147	608	64	818	4.2	1.2	2.8
	105	1612	211	1928	7.2	2.5	5.2
	96	2376	304	2776	9.6	2.4	5.9

O (or T) site to the double-force tensor or, put the other way round, for an unusually small contribution of the nearest neighbours, a situation which to some extent is simulated by pair potential (2). For these reasons we do not consider pair potential (2) as a serious candidate for a description of the H-Fe interaction. Therefore, the scenario shown in figure 5 is in our opinion not realistic.

3.3. Octahedral site occupation versus tetrahedral site occupation

The total energy differences between self-localized octahedral and the self-localized tetrahedral lowest energy state are shown in table 3 for the various hydrogen isotopes. It is found that for the three pair potentials used in this work the light hydrogen isotopes (μ^+ , π^+) occupy O sites whereas the heavier isotopes (d, t) occupy T sites. The proton is a borderline case for the two pair potentials which give rise to smaller values of trP. The energy differences are quite small and come about by three counteracting energy terms. The vibrational energy is lower in the self-trapped O state than in the self-trapped T state and thus taken alone would favour O-site occupation. The importance of the vibrational energy is larger for the lighter particles and thus the occupation of O sites by the lighter particles seems to be understandable. On the other hand, the energy E^{\min} of the potential minimum is lower at the T site than at the O site favouring T-site occupation. The same holds for the deformation energy E^{def} . E^{\min} as well as E^{def} depend on the isotope mass, E^{\min} decreases with decreasing isotope mass, whereas the deformation energy increases with decreasing particle mass. However, the sum $E^{\min} + E^{\text{def}}$ depends only very weakly on the particle mass (the variation is smaller than 10 meV between μ^+ and t for all three pair potentials. Even smaller is the mass dependence of the difference of $E^{\min} + E^{\text{def}}$ between the octahedral

and the tetrahedral state (less than 4 meV). In other words, the isotope effect in the site occupation is driven by the isotope dependence of the vibrational energy. The mass at which the transition between O- and T-site occupation occurs depends, of course, on the size of the difference of $E^{\text{min}} + E^{\text{def}}$ between O and T. The origin of the near independence of $E^{\text{min}} + E^{\text{def}}$ must lie in the non-linearities of the particle-host coupling (displacement dependence of the forces). The isotope dependence in the site occupation was found in all previous treatments of hydrogen in BCC metals (Sugimoto and Fukai 1980 and Puska and Nieminen for hydrogen isotopes in Nb, Klamt and Teichler 1986a, 1986b for Nb and Ta). Puska and Nieminen found that p in iron occupies O sites. In their calculations the energy difference between O and T sites came out to be -5 meV. This corresponds to the situation obtained with pair potential (2). In our opinion, however, pair potential (2) gives no adequate description of the Fe-H interaction and therefore p in Fe should occupy T sites.

Table 3. Total energy differences between the self-localized octahedral and the self-localized tetrahedral lowest energy state $\Delta E^{\text{tot}} = E^{\text{tot}}(\text{O}) - E^{\text{tot}}(\text{T})$ in Fe. For negative sign the O site is the stable one.

Pair potential	(2)	(3)	(4)
	ΔE^{tot} (meV)	ΔE^{tot} (meV)	ΔE^{tot} (meV)
μ^+	-57	-43	-25
π^+	-54	-37	-18
p	-2	+9	+32
d	+23	+23	+47
t	+37	+31	+53

Finally we want to comment on the stability of the site having the higher energy, which is the T site in the case of μ^+ , π^+ and the O site for the heavier hydrogen isotopes. It turns out that this site is always unstable and not metastable. Starting with the self-consistently determined higher energy state and relieving the constraint that the wavefunction vanishes outside a sphere around the site in question, a continuous transformation into the stable state takes place upon further iteration with continuously decreasing energy.

4. Conclusions

In order to determine the sites at which a hydrogen isotope, dependent on its mass, will form stable (or metastable) self-localized states in α -Fe, calculations have been performed using hydrogen-Fe pair potentials which have been constructed on the basis of *ab initio* data. Because of the restricted information on the forces exerted by hydrogen on its Fe neighbours three different pair potentials have been used which differ in this respect but describe the various energy versus displacement curves determined *ab initio* for FeH equally well.

It is found that the light hydrogen isotopes μ^+ , π^+ occupy O sites whereas p, d and t occupy T sites except for the potential giving rise to the smallest forces. In that case the O site for p is still lower in energy but by only 2 meV and the site change to T occurs for d. For the reasons outlined at the end of section 3.2 this scenario is not considered as realistic. It should be noted that the O site is a saddle point in the potential surface obtained by *ab initio* calculations in FeH. This configuration is stabilized only by a large and very

anisotropic local lattice distortion. It is found that of the two sites the one which is higher in energy is unstable against small lattice deformations and does not correspond to a metastable configuration. The small energy difference between the O and T site configuration should be reflected in the dynamics of the hydrogen isotopes in α -Fe.

For the two pair potentials corresponding to the stronger forces the shape of the potential wells created by self-trapping at the T or at the O site are practically independent of the particle mass. The wells created by the different isotopes are only slightly shifted in energy relative to each other. This means that the vibrational energies are unchanged if the calculation is performed with the potential created by a point-like particle. Moreover, the sum of the energy of the potential minimum and of the deformation energy is only slightly dependent on the isotopic mass. This holds for the O as well as for the T site.

From both facts taken together it can be concluded that effects of the wavefunction on the lattice relaxation give only very small contributions to the energy difference between O and T sites and that the origin of the isotope effect in the site occupation lies in the vibrational energy which is lower at the O site and more important for lighter particles. Since the energy differences are sometimes very small it seems wise to carry out the full calculation.

The situation is more complicated for the pair potential giving rise to the smallest forces. In that case the shape of the particle potential shows a pronounced mass dependence, but, as mentioned above, this situation is most likely not relevant to the description of hydrogen states in α -Fe.

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