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A THEORETICAL STUDY OF A H–H PAIR
ON THE BCC Fe(100) SURFACE

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Hydrogen adsorption on Fe(100) was analyzed using a semiempirical theoretical method. Calculations were performed using a Fe_{130} cluster. Adsorption sites for one and two hydrogen atoms on the surface correspond to local energy minima configurations.

Changes in the electronic structure of surface Fe atoms were analyzed for the system without hydrogen and with one and two adsorbed hydrogen atoms. Fe atoms close to H weaken their metallic bond. This is due to the formation of H–Fe bonds. Hydrogen influences only its nearest neighbor Fe atoms. The H–H interaction was also analyzed and our results show that H–Fe interaction is much stronger than any possible H–H interaction. No additional decohesion is observed in the Fe–Fe bonds; however, more Fe–Fe bonds are affected.

1. Introduction

Severe embrittlement can be produced in many metals by very small amounts of hydrogen. However, there is not a complete understanding of the hydrogen embrittlement mechanism.[1] Hydrogen is adsorbed into bulk iron at interstitial sites. Experimental studies of iron are very difficult to perform due to the low solubility of H.[2] Gas–metal interactions at surfaces, diffusion and absorption into bulk iron, and trapping of hydrogen have been the aim of intensive experimental and theoretical work.[3–6] There are also many studies devoted to the chemisorption of atomic H on a metal surface, based on LEED or HREELS measurements.[7,8]

A theoretical study of chemisorption of H on Fe(100) with corrected effective medium (CEM) calculations by Raeker and De Pristo reveals that H was found to bind at both threefold and long bridge sites with an equal binding energy and H did not induce any relaxation on the surface layer.[9] Cremaschi *et al.* also studied this system by *ab initio*

configuration interaction (CI) on an embedded cluster model of the Fe surface and found that H strongly binds to the Fe(110) surface at long bridge, short bridge and quasi-threefold sites with similar adsorption energies.[10] McCreery *et al.* described metal–hydrogen interaction using a semiempirical potential for examining a large number of configurations of a hydrogen molecule interacting with an iron surface, and all showed dissociative adsorption.[11]

Hydrogen adsorption on other Fe surfaces and the H–Fe interaction in the bulk of bcc iron and near-crystalline defects have been studied in previous works of our group.[12–17] Juan and Hoffmann[17] considered the H adsorption on Fe(110) using qualitative band structure calculations in the framework of the extended Hückel tight-binding theory and the ASED-MO cluster method. H adsorption on the Fe($\bar{1}$12) surface considering H–H pairs was also theoretically analyzed.[15]

In this work we study the H adsorption on Fe(100) considering the electronic changes on the

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Fe–Fe bonding after incorporating a second H atom and the possibility of any H–H interaction.

2.   The Fe(100) Surface Cluster Model and Its Interaction with H

Solid α-Fe has a bcc structure with a lattice parameter a, for the unit cell, of 2.86 Å. We simulate the solid Fe(100) surface with a cluster formed by 130 iron atoms distributed in three consecutive (100) layers of 60, 42 and 28 atoms, respectively. The surface is the plane formed by 60 atoms, which is the biggest layer. The selected geometry for each plane is hexagonal. The surface layer is an irregular hexagon with two sides of 14.31 Å (six atoms) and four sides of 12.14 Å (four atoms). The spacing between the Fe layers is 1.43 Å. A section of this cluster is shown in Fig. 1. The reference plane is the surface (upper), which is taken as the coordinate origin. All of the calculations were performed with hydrogen atoms at the central part of the cluster in order to avoid border effects.

When the H adsorption on the Fe(100) surface is analyzed, the adsorption energy is mapped at different heights. For each case the H is positioned at different locations along a plane parallel to the Fe(100) surface. The computed energy surface reveals the most favorable adsorption sites.

In order to calculate the H–H pair energy, several simplifications were made. The first H is set at a fixed position (see later), while the other H atom is moved along different positions in the region surrounding the first H atom to obtain another detailed energy plot.

The calculation method is described in the Appendix.

3.   Results and Discussions

3.1.   *Adsorption energies*

The energy of a hydrogen atom was evaluated in a region of the Fe(100) surface indicated in Fig. 1. Calculations were performed at 0.1 Å steps on both indicated axes. Three energy contour lines plots at different distances from the surface were considered, the one at 0.4 Å from the cluster surface being the most energetically favorable. After determining the adsorption site (parallel to the surface), we have optimized the distance of the site to the surface by moving the H atom toward the surface at 0.01 Å steps along the [001] direction, obtaining an energy minimum at 0.4 Å from the surface, as shown in Fig. 2. Figure 3 shows contour lines corresponding to the H adsorption energy surface on the mentioned region (at 0.4 Å from the surface). The absolute minima is -6.75 eV. The adsorption geometry is shown in Fig. 4, and reveals that H atom is close to three Fe atoms: two on the surface (Fe1 and Fe6) and one on the subsurface layer (Fe10); this almost corresponds to a tetrahedral interstitial site of the bcc lattice.
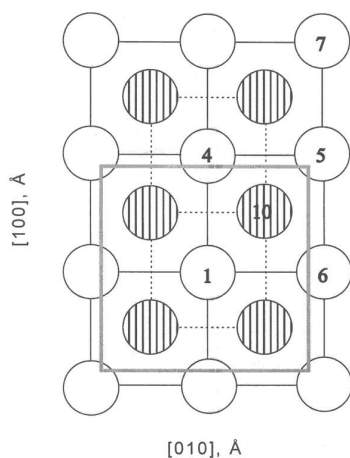

Fig. 1.   Schematic view of the Fe_{130} cluster. The H–Fe_{130} energies were evaluated on the region inside the gray square. ◯ 1st layer; ◍ 2nd layer.
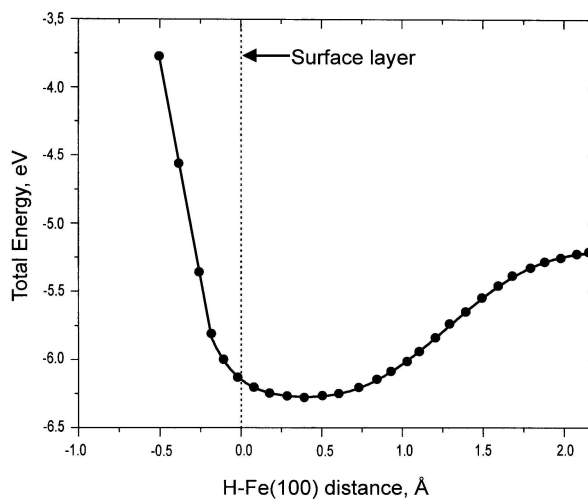

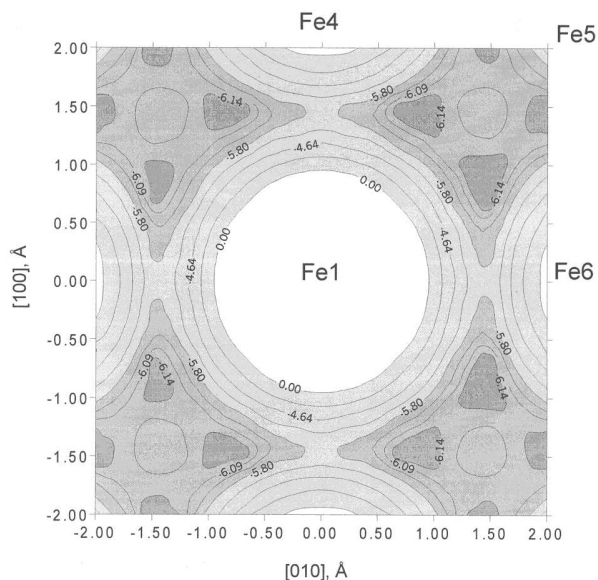Fig. 2.   H adsorption energy versus H distance to the surface.

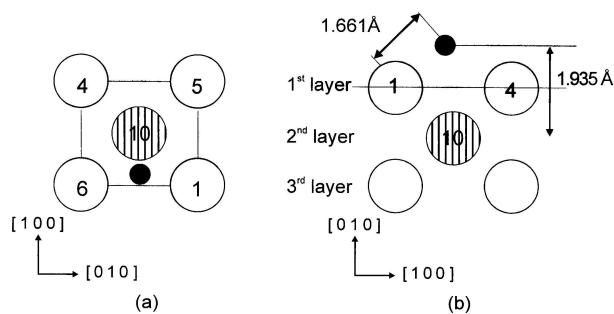Fig. 3. Contour lines corresponding to the energy for the system H–Fe$_{130}$ (eV).

Fig. 5. Contour lines corresponding to the energy for the system H2–H1–Fe$_{130}$ (eV) with H1 fixed (at the H1–Fe$_{130}$ absolute minimum position found previously).

Fig. 4. H adsorption geometry: upside view (a) and lateral view (b) of the minimum energy configuration. ◯ 1st layer; ⏣ 2nd layer; ● H1.
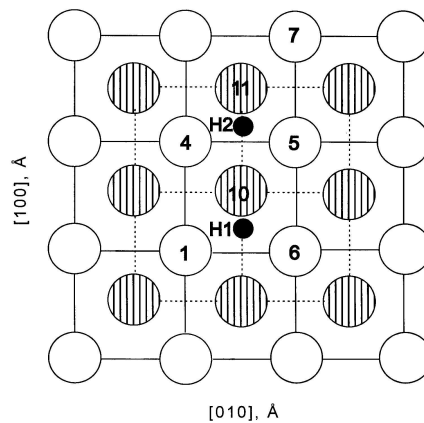
Fig. 6. H1–H2 adsorption geometry. ◯ 1st layer; ⏣ 2nd layer.

On Fe(110), Moritz *et al.* have concluded that H is adsorbed at a quasi-threefold site, with a H-surface distance of 0.9 ± 0.1.[18] Based on experimental studies, Nichtl–Pecher *et al.* and Hammer *et al.* have confirmed that H is indeed adsorbed at such a site.[19,20] Both experimental studies[21,22] and theoretical calculations[9,23] have found no significant difference in hydrogen adsorption energy among long bridge, short bridge and quasi-threefold sites on Fe(110) and W(110).

Figure 5 shows the energy of two hydrogen atoms when one of them is at a fixed position. The fixed position (H1) corresponds to the absolute minimum location found previously. There are several regions of stability for the second hydrogen location.
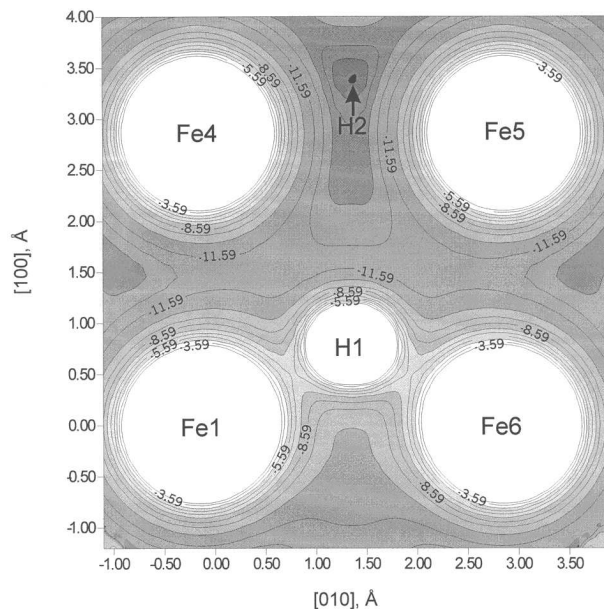
Figure 5 shows only one of them, in which the H–H pair distance results 2.64 Å (this is the smallest possible H–H distance). The location of the H–H pair is shown in Fig. 6. The binding energy for the H–H pair can be computed by noting that one H atom adsorbed on the Fe surface gains 6.27 eV, whereas for the H–H pair on the surface, the energy gain (in one of the minima configurations) is 12.57 eV. Thus the pairing energy is $12.57 - 2(6.27) = 0.03$ eV. This value shows a

very small H–H interaction on the surface which corresponds to a dissociated H_2 molecule. However, previous calculations of our group have shown that inside a cluster, some sort of H–H association close to lattice defects such as vacancies[13,16] and dislocations[14] could be possible.

3.2. *Electronic structure*

The electronic structure of the iron atoms in the cluster is analyzed first. The calculated orbital population for surface Fe atoms is $d^{7.084}$ $s^{0.713}$ $p^{0.266}$. This layer is negatively charged with respect to the inner layers; in particular, for the subsurface layer the electronic structure is $d^{5.431}$ $s^{0.681}$ $p^{0.343}$ (see Table 1). This is not unexpected, but has been discussed in detail in previous papers.[17] There are fewer nearest neighbors of a surface atom compared with the inner atoms. Iron atoms on the surface are second neighbors with each other (Fe1 and Fe4), and their OP value is 0.193 (see Table 2). For Fe–Fe pair first neighbors (Fe1 and Fe10) the OP value is 0.302.

When a H atom is located at the minimum energy site on the surface, the DOS curve is similar to that of the cluster without H except for a small peak at -15.43 eV [Fig. 7(a); total DOS not shown]. The small contribution of H to DOS is due to its low concentration. This peak is present in the projected DOS on H and on the first neighbor to H, as shown in Fig. 7(a), and is mainly the H 1s orbital stabilized by the H–Fe interaction.

As was mentioned before, H is positioned in an almost tetrahedral position, surrounded by three

Fe atoms. Two of them, Fe1 and Fe6, are on the surface; the third, Fe10, is on the subsurface layer (see Fig. 4). Comparing their atomic orbital occupation with and without H, we can see that H–Fe interaction mainly involves s and p bands; the contribution of d orbitals is much less important. Their net atomic orbital occupation diminishes. As a result, an increase in its positive charge is produced. There is an electron density transference to the H atom of 0.361 e^- mainly from neighboring Fe atoms.

The presence of H diminishes the OP value between Fe atoms surrounding it and its effect is mainly local; the OP reduction for Fe–Fe bonds on the surface (Fe1–Fe6) close to H is 20% (see Table 2). For Fe–Fe first neighbors (Fe1 and Fe10) the OP value is reduced by 34%. We can say, then, that a H–Fe bonding is achieved at the expense of weakening the bond between the Fe–Fe pairs nearest neighbors.

Figure 8 shows Fe–H and Fe–Fe COOP curves for Fe–Fe bonds first neighbor and second neighbor to H. Comparing the COOP curves for Fe–Fe bonds close to H with other Fe–Fe bonds on the surface (not shown in the figure), it can be seen that there is a peak at -15.43 eV due to Fe–H orbital mixing which is bonding in character; however, more Fe–Fe antibonding states appear and also the bonding surface

Table 1. Atomic orbital occupations and net charges for Fe and H atoms on the Fe_{130} cluster.

		s	p	d	Charge
Fe(100)	Fe1	0.713	0.266	7.084	−0.063
	Fe10	0.681	0.343	5.431	1.545
H/Fe(100)	Fe1	0.619	0.316	7.005	0.060
	Fe4	0.620	0.308	7.002	0.070
	Fe10	0.607	0.311	5.300	1.782
	H	1.361	0.000	0.000	−0.361
H–H/Fe(100)	Fe1	0.621	0.319	7.051	0.009
	Fe4	0.622	0.311	7.049	0.018
	Fe10	0.704	0.268	6.987	0.041
	H1	1.360	0.000	0.000	−0.360
	H2	1.355	0.000	0.000	−0.355

Table 2. Fe–Fe, Fe–H and H–H OP values for the system with and without H.

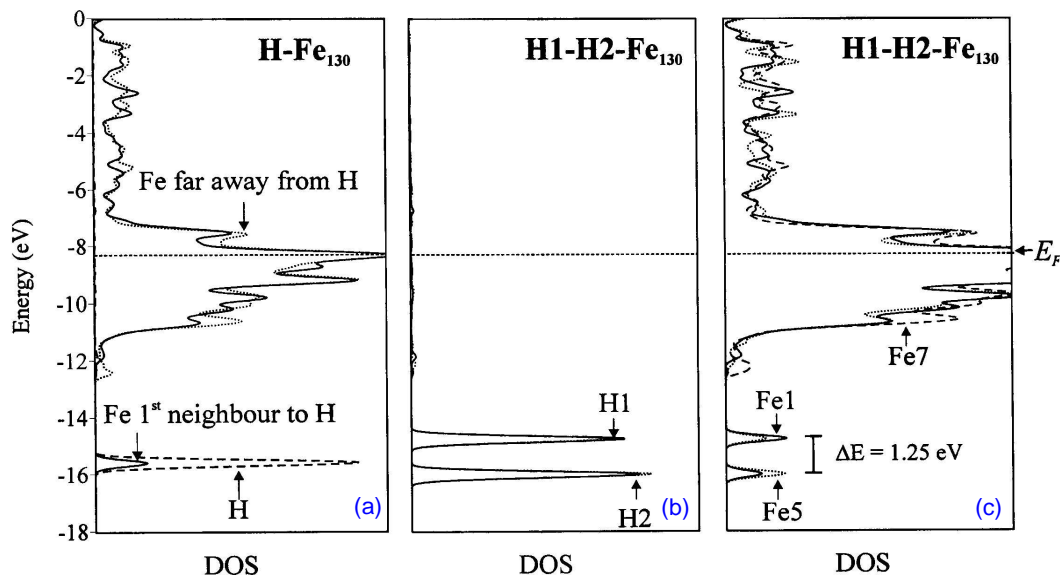|	Bond		OP	Distance (Å)
Fe(100)	Fe–Fe	Fe1–Fe6	0.193	2.86
		Fe1–Fe10	0.302	2.47
H/Fe(100)	Fe–Fe	Fe1–Fe6	0.154	2.86
		Fe1–Fe10	0.198	2.47
	H–Fe	H–Fe1	0.341	1.66
		H–Fe6	0.310	1.71
H–H/Fe(100)	Fe–Fe	Fe1–Fe6	0.154	2.86
		Fe1–Fe10	0.198	2.47
		Fe6–Fe5	0.157	2.86
		Fe6–Fe10	0.203	2.47
	Fe–H	H1–Fe1	0.350	1.66
		H1–Fe6	0.318	1.71
		H2–Fe4	0.382	1.57
		H2–Fe5	0.348	1.77
	H–H	H1–H2	0.000	2.64

Fig. 7. Projected DOS for the H–Fe$_{130}$ system on the H atom, Fe atom 1st neighbor to H (Fe1) and the Fe atom far from H (a). Projected DOS for the H1–H2–Fe$_{130}$ system on H1 and H2 (b) projections on the Fe atom 1st neighbor to H1 (Fe1), Fe atom 1st neighbor to H2 and 2nd neighbor to H1 (Fe5) and Fe atom 2nd neighbor to H2 (Fe7) (c).
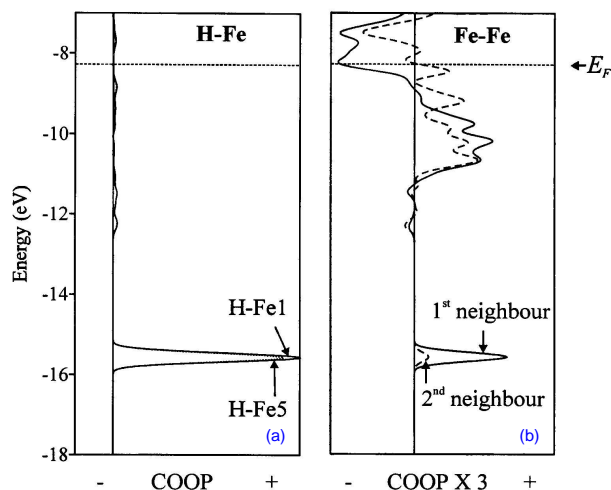

Fig. 8. H–Fe COOP curves for Fe close to H (a) 1st neighbor and 2nd neighbor Fe–Fe COOP curves for Fe pairs close to H (Fe1–Fe10 and Fe4–Fe5 respectivelly), (b) both for the H–Fe$_{130}$ system.

states are less bonding when H is present. As a net result Fe–Fe bonds gain an antibonding character when H is present, so integration up to the Fermi level produces a smaller OP value.

When two H atoms are considered, two new peaks emerge below the d metal band in the total DOS, as can be seen in the projected DOS of Figs. 7(b) and

7(c). The total DOS curves are similar to those obtained for the free cluster, except for two small peaks at −16.0 eV and −14.7 eV; these peaks have mainly contributions from the H 1s and Fe 4s and 4p orbitals. The two peaks present in the projected DOS for Fe close to H indicate that the H–Fe interaction is strong for nearest neighbors. There is no contribution from Fe atoms second neighbors to H (Fe7).

The charges are distributed from the Fe atoms close to the impurity, leaving the H atoms with charges of 0.360 e$^-$ and 0.355 e$^-$ (see Table 1). Fe–H COOP curves [Fig. 9(a)] present two bonding peaks, while the COOP curve corresponding to the interaction between both H atoms [Fig. 9(b)] presents a bonding peak at −16.0 eV and an antibonding peak at −14.7 eV. The resulting OP for the H–H bonding is almost null, revealing that there is almost no H–H interaction (H–H OP in the vacuum at the same distance is 0.177). The COOP curves between first neighbor iron atoms close to H atoms [Fig. 9(c)] present two bonding peaks below the d band, while the COOP curves for second neighbor iron atoms close to H present an antibonding and a bonding (the lower) peak. The electronic configuration for H atoms and the Fe atoms close to H, and the H–Fe OP are similar to the previous case (one H; see Table 2), so the presence of a second H does not
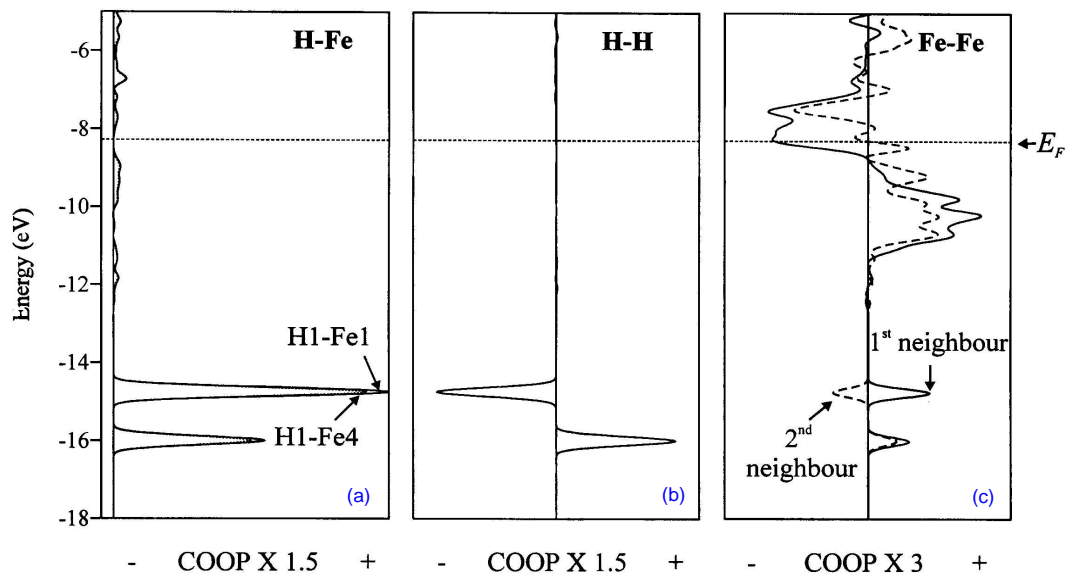
Fig. 9.   H–Fe COOP curves (a), H–H COOP curve (b) and 1st neighbors and 2nd neighbors Fe–Fe COOP curves (c), for H–H–Fe_{130}. COOP range triplicates the scale indicated in Fig. 7.

affect the bonding between the first H and its nearest Fe neighbors. We can say that H atoms prefer to be bonded to the surrounding Fe instead of bonding to each other.

4.   Conclusions

The energetic and electronic structure of hydrogen on the bcc Fe(100) surface has been studied by ASED-MO cluster calculations. First we have considered the Fe(100) clean surface, then we have considered the adsorption of a H atom, and finally the adsorption of a second H atom. The addition of a H atom diminishes the strength of the local Fe–Fe bond to about 34%. Our results show the decohesion of Fe–Fe bonds in the surface. The Fe–H interaction occurs mainly via Fe 4s and 4p and H 1s orbitals. The Fe–H bond is formed at the expense of the Fe–Fe bonding.

When two H atoms are adsorbed in the surface at a H–H distance of 2.64 Å, the results are qualitatively similar to that obtained for only one H atom; we can say that each H atom bonds to the surrounding Fe instead of bonding each other. The second H acts as an additional interstitial with almost no interaction with the first H present. The H–Fe interaction is much stronger than any possible H–H

interaction. No additional decohesion is observed in the Fe–Fe bonds; however, in this case more Fe–Fe bonds could be affected.

Appendix

The energies and optimized positions for H were calculated with a cluster approximation using the semiempirical molecular orbital ASED-MO method, which predicts molecular structures from atomic data (atomic wave functions and ionization potentials). This method is quite approximate but it is used because it provides a qualitative picture of H–Fe interactions.

Parameters necessary for calculations are listed in Table 3. Experimental values for ionization potentials were taken from spectroscopic data.[24] The values for the Slater exponent were those optimized by Nath and Anderson for describing Fe–Fe bulk interaction.[25]

The ASED-MO method is a modification of the extended Hückel method, which includes a repulsive term for the electrostatic interaction between nuclei.[26] The energy was computed as the difference ΔE between the H–Fe system when the H atom is absorbed at a specified geometry and when it is far away from the Fe cluster surface. It can be

Table 3. Parameters for ASED-MO calculations.

Atom	Orbital	Ionization potential (eV)	Slater exponent (au^{-1})	Linear coefficient	Electronegativity (Pauling)
H	1s	13.60	1.00		2.1
Fe	3d	9.00	5.35	0.5366	1.8
			1.80	0.6678	
	4s	7.87	1.70		
	4p	4.10	1.40		

expressed as

$$\Delta E_{\text{total}} = E(\text{H}_{1-2} - \text{Fe}_{130}) - E(\text{Fe}_{130}) - E(\text{H}_{1-2})$$

$$+ E_{\text{repulsion}},$$

where E is the electronic energy, and $E_{\text{repulsion}}$ is the repulsive energy for nucleus j in the presence of a fixed atom i:

$$E_{\text{repulsion}} = \frac{1}{2} \sum_i \sum_{j \neq i} E_{ij}$$

(E_{ij} is a pairwise electrostatic term). The summation extends over all Fe–Fe, H–Fe and H–H pairs.

To understand the H–Fe interaction we used the concept of DOS (density of states) and COOP (crystal orbital overlap population) curves. The DOS curve is a plot of the number of orbitals per unit volume per unit energy. The COOP curve is a plot of the overlap population weighted DOS versus energy. The integration of the COOP curve up to the Fermi level (E_{F}) gives the total overlap population of the bond specified and it is a measure of the bond strength.

Due to the approximate nature of the ASED method, the reported values for the energy should be interpreted in their *relative* terms.

Acknowledgments

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