Brief review of quantum chemical calculations on H-Fe interactions

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Introduction

We are interested in plasma interaction with reduced activation steels. However, thus far, there do not seem to be reports in the literature on the topics of erosion or retention of H/D/T in steels from DFT calculations.

There has been emphasis on the following topics:

- Hydrogen embrittlement of steels
- Hydrogen storage in alloys (Mg, Li, Al, Ti, other hydride-forming metals)

Hydrogen embrittlement I

- Interaction of hydrogen with steels induces structural weakening followed by crack formation

Source: http://en.wikipedia.org/wiki/Hydrogen_embrittlement

- Important phenomenon in hydrogen tanks and in nuclear fission reactors (zirconium hydride formation)
- Known for a long time: First time reported by W. H. Johnson, "On some remarkable change produced in iron and steel by the action of hydrogen and acids", Proc. Roy. Soc. London **23**, 168 (1873).

Hydrogen embrittlement II

- Mechanism starts with atomic **hydrogen diffusion into the metal** at elevated temperatures
- **H_2 formation** within the metal
- Buildup of **pressure** due to stable H_2 molecules inside the metal → **crack formation**
- Countermeasures: Acid treatment, followed by "baking out" hydrogen
- Problematic: carbon in steel; forms CH_4 molecules with hydrogen atoms, accelerates crack formation
- Another problem: oxygen impurities, form H_2O

Quantum chemical calculations

- DFT calculations of hydrogen diffusion in iron mostly performed by group of Emily A. Carter (Princeton University)

Emily A. Carter

Well known for development of orbital-free DFT method, treatment of electron correlation, and applications in energy-related materials

http://www.princeton.edu/carter/

Quantum chemical calculations I

PHYSICAL REVIEW B **70**, 064102 (2004)

Diffusion of interstitial hydrogen into and through bcc Fe from first principles

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(Received 17 December 2003; revised manuscript received 12 May 2004; published 6 August 2004)

Spin-polarized DFT calculations on hydrogen:

- adsorption
- absorption
- dissolution
- diffusion energetics

in bulk bcc Fe.

Quantum chemical calculations II

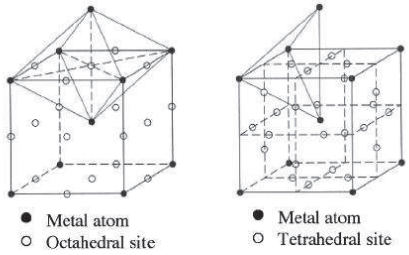
DFT Method: Spin-polarized PBE-PAW
Basis set: plane waves
Different unit cell sizes: Fe_2, Fe_{16}, Fe_{54}, Fe_{128}
Interaction energy of H with iron defined as:

$$\Delta E = E(\mathrm{Fe}_n\mathrm{H}) - E(\mathrm{Fe}_n) - \tfrac{1}{2}E[\mathrm{H}_{2(g)}].$$

Nudged elastic band (NEB) method for location of diffusion transition states

Quantum chemical calculations III

Which is the dominant absorption site? Tetrahedral site or octahedral site?



Quantum chemical calculations IV

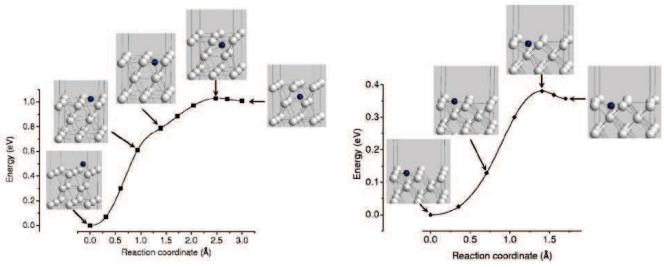
In bulk: H prefers tetrahedral site over octahedral site

TABLE II. The energy difference ($\Delta E = E_o - E_t$) between H in the o-site and t-site of bcc Fe for both unrelaxed and relaxed structures (for the unrelaxed structure, $a = 2.86$ Å).

Supercell	ΔE, unrelaxed (eV)	ΔE, relaxed (eV)
Fe_2H	0.51	0.01
$Fe_{16}H$	0.47	0.13
$Fe_{54}H$	0.46	0.13
$Fe_{128}H$	0.47	0.13

Quantum chemical calculations V

- H prefers to stay adsorbed on the surface:



Fe(110) Fe(100)

- Dissolution of H atoms in Fe **endothermic**: +0.3 eV

Quantum chemical calculations VI

- Dissolution energy agrees with experiment:

TABLE III. Dissolution energies (ΔE) of hydrogen in the t-site of bcc Fe with decreasing H concentration (C_H) for both unrelaxed and relaxed structures (for the unrelaxed structure, a=2.86 Å) and percent change in volume (ΔV). For the theoretical dissolution energies, the ZPE-corrected values are in parentheses.

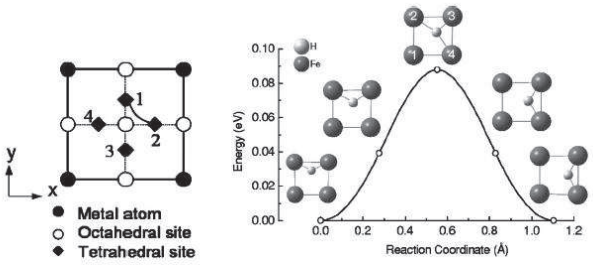
Method	Supercell	C_H (at.%)	ΔE, unrelaxed (eV)	ΔE, relaxed (eV))	ΔV (%)[a]
Current work	Fe_2H	33	0.45	0.20	11.5
	$Fe_{16}H$	5.9	0.27	0.16	2.10
	$Fe_{54}H$	1.8	0.28	0.19	0.57
	$Fe_{128}H$	0.78	0.29	0.20(0.30)	0.06
USPP-GGA[b]	$Fe_{16}H$	5.9		0.19(0.30)	
Experiment[c]				0.296	

[a]The volume increase of the relaxed Fe_nH cell with respect to the relaxed Fe_n cell.
[b]Ref. 20.
[c]Ref. 10.

- Dissolution of H atoms in Fe endothermic: +0.3 eV

Quantum chemical calculations VII

- H easily migrates from one t-site to the next:



Summary

- Dissolution of hydrogen into bulk iron is endothermic, associated with 0.4 – 1 eV barrier depending on the choice of surface
- H diffusion in iron fast via low-barrier jumps between t-sites

Outlook

- Need potentials for steels, either classical or tight-binding for MD simulations
- Tight-binding Fe-H parameters: A. T. Paxton and C. Elsaesser, PRB **82**, 235125 (2010)
- DFT too expensive for steels (extremely large unit cells required to treat non-stoichiometric composition; e.g. 0.1% carbon contents requires at least 1000 atom cell)