Study of impurities influence on the hydrogen dissolution energy in the bcc iron

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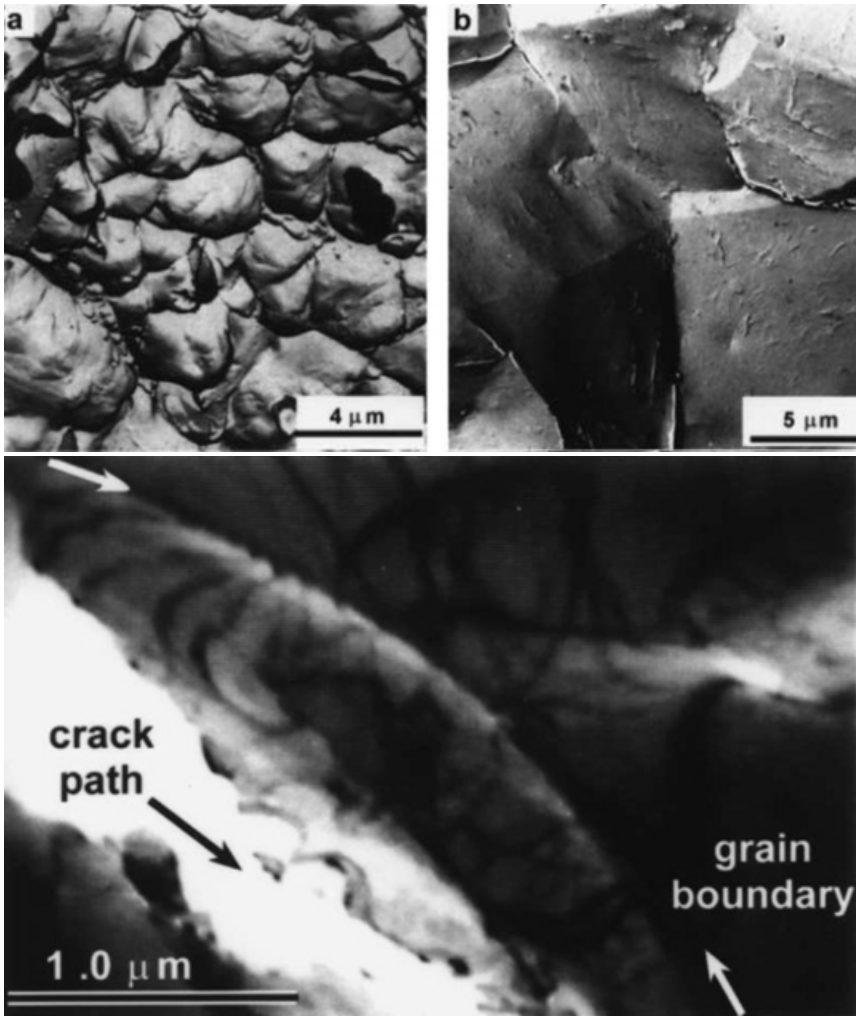
Outline

1. Introduction
2. Problem
3. Calculation method
4. Parameters of the simulation
5. Results
6. Conclusions

Hydrogen embrittlement of metals



I.M. Robertson / Engineering Fracture Mechanics 68 (2001) 671-692

The following processes can take place during cooling:

- Sharp decreasing of hydrogen solubility
- Defects formation (cracks, blisters)
- Plastisity decreasing and brittleness increasing
- Material degradation

Ways to avoid hydrogen embrittlement

- Vacuumizing during a melting process
- Purging of a liquid metal by noble gases

} Expensive!

- **Doping by impurities which are able to trap hydrogen and increase its solubility in iron**

$\Downarrow$

Simple and **accessible** way to control hydrogen content in iron

Interesting impurities: Palladium [1], Titanium [2, 3], Chromium [4], Vanadium [3], etc.

[1] Arkharov, et al. / PhChMM (USSR) 12 (1976) 47–51
[2] Myers, et al. / Rev. Mod. Phys. 64 (1992) 559–617
[3] Sigworth et al. / Metal Science 8 (1974) 298–310
[4] Thomas et al. / Metal. Trans. A. 33 (2002) 1991–2004

Problem

To understand influence of impurities on hydrogen dissolution we need to calculate dissolution energy of hydrogen in bcc iron with impurities and binding energy of hydrogen with the impurities.

To solve this problem we need:

1. Find optimal parameters of the simulation method.
2. Calculate dissolution energy and binding energy of hydrogen in bcc iron with the following impurities: Mg, Al, Si, $3d$ (Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn) and $4d$ (Y, Zr, Nb, Mo, Pd, Cd).
3. Calculate elastic and electronic contributions to the dissolution energies of hydrogen in bcc iron with the impurities.

Dissolution and binding energy of hydrogen

Dissolution energy of hydrogen in iron:

$$\underbrace{E_{\text{diss}}(\text{H})}_{\sim 0.1\ \text{eV}} = \underbrace{E(\text{Fe}_n\text{H})}_{\sim 10^4 \ldots 10^6\ \text{eV}} - \underbrace{E(\text{Fe}_n)}_{\sim 10^4 \ldots 10^6\ \text{eV}} - \frac{1}{2}E[\text{H}_{2(g)}]$$

$E_{\text{diss}}(\text{H})$ — dissolution energy of H in Fe
$E(\text{Fe}_n\text{H})$ — Fe_nH supercell total energy
$E(\text{Fe}_n)$ — Fe_n supercell total energy
$E[\text{H}_{2(g)}]$ — total energy of the hydrogen molecule
n — number of atoms in the ideal supercell

Binding energy of hydrogen with impurity metal **Me**:

$$E_{\text{b}}(\text{H-Me}) = \underbrace{(E(\text{Fe}_n\text{H}) - E(\text{Fe}_n))}_{E_{\text{diss}}(\text{H in Fe}_n\text{H})} - \underbrace{(E(\text{Fe}_{n-1}\text{MeH}) - E(\text{Fe}_{n-1}\text{Me}))}_{E_{\text{diss}}(\text{H in Fe}_{n-1}\text{MeH})}$$

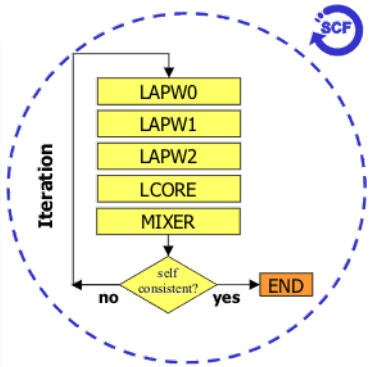
Calculation method

www.wien2k.at

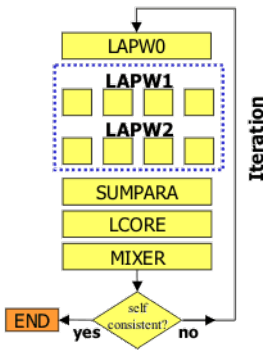
We used WIEN2k simulation package based on **Density Functional Theory (DFT)** with **Full-Potential Linearized Augmented Planewave Method (FP-LAPW)**.

Input:

Lattice constants (a,b,c)
Supercell
Lattice type (BCC, FCC, HCP, . . .)
NM, FM, AFM
RK_{max}
k-points
. . .



single mode



parallel mode

Output

Total energy
Forces on atoms
Optimized structure
DOS
Electronic density
. . .

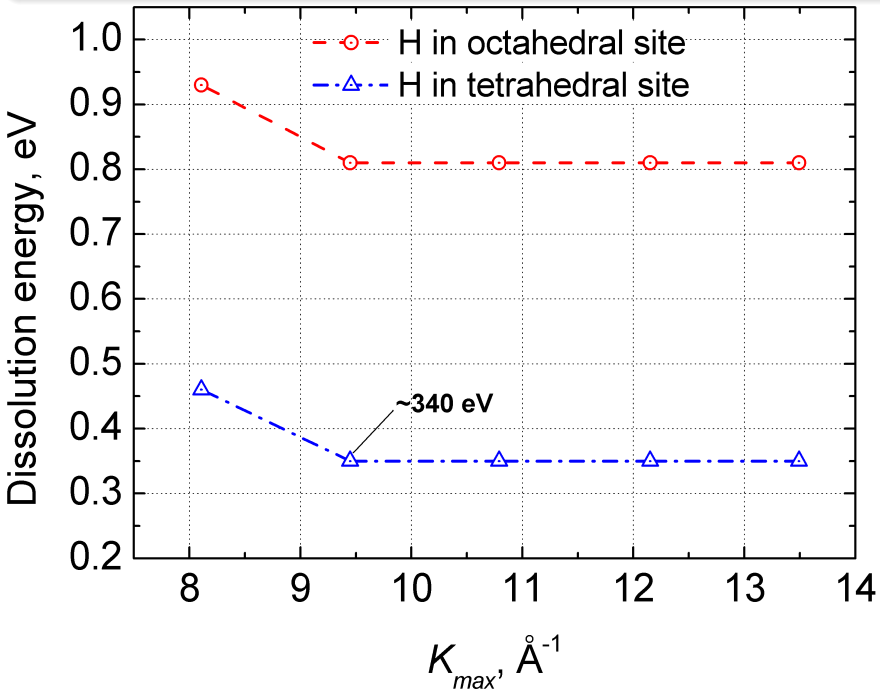
Parameters of the simulation

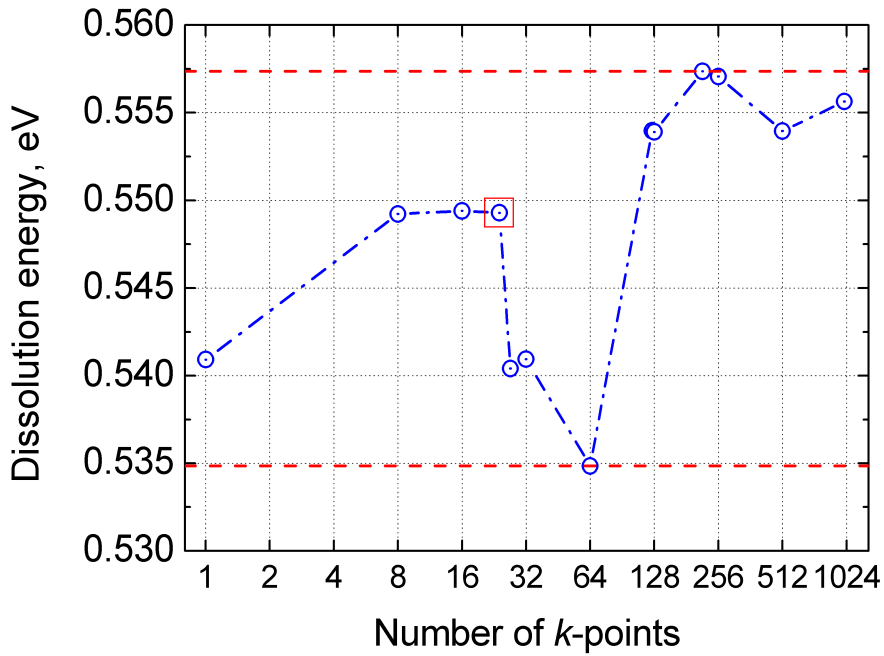
Main parameters:

Supercell with bcc structure:
(**53** atoms of Fe) + **1** impurity atom (Mg, Al, Si, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Pd, Cd) + (**1** atom of H)
R_{mt}(Fe): 1.06 Å (2.0 a.u.)
R_{mt}(impurities): 1.16 Å (2.2 a.u.)
R_{mt}(H): 0.37 Å (0.7 a.u.)
V_{xc}: GGA-PBE96
$E_{cut-off}$: 340 eV
Number of k-points: 24

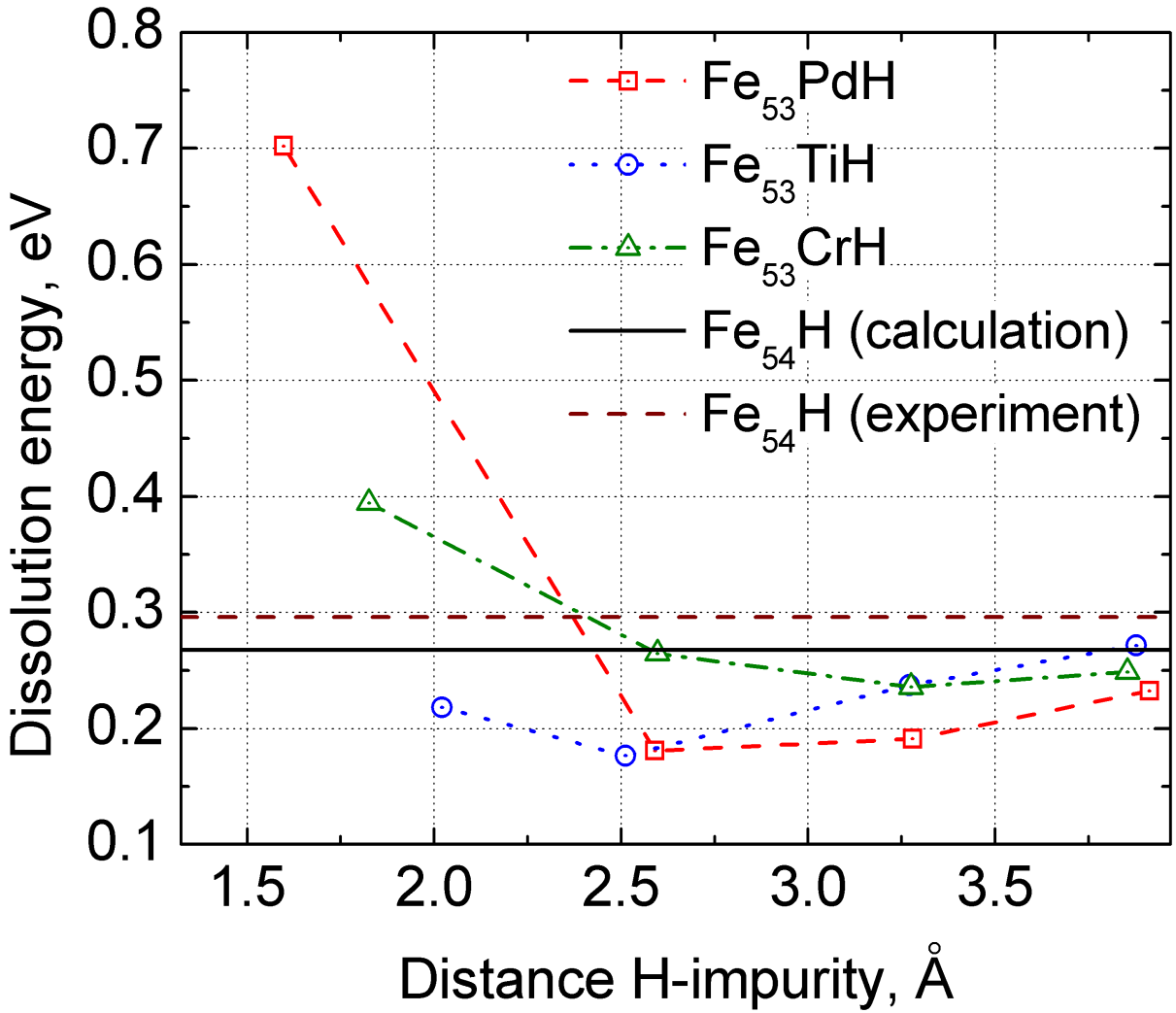
Convergence criteria

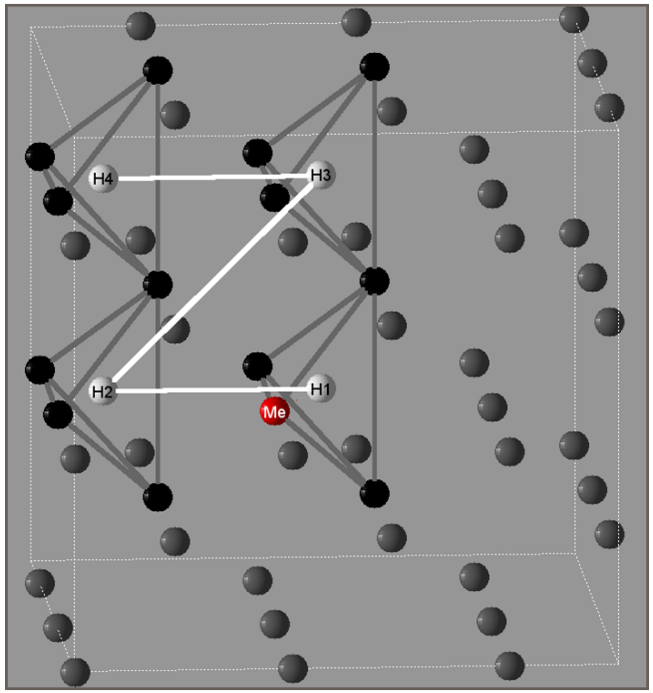
energy: 1.0 meV
charge: 0.001 e^-
forces: 0.01 eV/Å
(volopt + min_lapw on each step)





Dissolution energy of H in Fe with impurities





Contributions in the dissolution energy

$$E_{\text{diss}} = E^{\text{relax}}_{\text{Fe}_{53}\text{MeH}} - E^{\text{relax}}_{\text{Fe}_{53}\text{Me}} - \frac{1}{2}E_{\text{H}_2} = -E_{\text{elastic}} + E_{\text{electronic}}$$

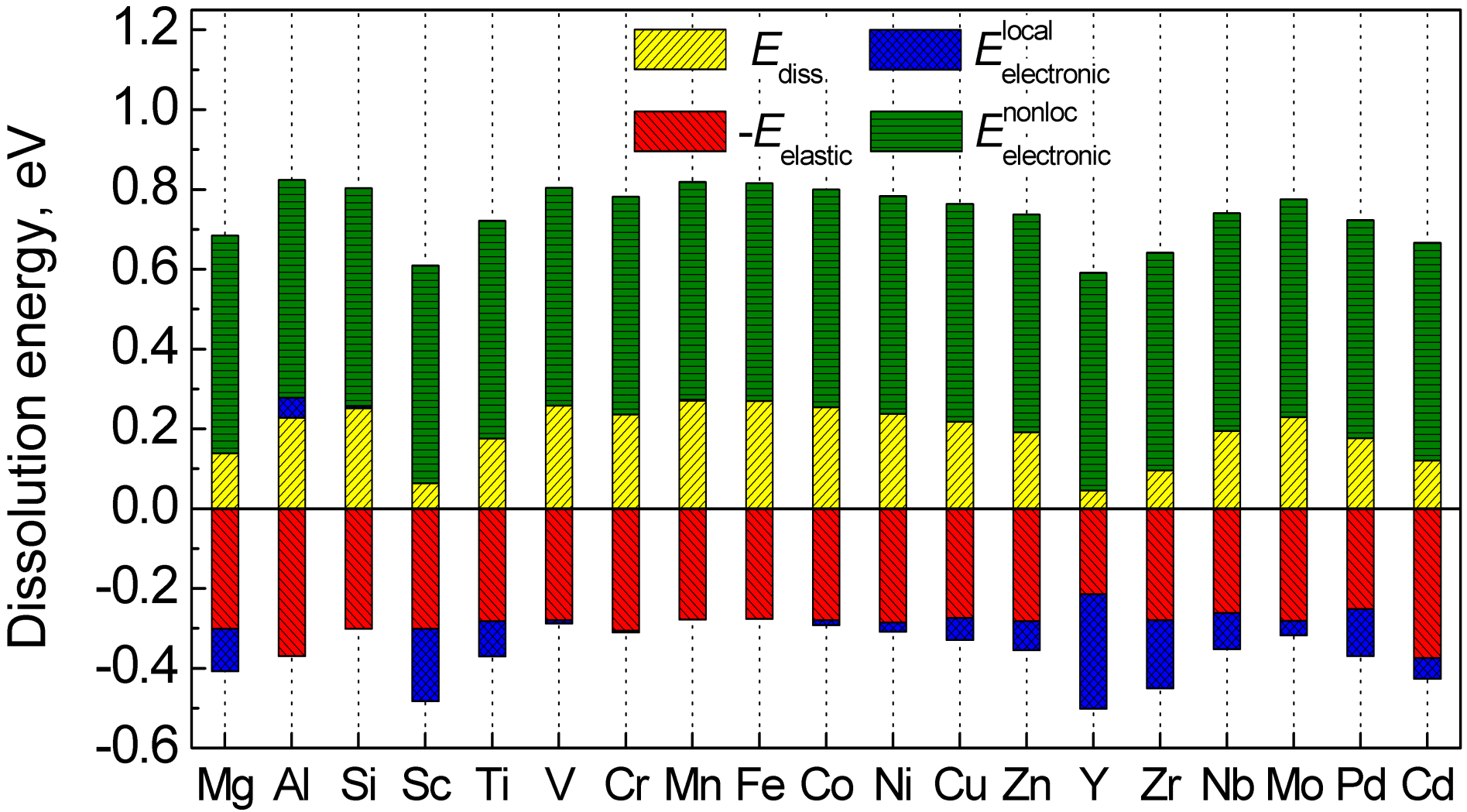
$$E_{\text{elastic}} = -E^{\text{relax}}_{\text{Fe}_{53}\text{MeH}} + E^{\text{nonrelax}}_{\text{Fe}_{53}\text{MeH}}$$

$$E_{\text{electronic}} = E^{\text{nonrelax}}_{\text{Fe}_{53}\text{MeH}} - E^{\text{relax}}_{\text{Fe}_{53}\text{Me}} - \frac{1}{2}E_{\text{H}_2} = E^{\text{local}}_{\text{electronic}} + E^{\text{nonloc}}_{\text{electronic}}$$

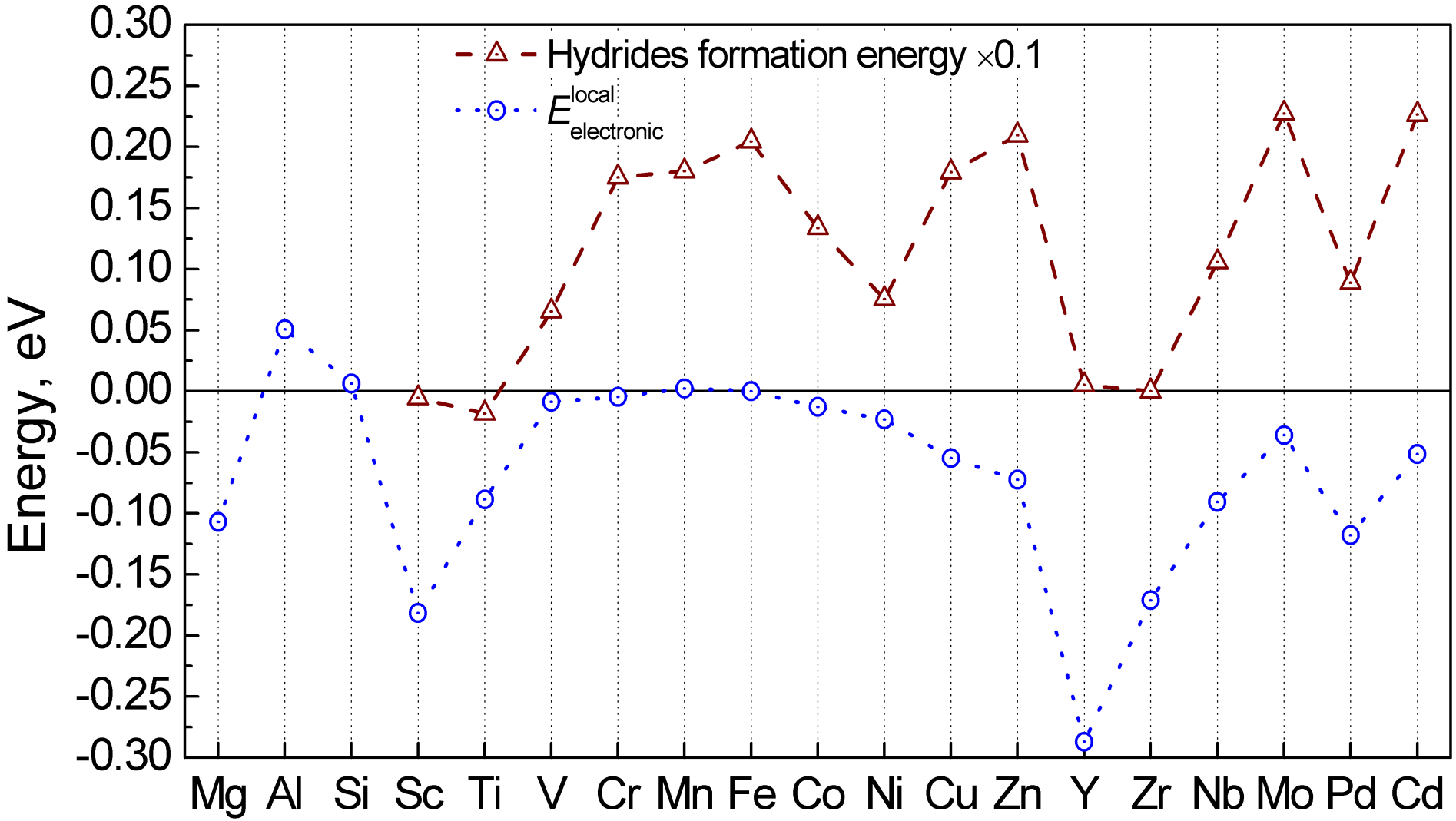
$$E^{\text{local}}_{\text{electronic}} = E^{\text{nonrelax}}_{\text{Fe}_{53}\text{MeH}} - E^{\text{relax}}_{\text{Fe}_{53}\text{Me}} - E^{\text{nonrelax}}_{\text{Fe}_{54}\text{H}} + E^{\text{relax}}_{\text{Fe}_{54}}$$

$$E^{\text{nonloc}}_{\text{electronic}} = E^{\text{nonrelax}}_{\text{Fe}_{54}\text{H}} - E^{\text{relax}}_{\text{Fe}_{54}} - \frac{1}{2}E_{\text{H}_2}$$

Contributions in dissolution energy of H in Fe with $3d$ and $4d$ metals

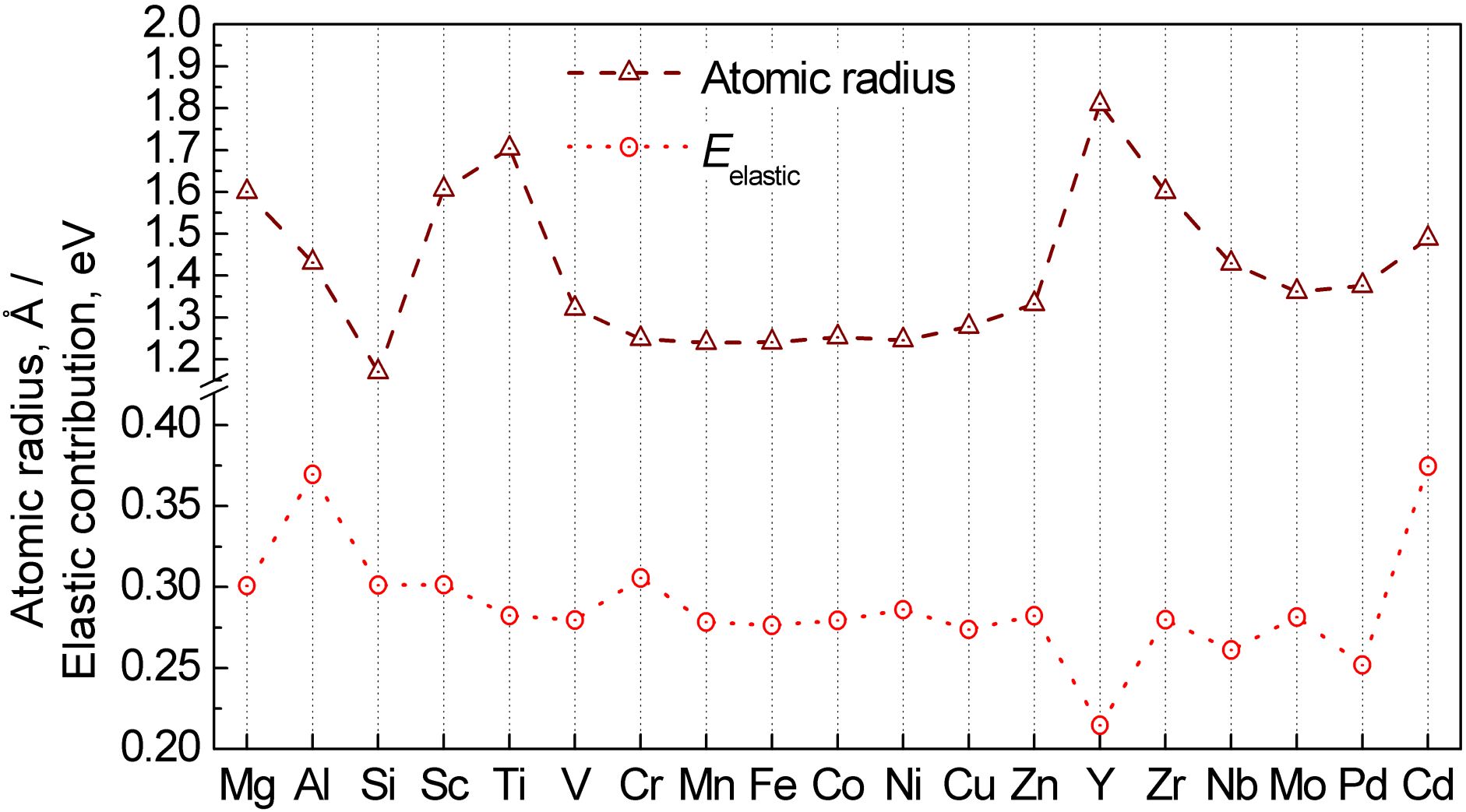


Comparison of local electronic contributions with hydrides formation energies

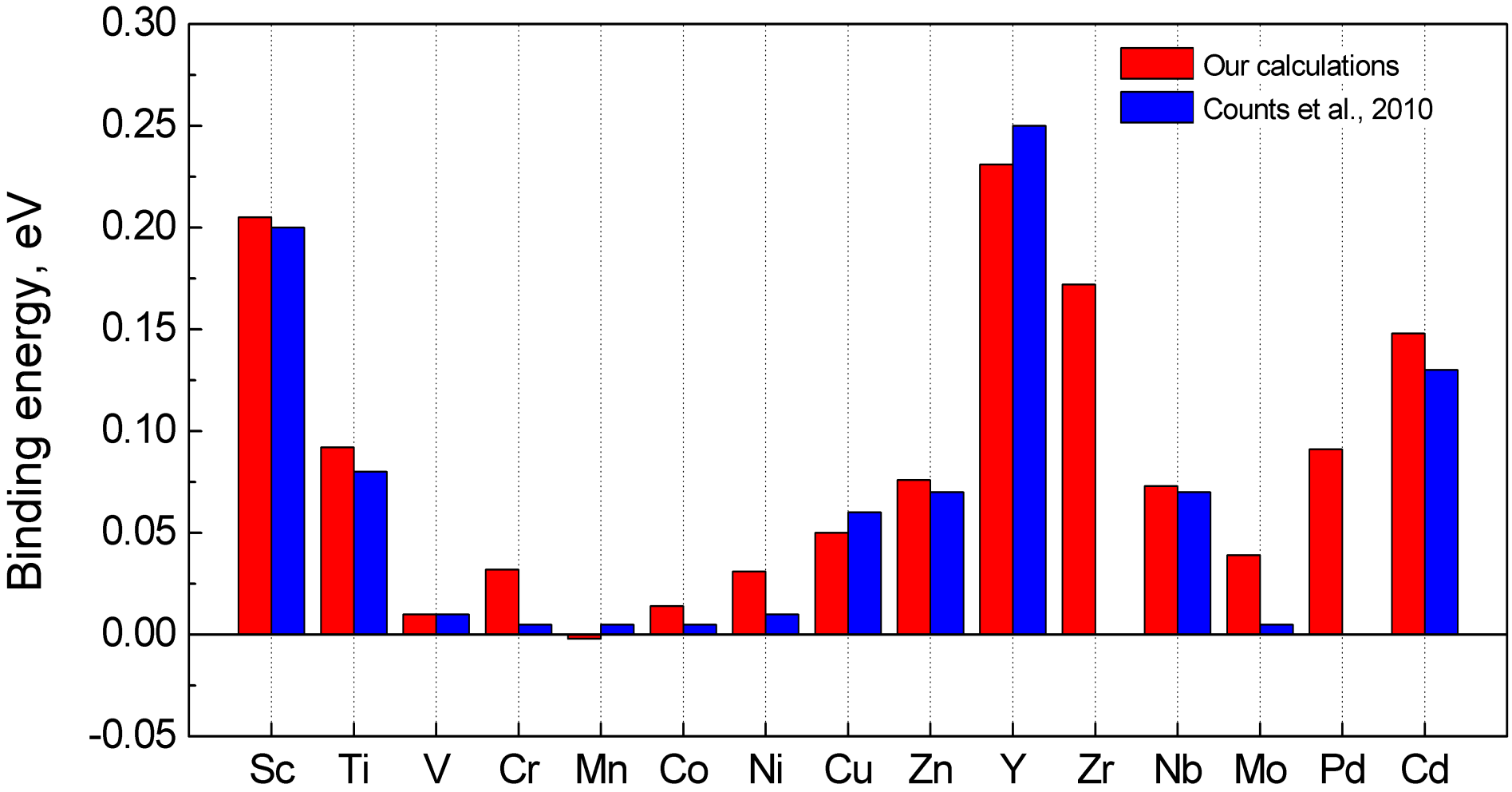


Smithson et al. / Phys. Rev. B 66, 144107 (2002)

Comparison of elastic energies with atomic radii of $3d$ and $4d$ metals



Binding energy with $3d$ and $4d$ metals



Conclusions

- Influence of Mg, Al, Si, $3d$ (Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn) and $4d$ (Y, Zr, Nb, Mo, Pd, Cd) metallic impurities on dissolution energy of hydrogen in bcc iron was examined using first principles calculations in WIEN2k *ab initio* simulation package.
- Elastic and electronic contributions to the dissolution energies of hydrogen in bcc iron with impurities were calculated. We found direct connection of the elastic contributions with the atomic radii of the metallic impurities, and electronic contributions with the hydrides formation energies of the corresponding metals.
- Binding energies of hydrogen with the impurities were computed and the highest binding energies were observed for hydrogen and Sc, Ti, Y, Zr, Pd, Cd. The data are in good agreement with the recent work of Counts et al. It is worth to note, that in the literature Zr and Pd are not present, and our investigation fills up the gap.

Main publications:

- Theory of hydrogen solubility in binary iron alloys based on *ab initio* calculation results / D. A. Mirzaev, A. A. Mirzoev, K. Yu. Okishev, M. S. Rakitin // *Molecular Physics*. — 2012. — V.110. — P. 1299–1304.
- Theory of Hydrogen Solubility in Binary Iron Alloys Based on First-Principles Calculation Results / A. A. Mirzoev, M. S. Rakitin, D. A. Mirzaev, K. Yu. Okishev // Thermodynamics 2011: Book of abstracts. — Athens, Greece. — 2011. — P. 524.
- *Rakitin, M. S.* Effect of palladium and titanium impurities on hydrogen solubility in bcc iron / M. S. Rakitin, A. A. Mirzoev // Summer School: Computational Materials Science: Contributions. — San Sebastian, Spain. — 2010. — P. 54–55.


Thank
You
Dank u wel
Merci
Gracias
Grazie mille
Arigato
Obrigado
Dankscheen
Mahalo
Juspaxar
Khawp khun
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Salamat
Efcharisto
Toda raba
Cám ơn
Dhanyawaad
Köszi
Kamsahamnida
Biyan
Shukria
Shukuria
Pidamayado
Dankon
Tusen takk
Terima kasih
Tashakkur
Doh je
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Merastawhy