Vacancy and interstitial type defects in Fe, W and other bcc metals

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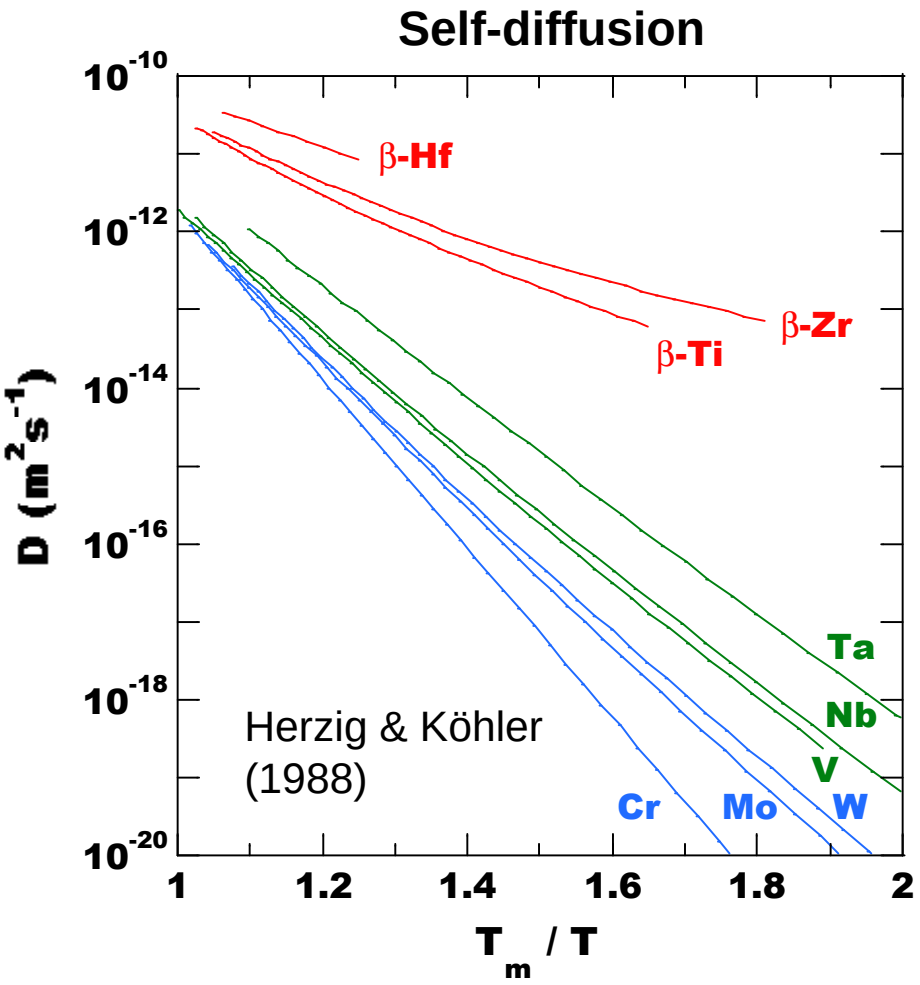
Group dependence of defect properties in BCC transition metals

3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
4d	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
5d	La	Hf	Ta	W	Re	Os	Ir	Pt	Au

- Strong group dependence of the properties of bcc metals: elastic constants, phonons, self-diffusion
- Related to bimodal shape of the electronic density of states
- Impact on radiation defect properties: vacancy clusters, self-interstitials and self-interstitial clusters ?



Tool box

♦ ***Ab initio* electronic structure calculations**

- Formalism: DFT, mostly, GGA-PBE, LDA or AM05
- Codes: SIESTA (localized basis) and plane-wave codes (PWSCF, ABINIT)
- Spin polarized calculations in Fe
- Supercell method (constant P or constant V)
- 128 and up to 432 atom supercells

♦ **Empirical potentials for iron**

M.I.Mendelev et al., Phil. Mag. (2003)

- Mendelev *et al.* 2003/2004 ; new fits
- Molecular statics
- Lattice dynamics
- Activation Relaxation Technique (ART) for systematic exploration of potential energy surface

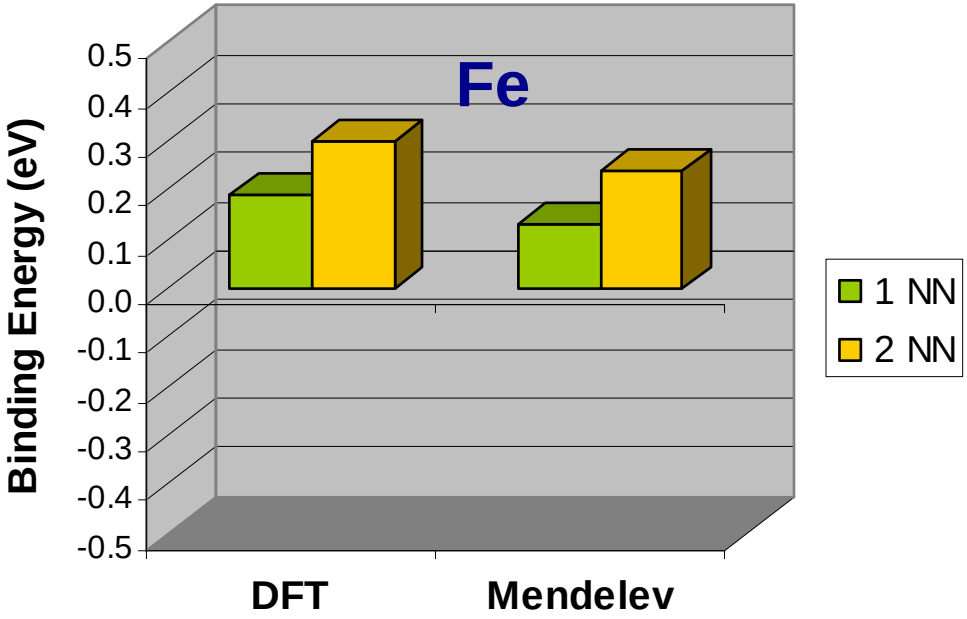
Ouline

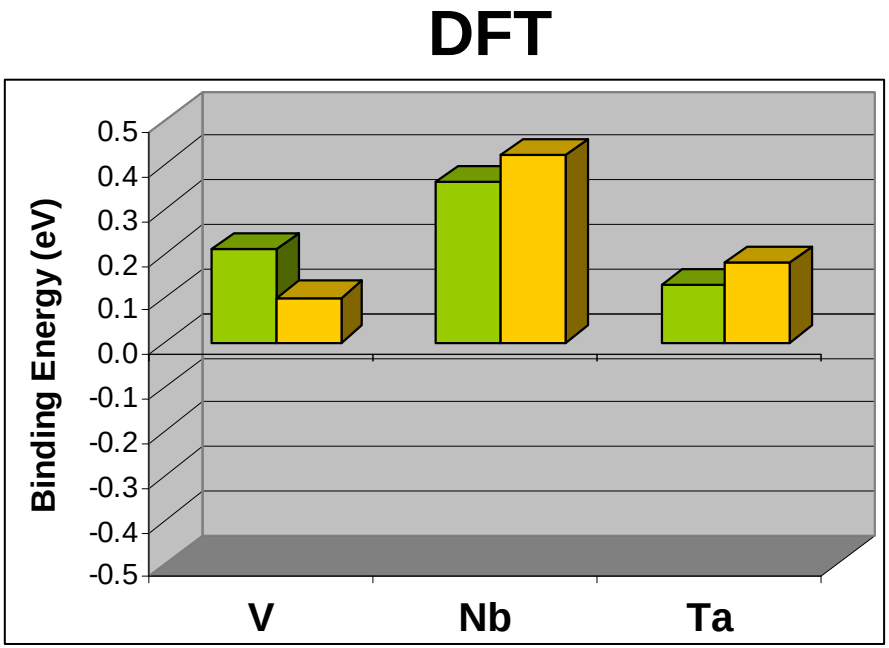
1. **Vacancy clusters**
   - **Di-vacancy binding energy**
   - **The case of W**
   - **Migration energies in Fe**

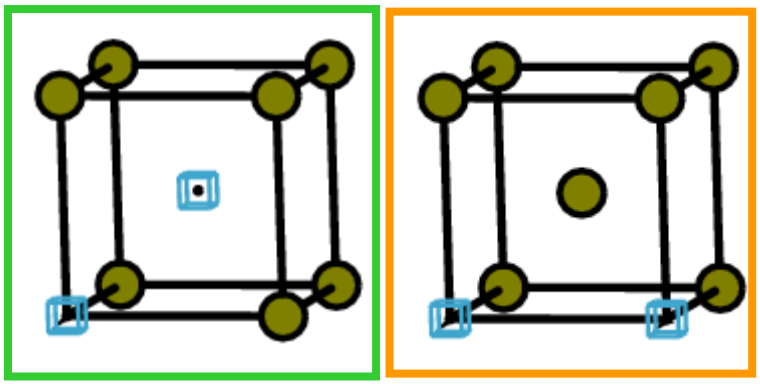
2. **Self-interstitial clusters**
   - **Structure of SIA**
   - **Complexity of SIA clusters in Fe**

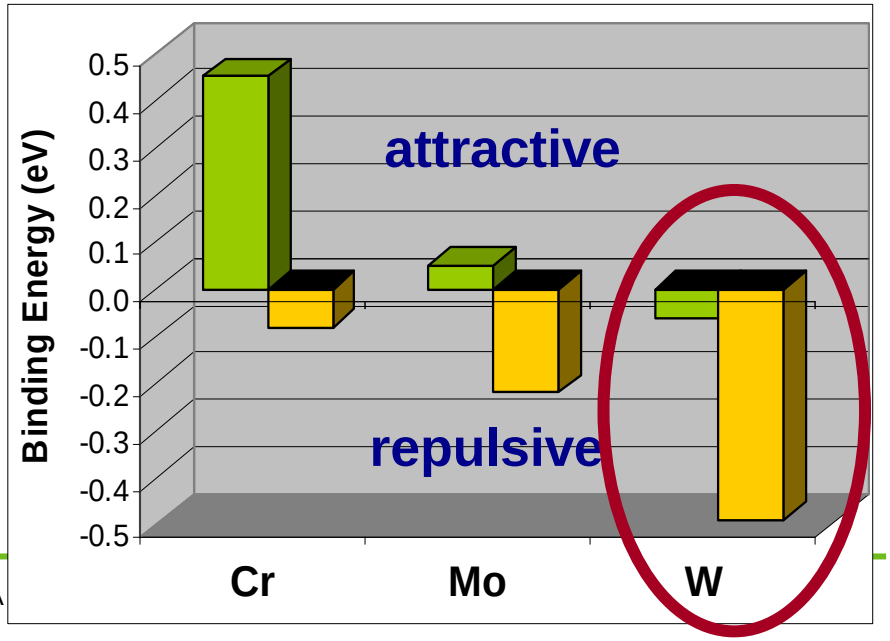
Vacancy clusters

Di-vacancy binding energies



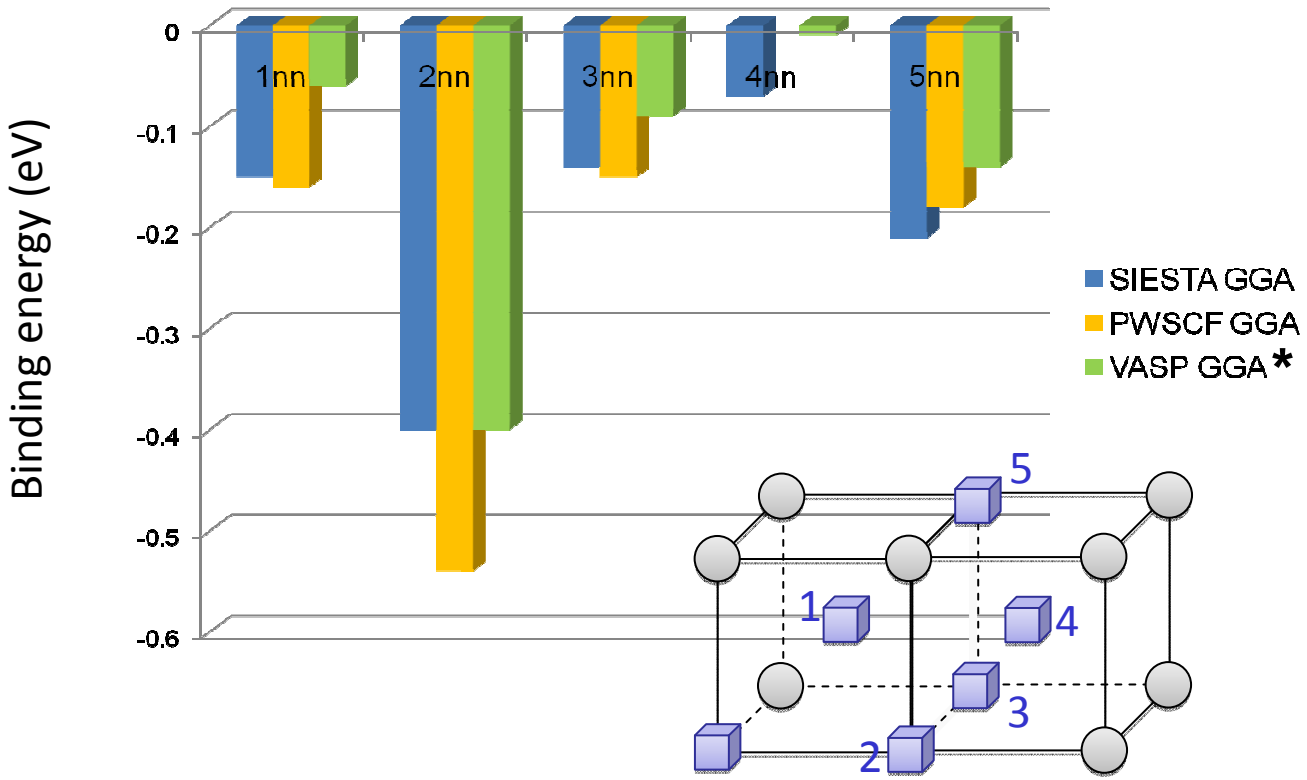






- Metal dependent
- Fe = « standard behavior » (EAM like)
- Anomalous behavior of W

Binding energies of di-vacancies in W



- Di-vacancies do not bind until 5th nearest neighbors
- Non-bonding character highly reproducable within DFT-GGA

*** C. Becquart and C. Domain, NIMB (2007)**

Contradiction with experimental evidence for di-vacancy binding and vacancy clustering

- Field-ion microscopy on quenched in defects in ultra-high purity W predicted the di-vacancy binding enthalpy to be 0.7 eV (J.Y. Park *et al.*, Philos. Mag. A **48**, 397 (1983)) – Surface effect ?
- Positron annihilation experiments (M.F. Barthe 2010): evidence for the formation of small vacancy clusters by vacancy migration

- DFT predicts that vacancies become attractive for larger clusters. But is it kinetically possible if di-vacancies do not bind ?
- Failure of DFT ?

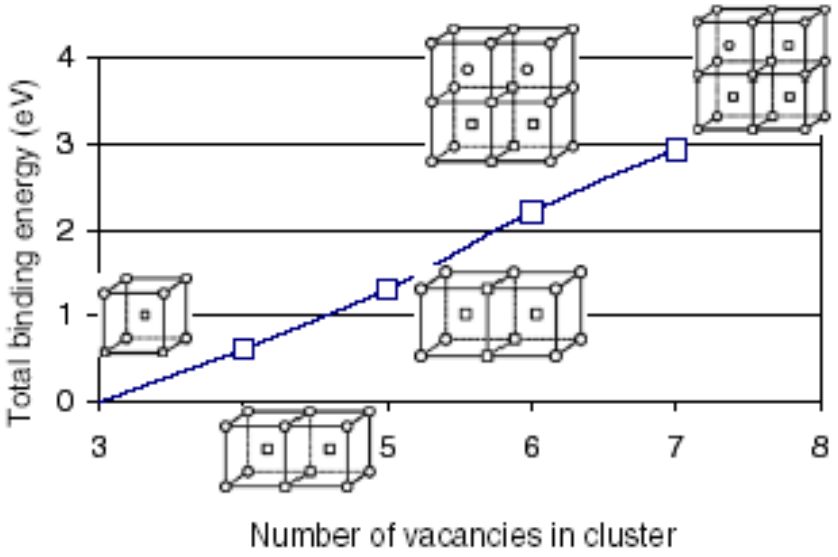


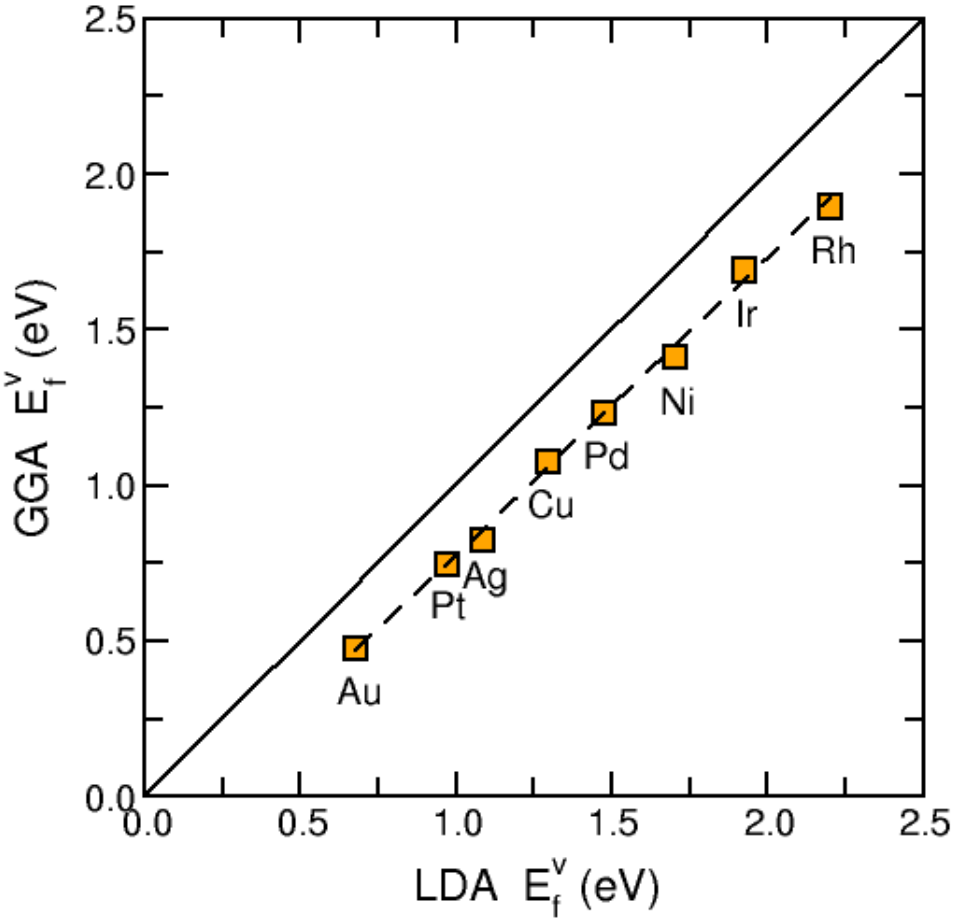
Fig. 2. Total binding energy for vacancy clusters versus the number of vacancies in the void.

*** C. Becquart and C. Domain, NIMB (2007)**

Effect of exchange correlation functional on vacancy properties

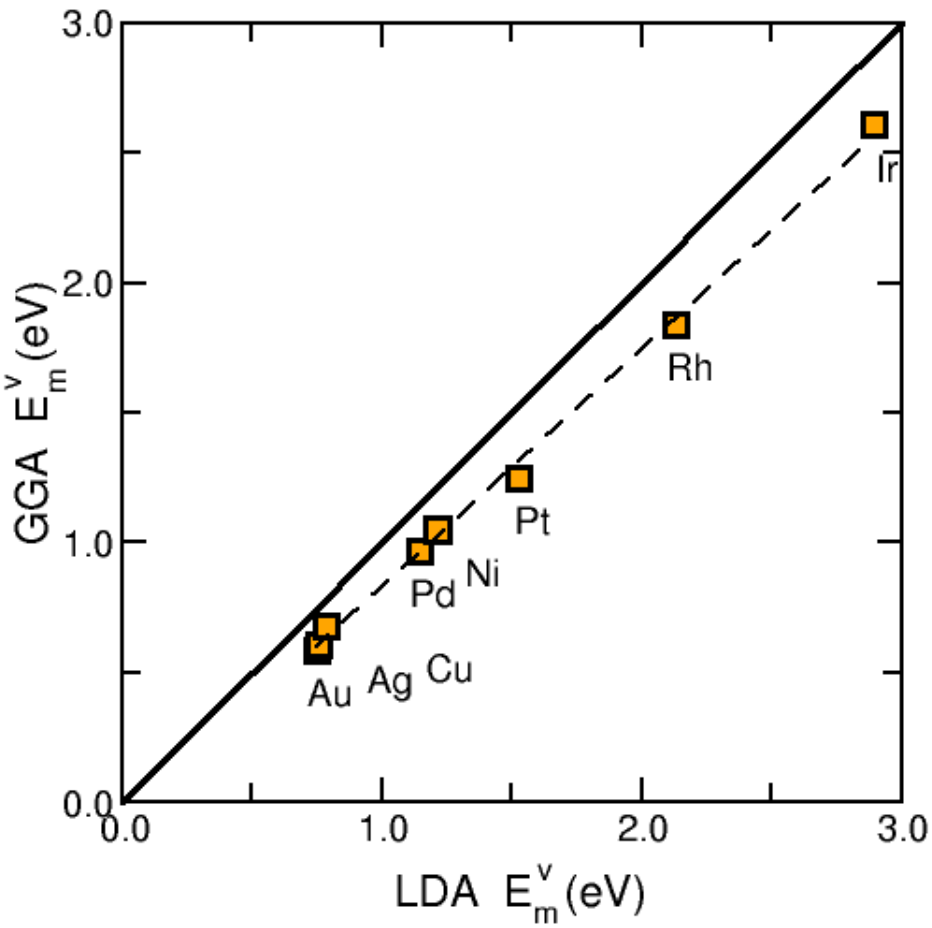
FCC metals

Vacancy <u>formation</u> energy



GGA values lower than LDA by 0.25±0.05 eV

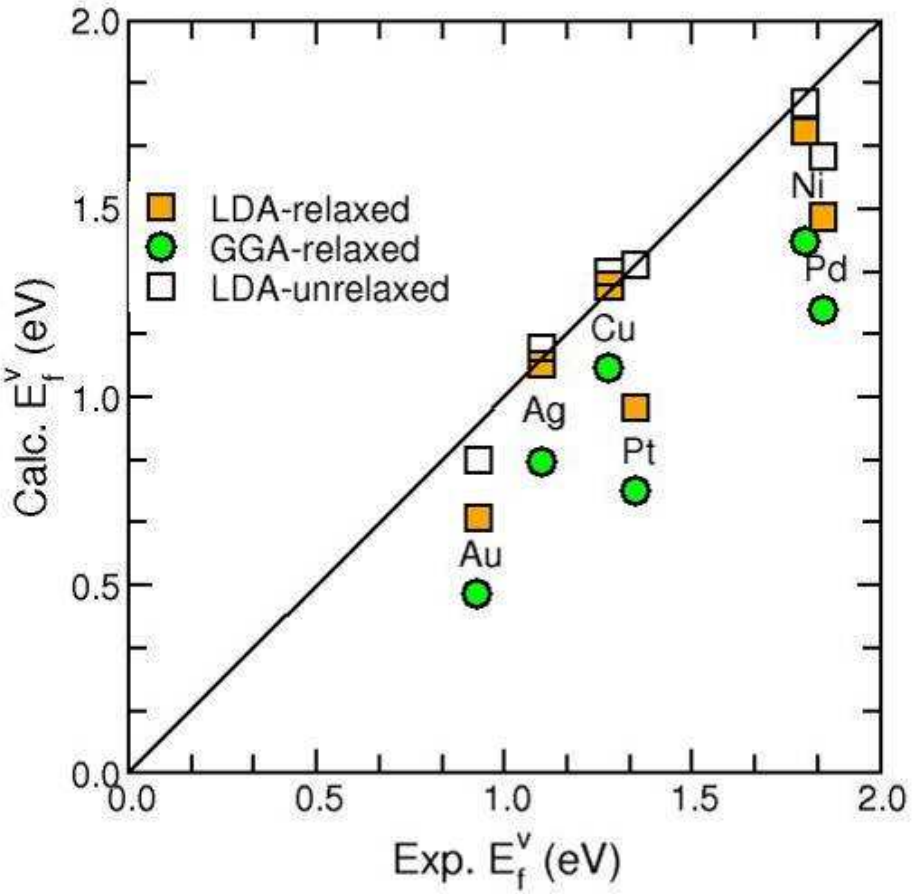
Vacancy <u>migration</u> energy



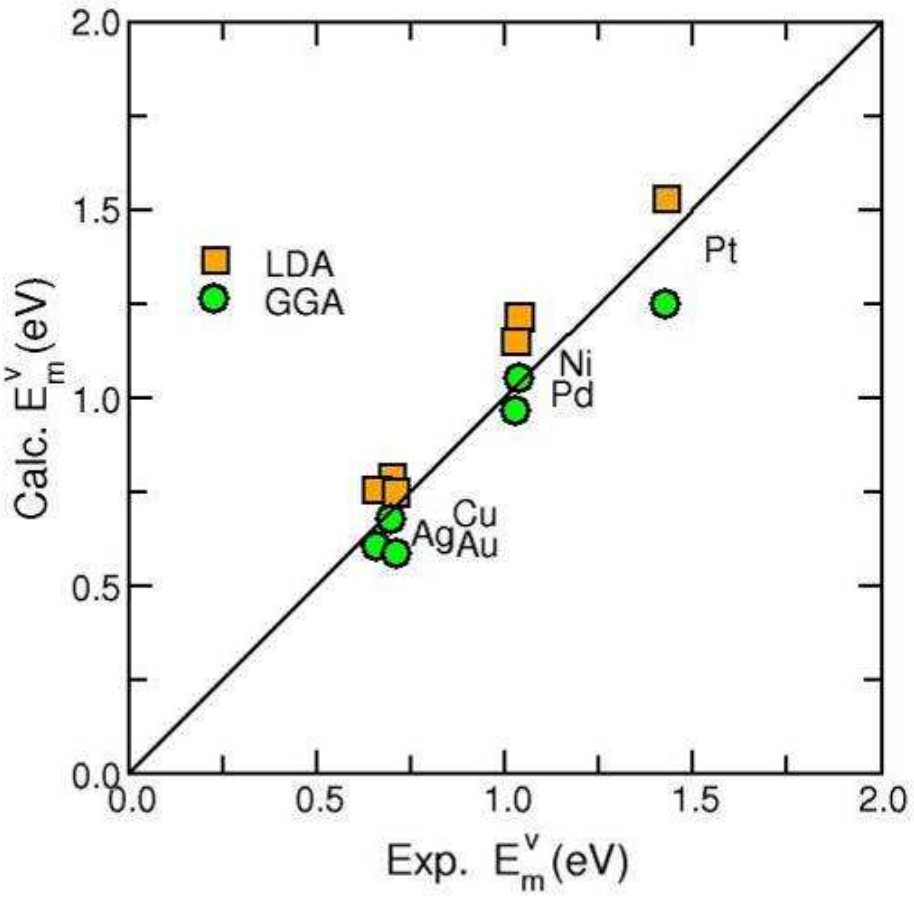
GGA values lower than LDA by ~ 10%

LDA vs GGA-PBE: vacancy properties of FCC metals

Vacancy formation energy



Vacancy migration energy



- LDA in better agreement with exp.
- GGA underestimates vac. form. energy

GGA < Expt. < LDA

FW (unpublished)

Effect of xc functional on vacancy properties in W

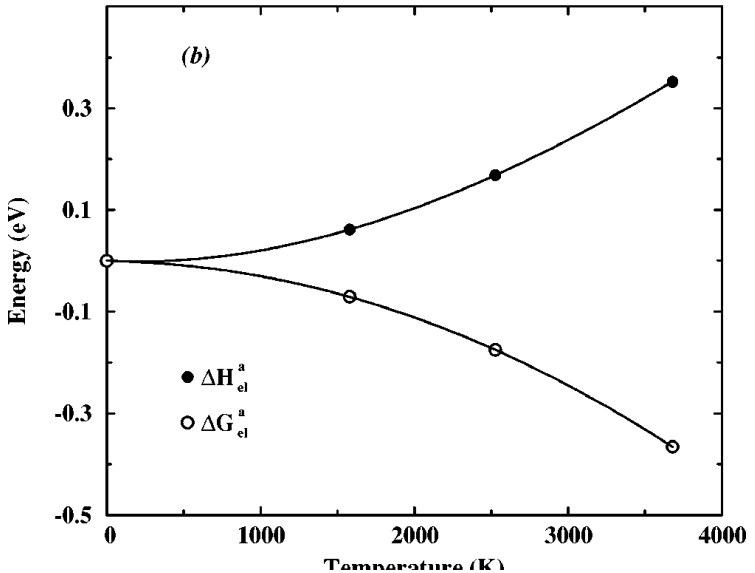
	GGA-PBE	LDA	AM05
E_f (V_1)	3.24 +/- 0.01	3.27	3.55
E_b (V_2 1nn)	-0.06 +/-0.03	-0.12	-0.06
E_b (V_2 2nn)	-0.44 +/- 0.03	-0.50	-0.43

- Significant effect on the vacancy formation energy
- Divacancy binding energy indenpendent on xc functional

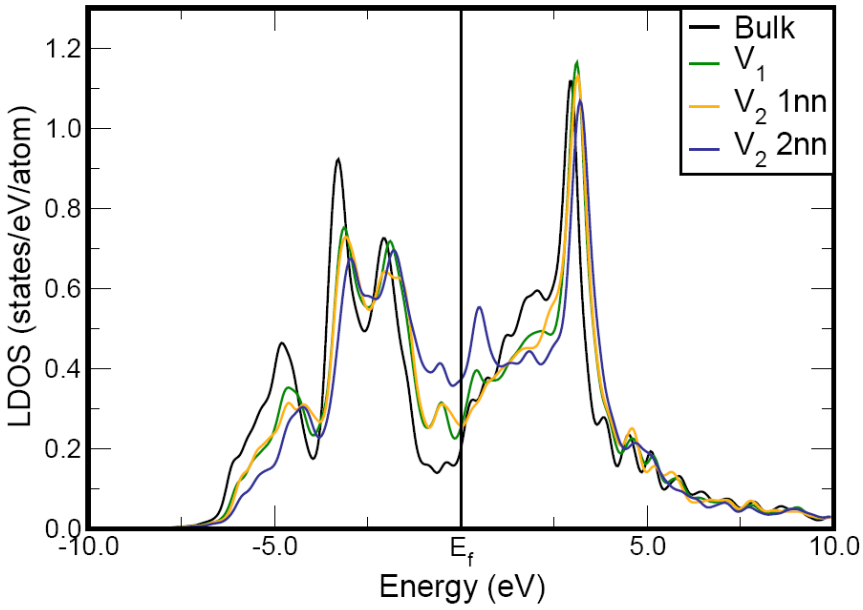
AM05: R. Armiento and A. E. Mattsson, Phys. Rev. B 72, 085108 (2005)

Finite temperature effect – electronic entropy

- Changes at E_{Fermi} in the LDOS of the nearest neighbors of the vacancy are known to have a strong impact on the Gibbs formation energy (Satta et al. PRB 1998)

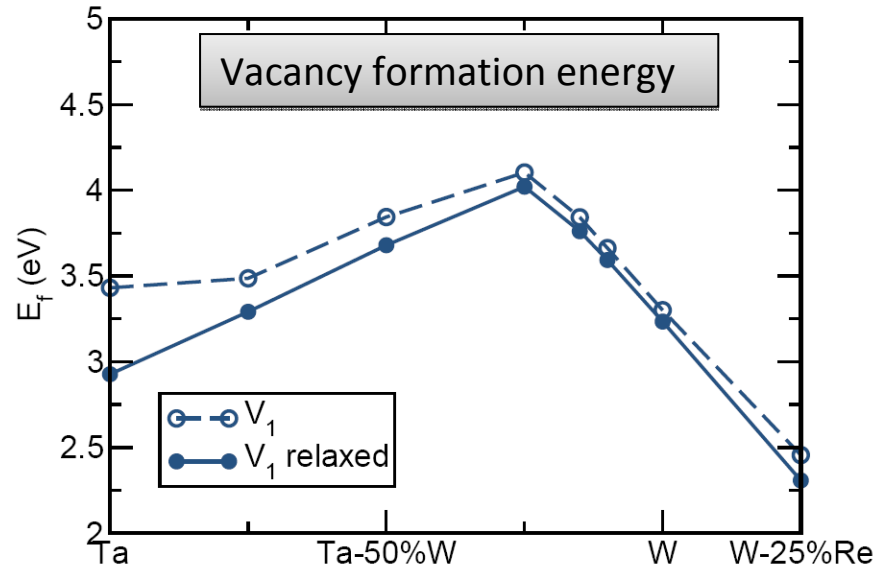


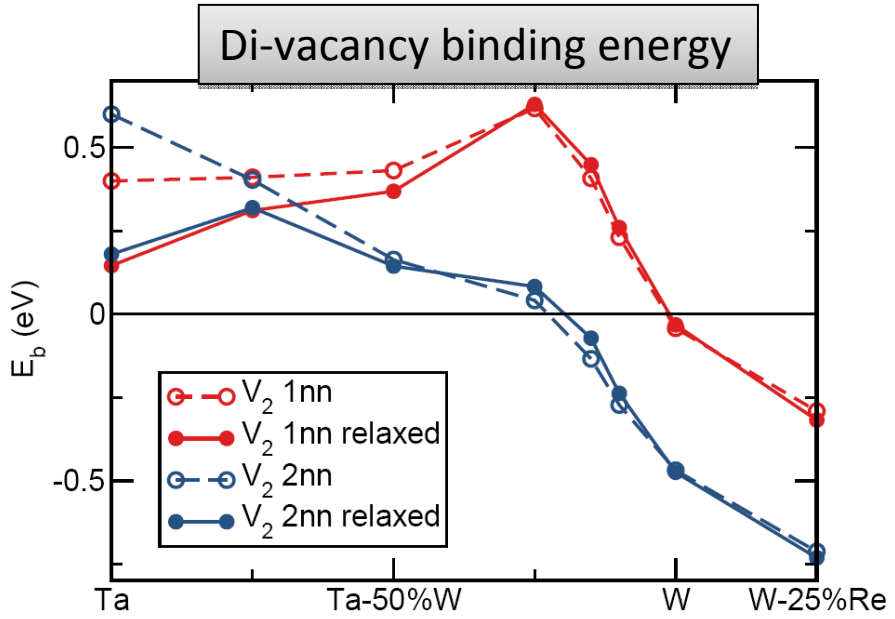
- Due to the electronic entropy, the 2NN di-vacancies become more attractive, at 3000 K:
- 1 NN: Eb=+0.09 eV (attractive)
- 2 NN: Eb=-0.27 eV (repulsive)



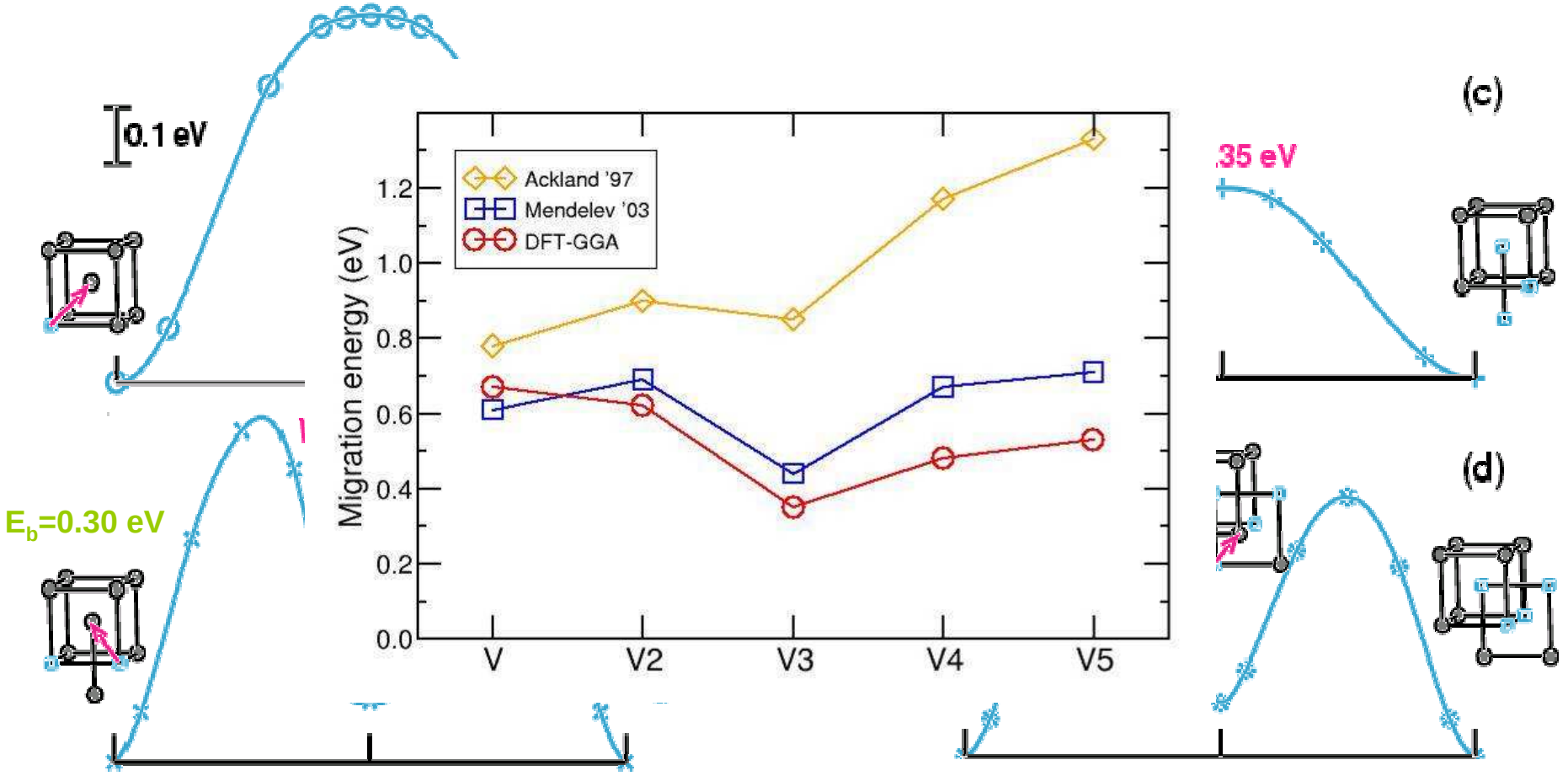
Alloying effects in the VCA approximation

- Virtual Crystal Approximation (VCA)
- Vacancy formation energy is maximum at $W_{0.75}Ta_{0.25}$
- Di-vacancies in W become attrative upon Ta alloying
- Solutes which decrease the d-band filling and bind with the vacancy (eg Hf) are predicted to make di-vacancies attractive





Migration of vacancy type defects (DFT)

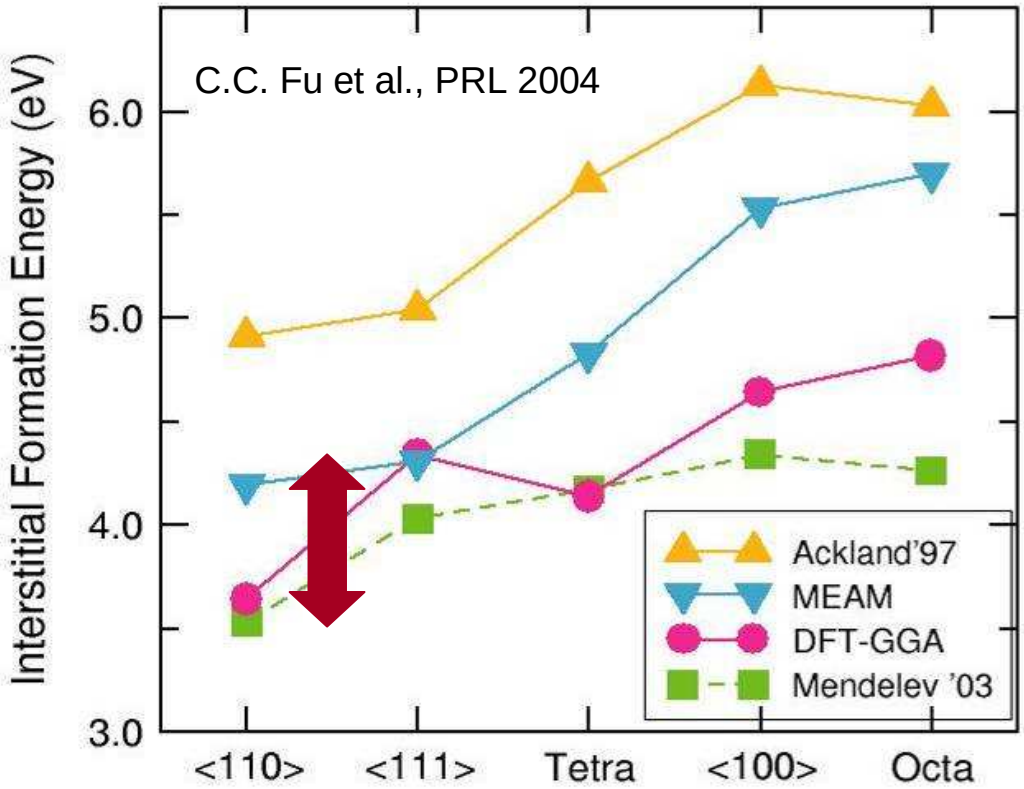


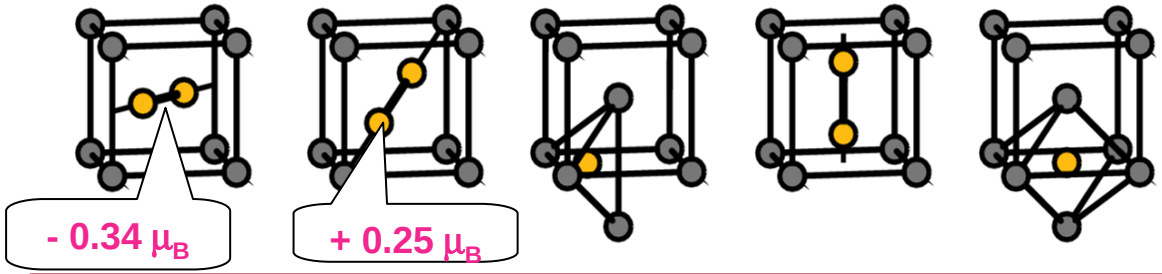
Unexpected high mobility of V_3 and V_4

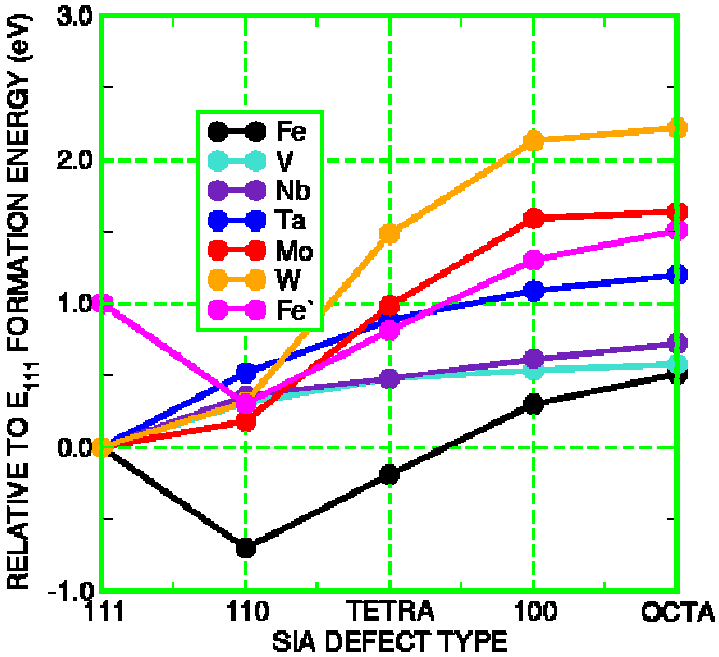
Fu, Dalla Torre, FW, Bocquet, Barbu, Nat. Mat. **4**, 68 (2005)

Self-interstitial clusters

Formation energy of self-interstitials in Fe







<111> dumbbell in all other BCC metals

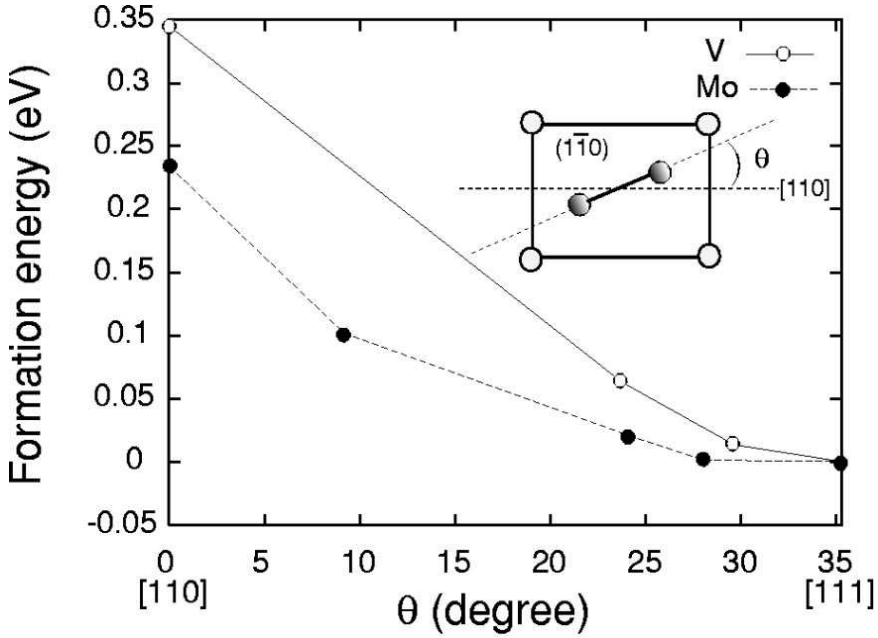
(Nguyen Manh, et al PRB 2006)

Large <111> -<110> energy difference can be reproduced but not predicted by empirical potentials

Orientation of SIAs in Cr, Mo, W: <111> or <11x> ?

- Experimental evidence X-Ray for non trigonal symmetry (Ehrhart, JNM 1978)

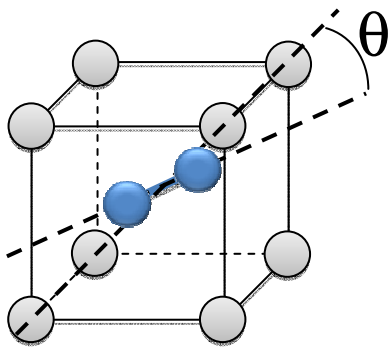
- DFT calculations in Mo don't exclude an orientation between <111> and <110> S. Han et al. PRB 2002

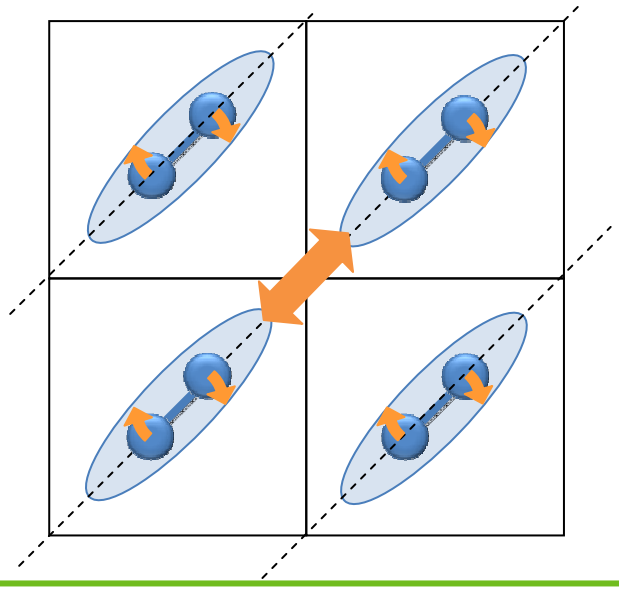


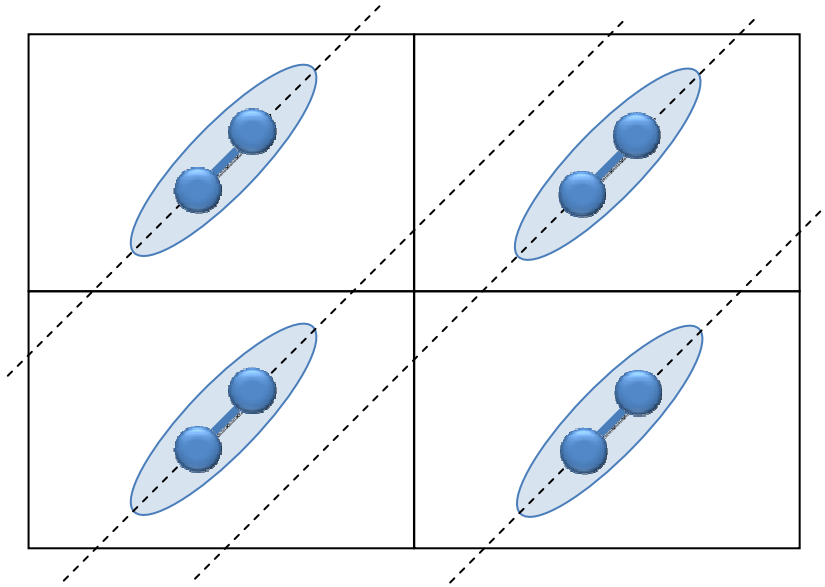
- DFT calculations in Cr show that SIA with an orientation close to <221> is 0.15 eV more stable than <111> crowdion Olsson (JNM 2009)

Orientation of SIAs in W: <111> or <11x> ?

- In *cubic* supercells the <11ξ> orientation is more stable by ~0.05 eV than <111>
  θ≈15° for cells with 128 to 432 atoms
- In *non cubic* cell (eg 5x6x6) <11ξ> relaxes towards <111>
- Interactions between periodic images yeald the <111> configuration to buckle in cubic cells







Conclusions

- Di-vacancies in bcc metals
  - Binding energy is strongly metal dependent
  - Tungsten has the most atypical behavior
    - *1NN and 2NN vacancies don't bind according to DFT*
    - *This result is independent on the exchange-correlation functional*
    - *VCA calculations show that alloying effect may strongly affect di-vacancy binding*

- Self interstitial defects
  - In W the <11ξ> configuration is an artefact to due periodic boundary conditions in cubic supercells
  - Self interstitial clusters in Fe
    - *configurations with non-parallel dumbbells are predicted to play a crucial role*
    - *Relative stability is temperature dependent*
    - *Methods such as ART are powerful tools to explore the complexity of their energy landscape*