

Ab initio calculations in fcc Fe + Ni,Cr + He,+ C,N + T.M.

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- Austenitic Fe-Cr-Ni based steel alloys are key structural materials in current nuclear applications (LWR Internals) and candidate materials for next generation fission and fusion systems.
- These high temperature, chemically corrosive and highly neutron irradiated environments lead to mechanical degradation by a number of mechanisms (IASCC, irradiation induced creep and swelling), which we wish to understand.
- An essential part is understanding and predicting the microstructural evolution of these materials under irradiation: primary (point defect) damage production, migration and interactions with other defects and alloying elements/impurities → evolution of observable microstructural features (voids, SFT, Frank loops etc.), radiation induced segregation and precipitation.
- Ab Initio electronic structure calculations allow the basic properties of point defects and their interactions to be studied in detail at 0K.
- In concentrated alloys the local and global composition dependence precludes a broad study. A useful first step is to study these in the dilute limits, as done in fcc Ni (Domain, PERFECT) and has been done here in both fcc Fe and Ni.

- First study in austenite and dilute Fe-Cr-Ni austenitic alloy (at 0K): T.P.C. Klaver, D.J. Hepburn and G.J. Ackland Phys. Rev. B **85** 174111 (2012).
 - Point defect (vacancies (V), self-interstitials (SI)) formation, migration, binding and clustering in austenite.
 - Solubility, binding and clustering of Ni and Cr in austenite at dilute concentrations.
 - Interactions between Ni and Cr solutes and point defects.
 - Vacancy-mediated tracer diffusion coefficients for Fe, Ni and Cr.
- Second study of He, C and N in austenite and Ni: D.J. Hepburn, D. Ferguson and S. Gardner, to be submitted to Phys. Rev. B.
 - Solute solubility, migration and binding in austenite and Ni
 - Solute interactions with Ni and Cr in dilute austenitic alloy.
 - Solute interactions with point defects in austenite and Ni.
 - Formation and stability of small solute-vacancy clusters in austenite.
- Third study of transition metal (T.M.) solute interactions with point defects in austenite: D.J. Hepburn and E. MacLeod.
 - Motivated by experimental results showing significant suppression of void nucleation and growth in FeCrNi alloys under irradiation by addition of small quantities of oversized T.M. solutes e.g. Zr and Hf.
 - Determine size factors for T.M. solutes and their interactions with vacancy and $\langle 001 \rangle$ dumbbell point defects in austenite.
 - Investigate relationship between solute size factors and interactions with defects.

General

- Density functional theory (DFT) code with plane wave basis.
- Generalised gradient approximation (GGA-PW91).
- Spin Interpolation by the Vosko-Wilk-Nusair scheme (VWN).
- Projector augmented wave potentials (PAW) supplied with VASP.
- Methfessel and Paxton smearing, $N=1$ and $\sigma = 0.2$ eV.
- Collinear magnetic (i.e. spin-polarised) calculations.

Bulk reference state calculations

- Plane wave energy cutoff, $E_{\text{cut}} = 400$ eV, Brillouin zone (BZ) sampling to absolute k-point convergence.

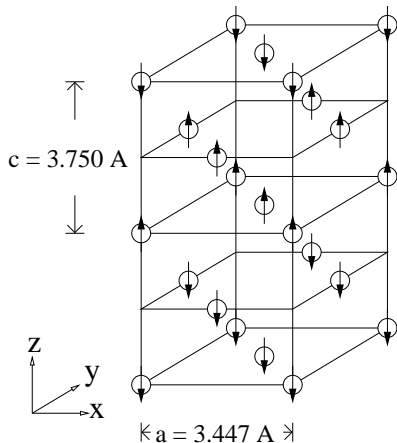
Main calculations

- Constant (equilibrium) volume with relaxed atomic positions.
- 256 ($\pm 1, \pm 2, \dots$) atom supercells ($4 \times 4 \times 4$ conventional cells).
- $E_{\text{cut}} = 350$ eV for Fe and Fe + T.M. solutes (300 eV for Fe + Ni/Cr in fct-afml) and 450 eV for Fe/Ni + He, C and N. BZ sampling using 2^3 Monkhorst-Pack grid.

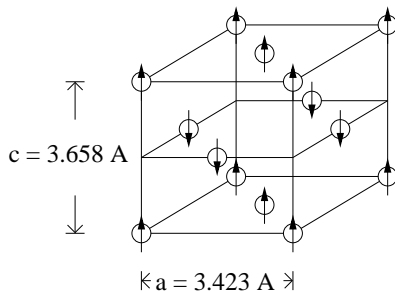
Magnetic reference states in Austenite and Ni (at 0K)

- Many distinct (collinear) magnetic configurations were investigated and tested for structural stability and stability under addition of point defects and solutes. The ferromagnetic low spin and high spin states were both unstable. Only the antiferromagnetic single layer (afml) and double layer (afmD) structures survived the tests:

fct afmD Fe



fct afmI Fe



fcc fm Ni

$a = c = 3.522 \text{ \AA}$

We define the formation energy, $E_f(\{n_X\})$, for a configuration of energy, $E(\{n_X\})$, containing n_X atoms of element X relative to a set of reference state energies, E_X^{ref} , for each element using

$$E_f(\{n_X\}) = E(\{n_X\}) - \sum_X n_X E_X^{\text{ref}}.$$

Reference states are as follows:

- For Fe, $E_{\text{Fe}}^{\text{ref}}$ is the energy per atom for bulk fct afmD or afml state.
- For C,N and He, E_X^{ref} is taken for the free atom.
- For T.M. Solutes, E_X^{ref} is the energy per atom for the bulk ground state crystal structure e.g. fcc-fm state for Ni, bcc-afm state for Cr.

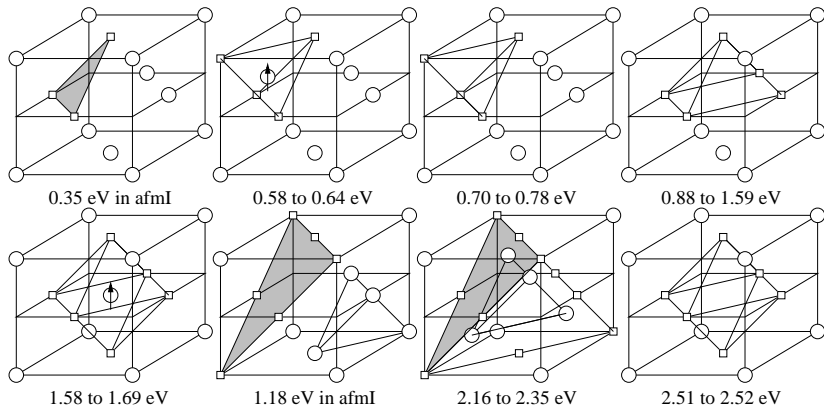
We define the binding energy, $E_b(\{A_i\})$, between a set of n species, $\{A_i\}$, where a species can be a defect, solute, cluster of defects and solutes etc., as

$$E_b(\{A_i\}) = \left[\sum_{i=1}^n E_f(A_i) \right] - E_f(\{A_i\}),$$

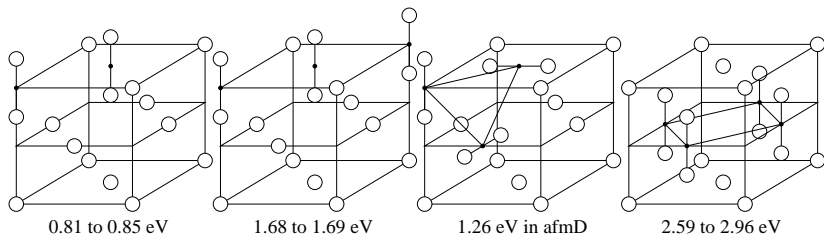
where $E_f(A_i)$ is the formation energy for the single species, A_i , and $E_f(\{A_i\})$ is the formation energy for a configuration containing all of the species in interaction.

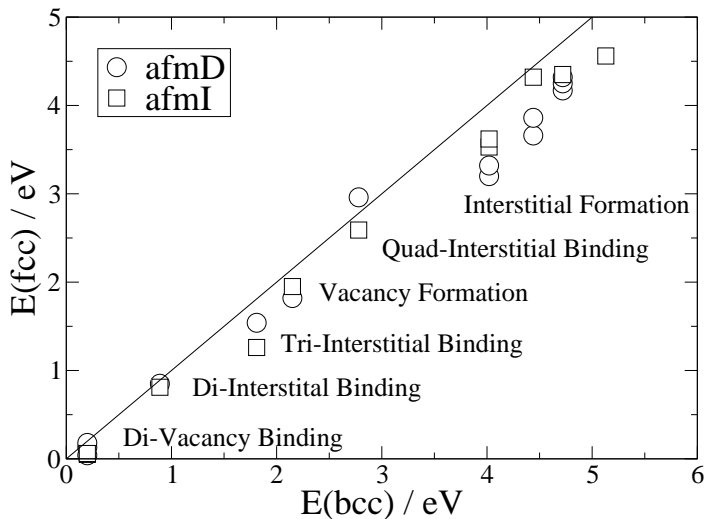
By this definition an attractive interaction between the species corresponds to a positive binding energy.

- Vacancy formation energy of 1.82 eV in afmD and 1.95 eV in afmI.
- Lowest vacancy migration barrier is 0.74 eV in afmD and 0.62 eV in afmI.
- Vacancy-Vacancy binding energies are on order of 0.1 eV at 1nn separation but larger clusters show significant binding:



- Most stable self-interstitial (SI) is $\langle 001 \rangle$ dumbbell with formation energy between 3.2 eV and 3.6 eV (including variation from reference state and tetragonal symmetry breaking effects). In agreement with other fcc metals e.g. Al, Cu and Ni.
- Lowest dumbbell migration barrier is between 0.20 and 0.25 eV for 1nn rotation-migration.
- Dumbbell-dumbbell binding energies are 0.85 eV in afmD and 0.81 eV in afmI c.f. binding energy of 0.97 eV in fcc Ni.
- $[001]$ dumbbell clusters exhibit steady, pair-additive, increase in binding. Finite volume errors are significant here and add up to 1eV to the binding energy (for 5 dumbbells).





Dilute Ni,Cr results (255 calculations) - Summary

- Substitution energies (from fcc-fm Ni and bcc-afm Cr) are small and positive (0.05 to 0.27 eV).
- Pair binding energies are greatest for Ni-Ni but by no more than 0.11 eV and lowest for Cr-Cr at no less than -0.10 eV.
- Binding energies for up to 5 solute clusters are pair additive and greatest for Ni-rich clusters in afm at 0.47 eV.
- Overall results suggest minimal short-range ordering effects but with some tendency for enhanced Ni-Ni ordering.
- Vacancy-solute binding of up to 0.1 eV for Ni, no significant binding of Cr.
- Barrier heights for solute-vacancy exchange are lowest for Cr at 0.56 eV (afmD) and 0.74 eV (afmI) and greatest for Ni at 0.89 eV (afmD) and 0.98 eV (afmI) c.f. Fe 0.74 eV (afmD) and 0.62 eV (afmI). Results in bcc iron are similar (Olsson 2007).
- Cr generally binds to overcoordinated defects e.g. mixed dumbbell by between 0.1 and 0.3 eV whereas Ni is generally repelled. Substitutional Cr binds to self-interstitial $\langle 100 \rangle$ dumbbells by 0.1 to 0.2 eV, generally in compressive sites and Ni binds by at most 0.1 eV in tensile sites.
- Barrier for solute exchange in mixed dumbbell 1nn migration-rotation estimated for Cr at 0.19 eV (afmD) and 0.25 eV (afmI) and for Ni at 0.37 eV (afmI) c.f. Fe at 0.20 eV (afmD) and 0.25 eV (afmI).

Dilute Ni,Cr results - (vacancy mediated) tracer diffusion coefficients 1

For vacancy mediated diffusion we use the 5-frequency model of Lidiard and LeClaire, which includes correlation effects between successive jumps. The 5 jump frequencies are as follows:

- w_0 : self-diffusion
- w_1 : vacancy-solvent exchange keeping vacancy at 1nn.
- w_2 : vacancy-solute exchange
- w_3 : vacancy-solvent exchange moving vacancy to 2nn,3nn or 4nn.
- w_4 : opposite process to w_3 .

Each jump frequency is modelled by an Arrhenius type expression:

$$w_i = C_{m,i} \exp(-\beta E_{m,i})$$

The ratio of the tracer diffusion coefficient for solute, $B = \text{Cr, Ni}$ to that for self-diffusion is then:

$$\frac{D_B^*}{D_{\text{Fe}}^*} = \frac{C_{m,2}}{C_{m,0}} C_b \exp(\beta E_{b,2}^{\text{B-TS}}) \frac{f_B}{f_0}$$
$$E_{b,i}^{\text{B-TS}} = E_{m,0} - E_{m,i} + E_{b,i}^{\text{B-V}}$$

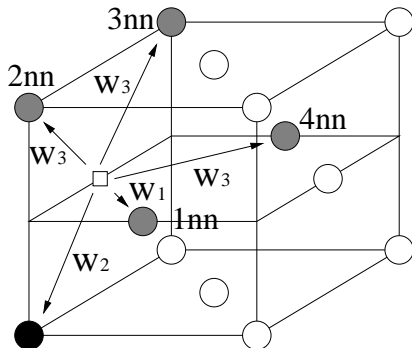
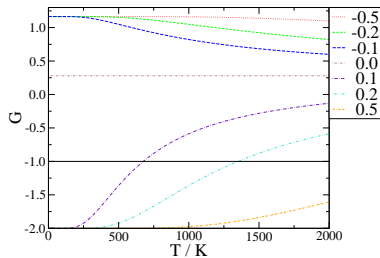
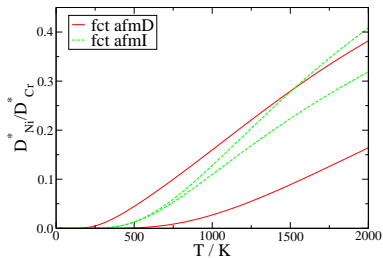
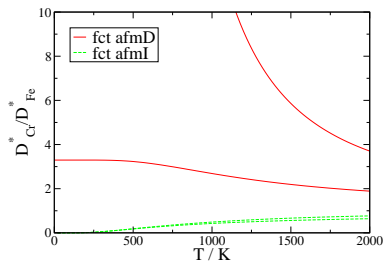
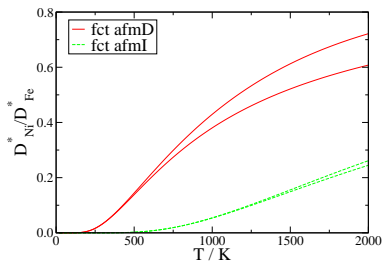


Figure: Jumps in 5-frequency model of Lidiard and LeClaire. Solute atom in black, solvent atoms either white or grey (if exchanging with a vacancy).

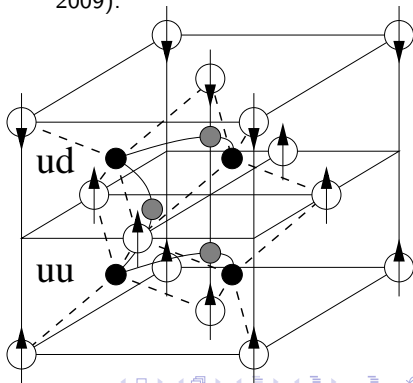
Dilute Ni,Cr results - (vacancy mediated) tracer diffusion coefficients 2



He results (210 Calculations) - He in defect free fcc Fe and Ni.

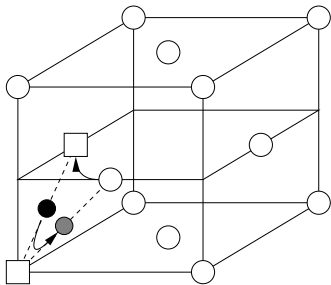
- Formation energies for He are large and positive: 4.02 to 4.18 eV in Fe and 3.18 eV in Ni substitutionally (sub-He) and 4.46 to 5.27 eV interstitially (int-He). As a closed shell noble gas element bonding interactions are repulsive. In Fe typical radius is 0.8 Å.
- Int-He is most stable in tetrahedral site (two sites in afmD with 0.07 eV difference), closely followed by octahedral with formation energy difference of 0.21 eV in afmD Fe, 0.06 eV in afml Fe and 0.13 eV in Ni. He most stable off-centre in region surrounding octahedral site.

- Migration energies range from 0.16 to 0.35 eV in afmD Fe, 0.07 to 0.11 eV in afml Fe and 0.13 eV in Ni. Experimental determination in Ni of 0.14 ± 0.03 eV (Philipps 1983). Similar energies found in other fcc metals: 0.10 eV in Al (Yang 2008), 0.07 eV in Pd (Zeng 2009).



He results - Interactions with point defects

- Int-He binds very strongly to a vacancy to form sub-He with a binding energy of 2.25 eV in afmD Fe, 2.74 eV in afmI Fe and 2.63 in Ni. Sub-He is, essentially, immobile.
- Diffusion requires either the dissociation of sub-He followed by interstitial migration until recaptured (dissociative mechanism) or the cooperation of vacancies (vacancy mechanism).



- Vacancy-mediated diffusion requires the presence of a vacancy at 1nn or 2nn to sub-He. We consider the formation and migration of an HeV_2 complex.
- Sub-He binds strongly to a vacancy at 1nn with a binding energy of 0.60 to 0.66 eV in Fe and 0.36 eV in Ni. He relaxes to the centre of the divacancy (HeV_2).
- Migration energy for HeV_2 is between 0.90 and 1.22 eV in Fe and 1.20 eV in Ni. (N.B. vacancy migration energy is between 0.62 and 0.74 eV in Fe and 1.06 eV in Ni).
- Int-He binds to the $\langle 001 \rangle$ dumbbell by up to 0.18 eV at 2nn in Fe and 0.20 eV at 1nn and 2nn in Ni. Binding is, therefore, likely at other overcoordinated defects (dislocations, grain boundaries). Could act as nucleation sites for int-He clustering and bubble formation.

He results - He binding to He_mV_n cluster

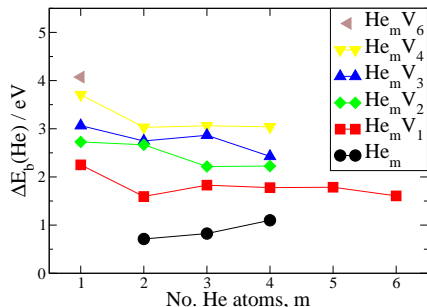


Figure: afmD Fe

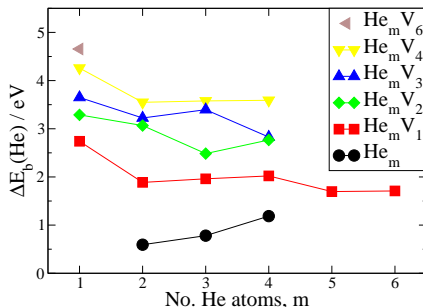


Figure: afml Fe

- $\Delta E_b^{(m,n)}(\text{He}) = E_b(\text{He}_m\text{V}_n) - E_b(\text{He}_{m-1}\text{V}_n) : \text{He}_m\text{V}_n \rightarrow \text{He}_{m-1}\text{V}_n + \text{He}$
- $\Delta E_b^{(m,n)}(\text{He})$ is always positive, plateaus as He is added at fixed n and consistently increases with n at fixed m .
- Even He_m clusters show strong additional binding of around 1 eV per He in Fe (and Ni).
- Data at $m = 1$ will converge to the formation energy of tetrahedral He as $n \rightarrow \infty$ i.e. 4.46 eV in afmD Fe and 4.97 in afml Fe.

He results - V binding to He_mV_n cluster

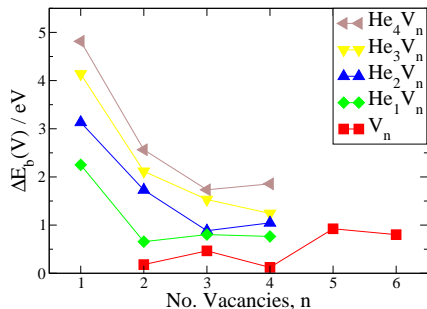


Figure: afmD Fe

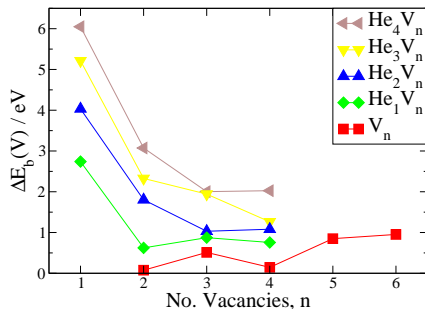


Figure: afmI Fe

- $\Delta E_b^{(m,n)}(\text{V}) = E_b(\text{He}_m\text{V}_n) - E_b(\text{He}_m\text{V}_{n-1}) : \text{He}_m\text{V}_n \rightarrow \text{He}_m\text{V}_{n-1} + \text{V}$
- $\Delta E_b^{(m,n)}(\text{V})$ is consistently positive.
- At fixed m additional binding rapidly decreases to a plateau as vacancies are added. All constant m curves should converge to the vacancy formation energy as $n \rightarrow \infty$.
- At fixed n additional binding steadily increases as He is added.

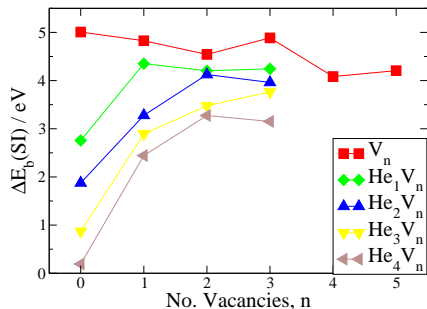


Figure: afmD Fe

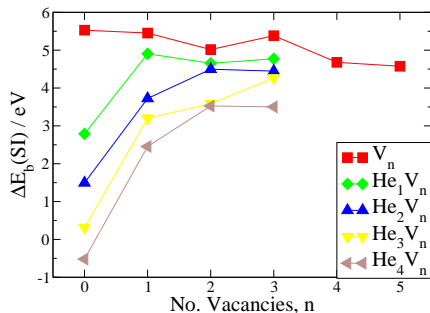


Figure: afmI Fe

- $\Delta E_b^{(m,n)}(\text{SI}) = E_f(\text{SI}) + E_f(\text{V}) - \Delta E_b(\text{He}_m\text{V}_{n+1})$
- $\Delta E_b^{(m,n)}(\text{SI})$ is the energy difference for the process $\text{He}_m\text{V}_n \rightarrow \text{He}_m\text{V}_{n+1} + \text{SI}$ i.e. emission of a self-interstitial.
- Adding He consistently reduces this energy for fixed n . Most pronounced for $n = 0$ i.e. spontaneous Frenkel-pair formation and is energetically favourable when $m = 4$ in afmI. There is direct experimental evidence for this process in gold, Thomas and Bastasz, J. Appl. Phys. **52**, 6426 (1981).

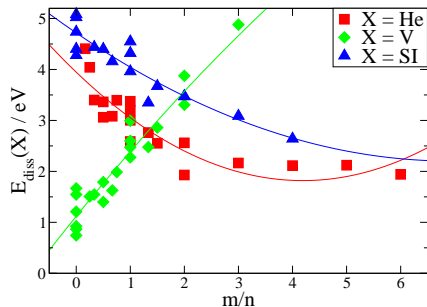


Figure: afmD Fe

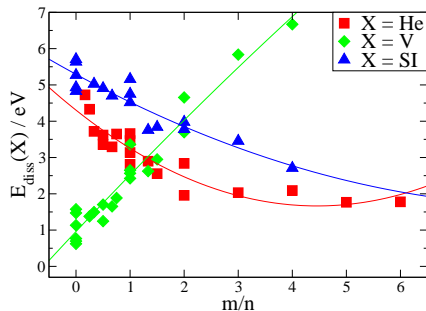


Figure: afmI Fe

- Take $E_{\text{diss}}(X) = \Delta E_{\text{b}}^{(m,n)}(X) + E_{\text{m}}(X)$ for $X = \text{He}, \text{V}, \text{SI}$ i.e. energy for species, X , to dissociate from the cluster.
- Clusters most prone to emission of vacancies below $m/n = 1.3$, He for $1.3 < m/n < 6$ and SI for $m/n > 6$. Data indicates spontaneous emission of SI at some value for $m/n > 6$. Clusters most stable when $m/n = 1.3$.
- Behaviour very similar to in bcc Fe (Fu and Willaime, Phys. Rev. B72,064117 (2005)) and fcc Al (Yang *et al.*, Physica B 403, 2719 (2008)).

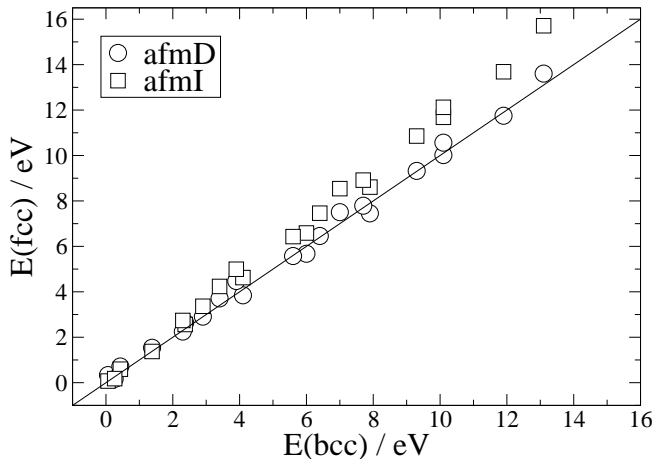
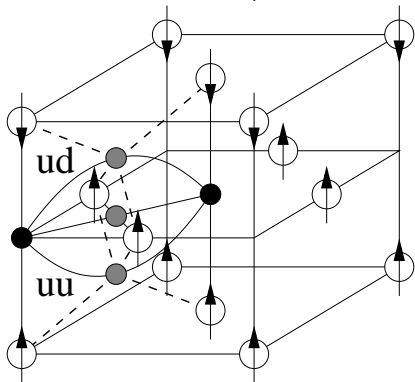


Figure: Comparison with results for He in bcc Fe by C.-C. Fu and F. Willaime, Phys. Rev. B72, 064117 (2005); J. Nucl. Mater.367-370, 244-250 (2007).

C,N results (236 calculations) - Defect free Fe

- Both C and N are most stable in the octahedral interstitial site.
- Migration can be via the $\langle 110 \rangle$ crowdion and tetrahedral interstitial sites, which we take to be the transition states (hypothesis to be tested using N.E.B. calculations).



- C migration is via $\langle 110 \rangle$ crowdion transition state. Barrier height for in plane migration is 2.03(2.44) eV in afmD(afml) and 1.31(2.11) eV out of plane. (Exp: 1.53 to 1.63 eV).
- Jiang and Carter, Phys. Rev. B67, 214103 (2003) found C to migrate via the crowdion in fcc fm-HS Fe (32 atom cell) with a barrier of 0.99 eV (crowdion at 0.98 eV).
- N migration in plane is via the tetra site with a barrier of 1.56(1.90) eV in afmD(afml). Out of plane migration is via the crowdion site in afmD and via the tetra site in afml with barriers of 1.38 and 1.90 eV respectively.
- Pair binding energies for C-C and N-N are repulsive up to 4nn. At 1nn and 2nn binding can be as low as -0.2 eV.

- Vacancy-C/N binding energies are positive and greatest at 1nn at up to 0.28(0.38) eV for C in afmD(afml) and up to 0.44(0.61) eV for N. In bcc Fe (Domain,Becquart,Foct, Phys. Rev. **B69**, 144112 (2004)), binding is 0.47 eV for C and 0.71 eV for N.
- A single vacancy can bind up to 2 C atoms with a maximum total binding energy of 0.48(0.80) eV for afmD(afml) (not C-C dumbbell as in bcc Fe although they are stable). Up to 6 N(4 N) can bind to a vacancy in afmD(afml) but additional binding energy reduces significantly after 2 N where the total binding energy is 0.98(1.30) eV.
- Overall C and N are likely to act as vacancy traps, as in bcc Fe.
- In larger vacancy clusters (proto-voids) single C and N generally bind at octa sites on surface with similar energies to those found for a single vacancy. Sites with enhanced binding were also found: 1.05(0.69) eV for C in afmD(afml) and 0.73(0.84) eV for N.
- Binding to $\langle 001 \rangle$ dumbbell repulsive at 1nn and 2nn (down to -0.3 eV) but shows small positive binding at 4nn of up to 0.05/0.08 eV for C in afmD/afml and up to 0.05/0.07 eV for N, similar to C in bcc Fe.

Transition metal solutes in fcc Fe

- Experimental results (Kato *et al.* 1991/1992) show that addition of small quantities (1% at.) of oversized TM solutes to FeCrNi austenitic steels significantly prolonged the incubation period for void nucleation and suppressed void growth. Vacancy trapping at the oversized atoms and the resultant enhancement in recombination is suggested as a central mechanism, with larger solutes showing more pronounced effects. Modelling by Stepanov, Pechenkin and Konobeev (J.Nucl.Mater **329-333**, 1214-1218 (2004)) showed that this mechanism could explain the reduction in void swelling and suppression of RIS.
- Final year project student, Ewan MacLeod, calculated size factors and binding energies of transition metal (TM) solutes to vacancy and $\langle 001 \rangle$ point defects at 1nn.
- Results give a size-factor ordering of $Zr > Hf > Nb > Ta > Ti > V$ for elements early in the TM series, which agrees well with similar work in bcc Fe (Olsson, Klaver, Domain, Phys. Rev. **B81**, 054102 (2010)). Results of Kato *et al.* show the ordering $Hf > Zr > Ta > Nb > Ti > V$ i.e. 4d and 5d elements are reversed relative to ab initio.
- Size factor measurements were found to be strongly correlated with binding energies to the vacancy and mixed dumbbell i.e. interaction is effectively elastic.
- Hf and Zr are the most effective vacancy traps, consistent with the experimental results. Sc and elements late in the transition metal series e.g. Cu, Ag, Au also show significant binding.