Ab initio study of transition metal solutes in austenite

D.J. Hepburn G.J. Ackland E. MacLeod

Institute for Condensed Matter and Complex Systems,
University of Edinburgh.

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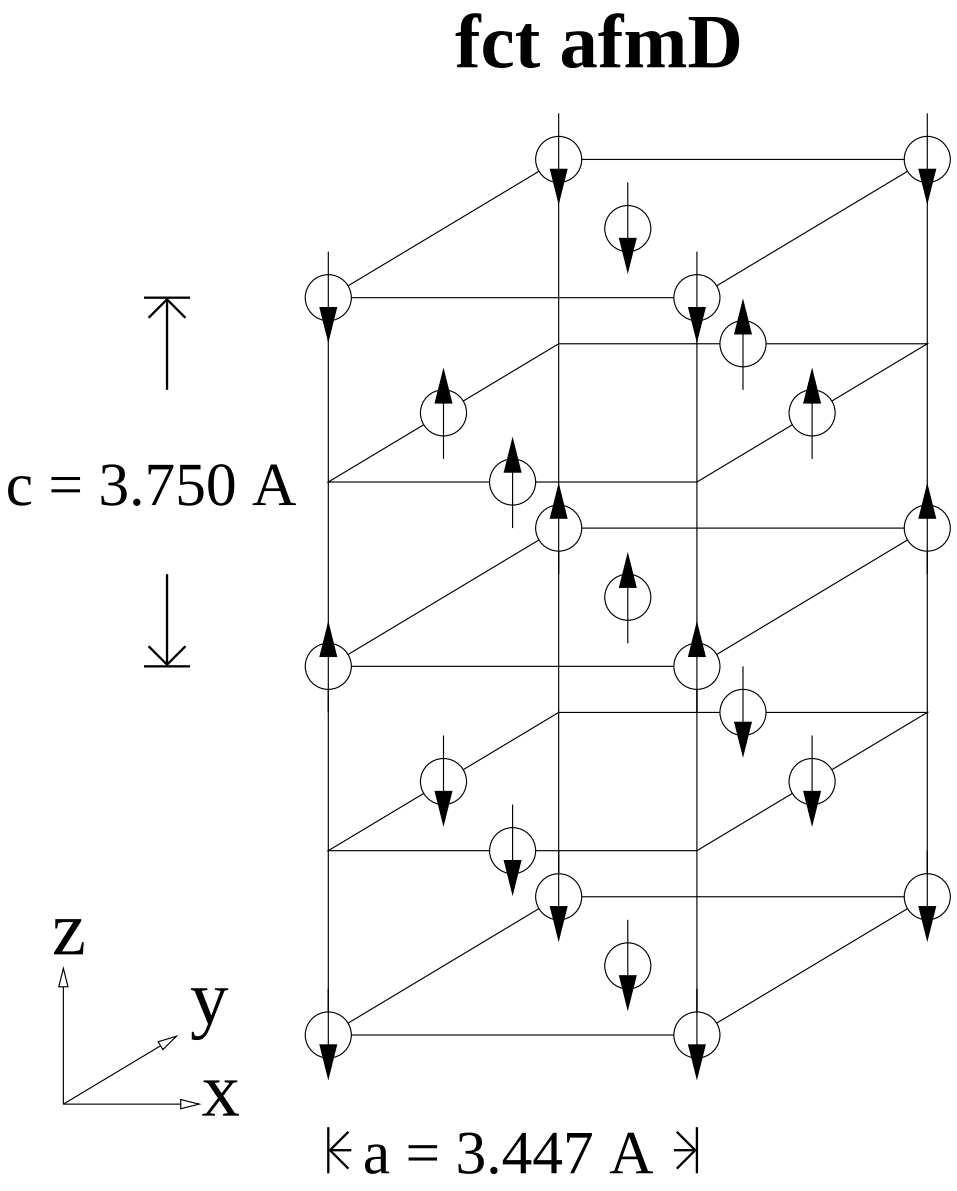
Introduction and Motivation

- Experimental results by Kato *et al.* (Mat. Trans. J.I.M. **32**, 921-930, (1991) ; J. Nucl. Mater. **189**, 167-174, (1992)) show that addition of small quantities (1% at.) of oversized transition metal (TM) solutes to type 316L austenitic stainless steels:
  - Significantly prolonged the incubation period for void nucleation and suppressed void growth.
  - Decreased the radiation-induced segregation (RIS) of Cr away from and Ni towards grain boundaries.
  - Effects increased with increasing size factor of the solute.
- Similar observations were made by Allen *et al.* (J. Nucl. Mater. **342**, 90-100, (2005)) upon adding Zr to Fe-18Cr-9.5Ni austenitic steel.
- The suggested mechanism is point defect (and in particular, vacancy) trapping by the oversized solutes leading to enhanced recombination and a reduction in net defect concentrations in the matrix, as well as a reduction in point defect mobility.
- Modelling by Stepanov *et al.* (J.Nucl.Mater**329-333**, 1214-1218 (2004)) showed that vacancy trapping at the oversized solutes could explain the observations.
- Following a similar methodology to that of Olsson *et al.* (Phys. Rev. B**81**, 054102 (2010)) for bcc Fe, we have performed ab initio calculations to measure TM size factors and binding energies to vacancy and $\langle 001 \rangle$ point defects in austenite (fcc Fe).

Magnetic reference states in Austenite (at 0K)

- In previous work we investigated many distinct (collinear) magnetic configurations 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 (afmI) and double layer (afmD) structures survived the tests.
- This work has been performed in the collinear magnetic ground state, namely the face-centred tetragonal (fct) afmD structure.



Computational details of ab initio calculations using VASP

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

- Fully relaxed calculations to determine lattice parameters.
- Plane wave cutoff energy and Brillouin zone k-point sampling chosen for full convergence of the energy, pressure and local magnetic moments, where appropriate.

Main calculations

- Constant (equilibrium) volume with relaxed atomic positions.
- 256 ($\pm$1,$\pm$2, . . .) atom supercells (4x4x4 conventional fct cells).
- Plane-wave cutoff energy, $E_{\mathrm{cut}} = 350$ eV.
- Brillouin zone sampling using 2^3 Monkhorst-Pack grid.

Definitions

- We define the solute size factor, $\Omega_{\mathrm{SF}} = \Delta V / \Omega_{\mathrm{Fe}}$, where ΔV is the change in volume at zero pressure upon substituting a solute atom for an Fe atom in the bulk phase and Ω_{Fe} is the volume per atom in the pure Fe reference phase. In our constant volume calculations, ΔV has been estimated using the bulk modulus and the excess pressure created by the solute.
- We define the formation energy, $E_{\mathrm{f}}(\{n_{\mathrm{X}}\})$, for a configuration of energy, $E(\{n_{\mathrm{X}}\})$, containing n_{X} atoms of element X relative to the energy per atom in the pure bulk reference states, $E_{\mathrm{X}}^{\mathrm{ref}}$, as

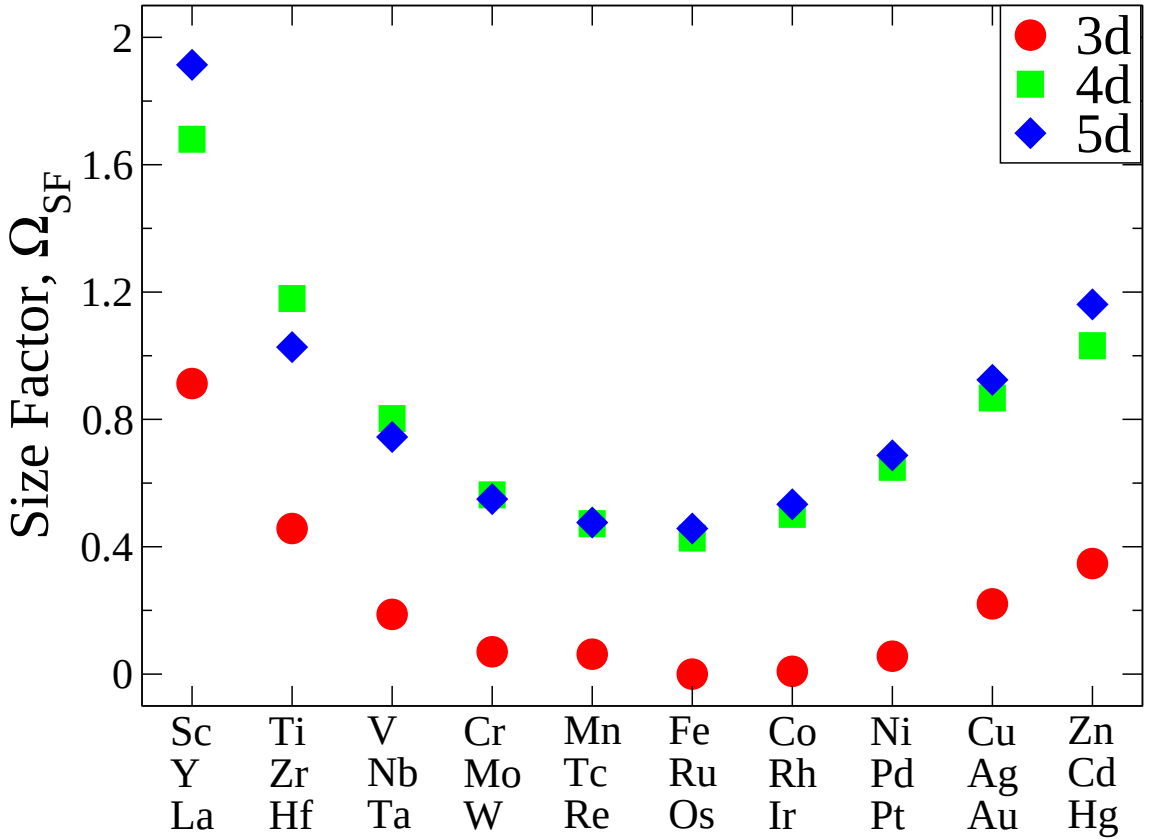
$$E_{\mathrm{f}}(\{n_{\mathrm{X}}\}) = E(\{n_{\mathrm{X}}\}) - \sum_{\mathrm{X}} n_{\mathrm{X}} E_{\mathrm{X}}^{\mathrm{ref}}.$$

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

$$E_{\mathrm{b}}(\{A_i\}) = \left[\sum_{i=1}^{n} E_{\mathrm{f}}(A_i)\right] - E_{\mathrm{f}}(\{A_i\}),$$

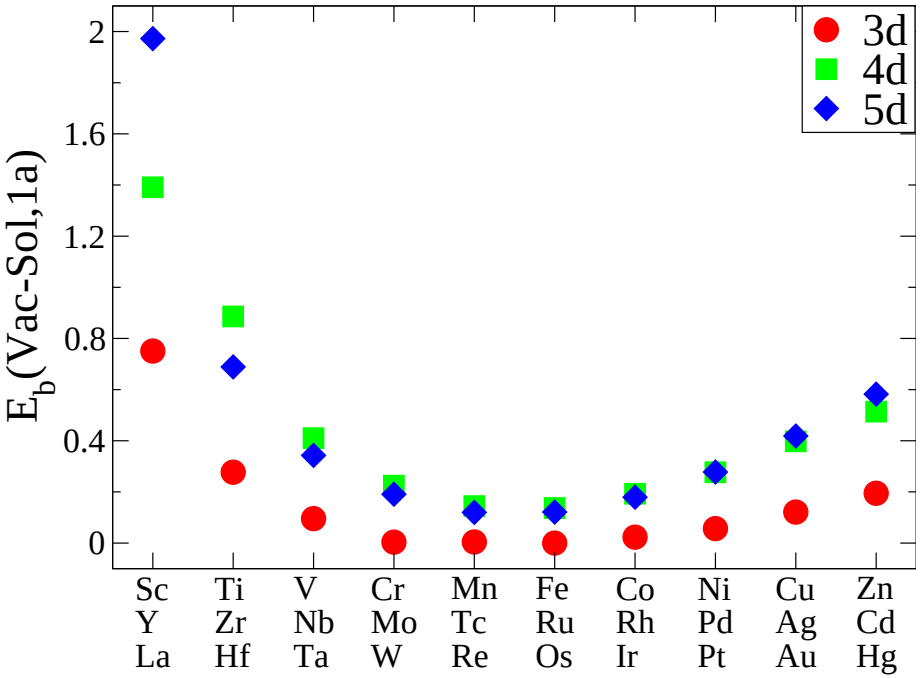
where $E_{\mathrm{f}}(A_i)$ is the formation energy for the single species, A_i, and $E_{\mathrm{f}}(\{A_i\})$ is the formation energy for a configuration containing all of the species in interaction. By this definition an attractive interaction corresponds to a positive binding energy.

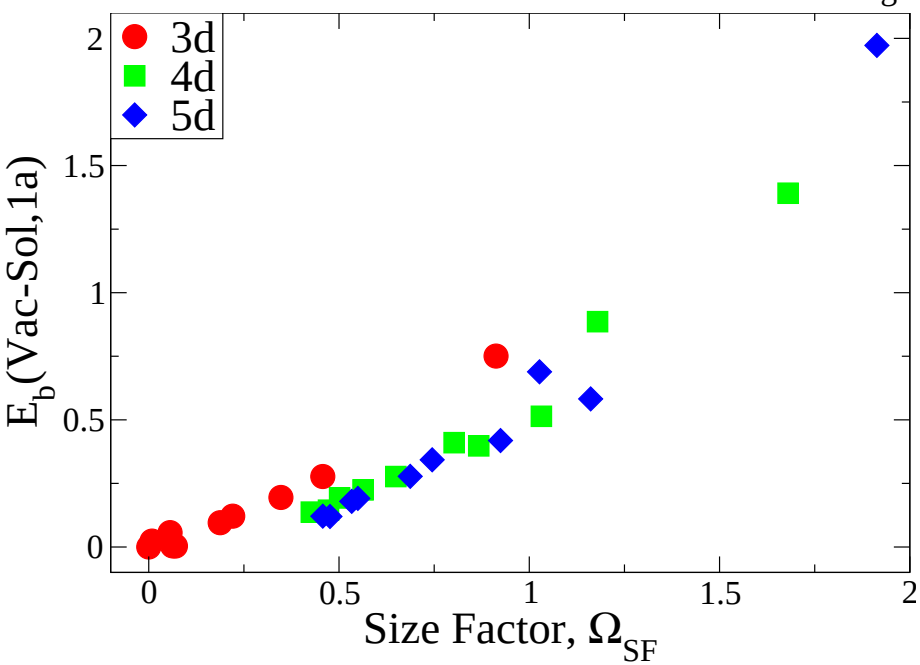
Solute size factors

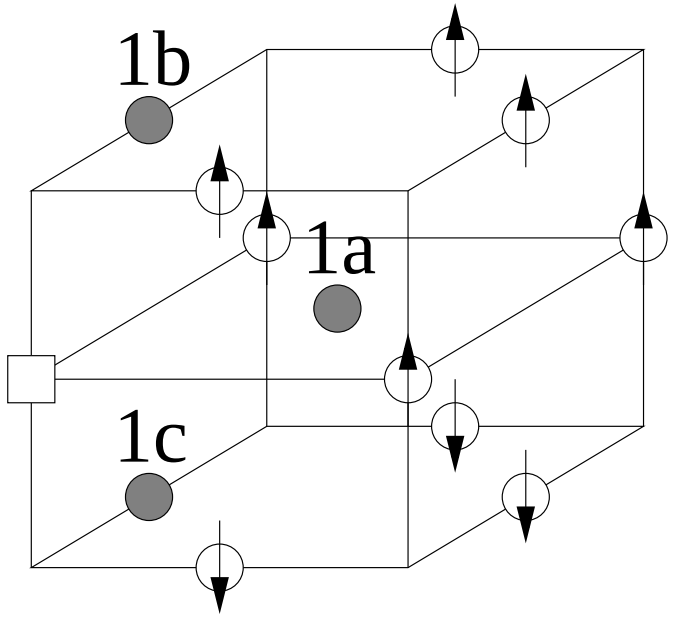


- Results show a high degree of correlation to those of Olsson *et al.* in bcc Fe.
- Kato *et al.* found a size-factor ordering of Hf>Zr>Ta>Nb>Ti>V for group IV and V elements whereas we find an ordering of Zr>Hf>Nb>Ta>Ti>V i.e. 4d and 5d elements are reversed.

Vacancy-solute binding energies at 1nn

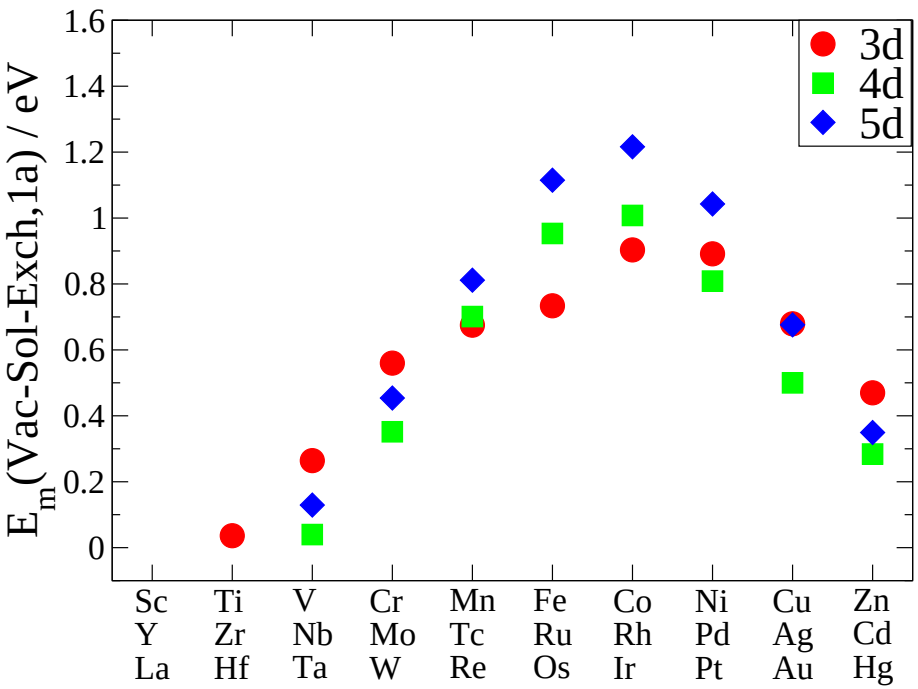


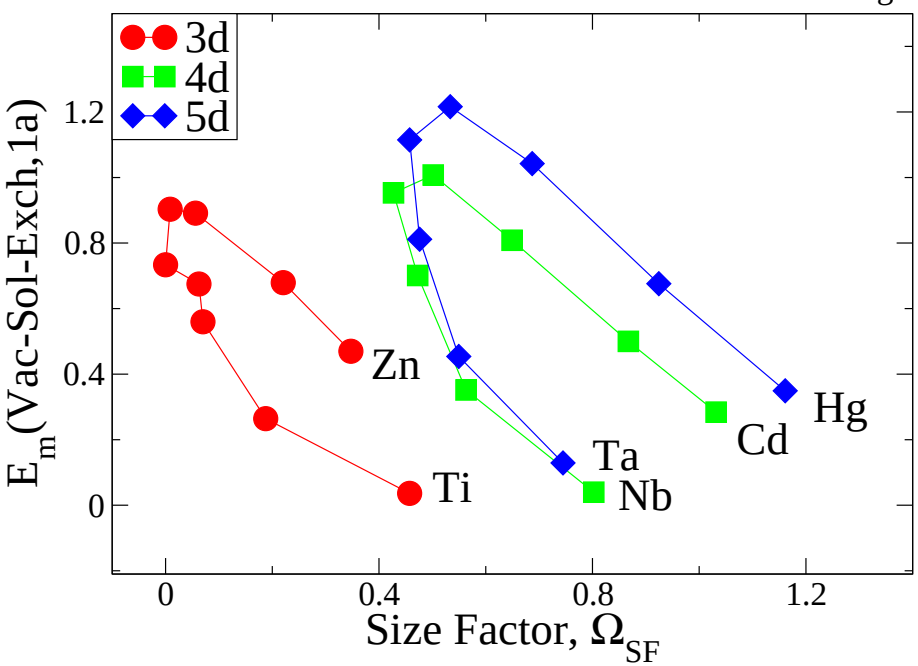


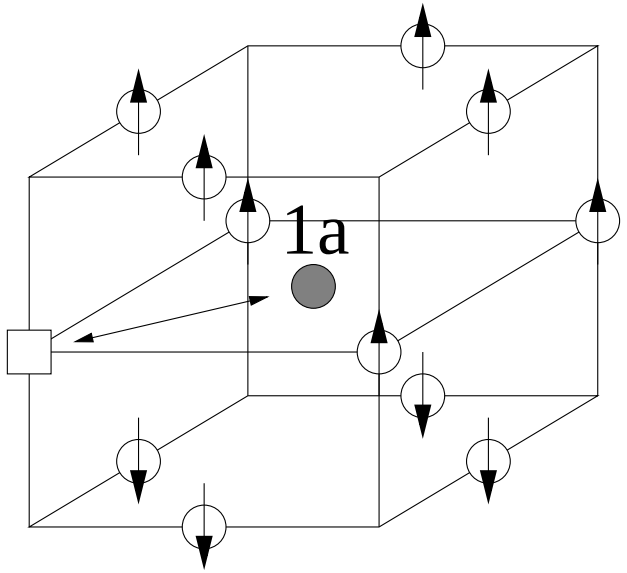


- In fct afmD Fe there are 3 distinct 1nn positions. Results are similar for all so only those for position 1a.
- Group III, IV and V elements make the strongest vacancy traps but elements in groups IX and X also show significant binding.
- Binding energies between vacancy and solute were found to be strongly correlated to size factor.

Vacancy-solute exchange at 1nn - migration energy

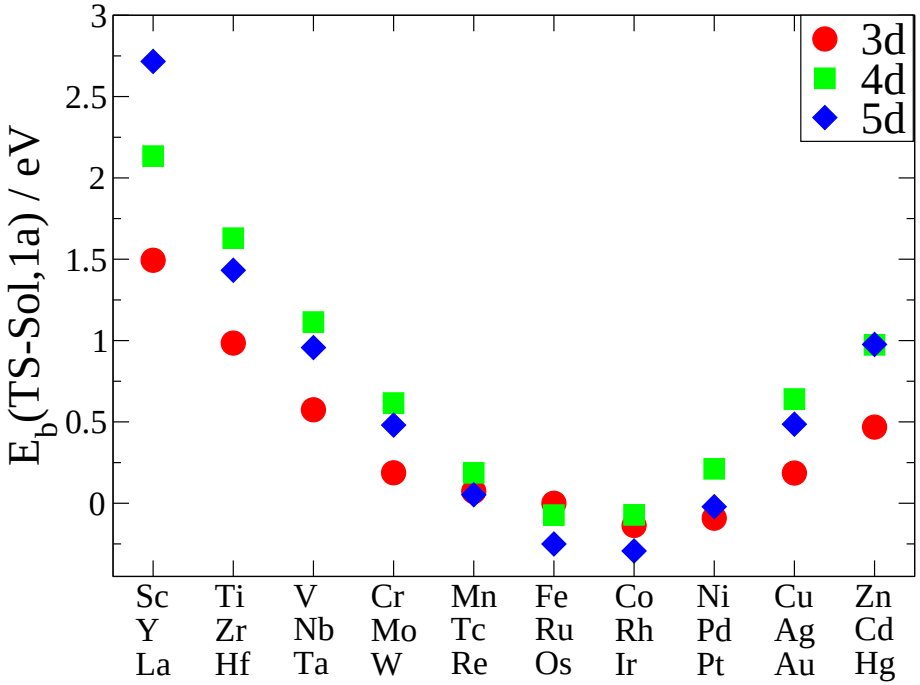


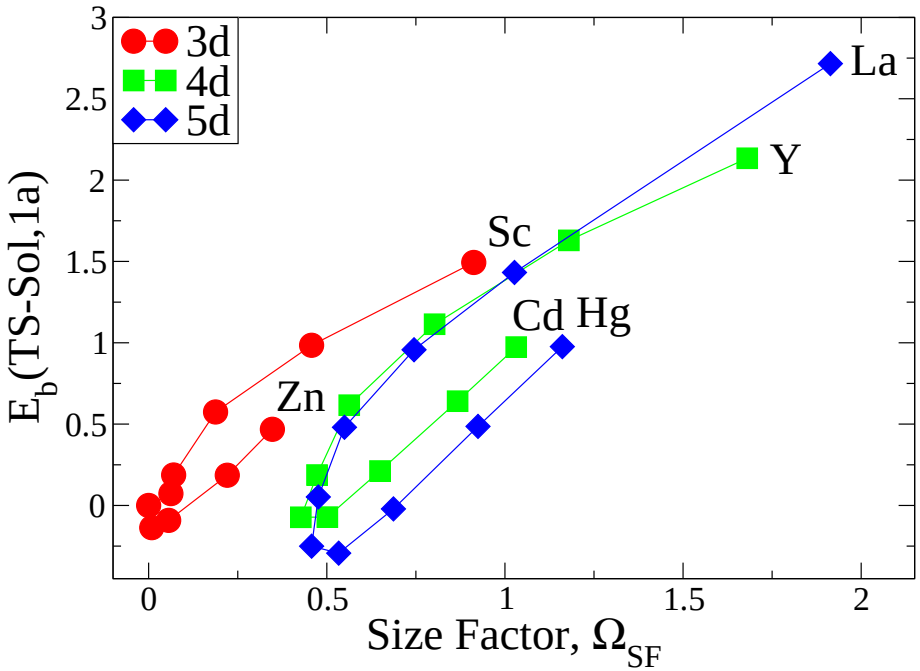


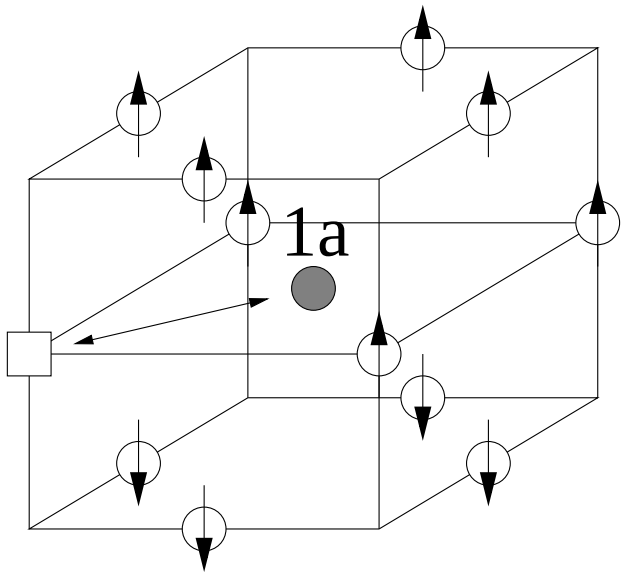


- Energy barriers for solute-vacancy exchange show a clear trend across the TM series with the largest solutes exhibiting the smallest barriers.
- For the largest solutes (Sc,Y,La,Zr,Hf) no barrier exists and solute relaxes to the centre of a 1nn divacancy.
- Despite there being a clear trend, no simple functional dependence of the migration barrier on solute size factor is exhibited in the data.

Vacancy-solute exchange at 1nn - transition state binding energy

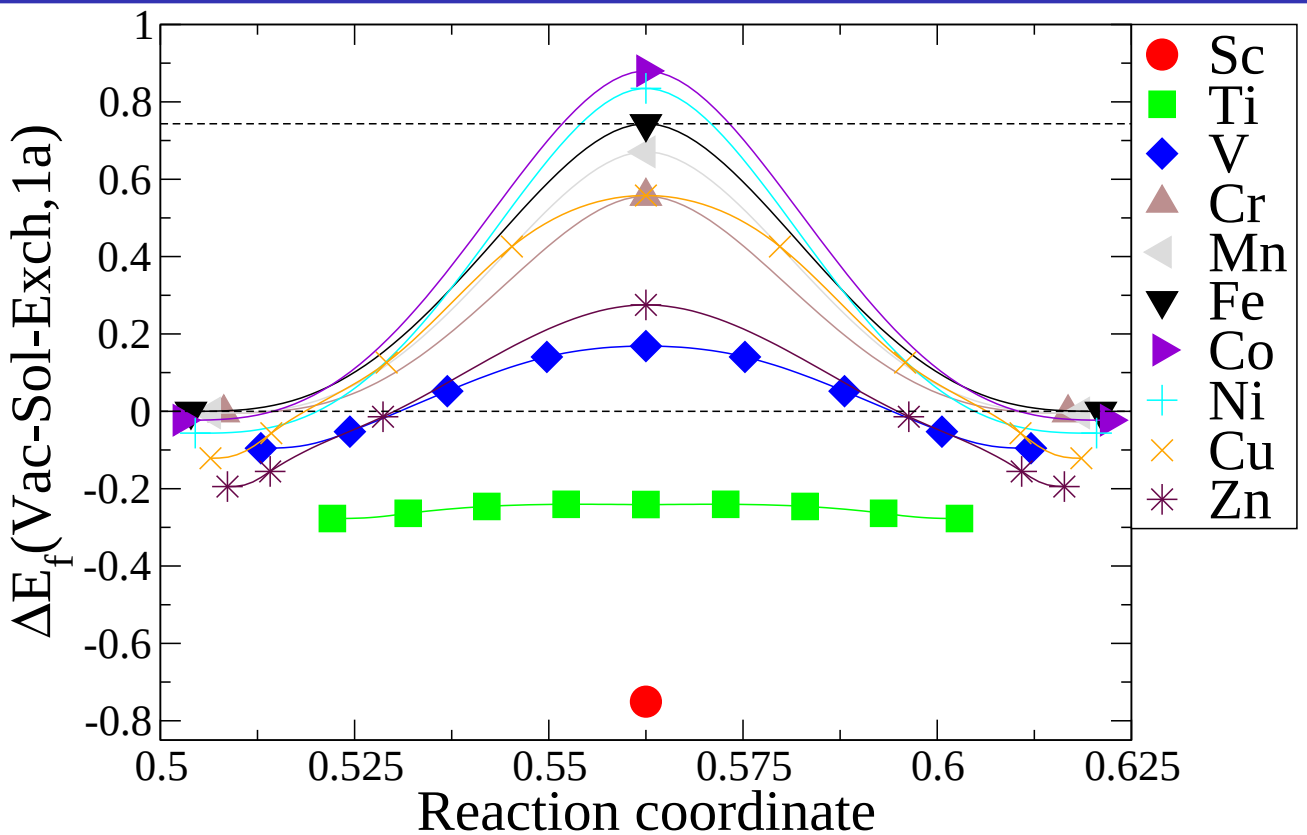






- Instead of the migration energy one can consider the binding energy of the solute to the transition state (TS) for vacancy (self-)migration.
- Binding to the TS is, generally, greater than for the on-site vacancy and solute, leading to a reduction in migration energy relative to pure Fe.
- There is clearly a strong positive correlation with solute size factor but a clear functional dependence is still absent.

Vacancy-solute exchange at 1nn - migration energy barrier

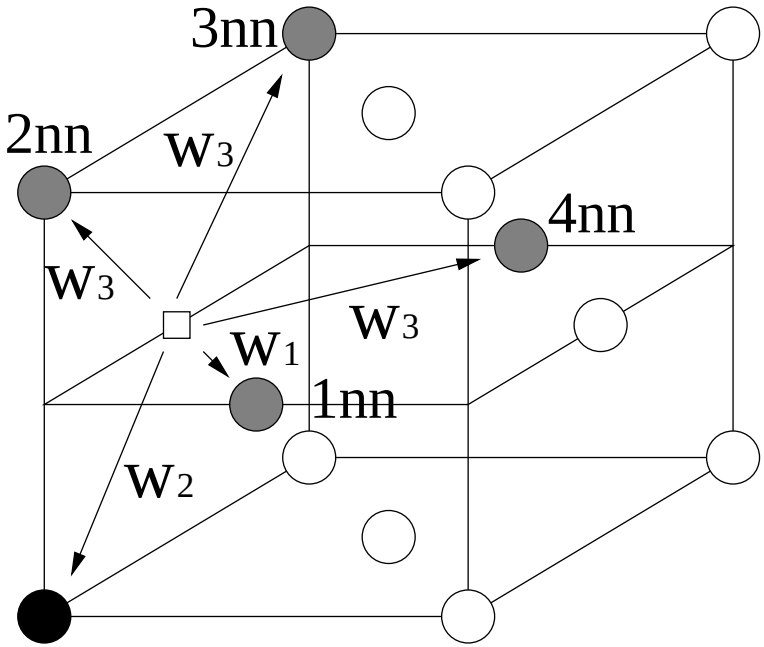


- The migration barriers for 3d TM solute-vacancy exchange are given as the change in formation energy along the migration path relative to that of an isolated solute and vacancy i.e. $\Delta E_{\mathrm{f}} = -E_{\mathrm{b}}(\mathrm{Vac}, \mathrm{Sol})$.
- With this definition, the drop in energy for the transition state relative to that for pure Fe (dotted line at 0.74 eV) corresponds to the TS-solute binding energy discussed previously.
- As the size-factor of the solute increases, the relaxed on-site solute moves closer to the centre of the divacancy and binds to the vacancy more strongly. TS-solute binding increases at an even greater rate, leading to a reduction in overall migration barrier height. This continues until we reach Sc, where there is no energy barrier and the stable configuration has Sc at the centre of a divacancy.

Vacancy-mediated solute diffusion - preliminary results for Y

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.



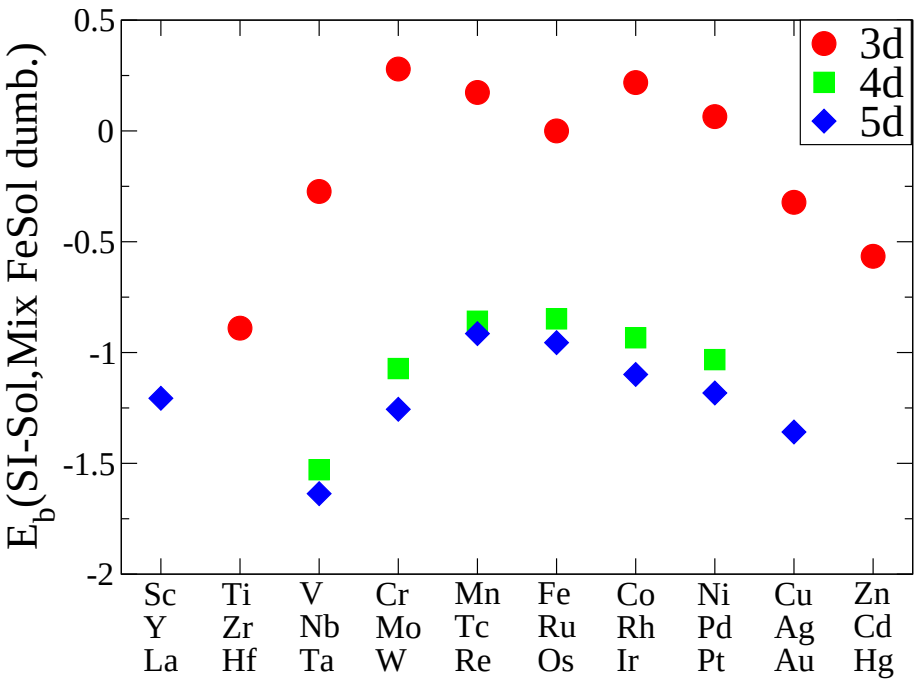
Each jump frequency is modelled by an Arrhenius type expression:

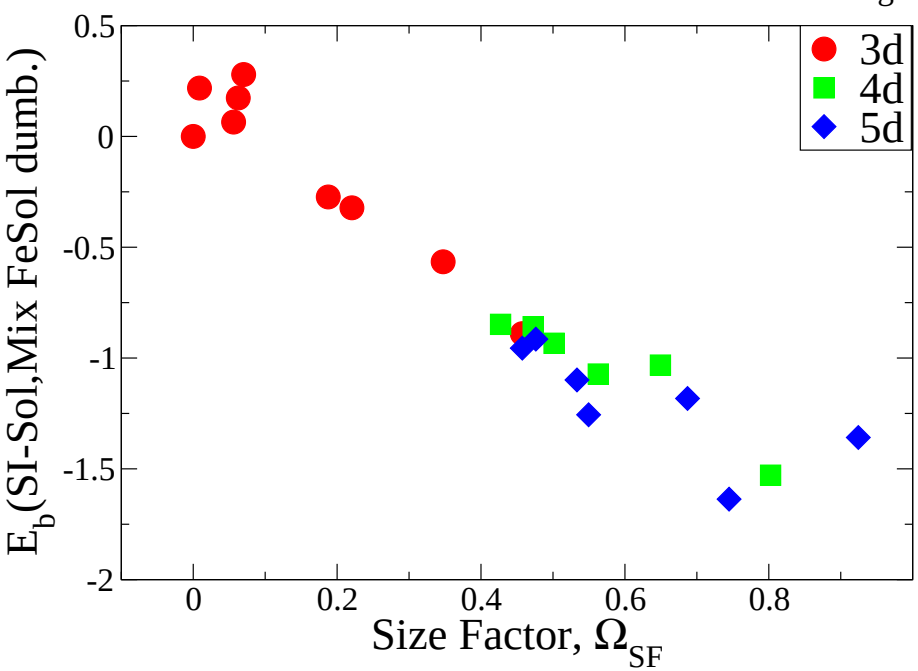
$$w_i = C_{\mathrm{m},i} \exp(-\beta E_{\mathrm{m},i})$$

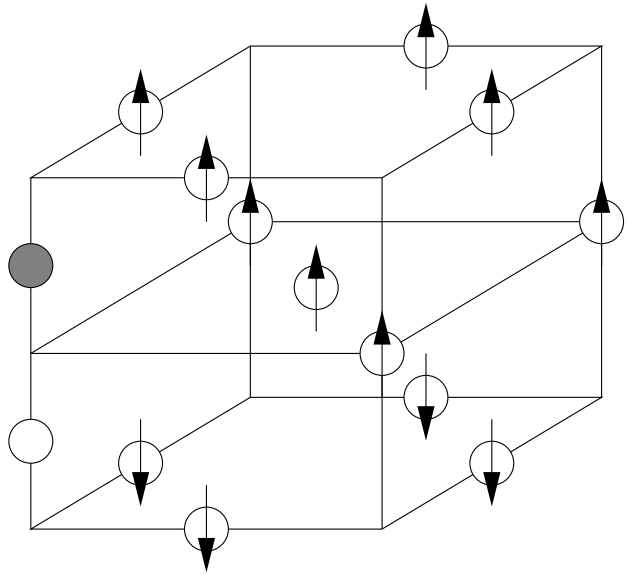
For Y, the preliminary results are as follows:
$E_{\mathrm{m},0} = 0.7 - 1.0$ eV, $E_{\mathrm{m},2} < 0$,
$E_{\mathrm{m},1} = 1.9 - 2.6$ eV,
$E_{\mathrm{m},3}(2nn) = 1.8 - 2.1$ eV,
$E_{\mathrm{m},3}(3nn) = 1.2 - 1.7$ eV,
$E_{\mathrm{m},3}(4nn) = 1.3 - 1.4$ eV,
$E_{\mathrm{m},4}(2nn) = 0.3 - 0.9$ eV,
$E_{\mathrm{m},4}(3nn) = 0.1 - 0.3$ eV,
$E_{\mathrm{m},4}(4nn) = 0.1 - 0.2$ eV.

- w_1 jumps are significantly suppressed relative to free vacancy migration (w_0). Y sits at the 1nn divacancy centre ($w_2 < 0$).
- Dissociative w_3 jumps also exhibit an enhance barrier height, whereas associative w_4 jumps have a significantly lower barrier than for free vacancy migration.
- Result is that Y will tend to trap a vacancy from as far as 4nn separation and the resulting complex will be effectively immobile.

[001] SI-solute binding energies for mixed dumbbell

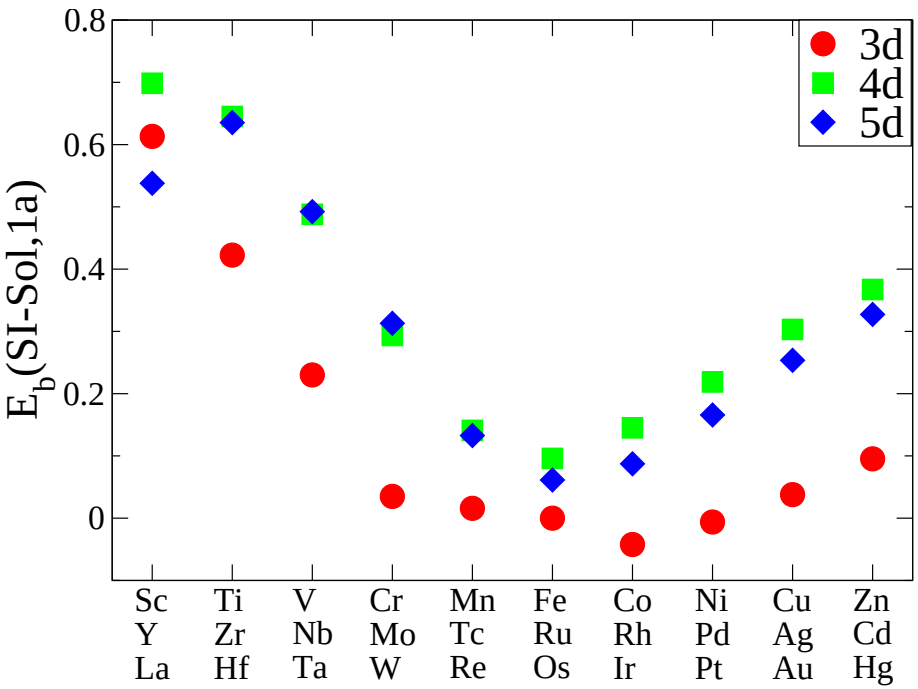


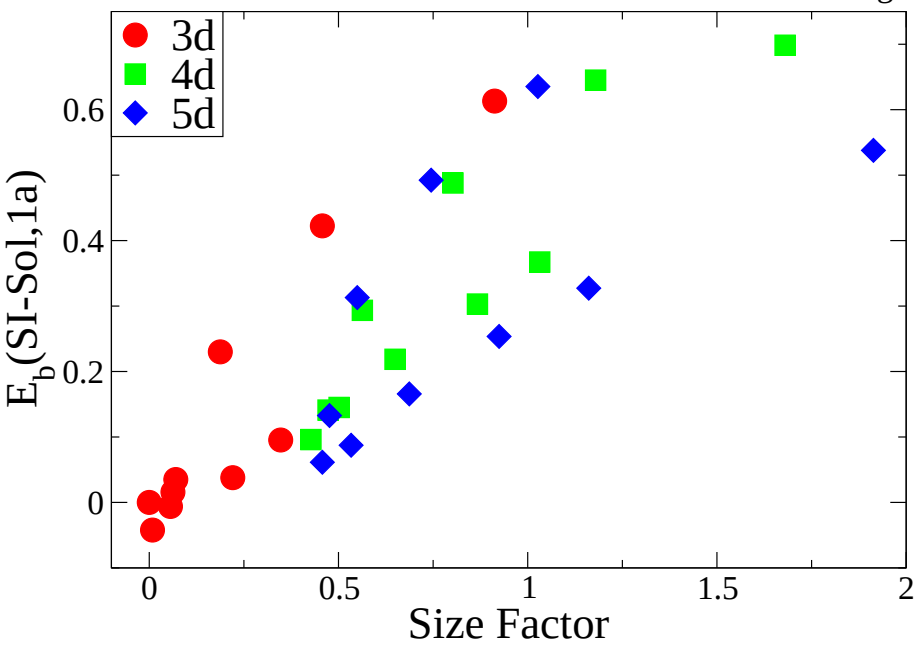


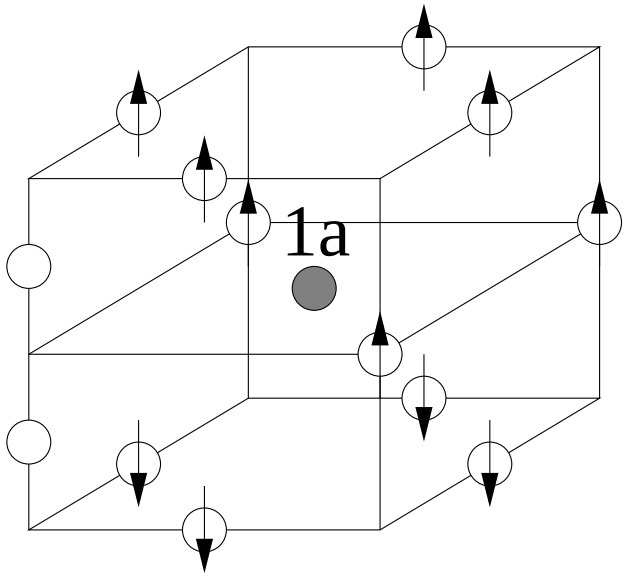


- TM solutes generally repelled from mixed dumbbell positions. The exceptions are the magnetic elements, Cr,Mn,Co and Ni.
- For the largest solutes (Sc,Y,Zr,Hf), no stable mixed dumbbell configuration could be found. The system relaxed to form an [001] self-interstitial with solute positively bound at 2nn.
- Solute binding energies in the mixed dumbbell show a strong correlation to size factor.

[001] SI-solute binding energies for solute in 1nn tensile site (1a)







- Positive binding to the [001] self-interstitial was observed at both 1nn and 2nn separation but was strongest for the 1nn tensile site, position 1a.
- Binding energies are significant, particularly for the largest solutes, but is generally less than that to the vacancy.
- Binding energies show a strong correlation to size factor but there is no simple functional dependence.

Summary and Conclusions

- Size factor data shows very similar trends to experimental results and exhibits significant correlations to results in bcc Fe. A quantitative comparison with experiment is still to be completed.
- Solute-Vacancy binding energies are strongly correlated to size factor with elements early and late in the transition metal series making the strongest vacancy traps.
- The energy barrier for solute-vacancy exchange shows no clear correlation for all transition metal solutes but larger solutes still tend to have smaller barriers. Further investigation is necessary.
- The solute binding energy to the transition state for solute-vacancy exchange shows improved correlation to the size factor but no clear functional dependence is exhibited by the data. This will be investigated further.
- For the largest solutes (Sc,Y,La,Zr,Hf) there is no barrier to solute-vacancy exchange and the most stable solute position is at the centre of the 1nn divacancy.
- Despite the energy barrier for solute-vacancy exchange reducing as solute size increases, oversized solutes will tend to trap vacancies and exhibit low vacancy-mediated diffusivity, as preliminary calculations for Y indicate.

Summary and Conclusions (cont.)

- Most transition metal solutes are repelled from the mixed [001] dumbbell, except for the magnetic elements, Cr, Mn, Co and Ni (although binding for Co and Ni is configuration dependent). The repulsion is so strong for the largest solutes (Sc,Y,Zr,Hf) that the mixed dumbbell relaxed to form a self-interstitial dumbbell with solute positively bound at 2nn. Binding to the mixed dumbbell shows significant correlation to size factor.
- Other compressive sites near an [001] self-interstitial dumbbell exhibited similar results to the mixed dumbbell but with reduced interaction strength.
- Positive binding of solutes to the [001] self-interstitial was observed in many sites and most strongly in the tensile site at 1nn. Binding energies show reasonable correlation to the size factor but further analysis is necessary to understand the trends.
- Oversized solutes act as both vacancy and self-interstitial traps. This should lead to enhanced point defect recombination and reduced net defect concentrations in the matrix and hence to a corresponding reduction of void swelling and radiation induced segregation.