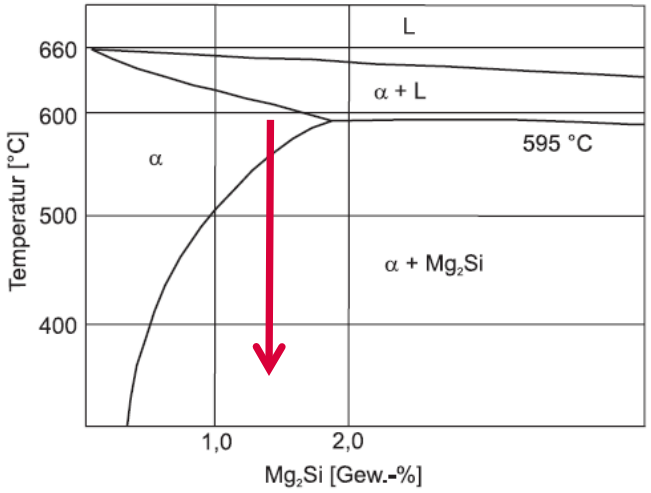
VACANCY-SOLUTE CLUSTERS IN AL-ALLOYS AB INITIO STUDIES

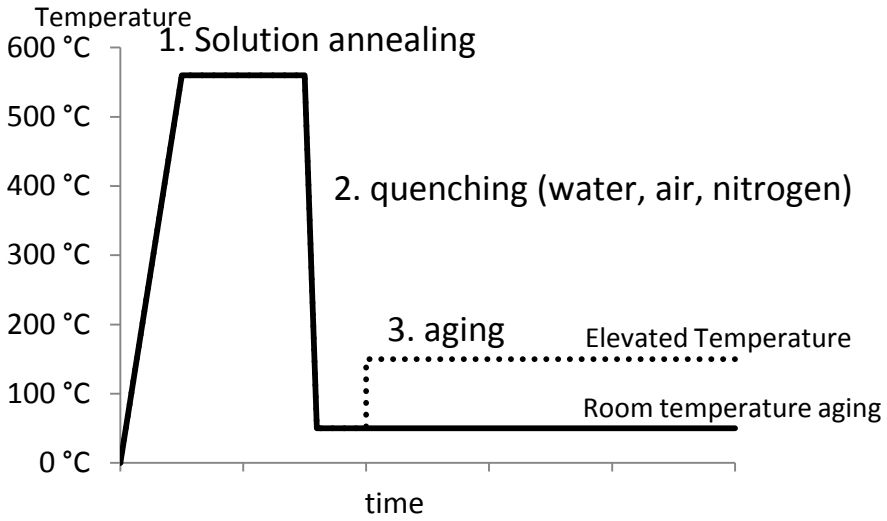
Peter Lang

Phase diagram and heat treatment (simplified)

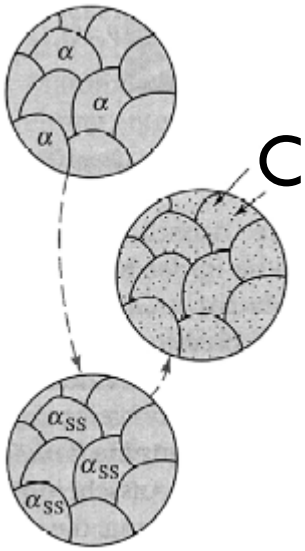


L… liquid
α+L … alpha + liquid
α… alpha crystal (fcc – Al)
α+Mg2Si… 2 phase region

1. solutionizing: temp. appr. 550 C; homogenization
2. quenching: as fast as possible – lead to supersaturated solid solution
3. aging: formation of metastable phases

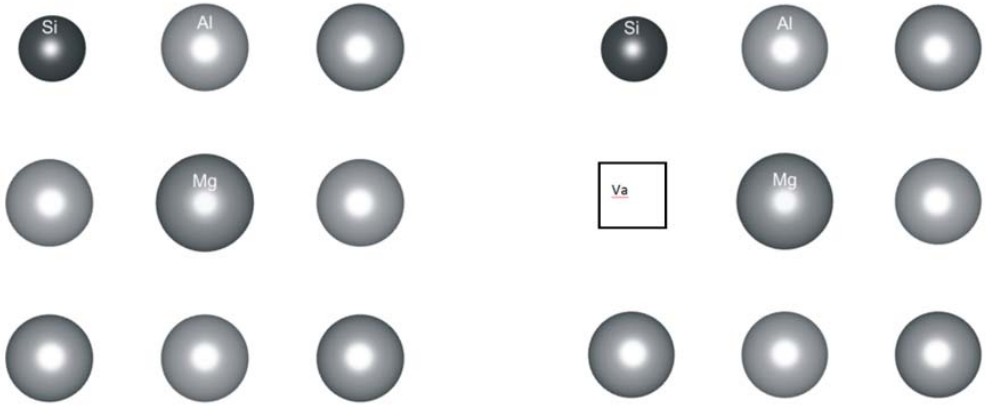


Co-cluster formation after/during quenching



Cluster formation in matrix

2 atom cluster = dimer



Mg-Si co-cluster (left), Mg-Si-Va co-cluster

First principle methodology

Based on the density functional theory (DFT)

implemented in

Using VASP 5.2.10

PAW potentials (kind of GGA) [1]

Al… PAW_PBE Al 04Jan2001

Mg… PAW_PBE Mg 13Apr2007

Si… PAW_PBE Si 05Jan2001

System fully relaxed with respect to volume as well as all cell-internal and external coordinates (tag ISIF = 3)

[1] G. Kresse, and J. Joubert, "From ultrasoft pseudopotentials to the projector augmented wave method", Phys. Rev. B **59**, 1758 (1999).

Settings in our studies; 32 atomic sites
Al + 1Mg + 1Si +1Va

INCAR file…

fcc Al+Mg+Va NN

ISMEAR = 0

SIGMA = 0.1

IBRION = 1

ISIF = 3

NSW = 15

KPOINTS file…

0

Monkhorst Pack

3 3 3

0 0 0

POTCAR file…

PAW_PBE Al 04Jan2001

PAW_PBE Mg 03Apr2007

PAW_PBE Si 05Jan2001

POSCAR file…

p(2x2) Al PBE
4.05
2.0 0.0 0.0
0.0 2.0 0.0
0.0 0.0 2.0
Al Mg Si
253 1 1
Direct
0.000 0.000 0.500 Al
0.000 0.500 0.000 Al
0.000 0.500 0.500 Al
⋮
0.000 0.000 0.000 Mg
0.000 0.250 0.250 Si
0.000 0.000 0.500 Va

Simulation setup

- Create a perfect crystal. Calculate the total energy of the pure Al system.
- Remove one atom and replace it by different occupancy (Mg/Si/Va);

  basis systems = starting conditions
- Remove two atoms and replace two different (Mg+Si) substituting elements = reference energy
- Remove three atoms and replace two different substituting elements with one vacancy (Mg+Si+Va) in the next neighbour shells.
- Relax the system with respect to volume as well as all cell-internal atomic coordinates.
- Evaluate energy states based on different cluster structures.
- Compare the total energies of the different configurations.

Binding energy

- Binding energy (two substitutes)

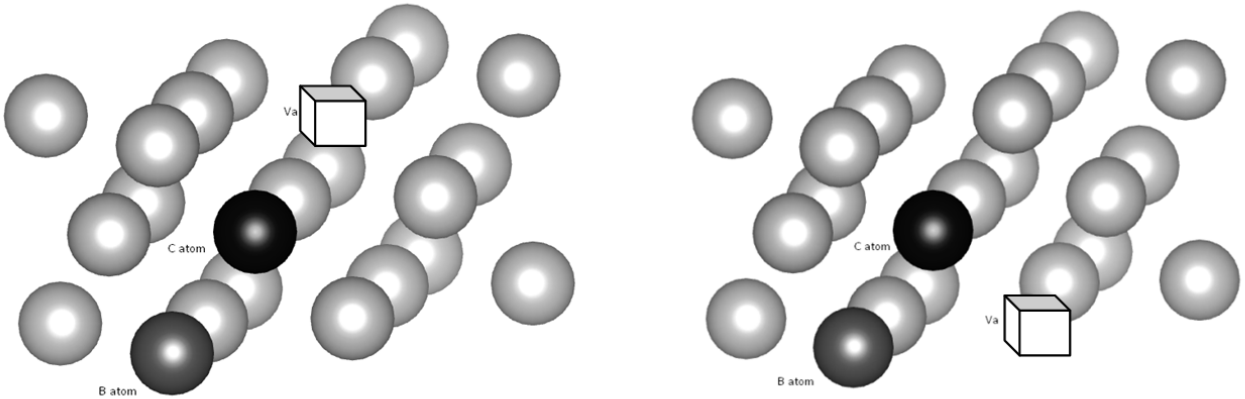
$$E_{\mathrm{b}}(A,B) = [E(N-1+A) + E(N-1+B)] - [E(N-2+A+B) + E_{\mathrm{ref}}].$$

  - Extension to more substitutes

$$E_{\mathrm{b}}(A_1, A_2, \ldots, A_n) = \sum_{i=1,\ldots,n} E(A_i) - [E(A_1 + A_2 + \cdots + A_n) + (n-1)E_{\mathrm{ref}}].$$

Simulation geometries

- Implementation of one vacancy



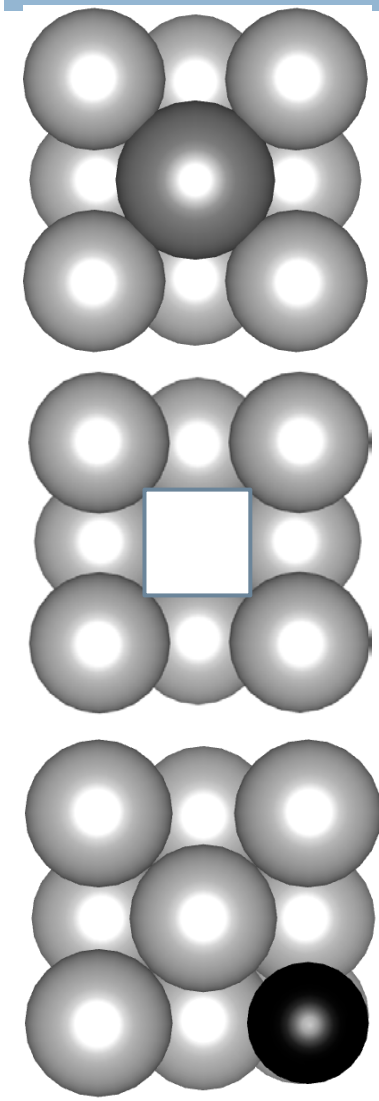
Arrangement of co-cluster dimer; Va in row (left side), Va in triangle (right side) structure

A atom: for system Al-Mg-Si….. Mg; for system Al-Zn-Mg…..Mg

B atom: for system Al-Mg-Si…..Si; for system Al-Zn-Mg…..Zn

Vacancy

Subsystems…

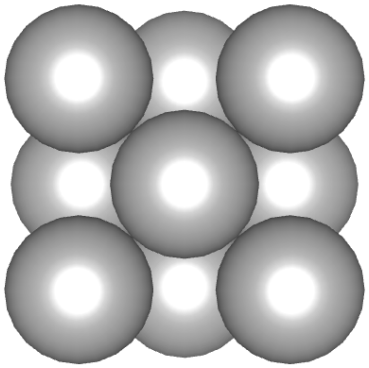


E(Al + Mg atom)

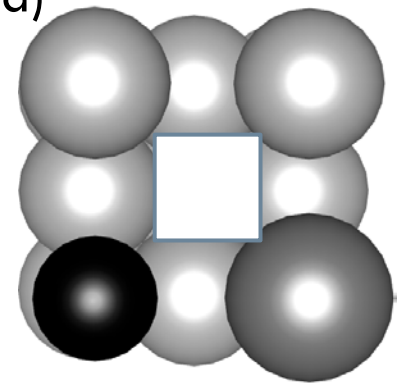
E(Al + Va)

E(Al + Si atom)

2 x E (pure Al)



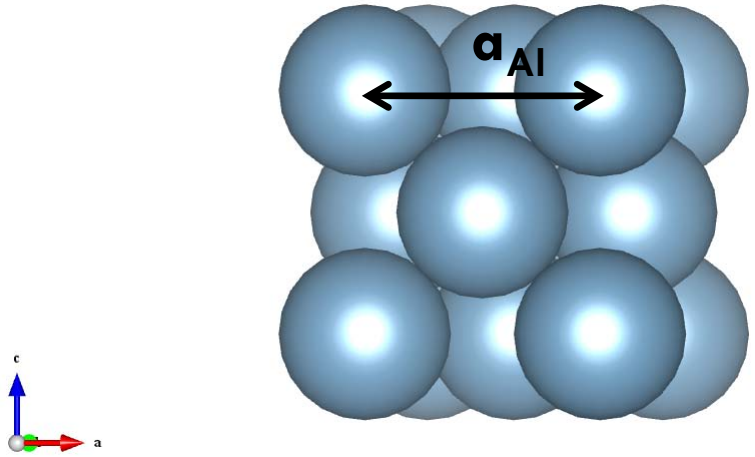
E(Al + Mg + Si + Va)



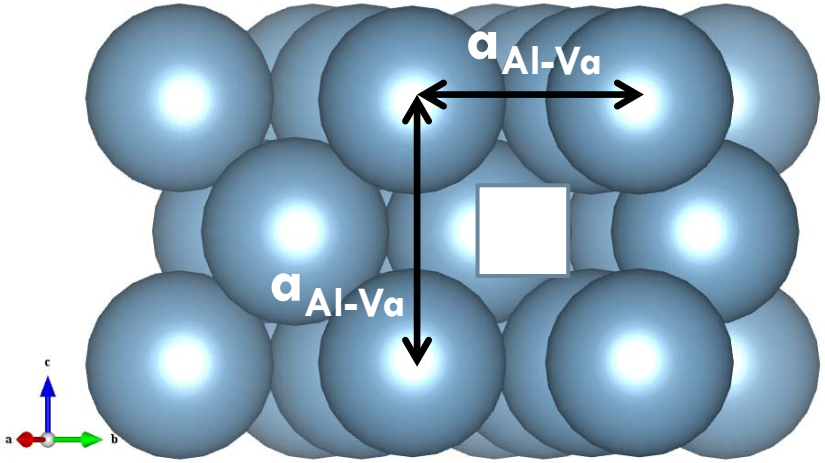
lattice parameter of Al-matrix

- Set lattice constant: 4.050Å
  - After fully relaxation: 4.041Å
    - Experimental value: 4.050Å

<u>Pure, undisturbed Al matrix</u>



- One Vacancy
  - After fully relaxation: 3.976Å
  - Formation energy 0.66eV
    - Exp. Value: 0.69±0.03 [1]



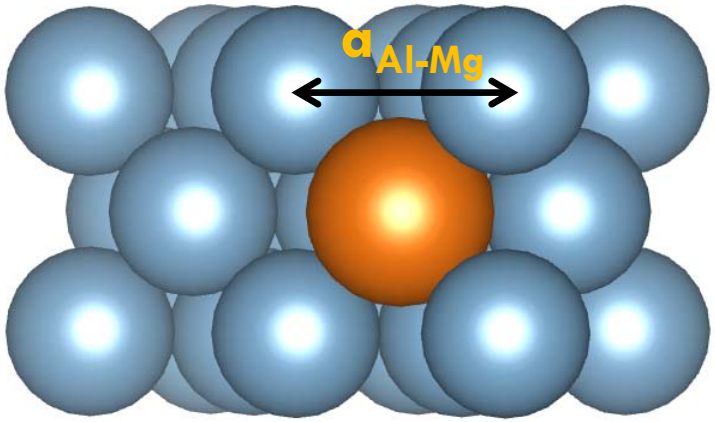
… symbol for Va

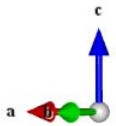
[1] Tzanetakis et al.; The formation energy of vacancies in Aluminium and Magnesium; physica status solidi; Vol.75,issue 2, 1976, 433-439

Lattice parameter with defects

- Magnesium in Al matrix
  - After fully relaxation: 4.094Å
    … expansion

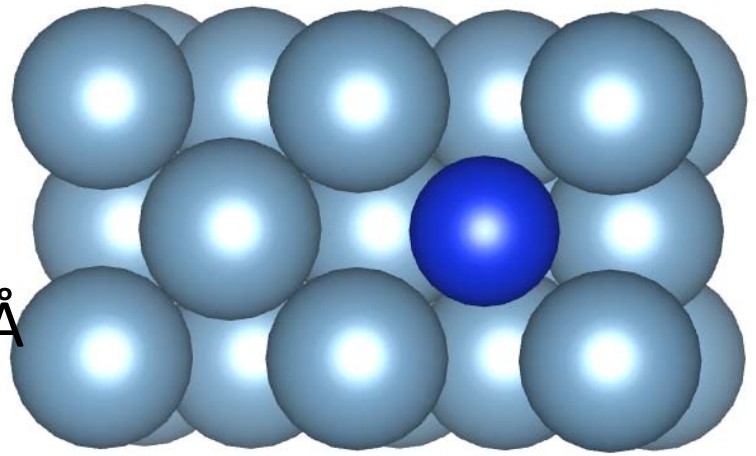
atom radius$_{Mg}$ 150pm

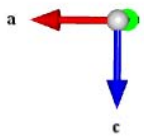




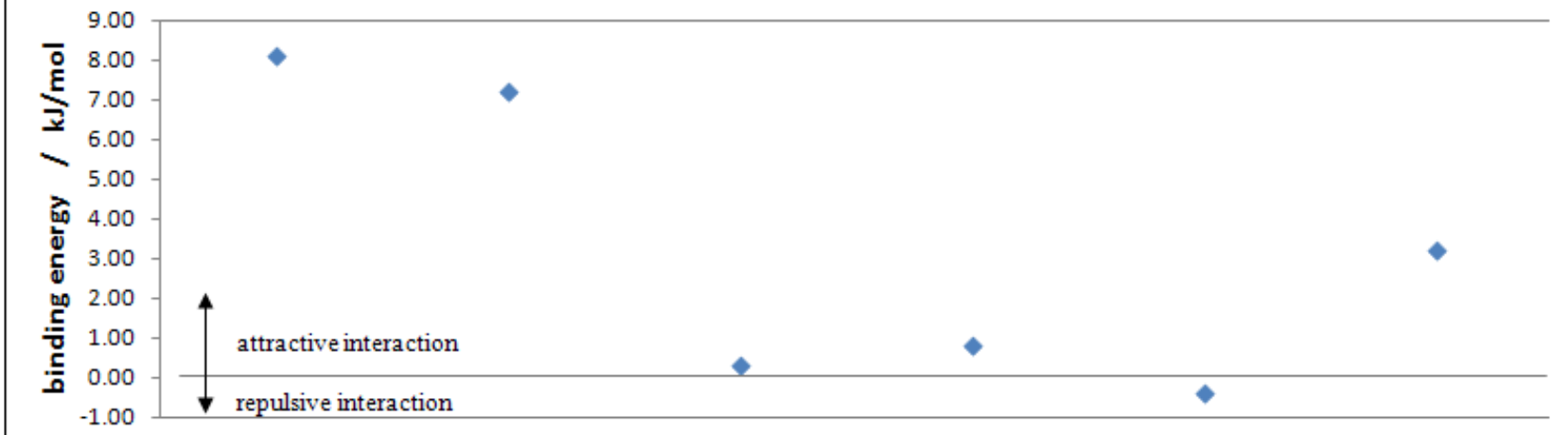
- Silicium in Al matrix
  - After fully relaxation: 4.012Å
    … compression

atom radius$_{Si}$ 110pm

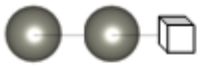
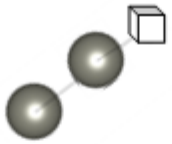
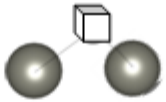
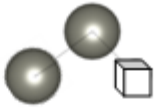
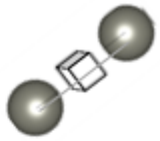
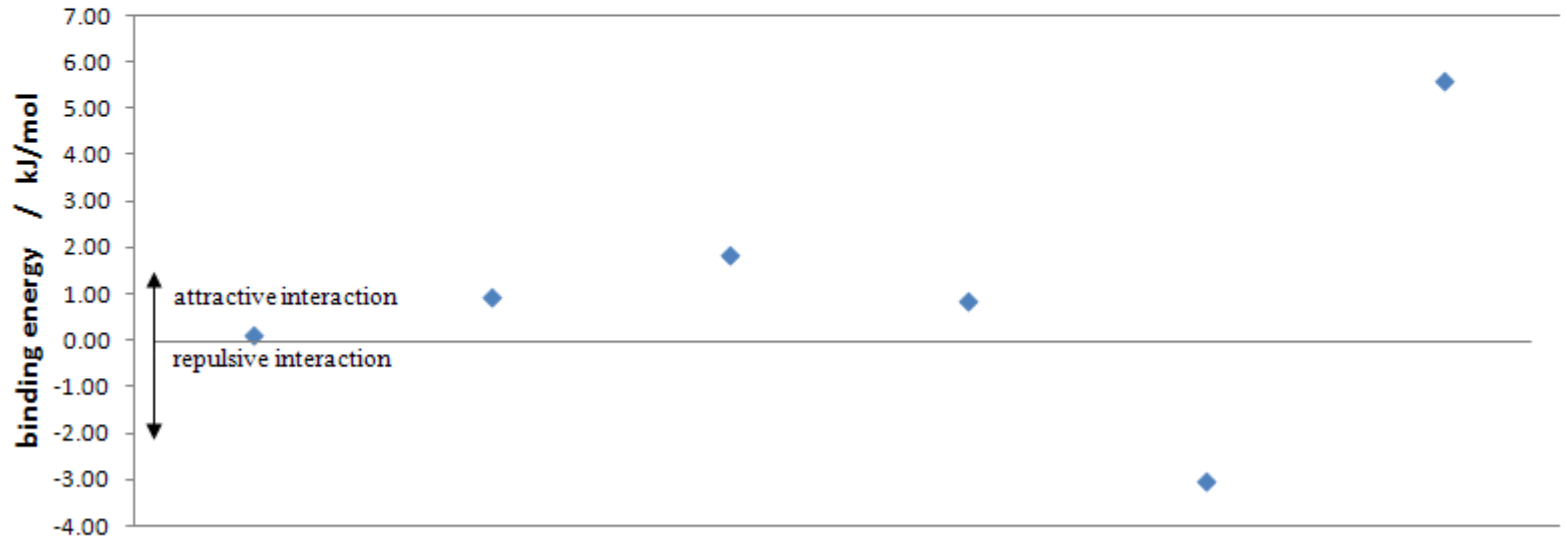




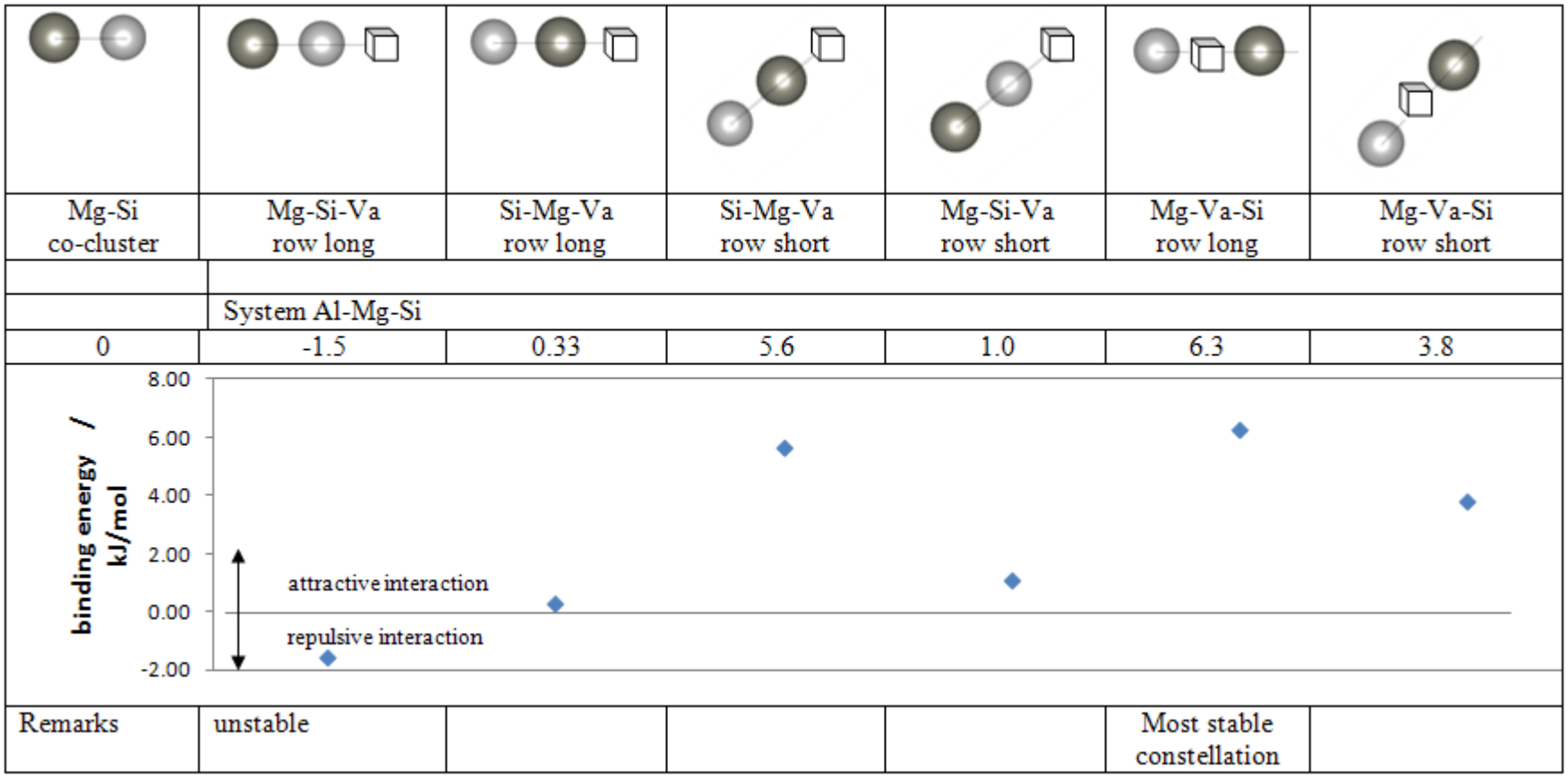
Results Al-Mg-Mg system

Ref.-energy						
Mg-Mg cluster	Mg-Mg-Va row long	Mg-Mg-Va row short	Mg-Va-Mg triangle	Mg-Mg-Va triangle	Mg-Va-Mg row long	Mg-Va-Mg row short
System Al-Mg-Mg						
0	8.11	7.21	0.31	0.81	-0.4	3.21
						
Remarks	Most stable: Va next Mg in row				unstable	

Results Al-Si-Si system

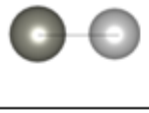
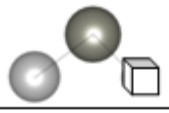
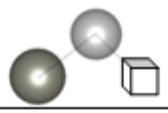
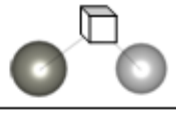
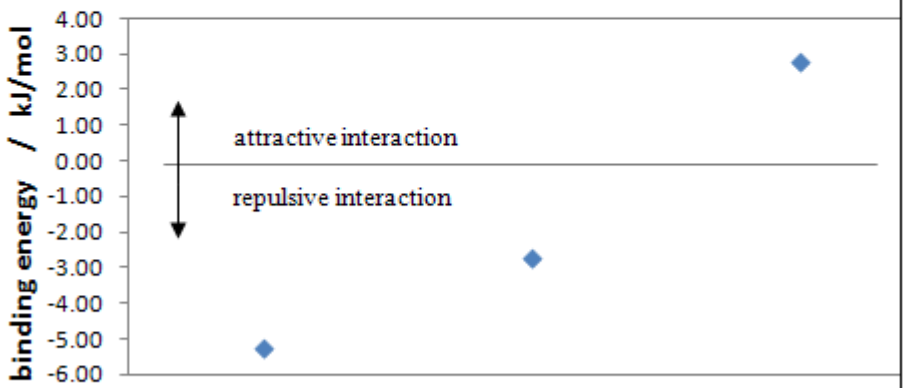
Ref.-energy						
Si-Si cluster	Si-Si-Va row long	Si-Si-Va row short	Si-Va-Si triangle	Si-Si-Va triangle	Si-Va-Si row long	Si-Va-Si row short
System Al-Si-Si						
0	0.11	0.95	1.84	0.85	-3.05	5.57
						
Remarks					unstable	Most stable: Va in-between row

Results Al-Mg-Si system



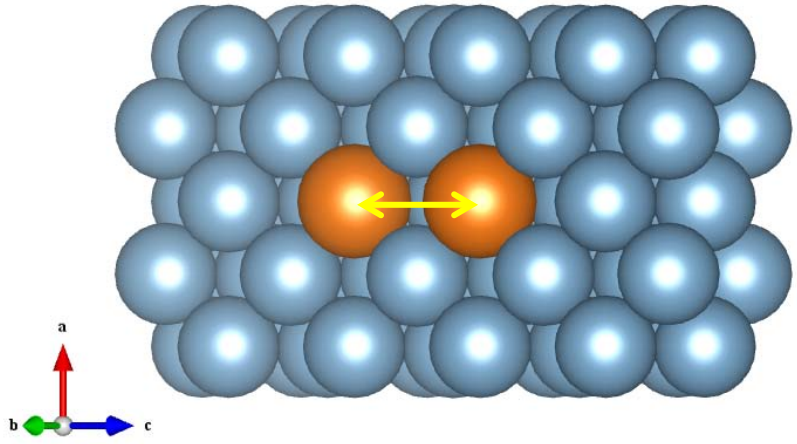
Mg-Si co-cluster	Mg-Si-Va row long	Si-Mg-Va row long	Si-Mg-Va row short	Mg-Si-Va row short	Mg-Va-Si row long	Mg-Va-Si row short
	System Al-Mg-Si					
0	-1.5	0.33	5.6	1.0	6.3	3.8
Remarks	unstable				Most stable constellation	

Results Al-Mg-Si system

			
Mg-Si co-cluster	Si-Mg-Va triangle	Mg-Si-Va triangle	Si-Va-Mg triangle
	System Al-Mg-Si		
0	-1.5	0.33	5.6
			
Remarks	unstable		

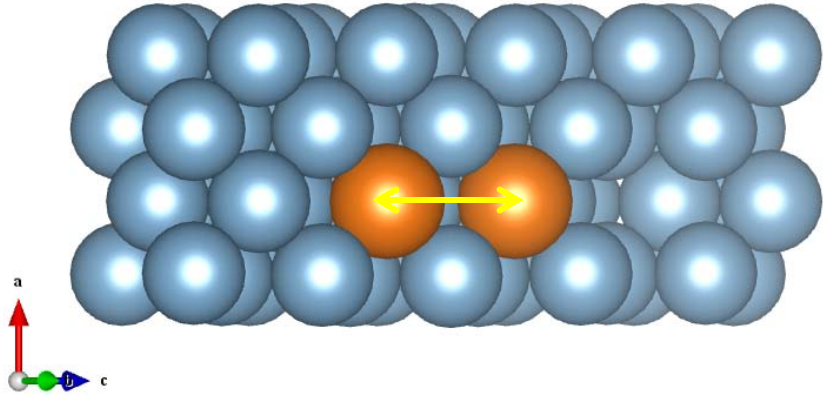
Most stable Mg-Mg-Va cluster

- Mg-Mg cluster, higher mechanical stress atoms more close to each other – not favourable



Distance Mg-Mg: 4.035Å

- Mg-Mg-Va cluster, reduction of mechanical stresses, atoms can move



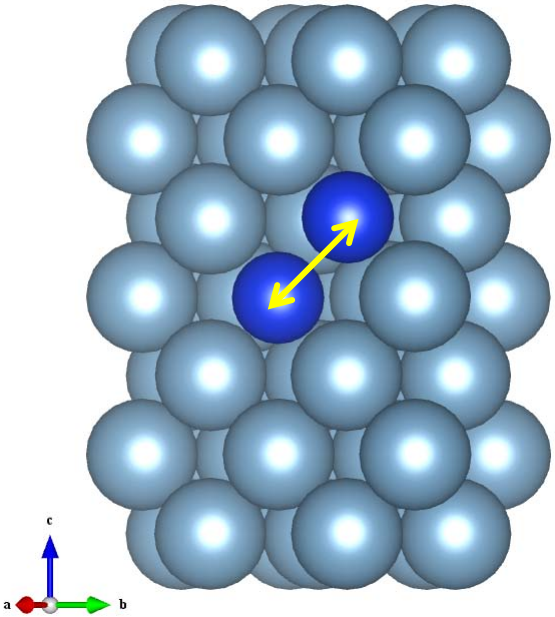
Distance Mg-Mg: 4.068Å – less mechanical forces (amongst chemical forces)

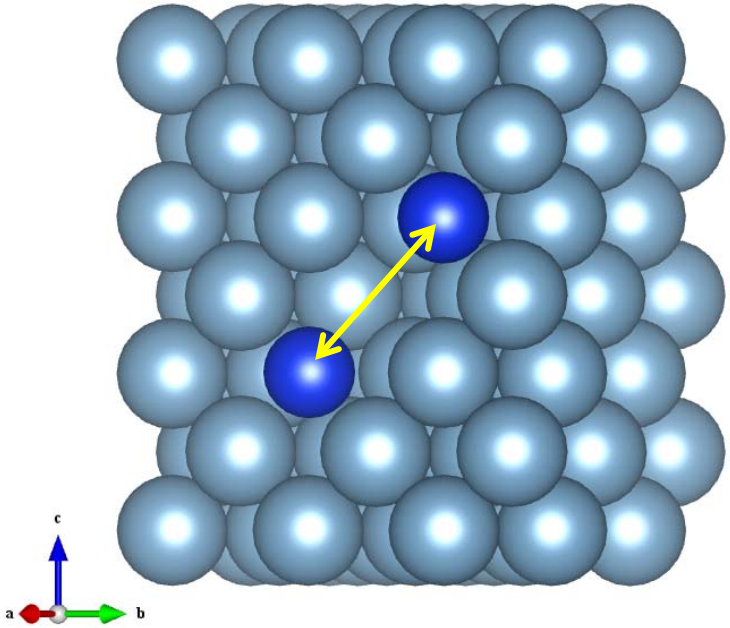
Most stable Si-Si-Va cluster

- Si-Si cluster,

  higher chemical stresses

  Distance Si-Si: 2.906Å





- Si-Si-Va cluster,

  Distance Si-Si: 5.619Å

  most favourable Cluster constellation

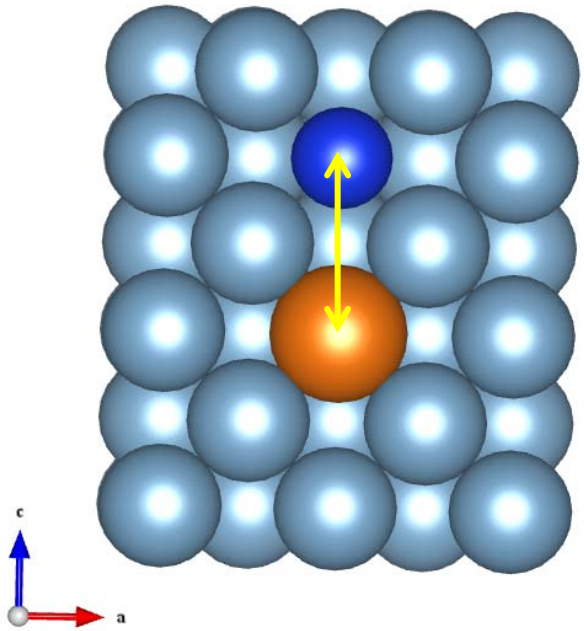
Most stable Si-Si-Va cluster

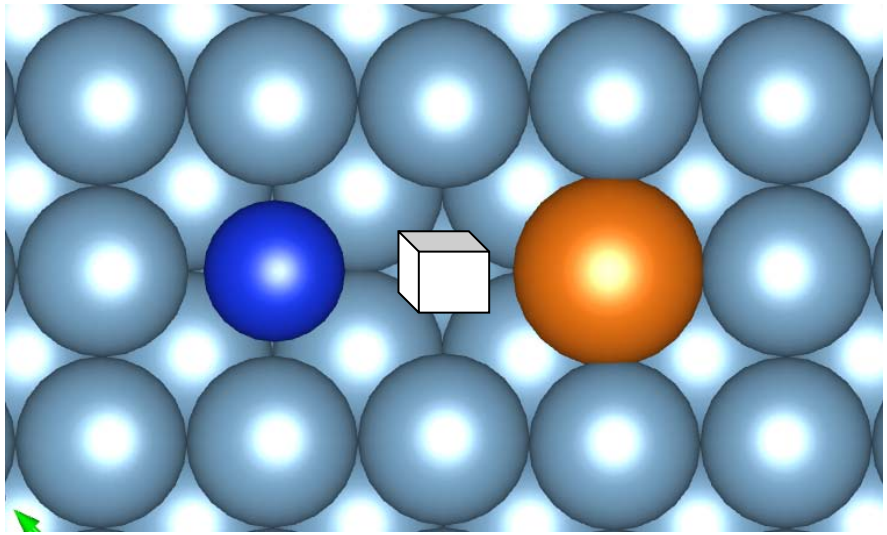
- Mg-Si cluster,

  nearly compensation of

  compression and tension

  Distance Mg-Si: 4.059Å





- most favourable

  Mg-Si-Va cluster,

$\Delta E_{bind} = 6.3$ kJ/mol

Conclusions

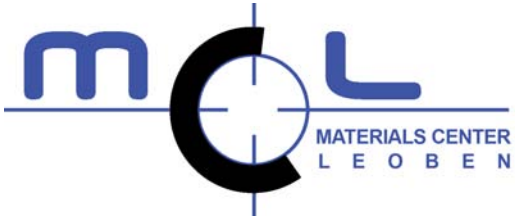
- Some co-cluster arrangements energetically favourable with vacancy

- First-principles calculations:

  capable of producing quantitatively accurate

  solute – vacancy binding energies

Acknowledgements



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