

First-principles calculations of solute-vacancy binding in magnesium

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Introduction

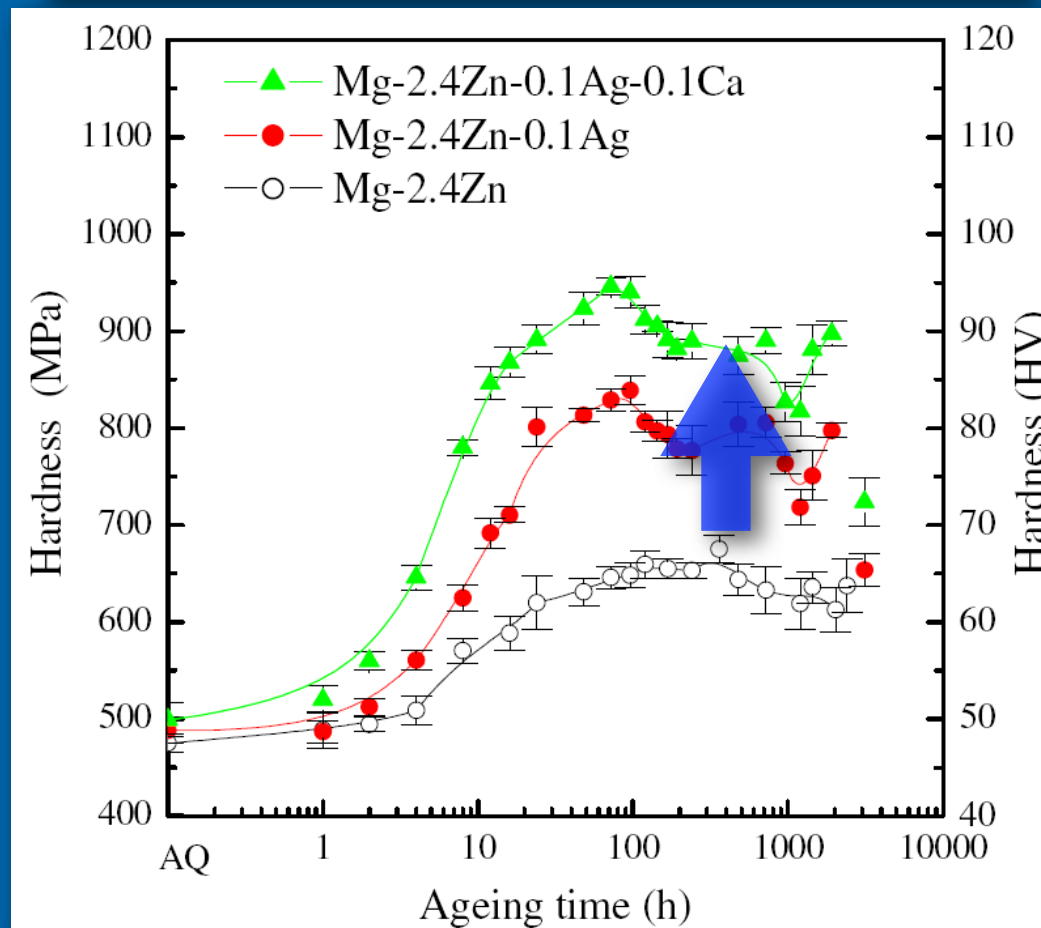
- Magnesium alloys
 - Fuel efficiency in automobiles
 - May substitute for heavier aluminum and steel based counterpart in the future
 - Relatively low strength and creep resistance compared with aluminum alloys
- How to increase mechanical properties?
 - Searching for precipitate hardenable Mg alloys
 - Fine distribution of precipitates in Mg matrix

Microalloying!

Enhanced age hardening in a Mg-2.4 at.% Zn alloy by trace additions of Ag and Ca

C.L. Mendis,* K. Oh-ishi and K. Hono

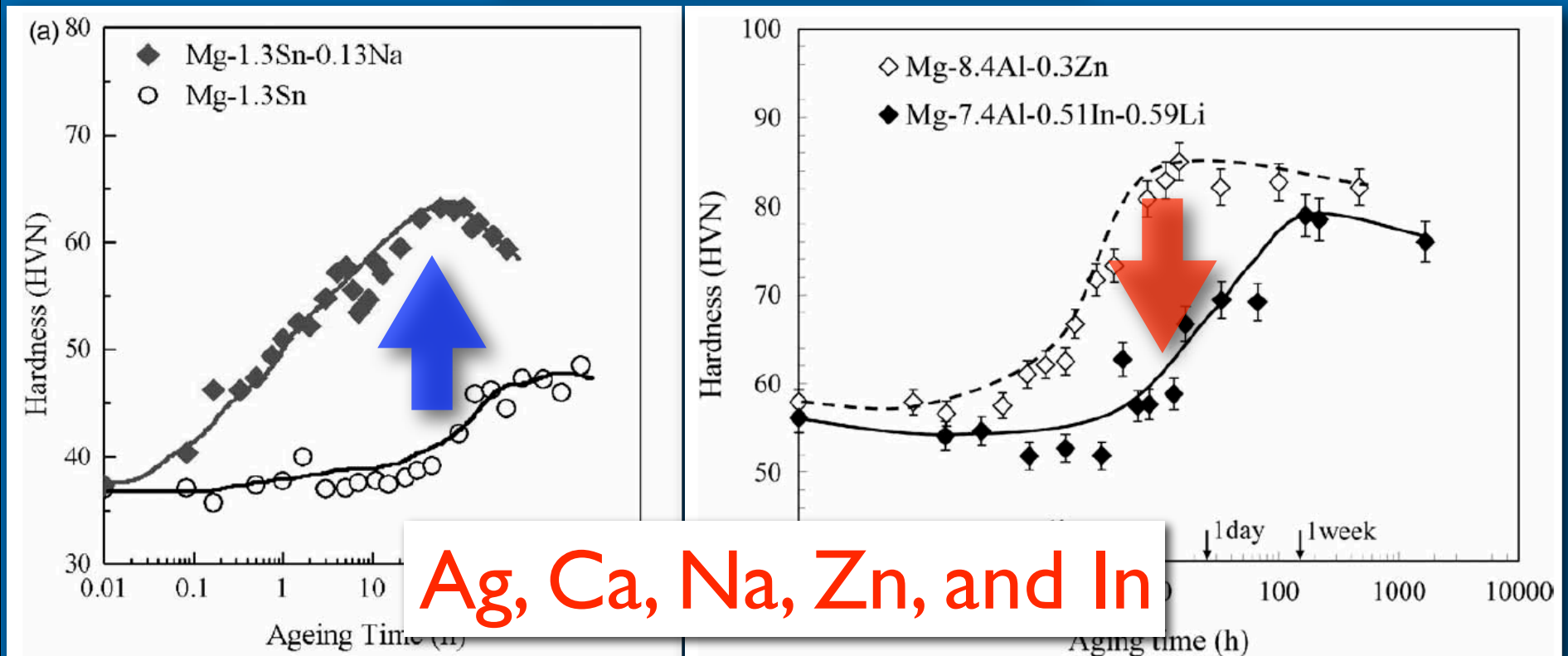
Scripta Materialia 57 (2007) 485–488



Refinement of precipitate distributions in an age-hardenable Mg–Sn alloy through microalloying

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Introduction

- Why microalloying improves mechanical property?
 - Not yet clearly explained for magnesium alloys
 - Analogous to Sn addition to Al-Cu
- Al-Cu alloys
 - Sn is reported to decrease natural aging of Al-Cu
 - Kimura and Hasiguti, *Acta Metal.* (1961) suggested:
 - Sn impurity and vacancy bonding starves the diffusing Cu atoms to vacancies
 - Suppress Cu clustering or GP zone formation
 - Promote precipitates' nucleation in Al matrix
 - Many researchers have measured solute-vacancy binding energy in Al

Solute-vacancy binding energy

- Largely unknown for magnesium → **first-principles !**
- Difference between ‘infinite separation’ of defects (vacancy and solute) and NN separation

$$-E_{\text{bind}}(X - \square) = E(\text{Mg}_{N-2}X_1\square_1) + E(\text{Mg}_N) - E(\text{Mg}_{N-1}X_1) - E(\text{Mg}_{N-1}\square_1)$$

- As byproducts, we also can get
 - Vacancy formation energy

$$E_{\text{vac}}(\square) = E(\text{Mg}_{N-1}\square_1) - \frac{N-1}{N}E(\text{Mg}_N)$$

- Mixing enthalpy

$$E_{\text{mix}}(X) = E(\text{Mg}_{N-1}X_1) - \frac{N-1}{N}E(\text{Mg}_N) - E(X)$$

N : Number of lattice sites in a supercell, X : Solute, \square : Vacancy

Supercell construction

lattice sites	supercell size*	k -points	ratio (a:b:c)
48	$3 \times 2 \times 2$	$12 \times 12 \times 12$	1:1.15:1.09
64	$4 \times 2 \times 2$	$10 \times 10 \times 10$	1:0.87:0.82
96	$4 \times 2 \times 3$	$8 \times 8 \times 8$	1:0.87:1.23
144	$4 \times 3 \times 3$	$6 \times 6 \times 6$	1:1.30:1.23

* 4 atoms orthorhombic hcp unit cell has been used as a basis

Experimental validation

		First-principles (This work)	Value	Previous Method
Vacancy formation (E_f)		0.74 ± 0.05	0.89 ± 0.06	Exp ($\Delta\rho_q$)
		$0.83 \pm 0.01^{\S}$	0.81 ± 0.02	Exp ($\Delta\rho_{eq}$)
			0.58 ± 0.01	Exp (DD)
			0.79 ± 0.03	Exp ($\Delta\rho_q$)
			0.90 ± 0.1	Exp (PAS)
			0.83^{\dagger}	DFT
			$0.83 \pm 0.07^{\ddagger}$	DFT
Solute-Vacancy binding (E_b)	Zn-□	0.05	0.07 ± 0.02	Exp ($\Delta\rho_q$)
	Al-□	0.03	0.29 ± 0.02	Exp (H_v)

\S LDA, $N = 48, 64, 96,$ and 144

\dagger LDA, $N=96$

\ddagger LDA, $N=16, 36,$ and 54

$\Delta\rho_{q,eq}$: Electrical resistivity of quenched, thermal equilibrium samples respectively

H_v : Vickers hardness

DD: Differential dilatometry

PAS: Position-annihilation spectroscopy

Vacancies in Metals: From First-Principles Calculations to Experimental Data

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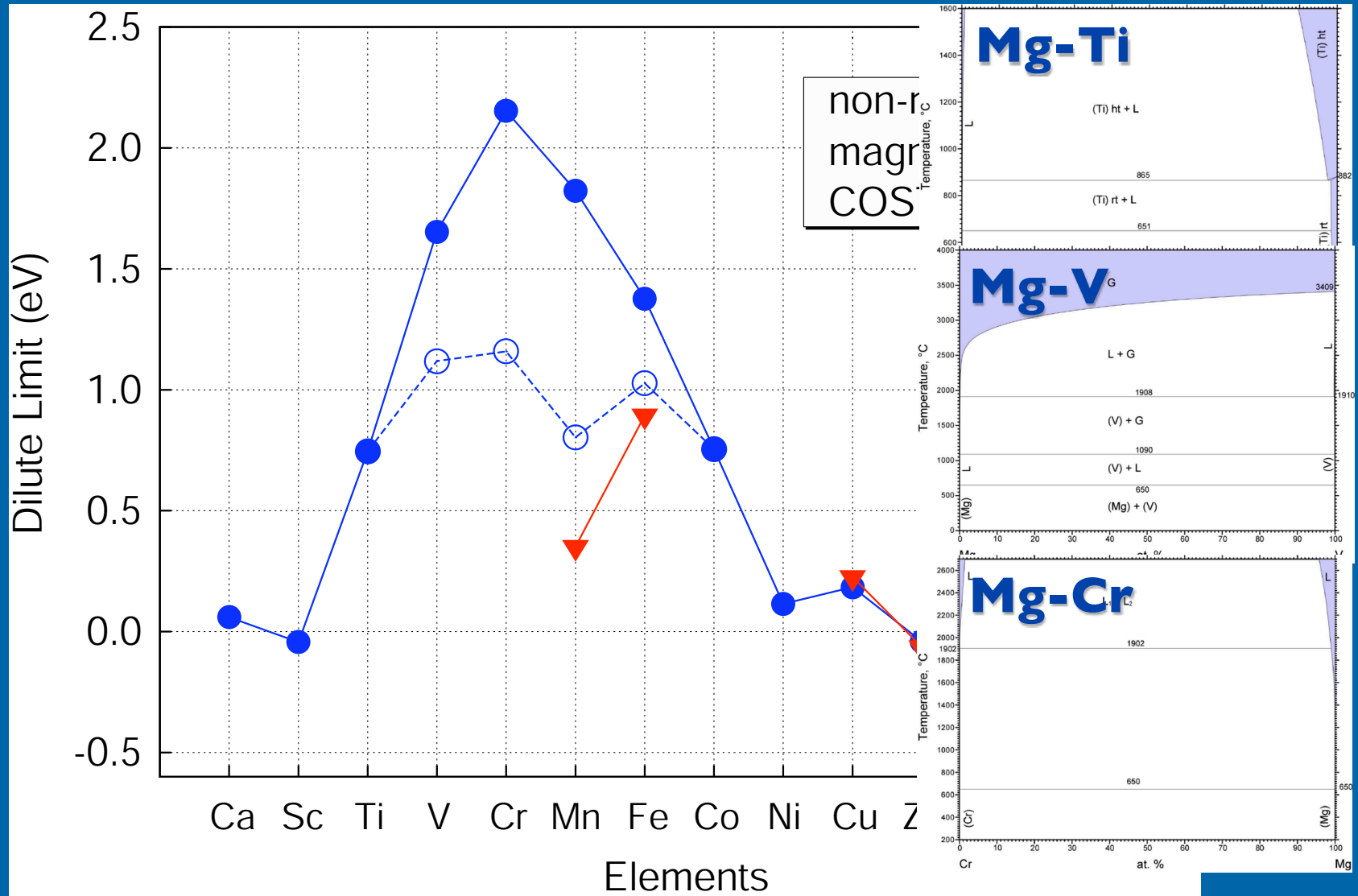
(Received 30 May 2000)

TABLE III. Fundamental properties of Al. Lattice constant a , bulk modulus B , cohesive energy E_c , vacancy formation energy H_V^F , including surface corrections H_V^{F*} , and binding energy for the nearest-neighbor divacancy $H_{2V,nn}^B = 2H_V^F - H_{2V,nn}^F$. Expt.: experimental data from the literature (a at $T = 0$ K, $B = (c_{11} + 2c_{12})/3$, and E_c at $T = 0$ K and 1 atm). Expt.*: our reinterpretation of the experimental results in Ref. [8]. Computed DFT data from the literature (full potential [14] and pseudopotential [23]) together with the present DFT data. The theoretical values for E_c are not corrected for the zero-point energy (≈ 39 meV). Our surface corrected data for the vacancy formation energy is shown in bold.

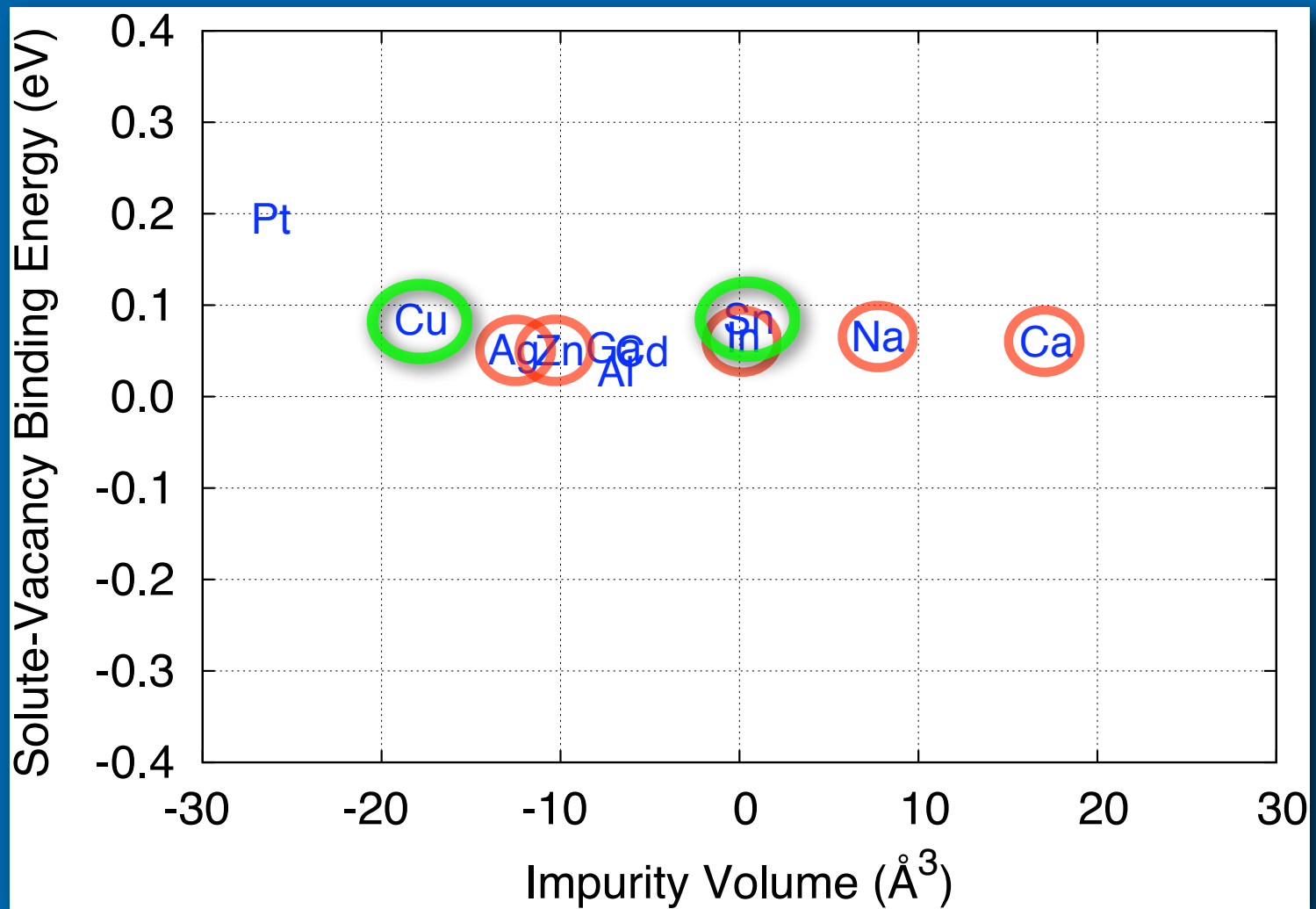
Method	a (Å)		B (Mbar)		E_c (eV)	H_V^F (eV)	H_V^{F*} (eV)	$H_{2V,nn}^B$ (eV)
Expt.	4.03 [20]		0.77 [21]		3.39 [22]	0.67 ± 0.03 [7]		0.2, 0.3 [7]
Expt.*	0.68		0.00
GGA	4.039 [14]	4.042 [23]	0.773 [14]	0.744 [23]	3.415 [23]	0.54	0.69	-0.08
LDA	3.983 [14]	3.961 [23]	0.840 [14]	0.830 [23]	4.034 [23]	0.70	0.76	-0.07

LDA: 0.06 eV, GGA: 0.15 eV for Al

Mg-X: mixing enthalpy (Mg63X)



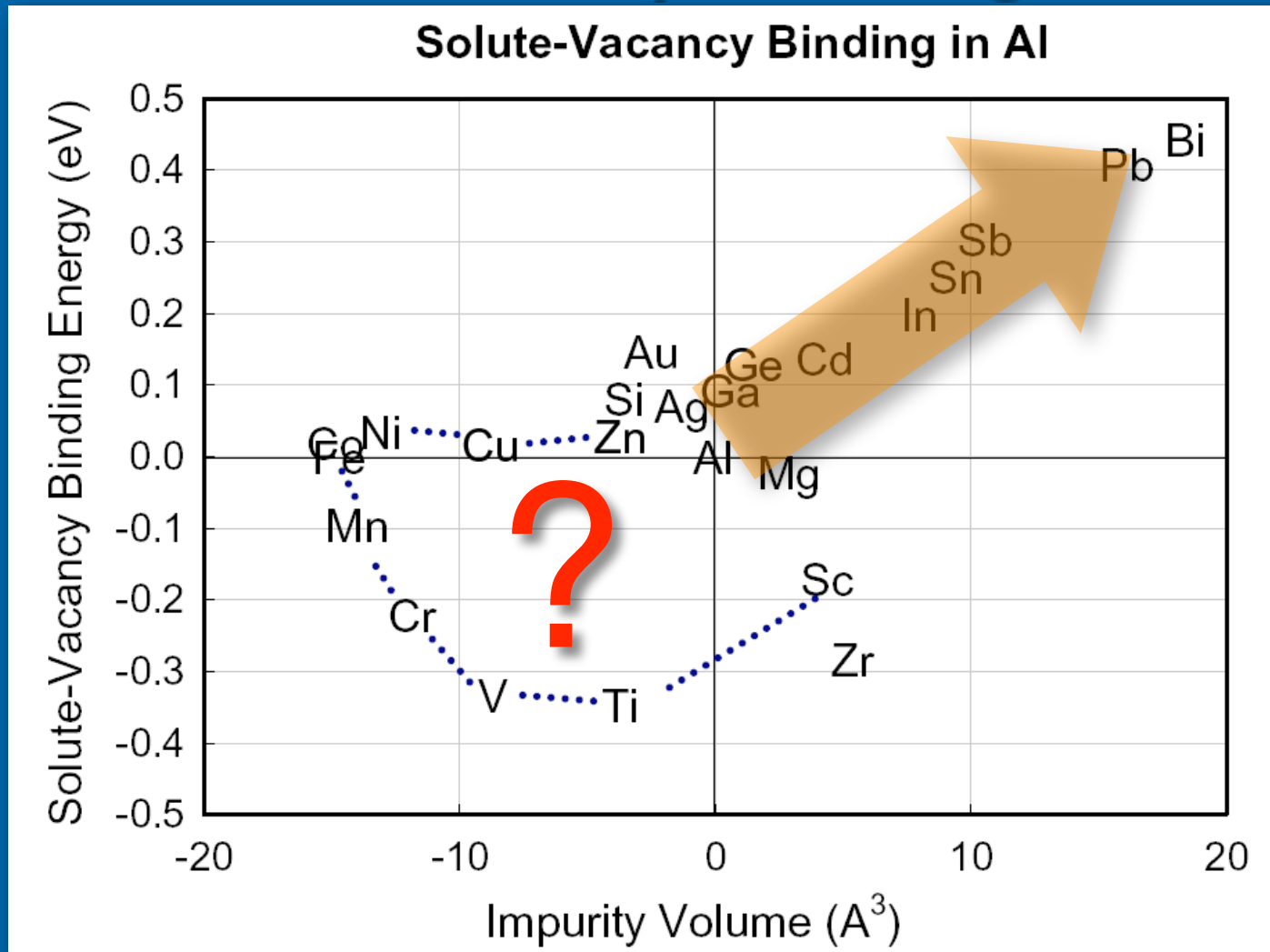
Solute-vacancy binding in Mg



What factors control solute-vacancy binding?

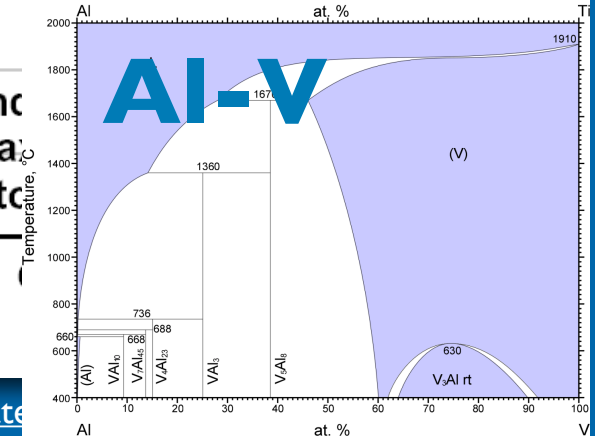
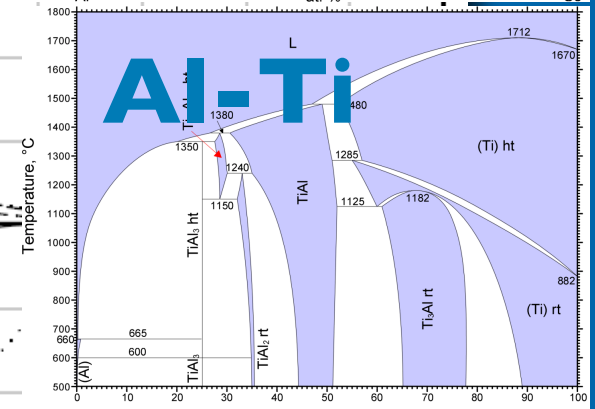
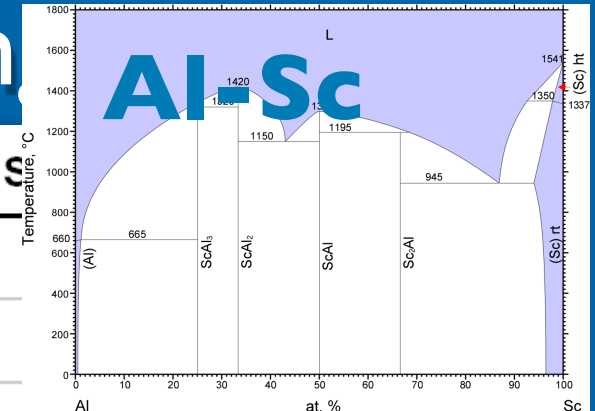
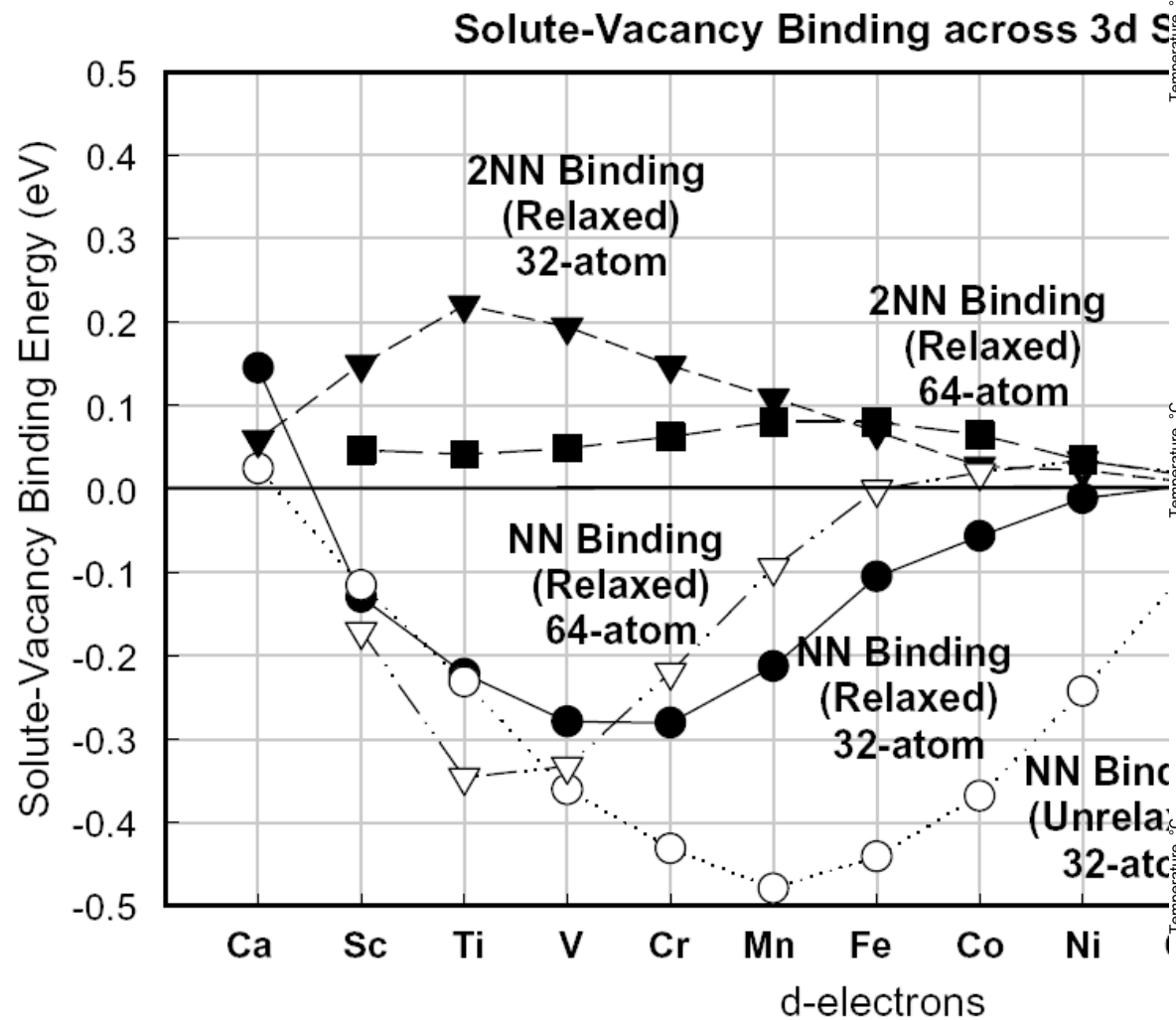
- Strain due to the size effect
 - Strain induced by a bigger solute can be reduced by putting a vacancy near a solute atom
 - Larger solute-vacancy binding as the size of solute increases
- Bond-breaking model
 - T. Hoshino *et al.*, PRB, 1996: for Al-X (3d trans metals)
 - Very strong $sp-d$ (host-impurity) bonds
 - “Unhappy” with the breakup the $sp-d$ bonds
 - Repulsive interaction of vacancy with 3d solutes

Solute-vacancy binding in Al



Wolverton, C. (2007). "Solute-vacancy binding in aluminum." *Acta Mater.* **55**(17): 5867-5872.

Solute-vacancy binding

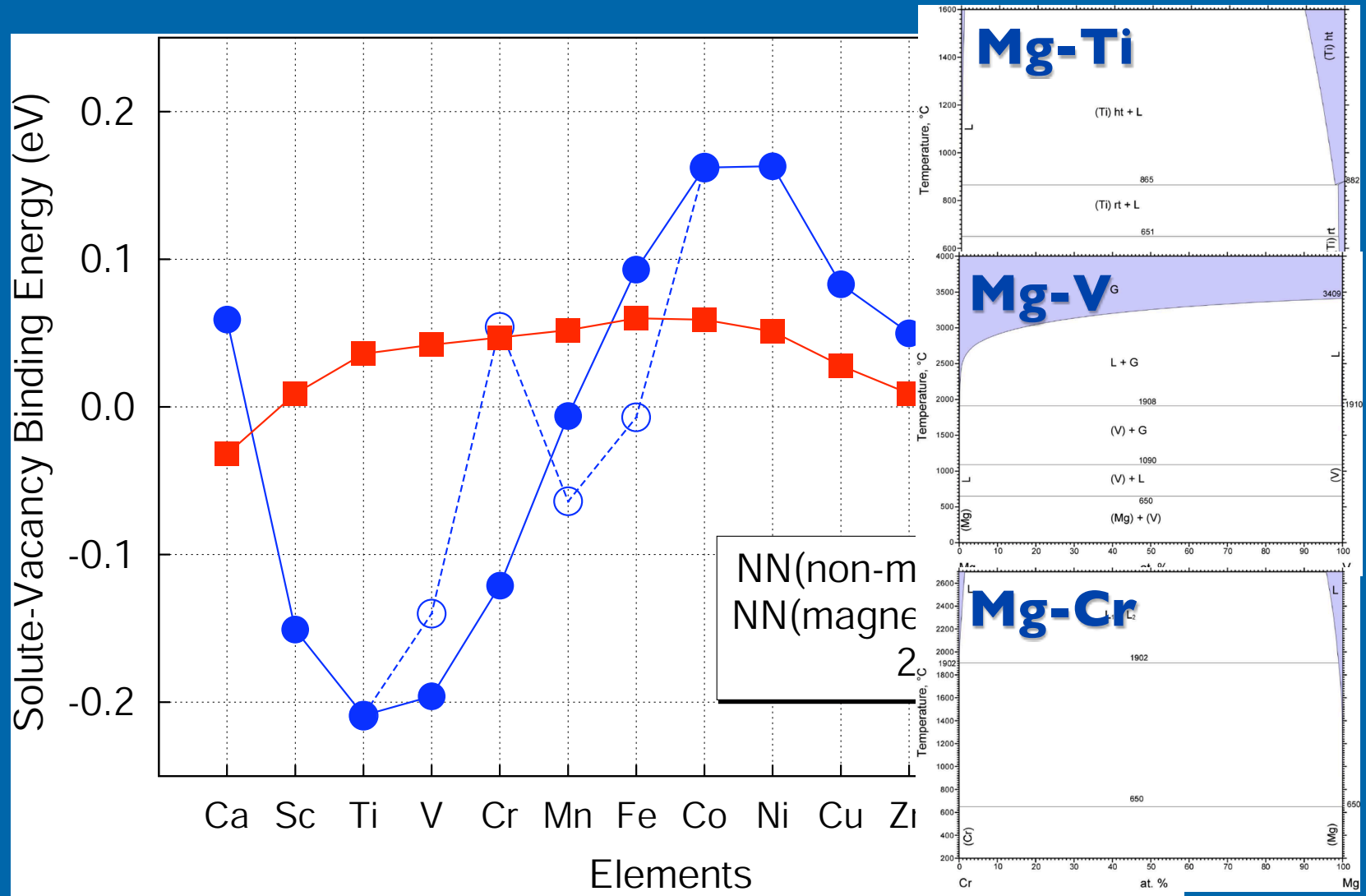


Wolverton, C. (2007). "Solute-vacancy binding in aluminum." [Acta Mater](#)

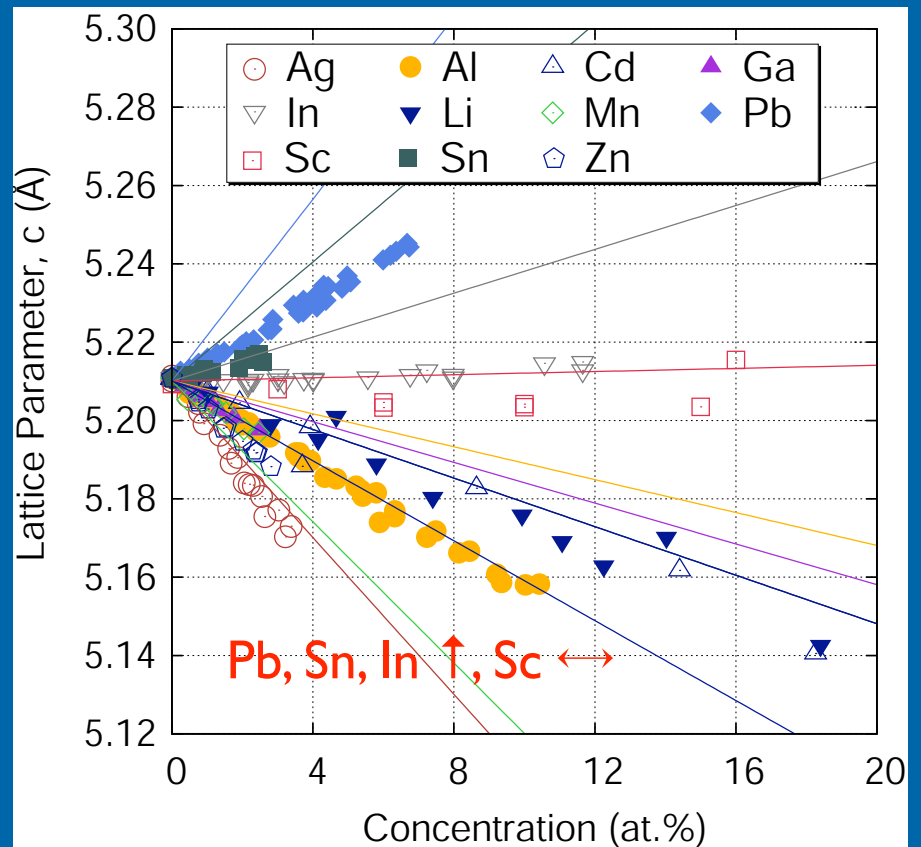
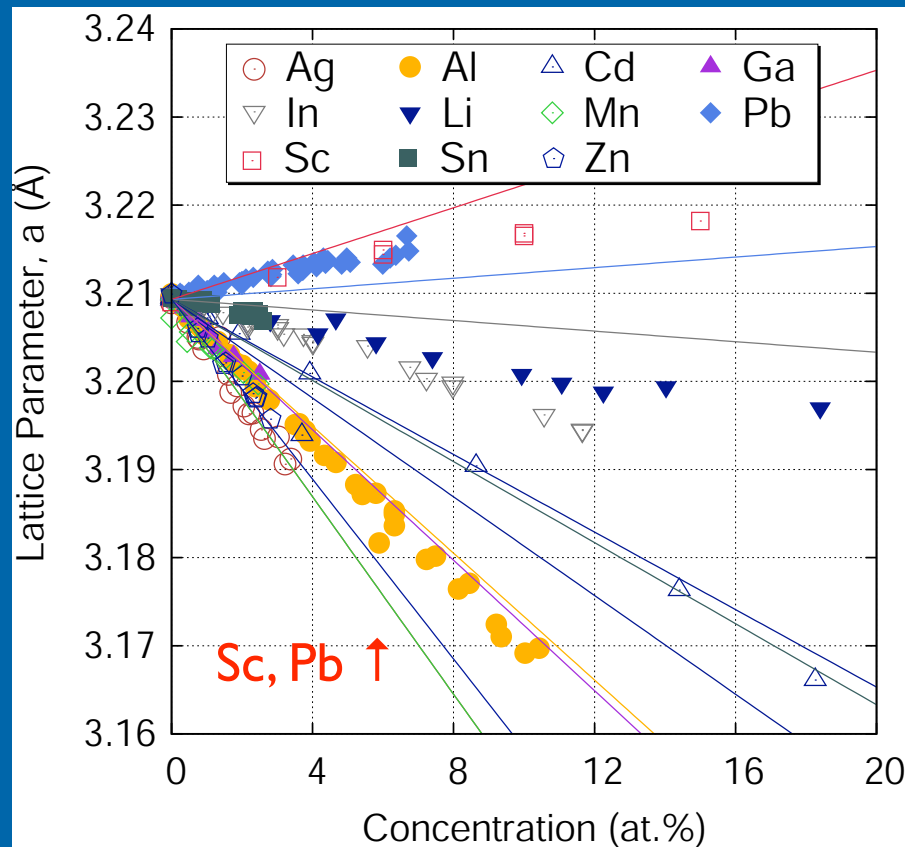
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Solute-vacancy binding in Mg

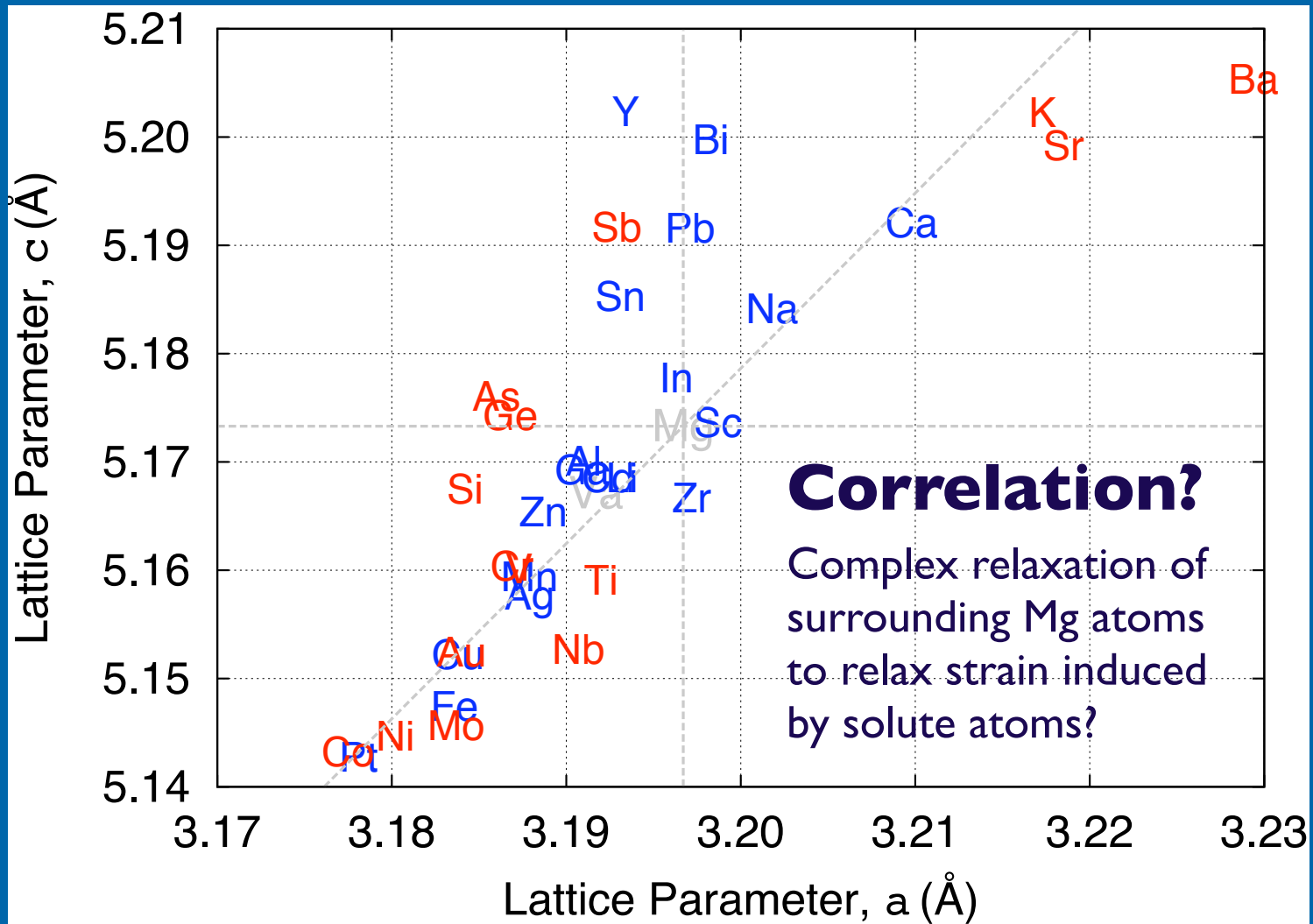


Mg lattice parameters



- Mg lattice parameters are deduced from Mg63X calculations
- Slopes represent first-principles calculations

Mg lattice parameters



Summary

- Previously unknown solute-vacancy binding energies for various elements in Mg alloys have been calculated from first-principles supercell approach
- Calculated mono-vacancy formation energy in Mg agree well with experimental measurements
- Favorable solute-vacancy binding has been predicted for the elements that are experimentally shown to increase age-hardening response in Mg-alloys: Ag, Ca, Na, Zn, and In
- Calculated lattice parameters show that relaxation of surrounding Mg atoms to relieve strain induced by solute atoms may be complex
- Solute-vacancy binding in Mg may have to go beyond strain effect due to size mismatch and simple bonding breaking model