Metallic Dopants in Mo Grain Boundaries:

A DFT Approach

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Outline

- ❑Background and motivation
- ❑Models and quantities
- ❑Segregation energy
- ❑Strengthening energy
- ❑Conclusion

Why Molybdenum?

Under high T environments:

- Excellent strength-to-density ratio
- Stable phase
- Low coefficient of thermal expansion

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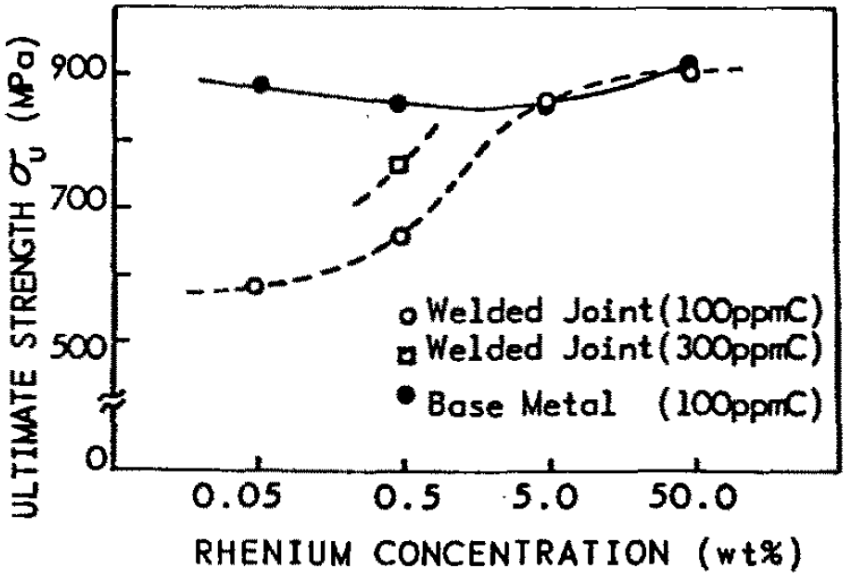
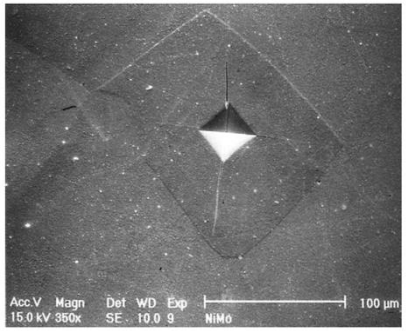
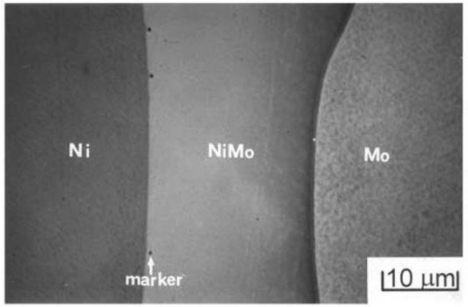
Igata, N., et al. *J. Nucl. Mater.* 85-86, 895–899 (1979).
Hwang, K. S. & Huang, H. S. *Acta Mater.* 51, 3915–3926 (2003).

Why Molybdenum?







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Quantities of interest

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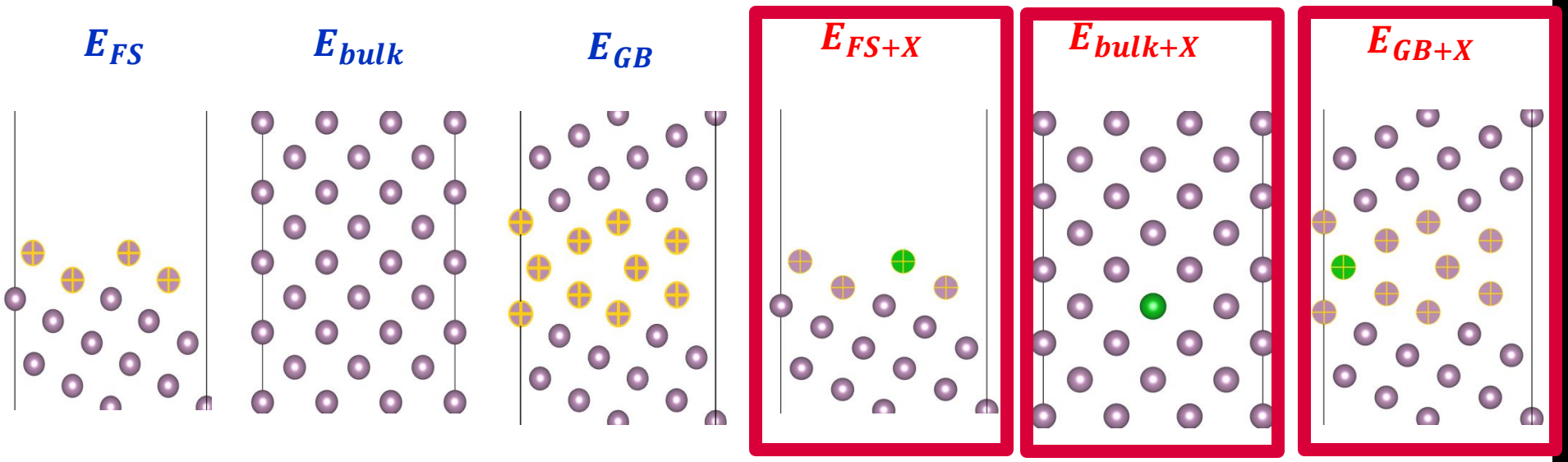
Segregation energy:

$$E_{seg}^{GB} \approx 0 \rightarrow E_{GB/FS+x} - E_{GB/FS} \approx E_{Bulk+X} - E_{Bulk}$$

Interfacial energy:

$$\gamma_{GB/FS} = \frac{1}{2A_{GB/FS}}\left(E_{GB/FS} - E_{bulk/atom} \times n_{GB/FS}\right) - \left(E_{GB/FS+x} - E_{GB/FS}\right) - \left(E_{Bulk+X} - E_{Bulk}\right)$$



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Tran, R. *et al. Acta Mater.* 117, 91–99 (2016).

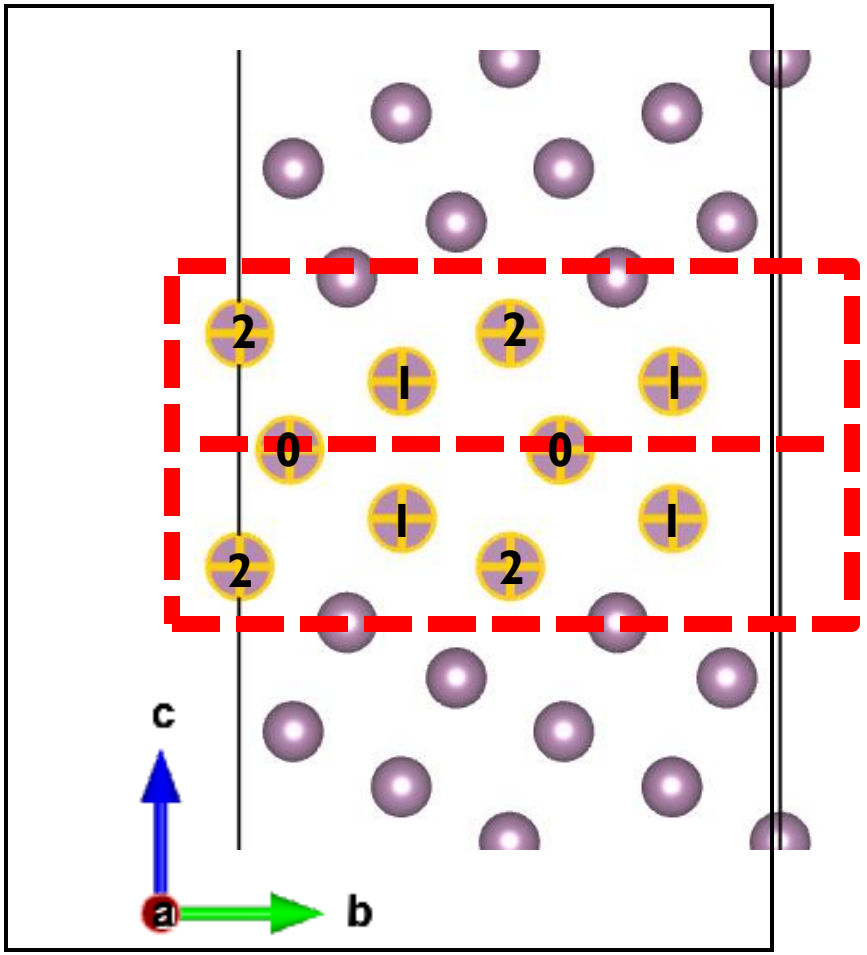
Σ5 (310) tilt

144 atoms

9.44 x 9.44 x 27.76 $Å^3$

Γ_{GB}=0.012 $Å^{-2}$

Site	CN	Volume ($Å^3$)
0	7	31.97
1	8	26.73
2	8	31.87



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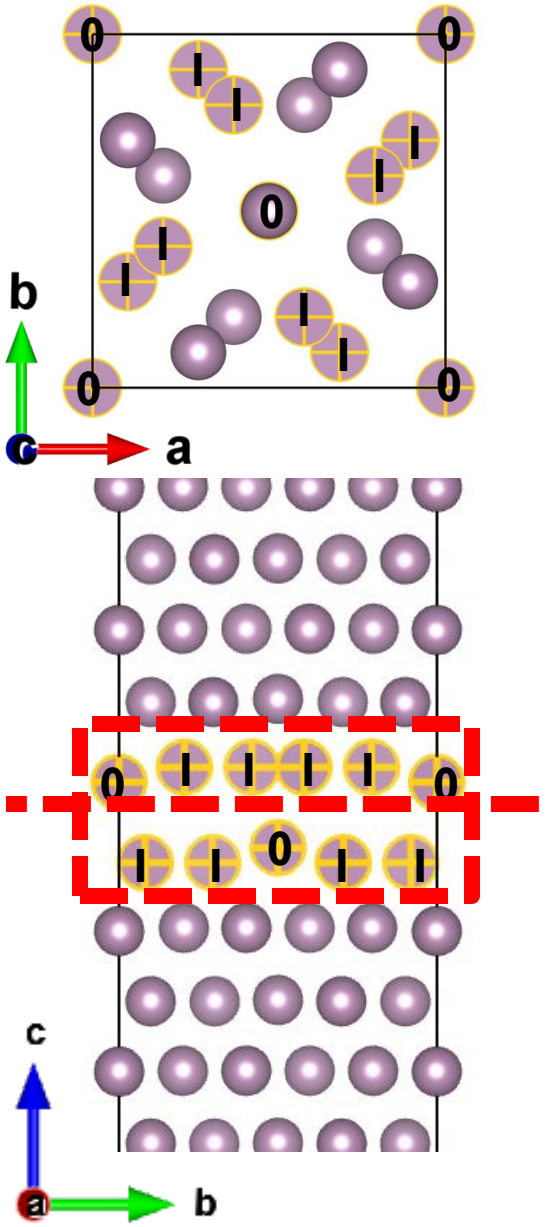
Σ5 (100) twist

- **80 atoms**
- **7.08 x 7.08 x 25.34 $Å^3$**
- **Γ_{Gb}=0.02 $Å^{-2}$**

Site	CN	Volume ($Å^3$)
O	8	39.04
I	6	20.11



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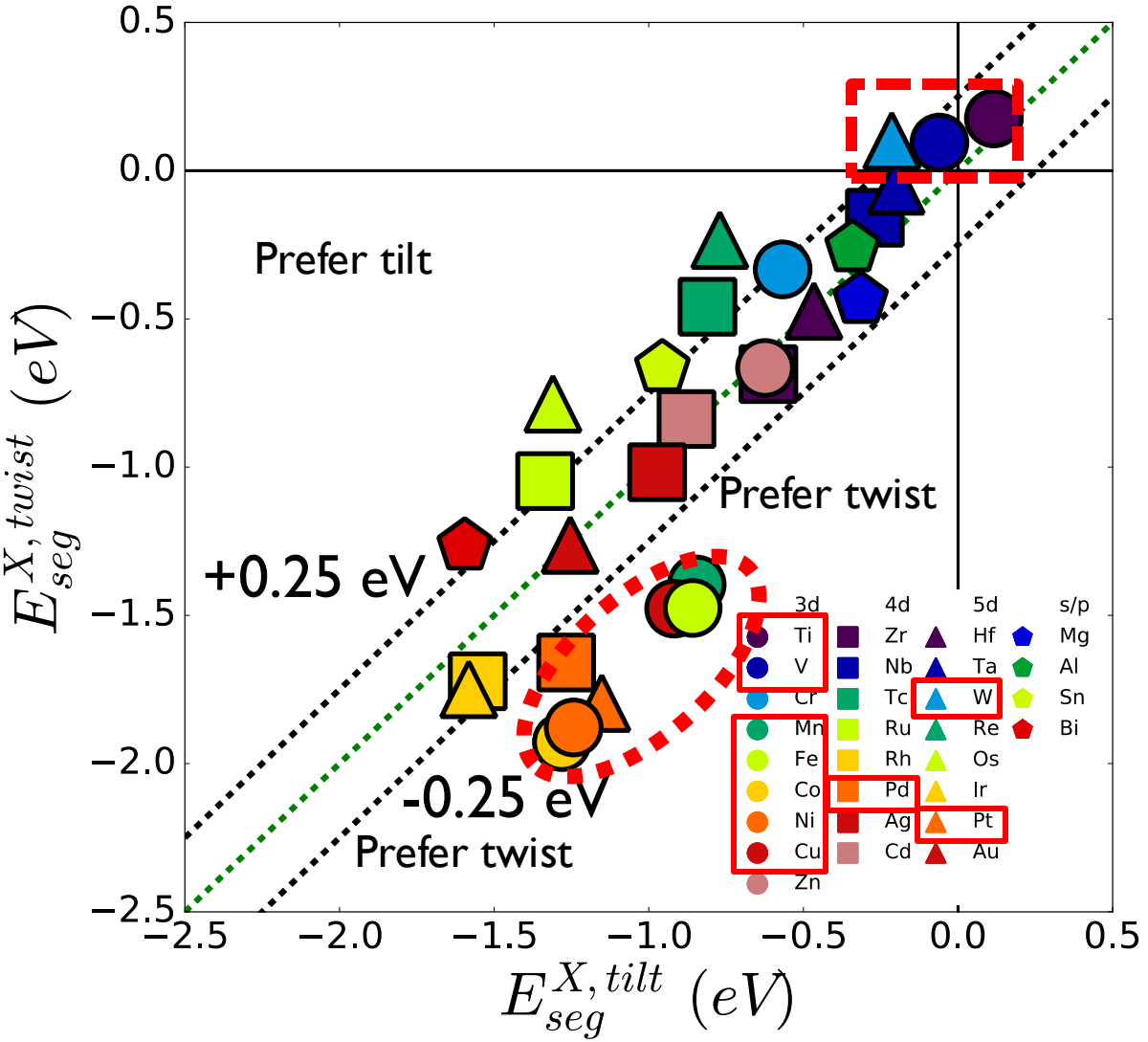
Twist vs tilt

$$V_1^{twist} = 20.11 Å^3$$

$$V_1^{tilt} = 26.73 Å^3$$

$$\gamma_{twist} = 2.43 J/m^2$$

$$\gamma_{tilt} = 1.83 J/m^2$$



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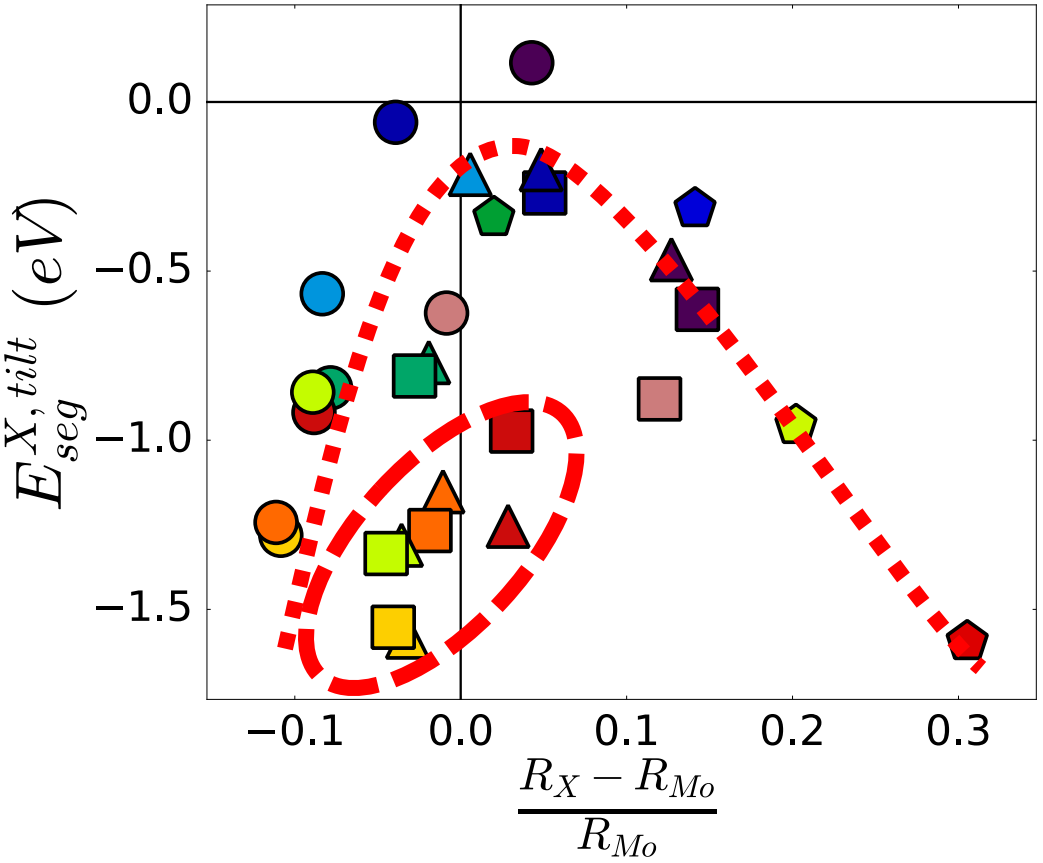
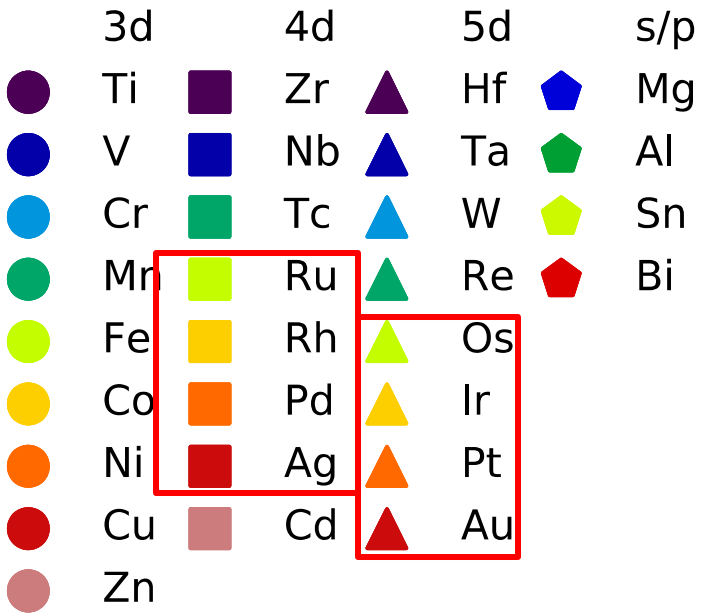
Tran, R. *et al. Acta Mater.* 117, 91–99 (2016).

Size effects and segregation





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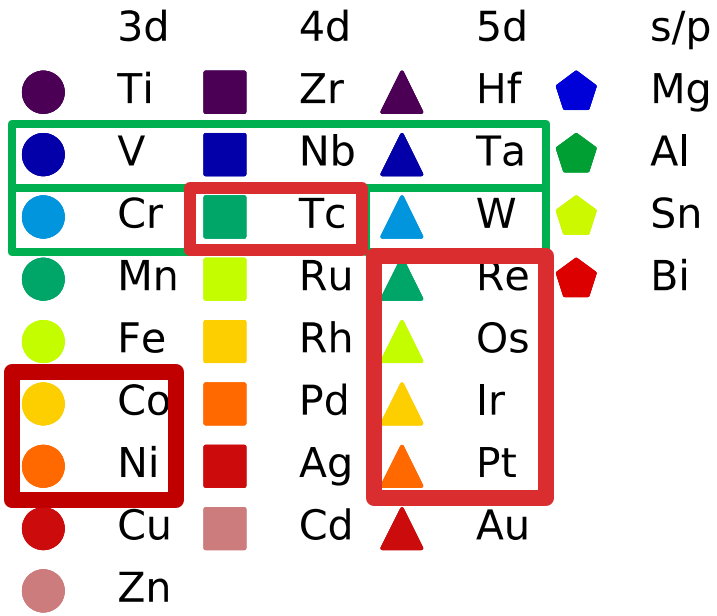
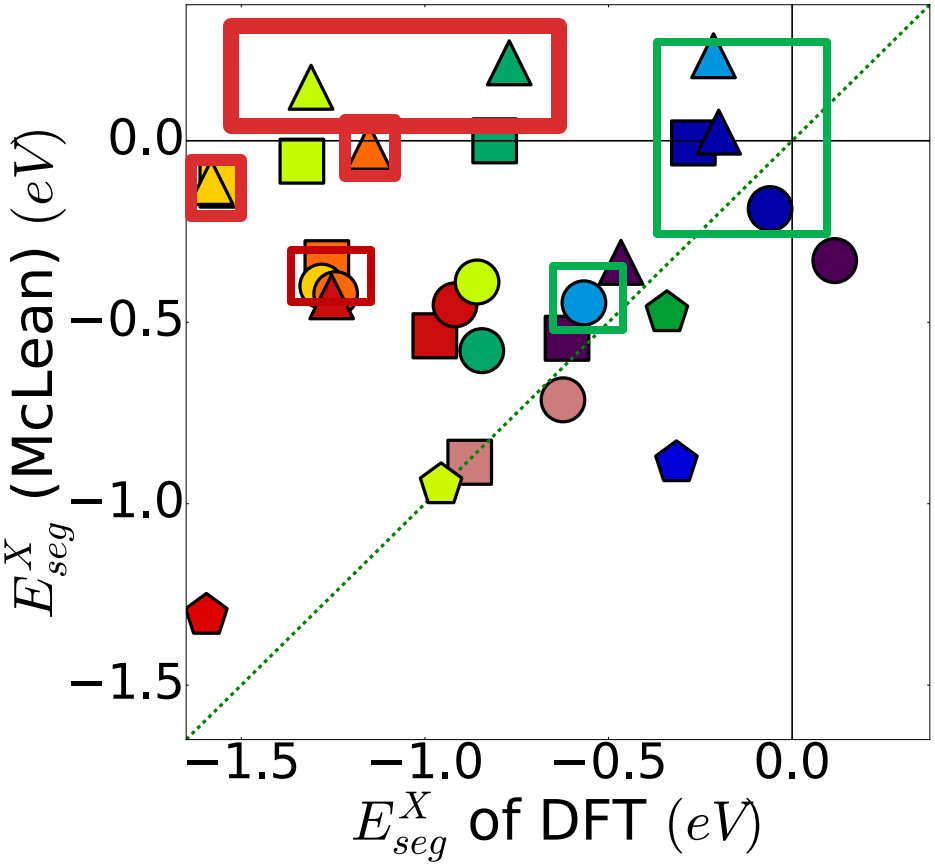
McLean's empirical model





McLean model:

$$\Delta \mathbf{H}_{\mathbf{el}}^{\boldsymbol{seg}} = \frac{24\pi K_{Mo} G_X r_{Mo} r_X (r_{Mo} - r_X)^2}{3K_{Mo} r_{Mo} + 4G_X r_X}$$

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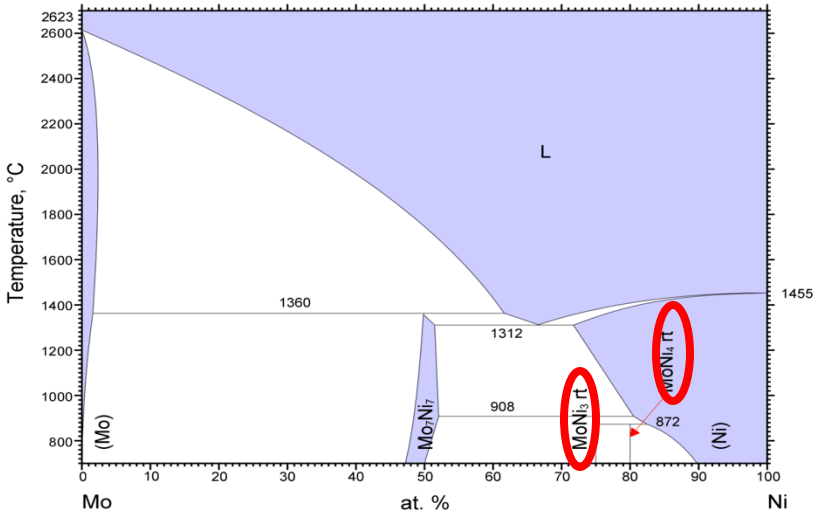
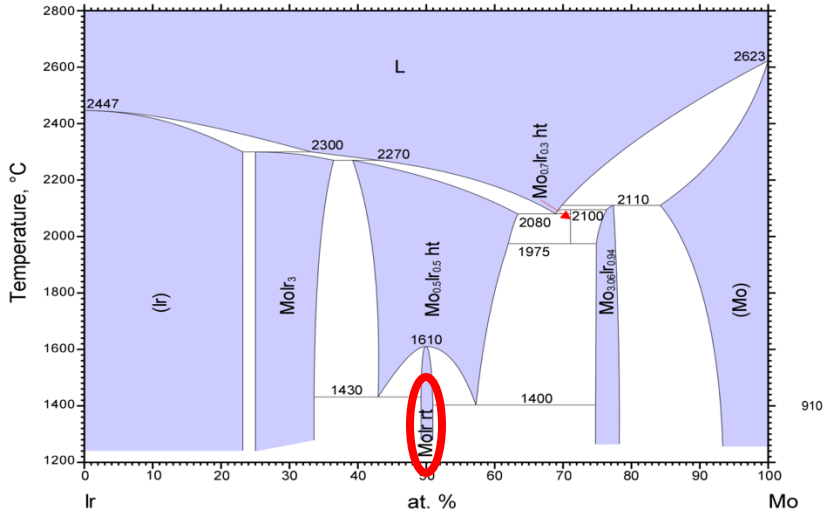
A-B-C Phase Diagram, ASM Alloy Phase Diagrams Database. ASM International (2006).

Intermetallic compounds

3d	4d	5d	s/p
Ti	Zr	Hf	Mg
V	Nb	Ta	Al
Cr	Tc	W	Sn
Mn	Ru	Re	Bi
Fe	Rh	Os	
Co	Pd	Ir	
Ni	Ag	Pt	
Cu	Cd	Au	
Zn			

@ RT
Mo_7Ni_7
$MoNi_3$
MoIr





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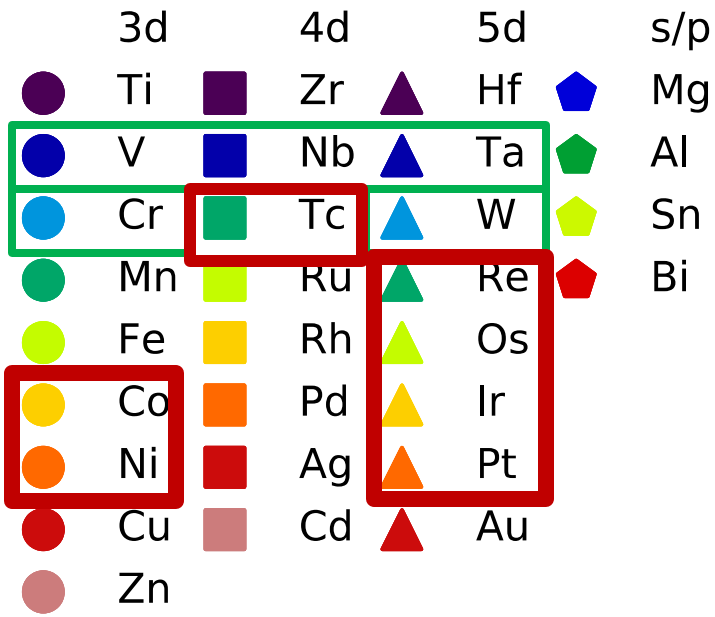
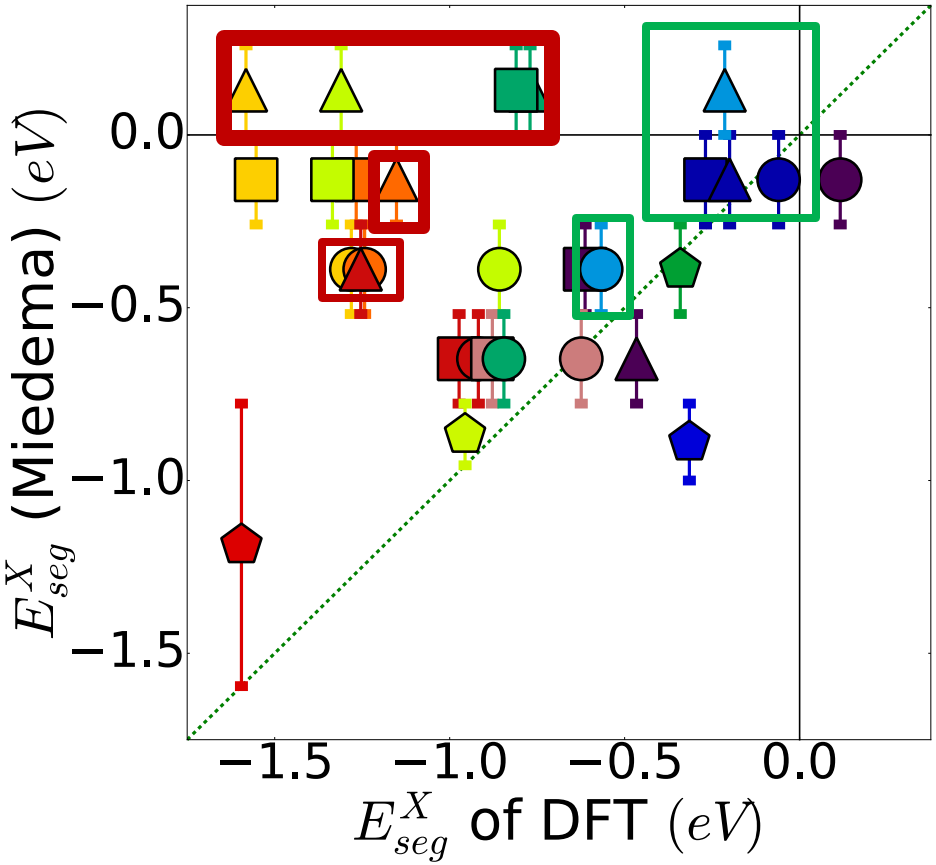
Tran, R. *et al. Acta Mater.* 117, 91–99 (2016).

Miedema's empirical model





Miedema model:

$$\mathbf{\Delta H_{el}^{seg}} = -0.71 \times \frac{1}{3} \times \nu \times \left(-\Delta \mathbf{H_{sol}^{Mo}} c_0 \gamma_{Mo}^{S} V_{Mo}^{2/3} + c_0 \gamma_X^S V_X^{2/3} \right) + \mathbf{\Delta E_{el}}$$

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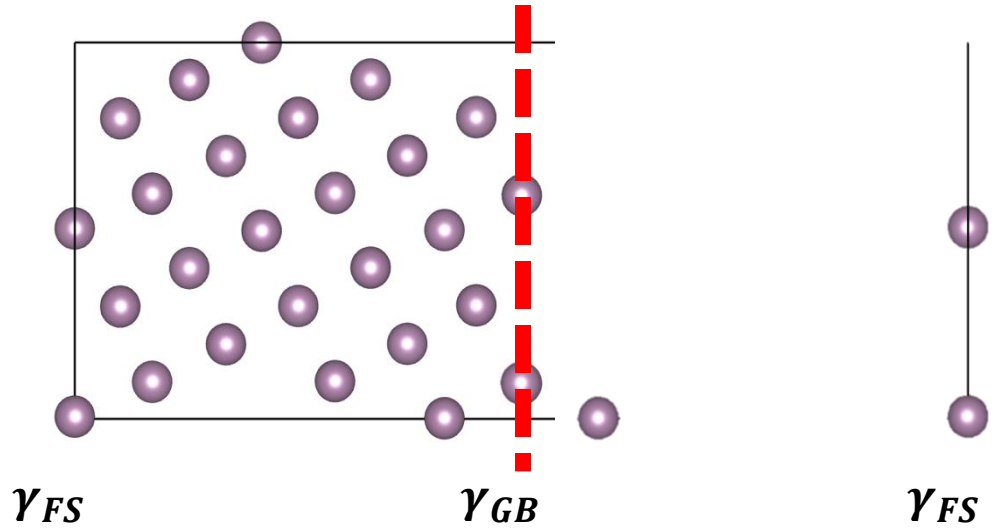
The work of separation



Interfacial energy:

$$\gamma_{GB/FS} = \frac{E_{GB/FS} - E_{bulk/atom} \times n_{GB/FS}}{2A_{GB/FS}}$$

Work of separation:

$$W_{sep} = 2\gamma_{FS} - \gamma_{GB}$$

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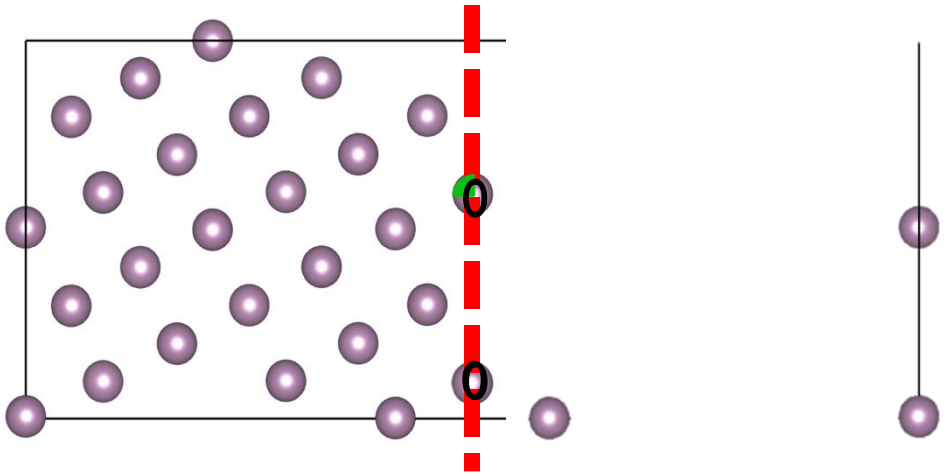
Modelling strengthening energy



$$E_{SE} \gtrless 0 \rightarrow E_{GB+x} - E_{GB} \gtrless E_{FS+X} - E_{FS}$$

Strengthening

Segregating energy:

$$E_{seg}^{GB} = (E_{GB+x} - E_{GB}) - (E_{FS+X} - E_{FS})_{Bulk}$$

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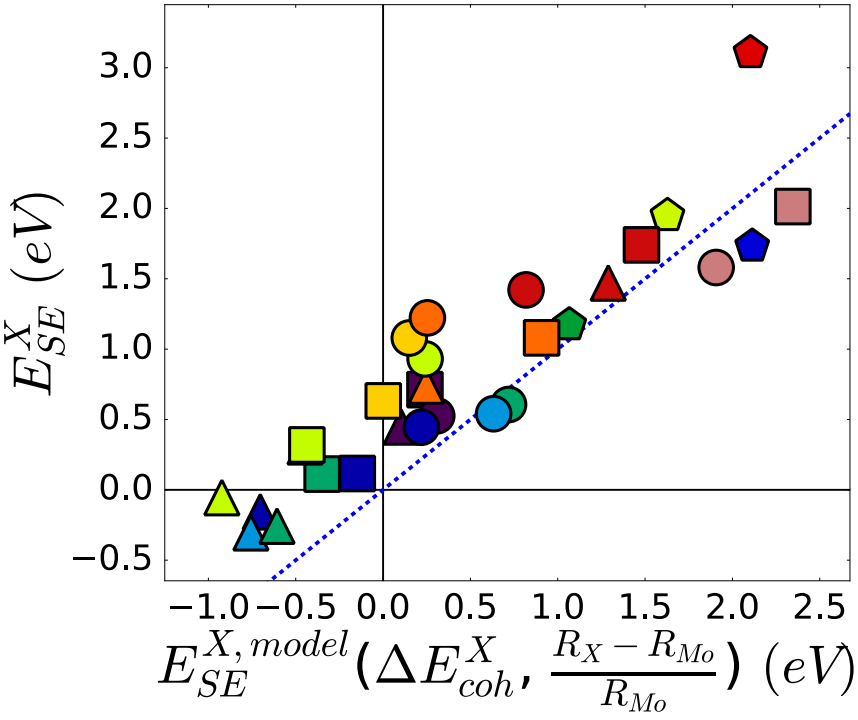
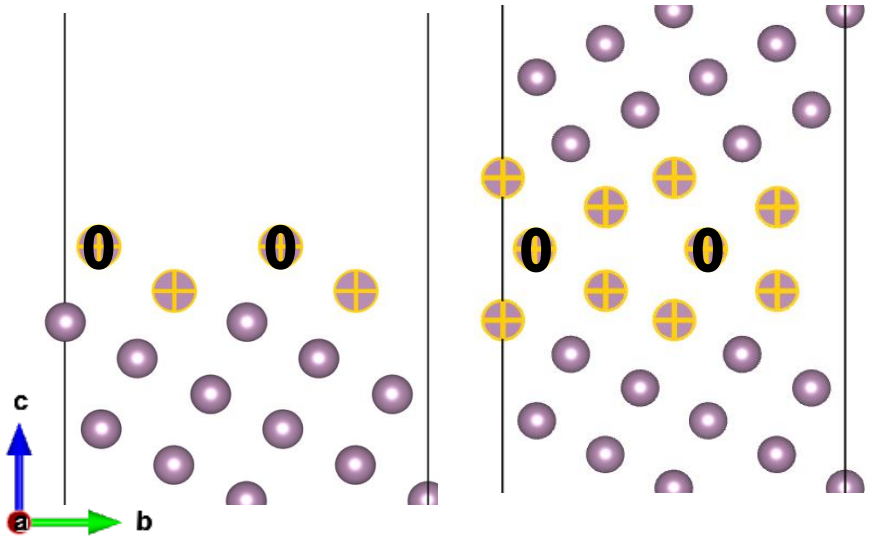
Seah, M. P. *Acta Metall.* 28, 955–962 (1980).

Trends in strengthening energy



$$k_{coh} = 0.39 \pm 0.042$$
$$k_R = 2.40 \pm 1.076$$



$$E_{SE}^{X,model}\left(\Delta E_{coh}^{X}, \frac{R_X - R_{Mo}}{R_{Mo}}\right) = k_{coh}\Delta E_{coh}^{X} + k_R \frac{R_X - R_{Mo}}{R_{Mo}}$$

3d	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
4d	Zr	Nb	Tc	Ru	Rh	Pd	Ag	Cd		
5d	Hf	Ta	W	Re	Os	Ir	Pt	Au		
s/p	Mg	Al	Sn	Bi						

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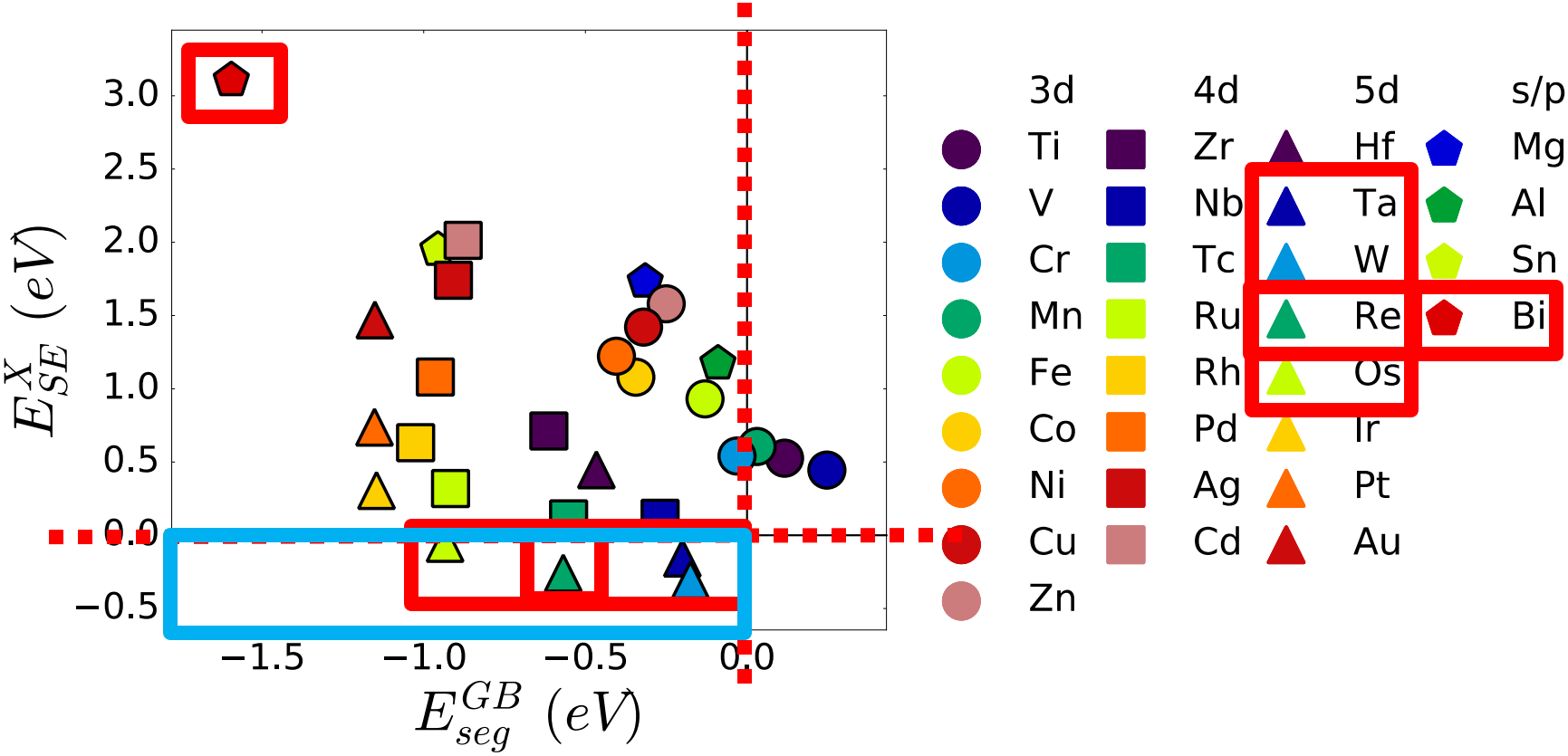
Viable dopants



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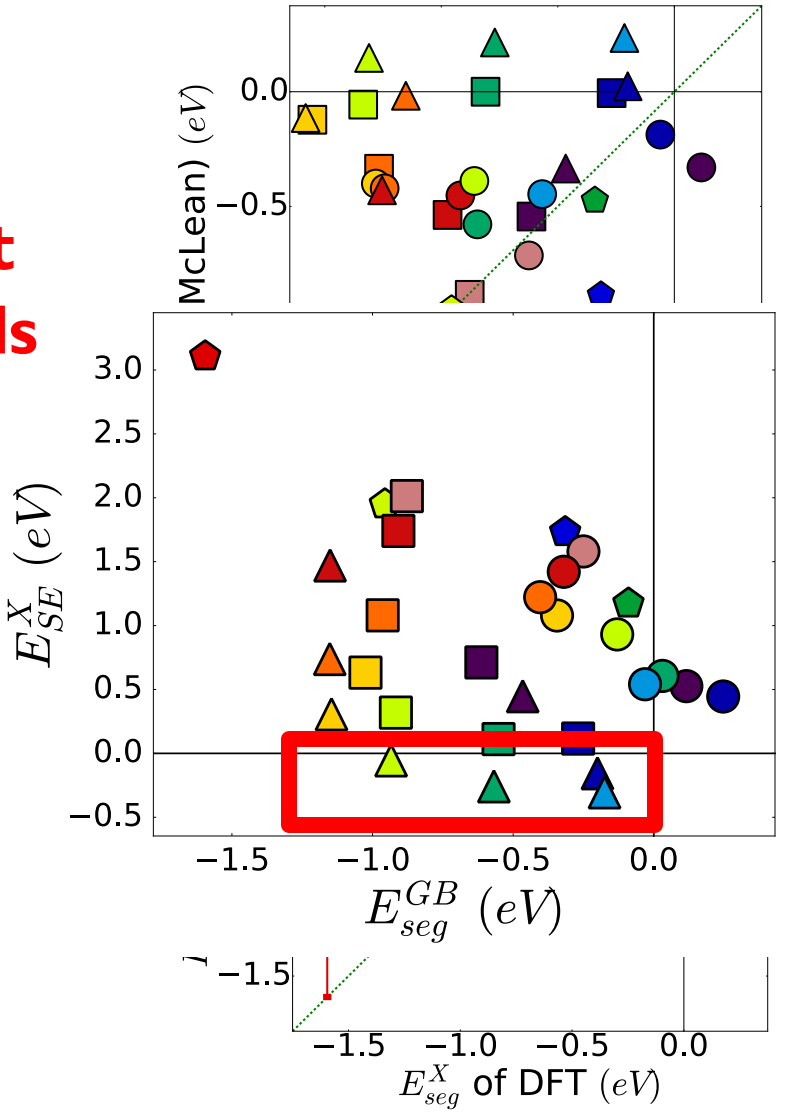
Conclusion

- **Empirical models compare poorly to DFT for metals that form intermetallic compounds with bulk Mo**
- **Dopant strain and cohesion effects strengthening properties**
- **Ta, W, Re, and Os are viable strengthening components for Mo**



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