# Computational Materials Physics

narrated by


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thanks to

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O. Eriksson
N.E. Christensen
T. Bligård
O.K. Andersen
M. Aldén
I. Abrikosov

# Wigner and Seitz

If one had a great calculating machine, one might apply it to the problem of solving the Schrödinger equation for each metal and obtain thereby the interesting physical properties, such as the cohesive energy, the lattice constant, and similar parameters. It not clear, however, that a great deal would be gained by this. Presumably the results would agree with the experimentally determined quantities and nothing vastly new would be learned from the calculation.

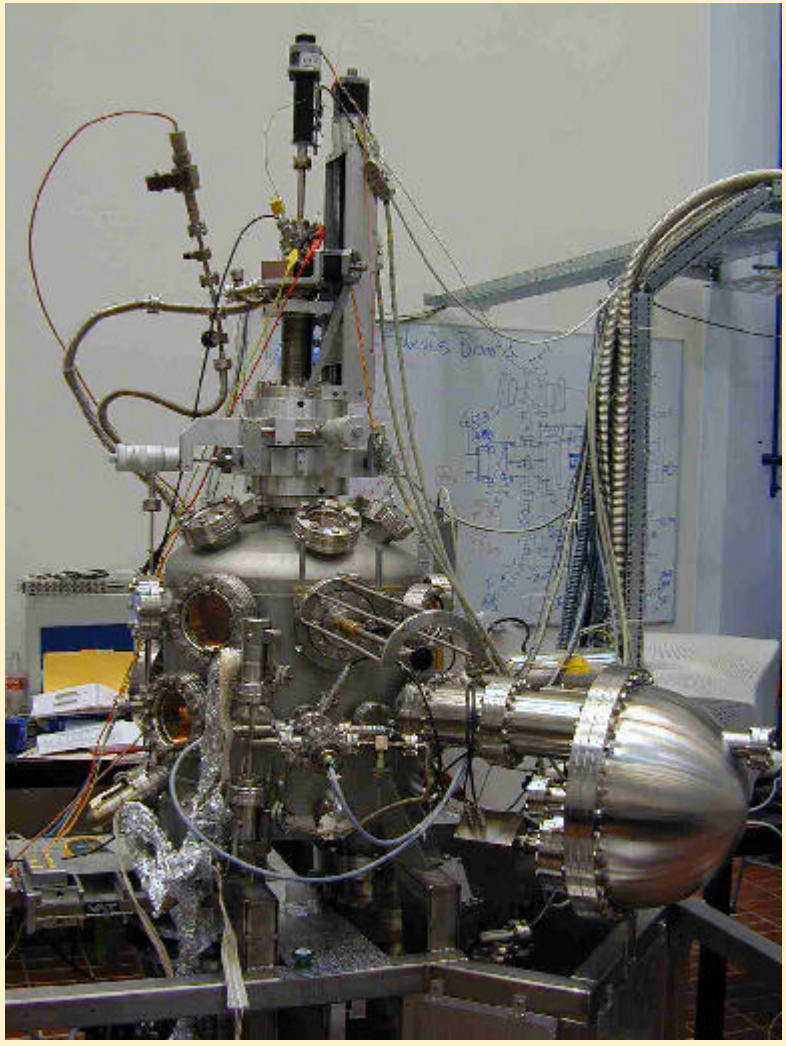
It would be preferable instead to have a vivid picture of the behaviour of the wave functions, a simple description of the essence of the factors which determine cohesion and an understanding of the origins of variation in properties from metal to metal.

The task before us is not a purely scientific one; it is partly pedagogic.

**Eugene Wigner and Frederick Seitz (1955)**

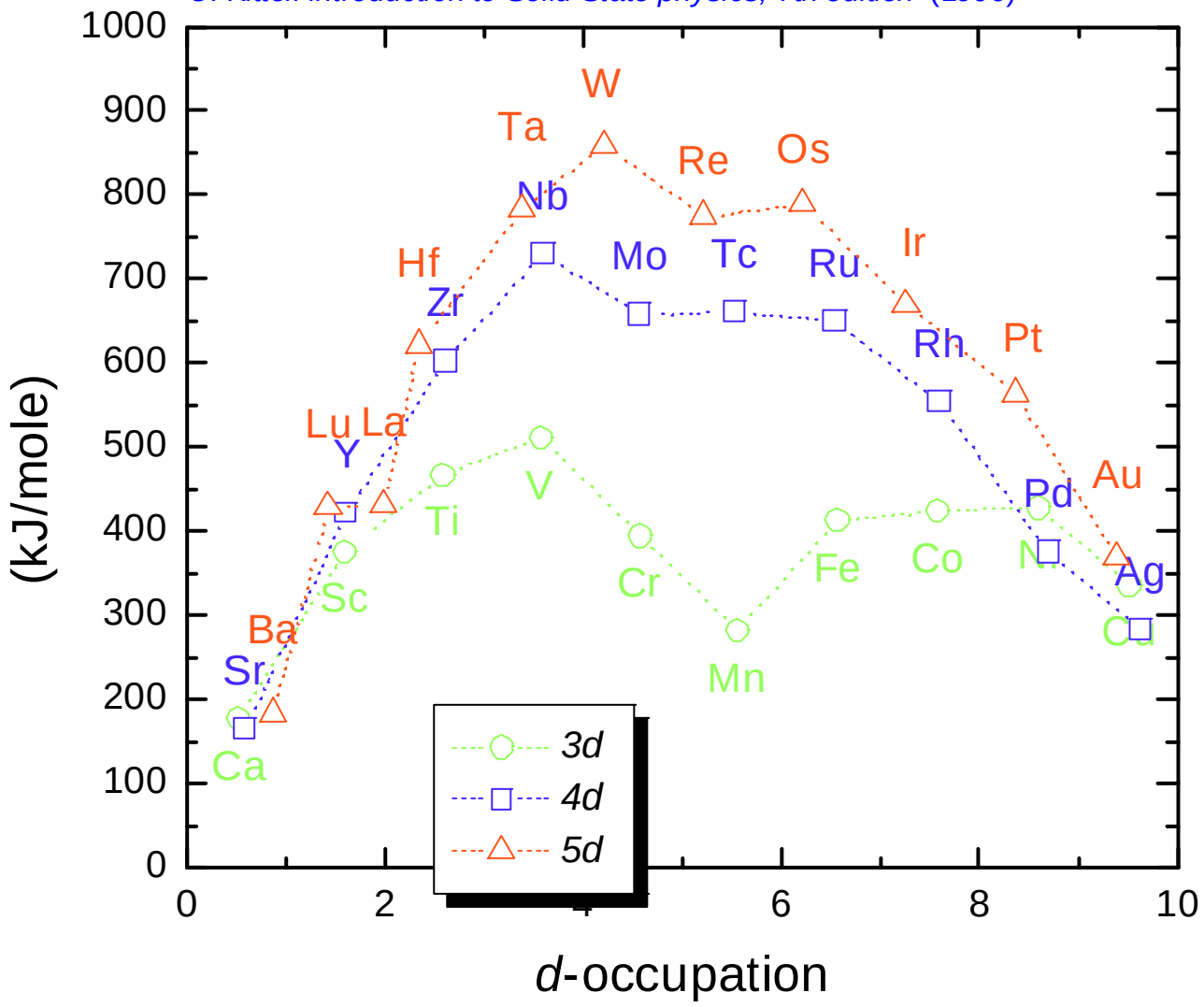
# Eriksen's Theorem

Physics is an experimental science



# Measured Cohesive Energies

C. Kittel: *Introduction to Solid State physics*, 7th edition (1996)



# Cohesive Energy

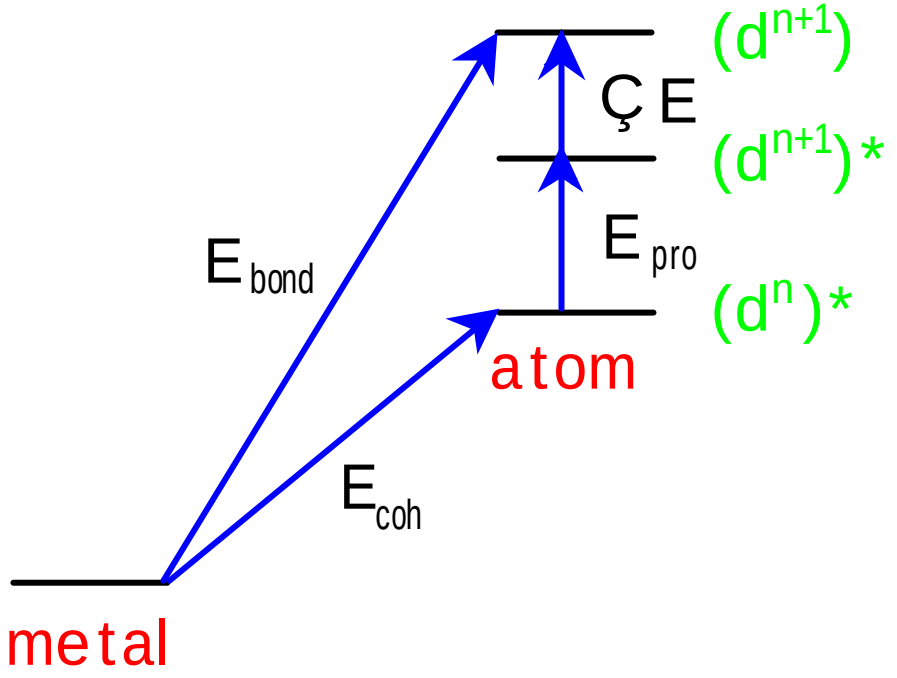
Energy difference between atom in the ground state and the energy of the solid per atom at zero temperature

$$E_{coh} = E_{bond} - \Sigma E_{atom}$$

$$\Sigma E_{atom} = E_{pro} + \Sigma E$$

$\Sigma E$ : Calculated from local exchange integrals

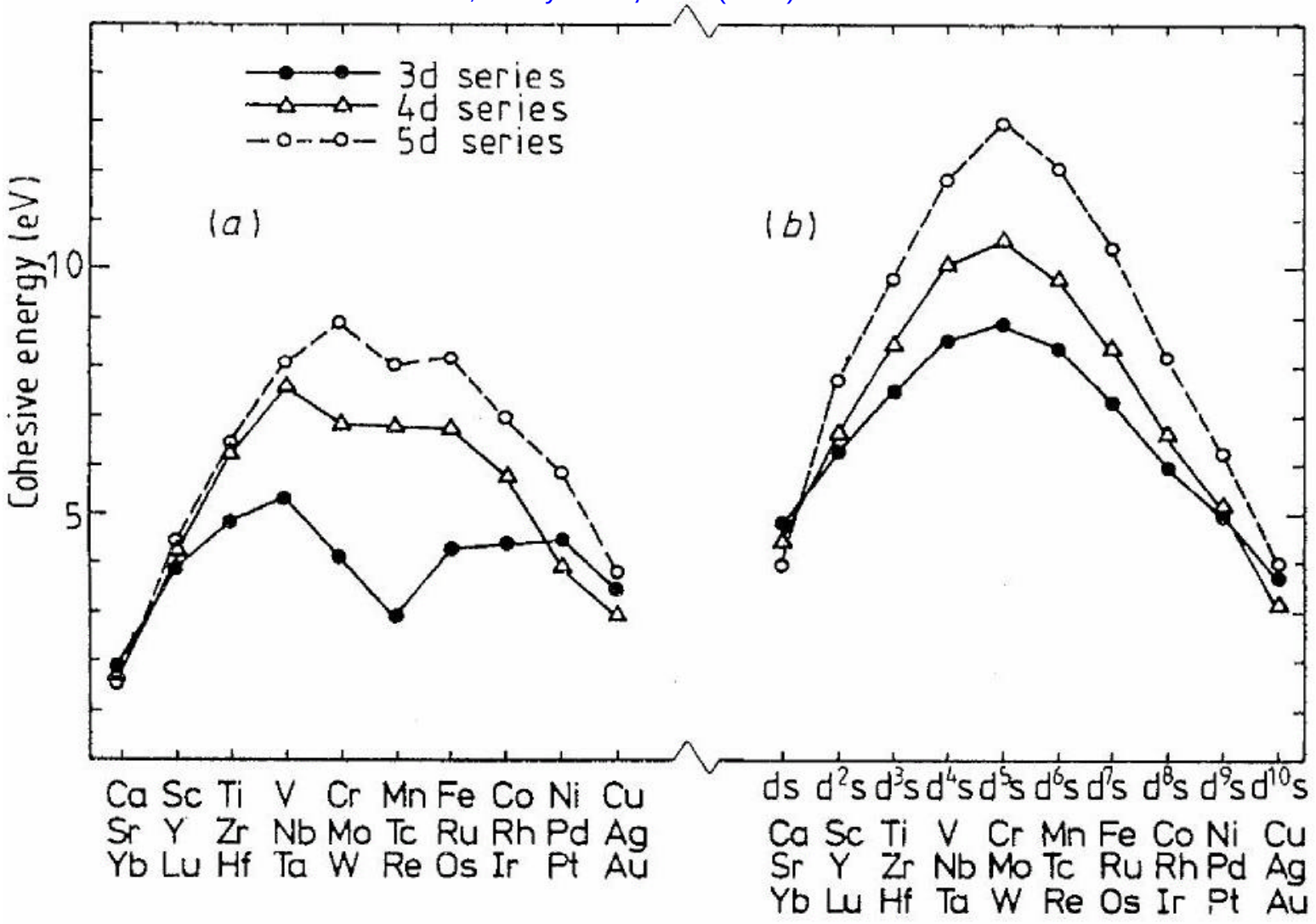
$E_{pro}$ : From experiment (Moore 1958)




M.S. Brooks and B. Johansson, J. Phys. **F13,** L197 (1983)

# Cohesive Energy

M.S. Brooks and B. Johansson, J. Phys. **F13,** L197 (1983)

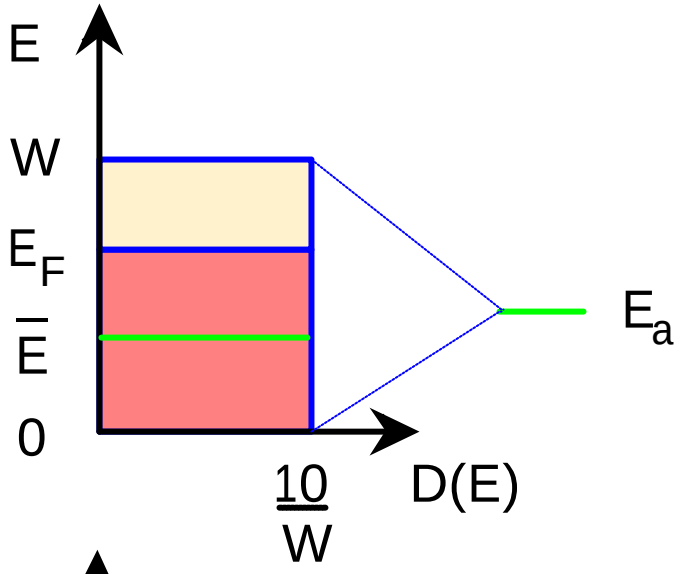


# The Friedel Model

J. Friedel in *The Physics of Metals* (ed. J.M. Ziman, 1969)

d-band occupation:

$$n_d = \int_0^{E_F} D(E)\, dE$$

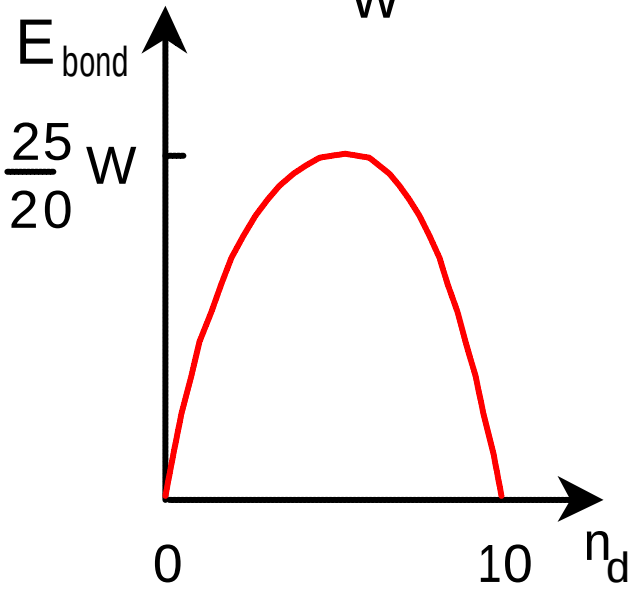



Bonding energy:

$$E_{bond} = \int_0^{E_F} D(E)\,(E - E_a)\, dE$$

$$= -(\bar{E} - E_a)\, n_d$$

$$= \frac{W}{20}\, n_d\, (10 - n_d)$$



# Local Density Theory of Metallic Cohesion

Calculations by

V.L. Morruzzi, A.R. Williams and J.F. Janak,
Phys. Rev. B**15,** 2854 (1977)

using

DFT
P. Hohenberg and W. Kohn,
Phys. Rev. **136,** B864 (1964)
W. Kohn and L. Sham,
Phys. Rev. **140,** A1133 (1965)

LDA
L. Hedin and B.I. Lundqvist,
J. Phys. C **4,** 2064 (1971)

LSD
U. von Barth and L. Hedin,
J. Phys. C **5,** 1629 (1972)

and fast KKR

A.R. Williams, J.F. Janak and V.L. Morruzzi,
Phys. Rev. B**6,** 4509 (1972)

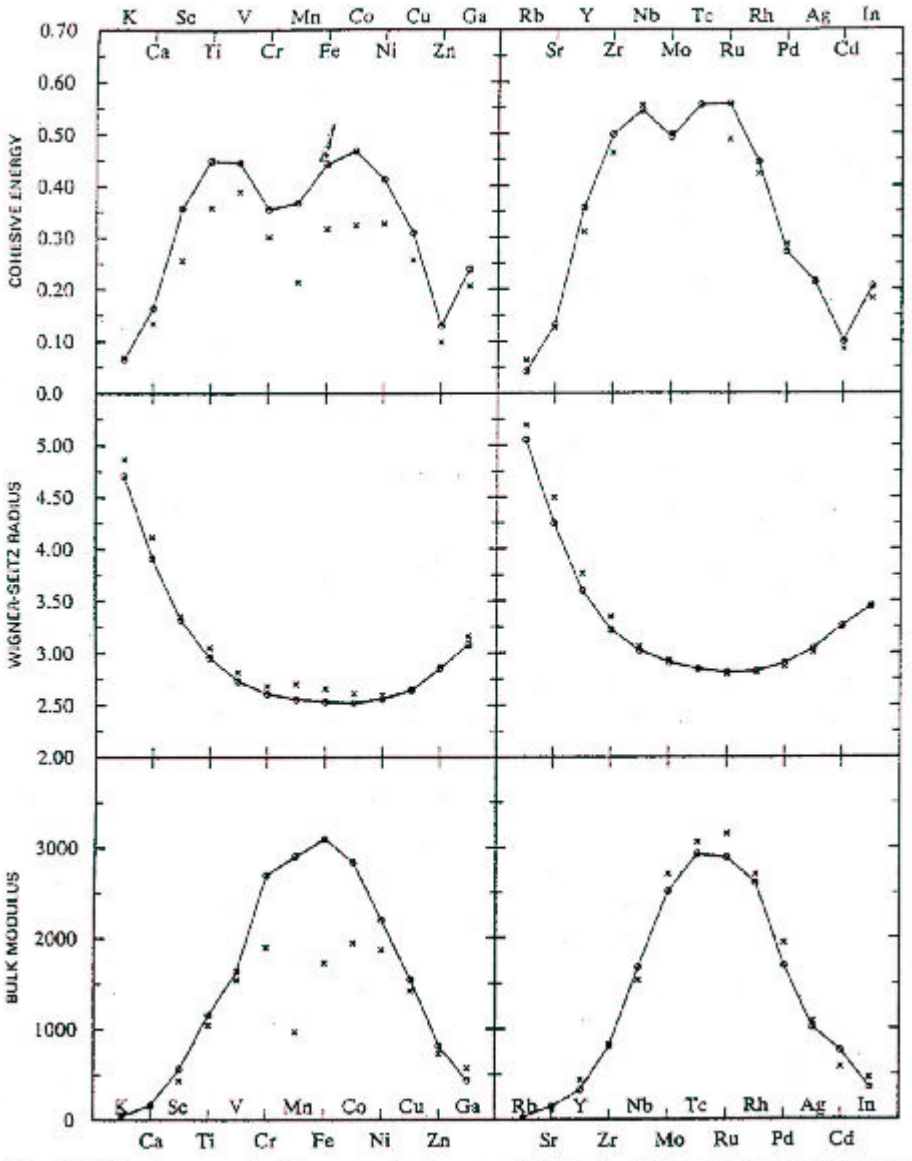
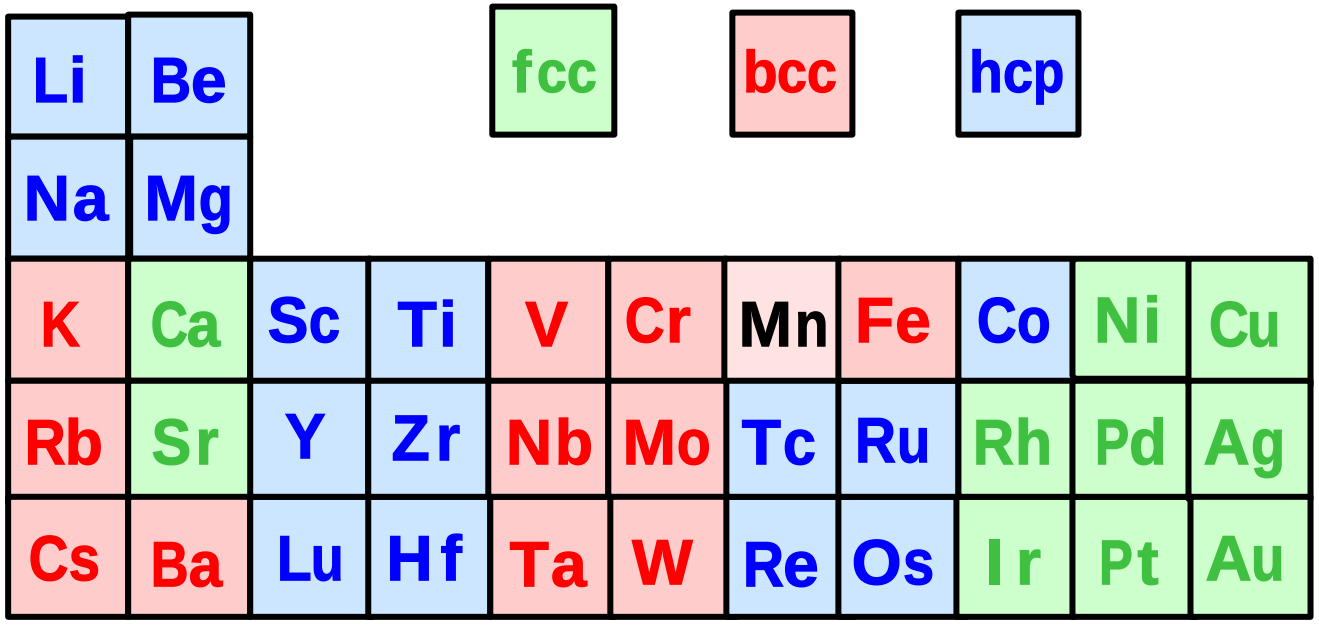


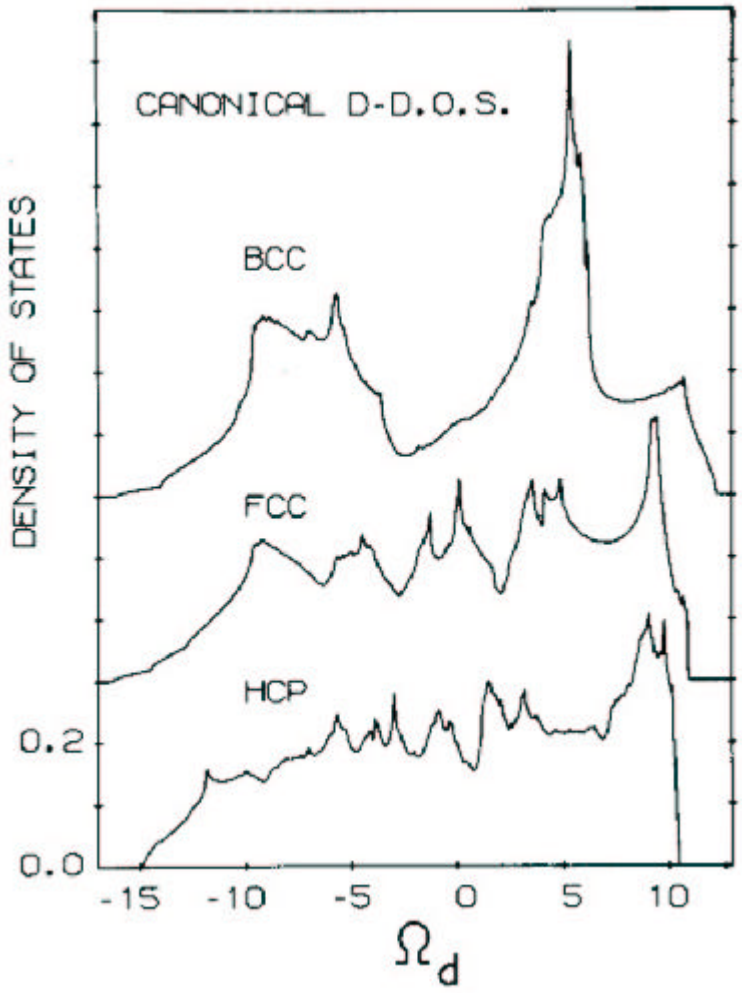

Figure 1.1 Cohesive properties. Top row- cohesive energy (Ry/atom). Middle row- Wigner-Seitz radius (a.u.). Bottom row- bulk modulus (Kbar). Measured values are indicated by crosses.

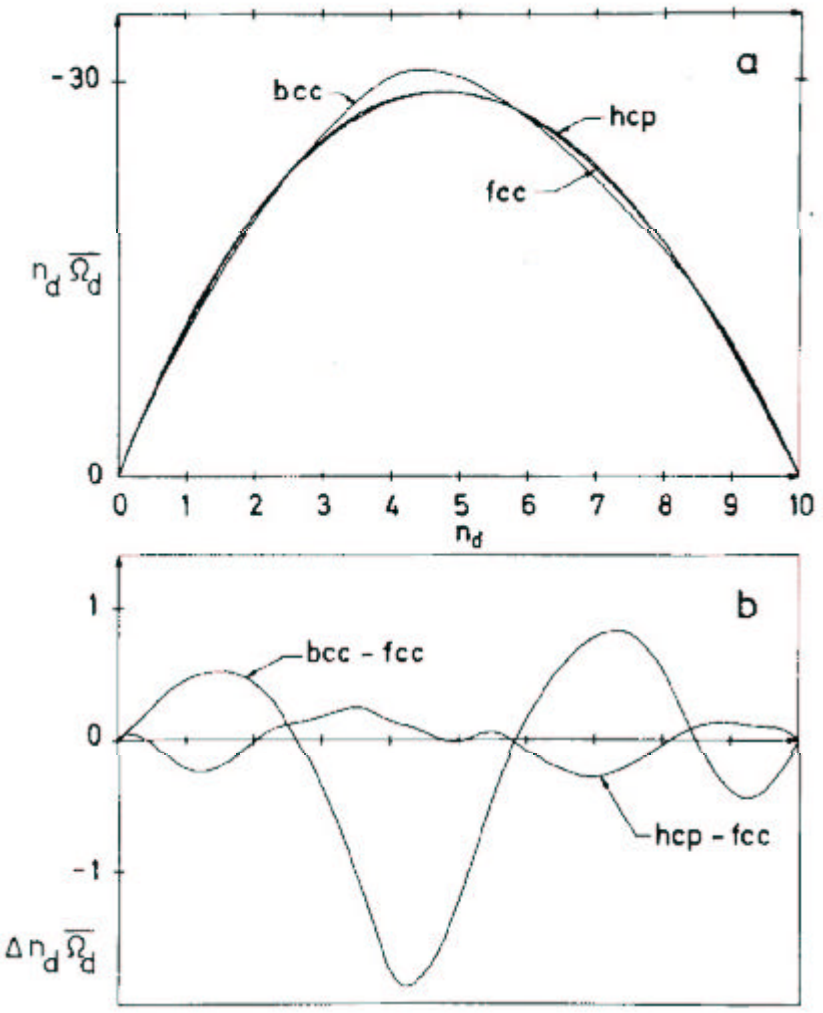
# Crystal Structures



# Canonical Band Theory

O.K. Andersen, J. Madsen, U.K. Poulsen,
O. Jepsen and J. Kollar,
Physica **86-88B,** 249 (1977)



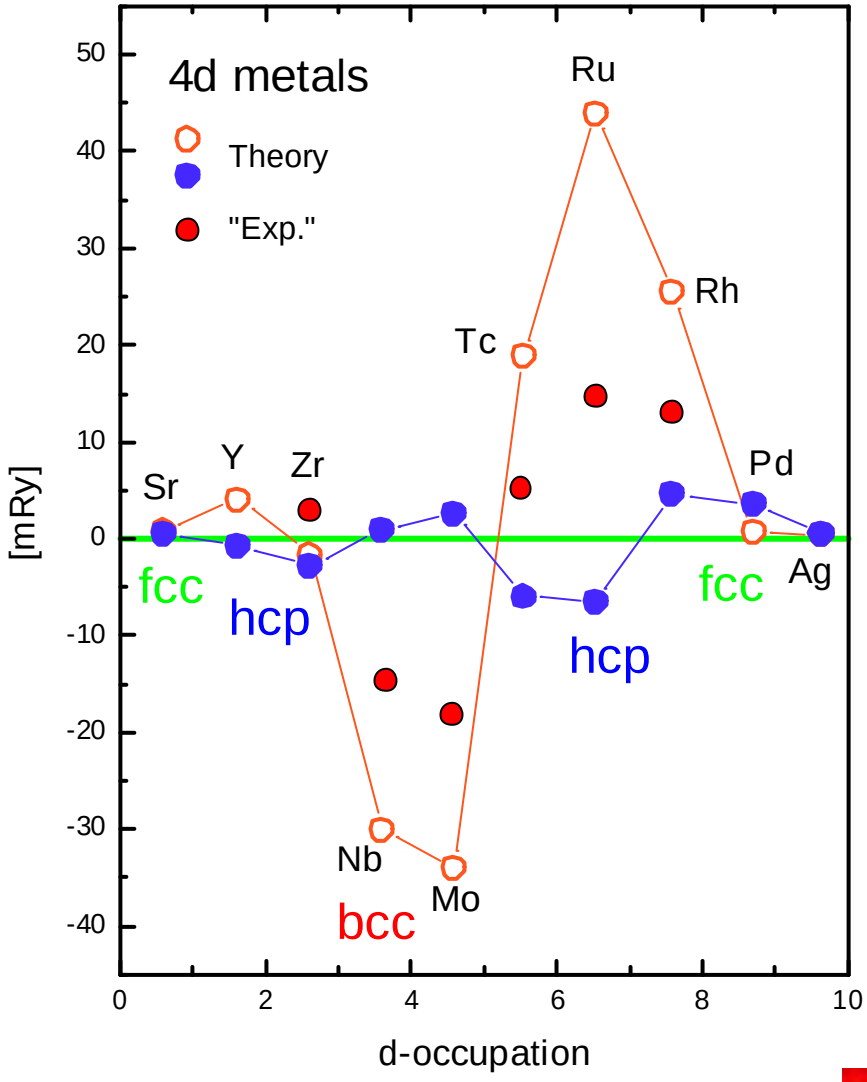
# Calculated Structural Energy

H.L. Skriver, Phys. Rev. **B31,** 1909 (1985)

A.R. Miedema and A.K. Niessen, *CALPHAD* **7,** 27 (1983)

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Li | Be | | | | | | | | | |
| Na | Mg | | | | | | | | | |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag |
| Cs | Ba | Lu | Hf | Ta | W | Re | Os | Ir | Pt | Au |

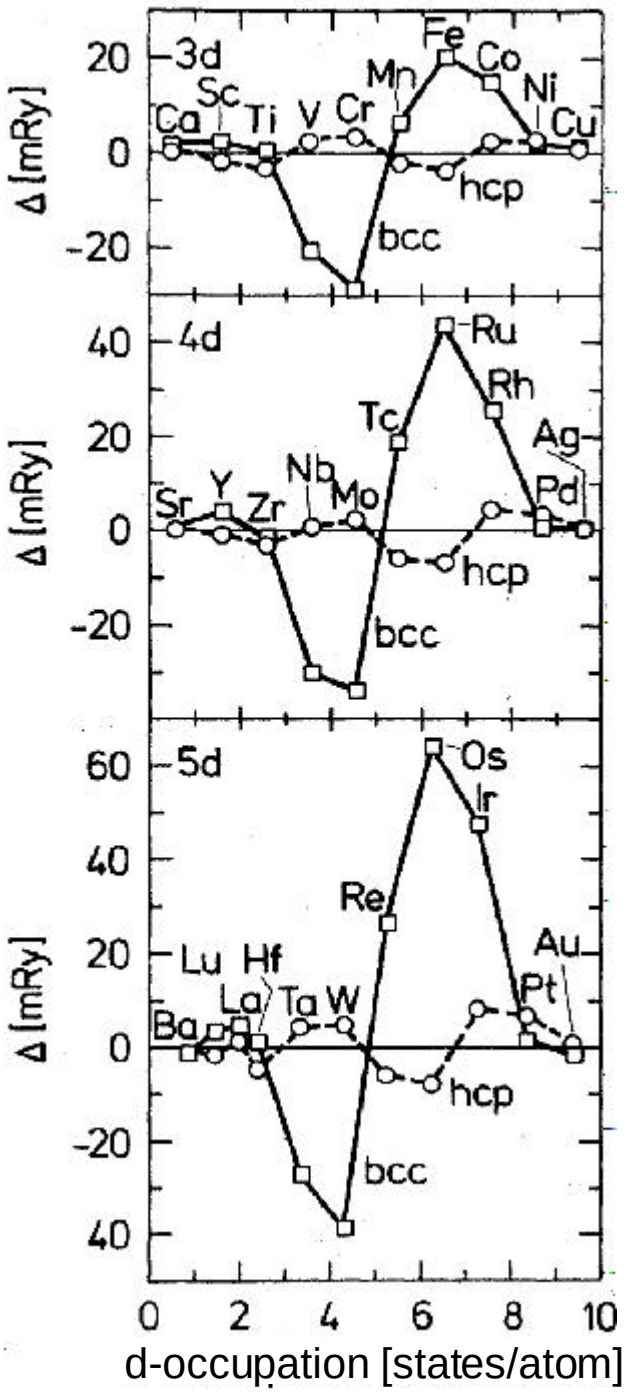
fcc bcc hcp



# Database:

Calculated Structural energy differences

- Li - Pa at experimental volume
- LMTO-ASA plus Madelung correction
- Andersen's force theorem
- Barth-Hedin XC





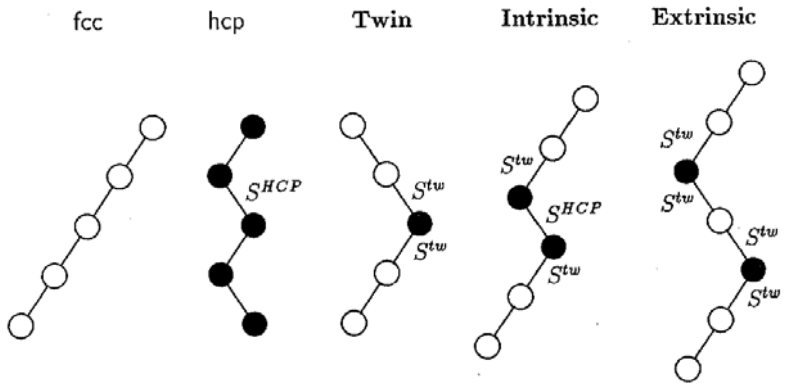
H.L. Skriver, Phys. Rev. B**31,** 1909 (1985)

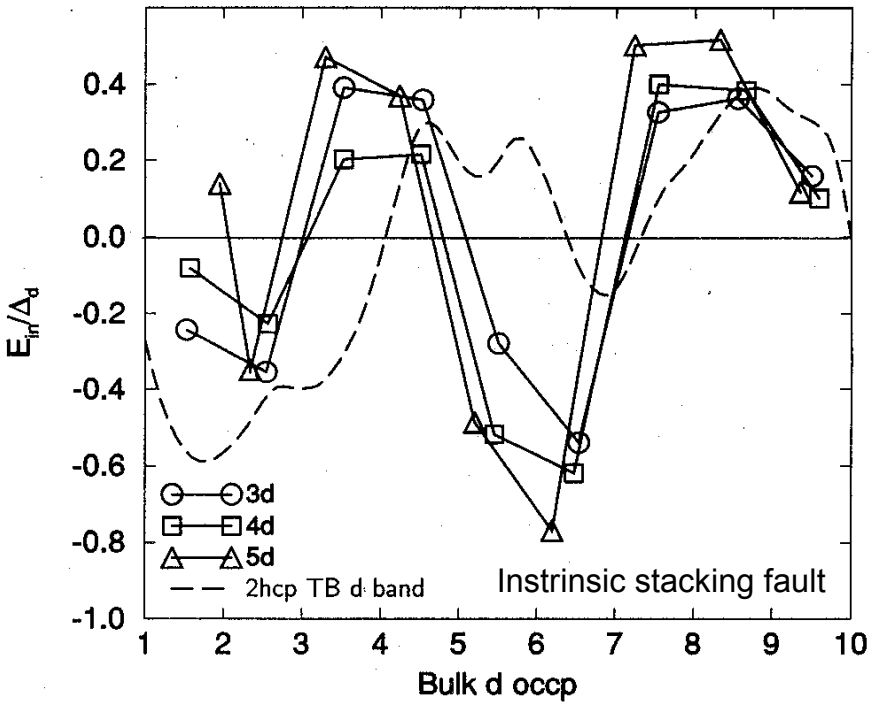
H.L. Skriver, Phys. Rev. Lett. **49,** 1768 (1982)

# Database:

Calculated Stacking fault energy

- Transition metals at experimental volume
- LMTO-ASA
- Green function approach, semi-infinite geometry
- LDA: Perdew-Zunger, Ceperley-Alder

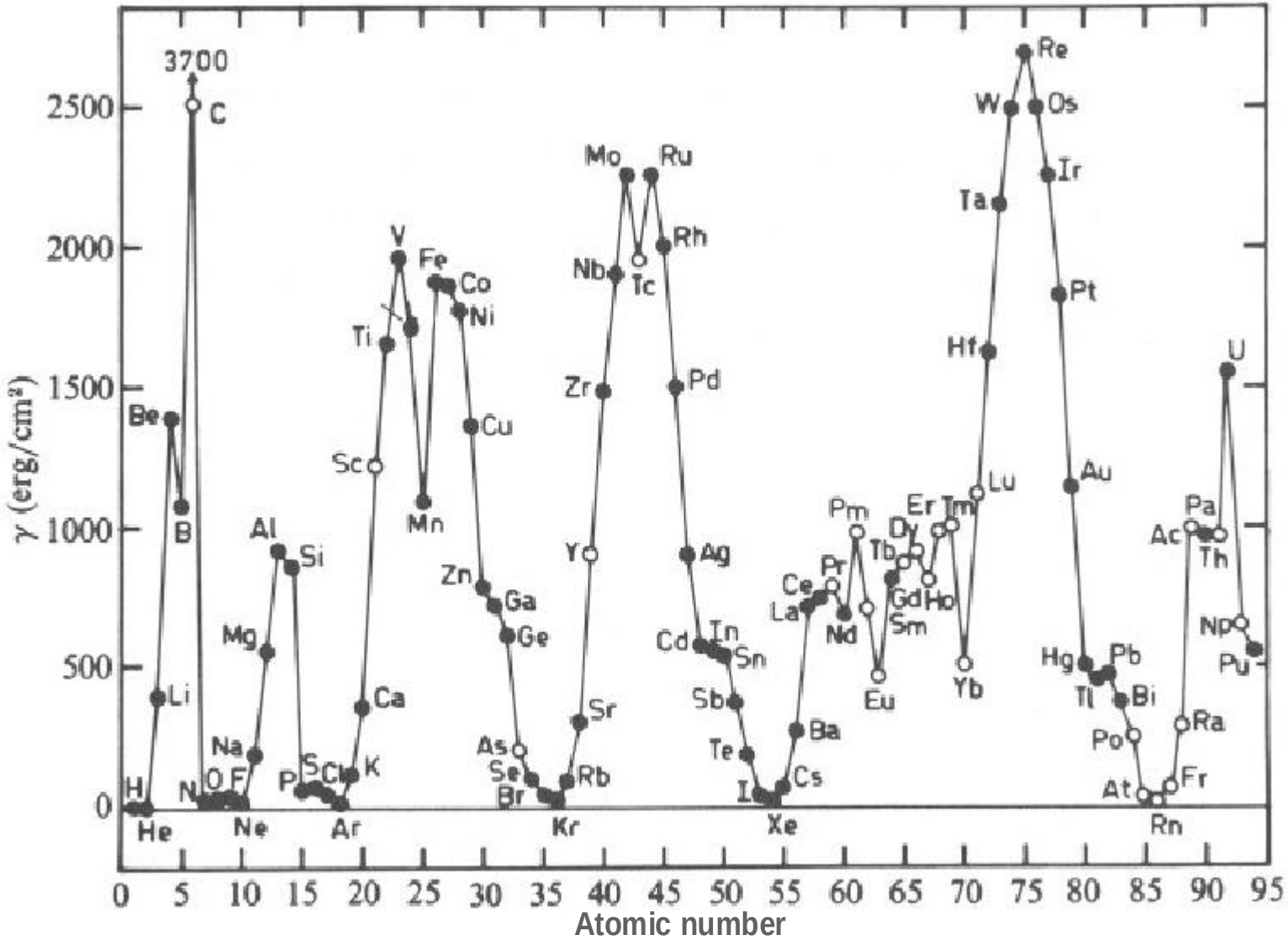



N.M. Rosengaard, H.L. Skriver,
Phys. Rev. B**47,** 12 865 (1993)

# Experimental Surface Tension

J.N. Schmit: Ph.D. Thesis (1978), University of Liege; in Zangwill: *Physics at Surfaces* (1988)



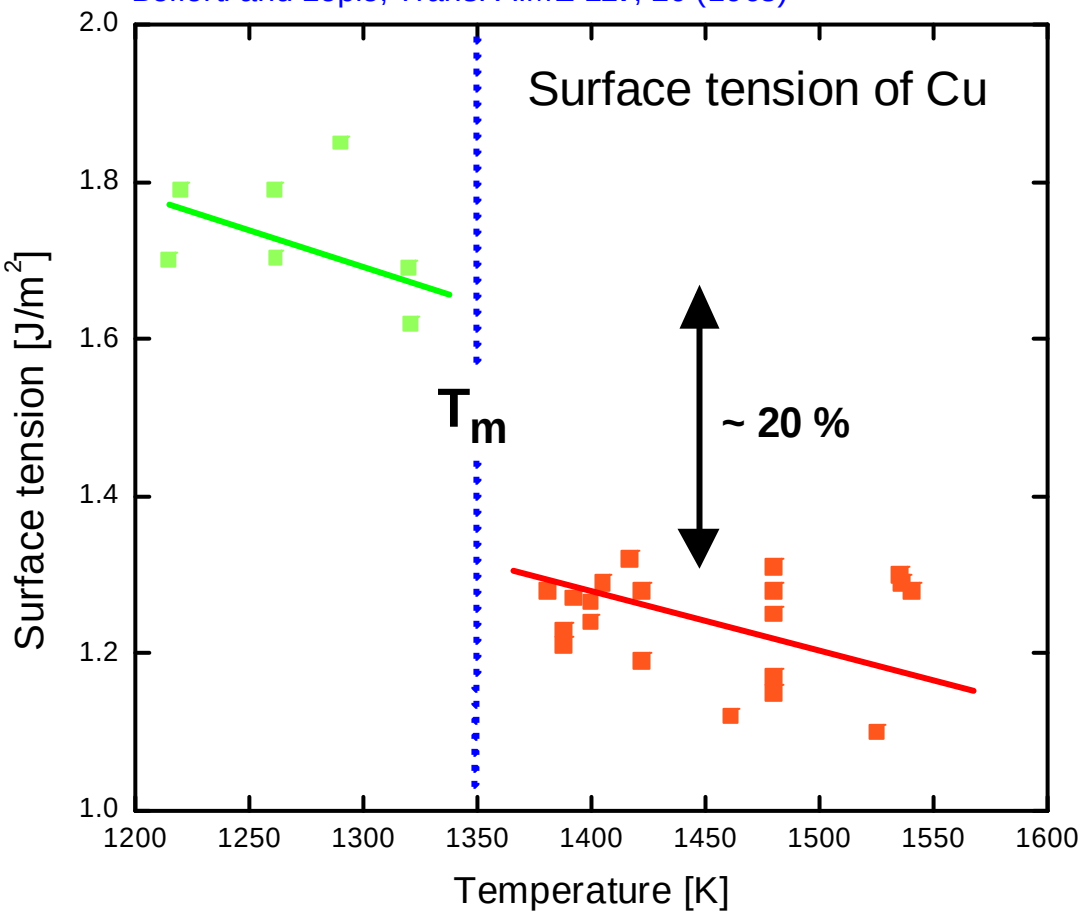
# Eötvös Law

Surface tension (energy) is linear in temperature.

Discontinuity at melting is approximately 20 %.

$$\sigma(T) = \sigma(T_m) + \beta(T_m - T)$$

Shaler and Wulff, *Trans. AIME* **185**, 186 (1949)
Belforti and Lopie, *Trans. AIME* **227**, 20 (1963)



# Surface Energy

Energy required to transform a bulk atom into a surface atom with a corresponding increase in surface area

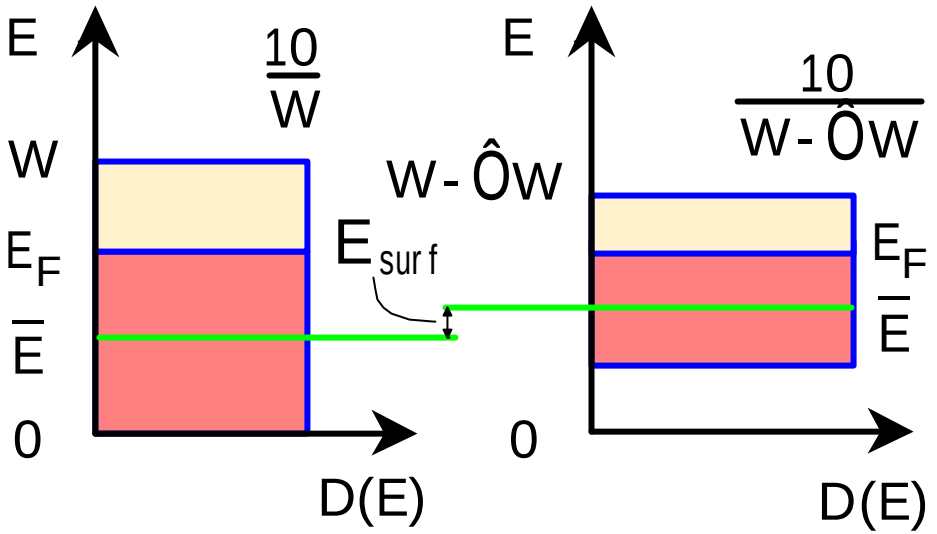
Friedel:

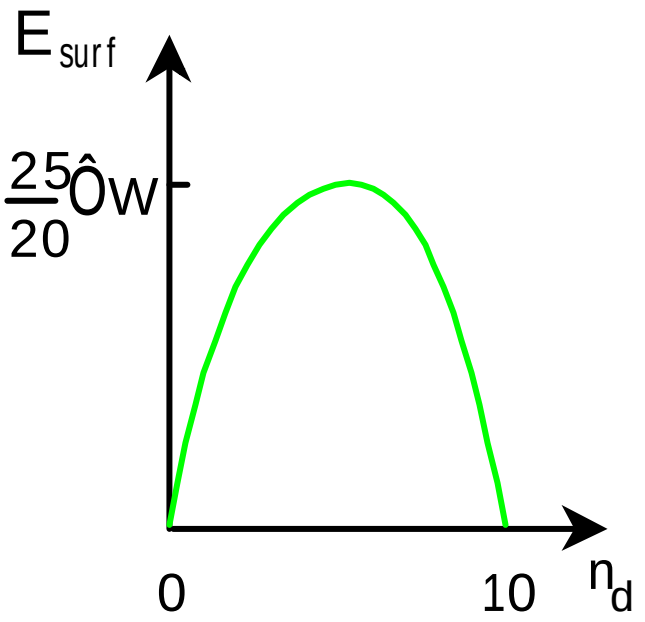
$$E_{coh} = \frac{W}{20} n_d ( 10 - n_d )$$

$$E_{surf} = \frac{\hat{O}W}{20} n_d ( 10 - n_d )$$

Tight-Binding:

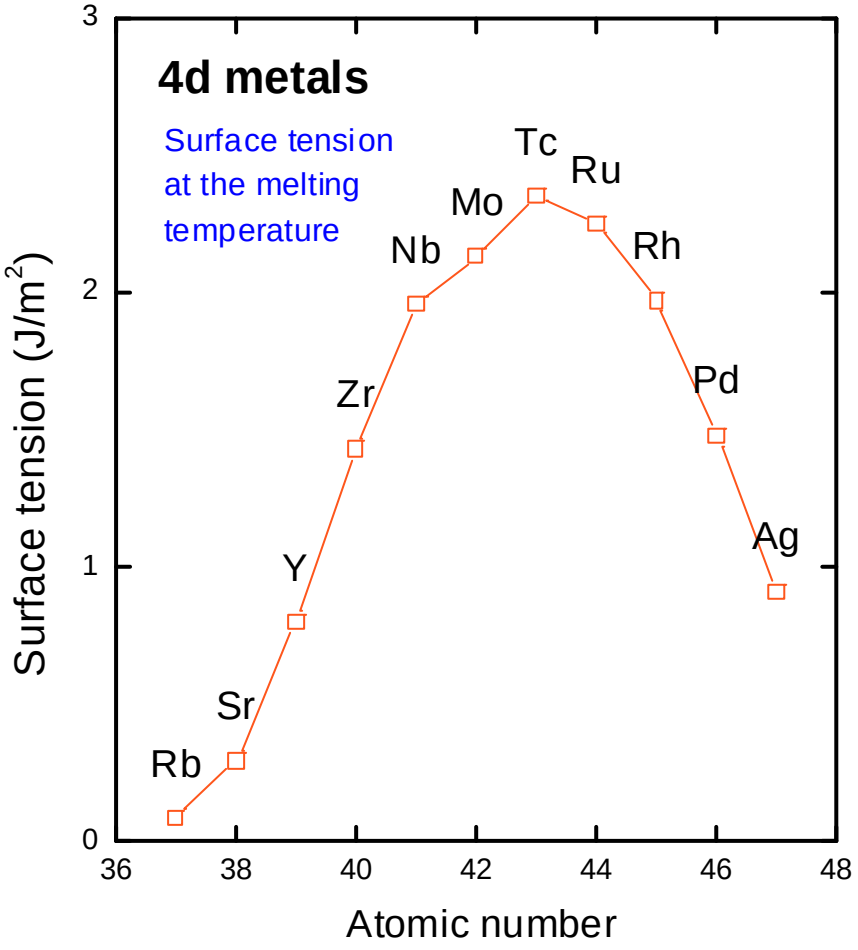
$$\hat{O}W = 1 - (8/12)^{1/2} \sim 0.19$$



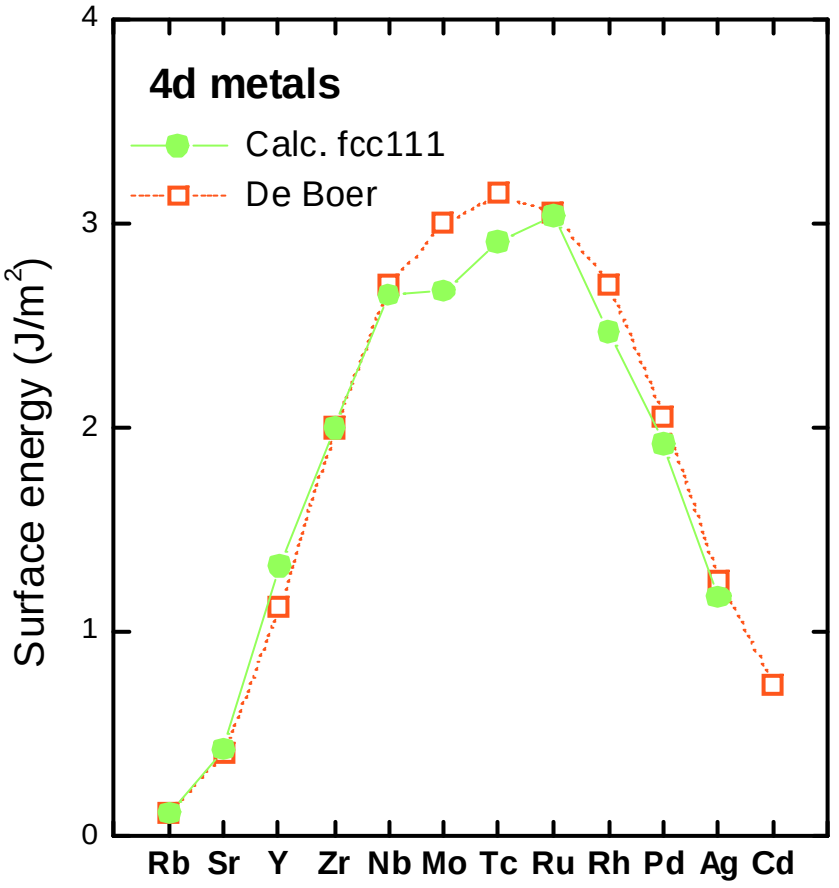



# "Experimental" Surface Energy

□: de Boer *et al.*, *Transition Metals Alloys* in *Cohesion and Structure, Vol 1 (North-Holland, 1988)*

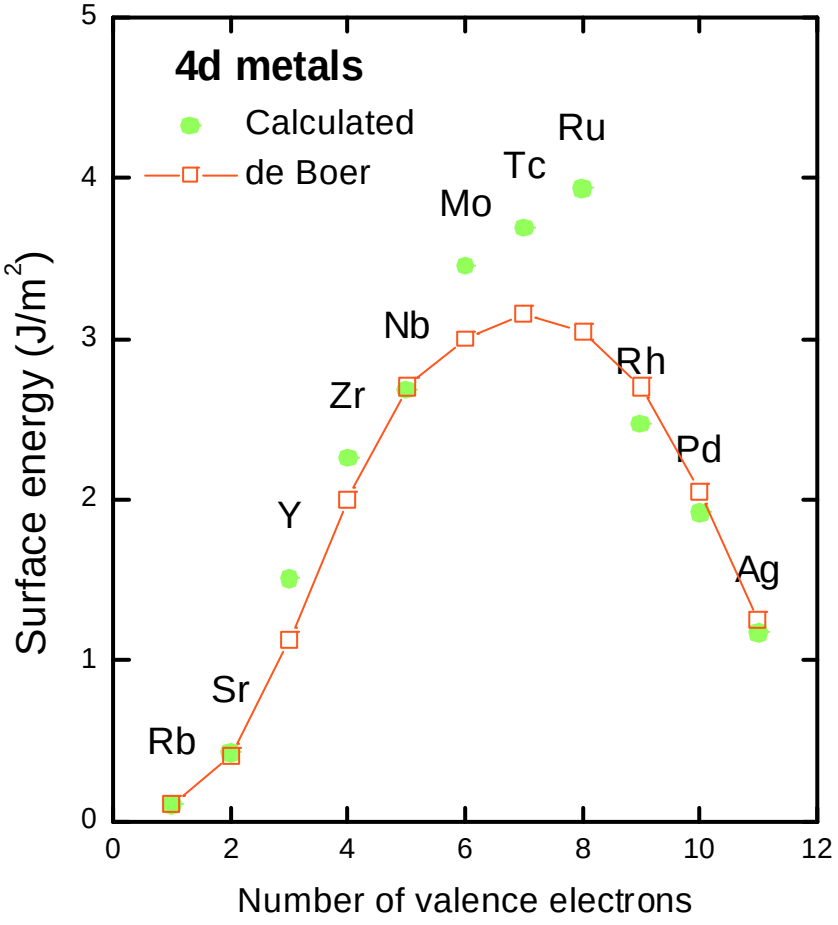



●: Vitos *et al.*, *Surf. Sci.* **411**, 186 (1998); DFT-LMTO-FCD

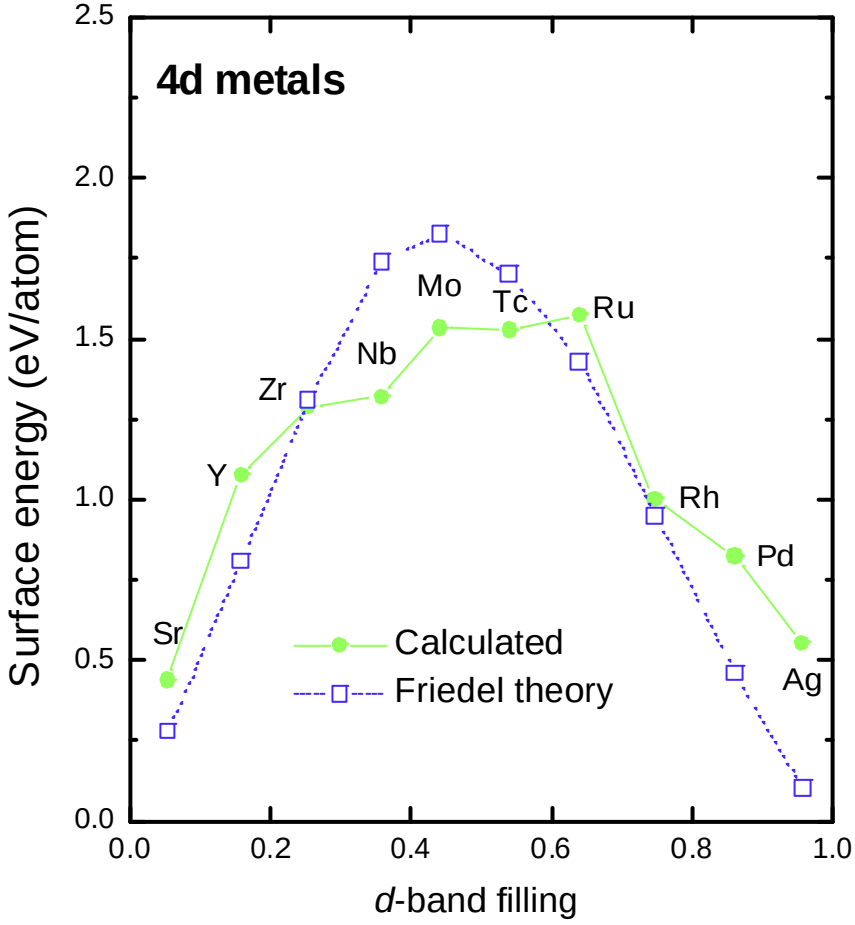


# Calculated Surface Energy

□: de Boer *et al.*, *Transition Metals Alloys* in *Cohesion and Structure, Vol 1 (North-Holland, 1988)*




●: Vitos *et al.*, *Surf. Sci.* **411**, 186 (1998); DFT-LMTO-FCD



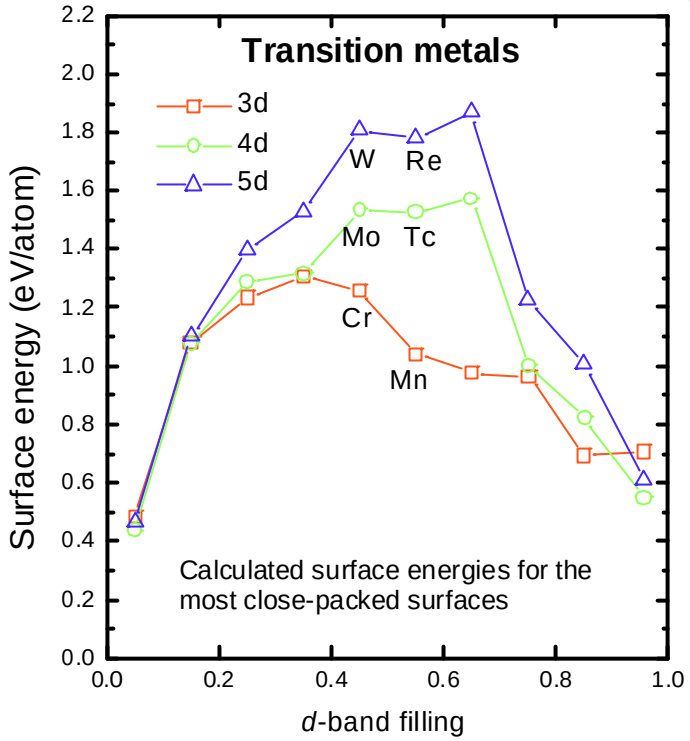
# Database:

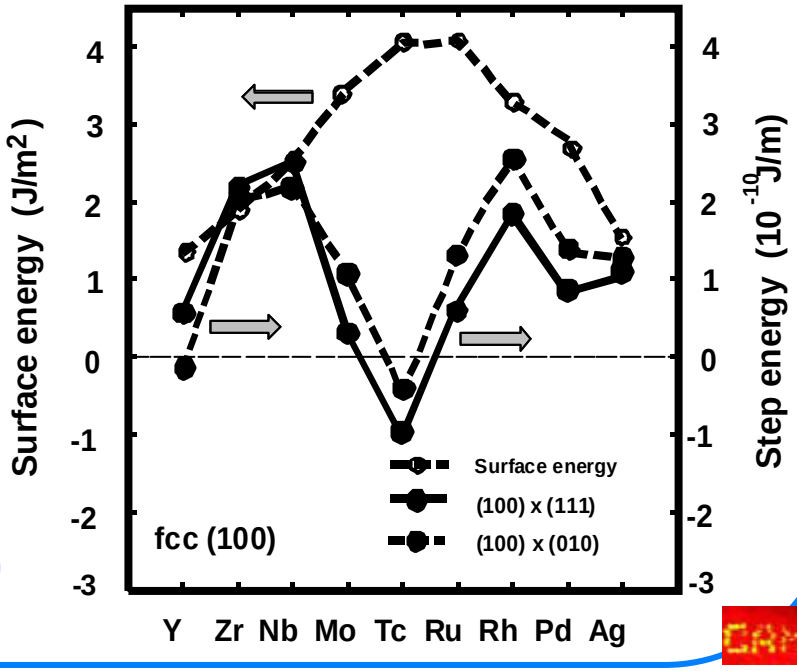
Calculated Surface, step and kink energy

- Li - Pu at calculated volume
- LMTO-ASA plus full charge-density correction FCD
- Green function approach, semi-infinite geometry

$$E_{surf} = E_{2D}^{FCD}(N_{atom} + N_{vac}) - N_{atom} E_{3D}^{FCD}$$

- Perdew, Burke, Ernzerhof GGA





L. Vitos, A.R. Ruban, H.L. Skriver, J. Kollar, Surf. Sci. **411,** 186 (1998)

L. Vitos, H.L. Skriver, J. Kollar, Surf. Sci. **425,** 212 (1999)

# Surface Segregation Energy

Bulk $A_{1-c}B_c$

$$\ddot{U} = \left.\frac{dE_{bulk}}{dc}\right|_{c=0}$$

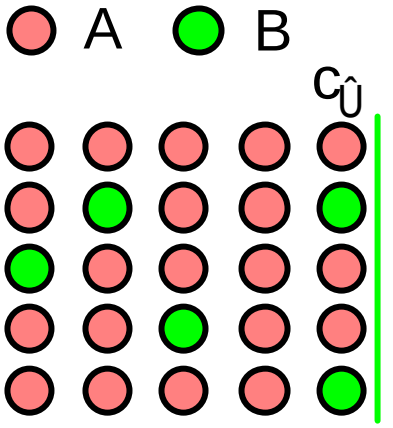
Surface $A_{1-c_{\hat{U}}}B_{c_{\hat{U}}}$

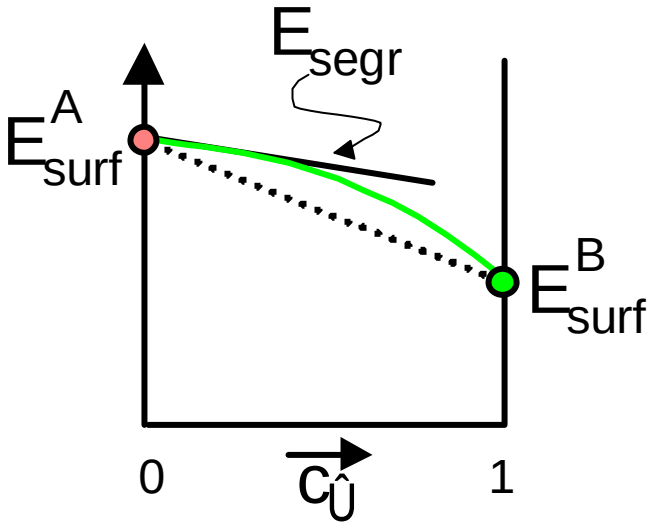
$$E_{surf} = \grave{I}_{\hat{U}} (E_{\hat{U}} - E_{bulk}) - \ddot{U} c_{\hat{U}}$$

$$E^{B \to A}_{segr,\hat{U}} = \left.\frac{dE_{surf}}{dc_{\hat{U}}}\right|_{c_{\hat{U}}=0}$$

Friedel model

$$E^{B \to A}_{segr} \sim E^{B}_{surf} - E^{A}_{surf}$$



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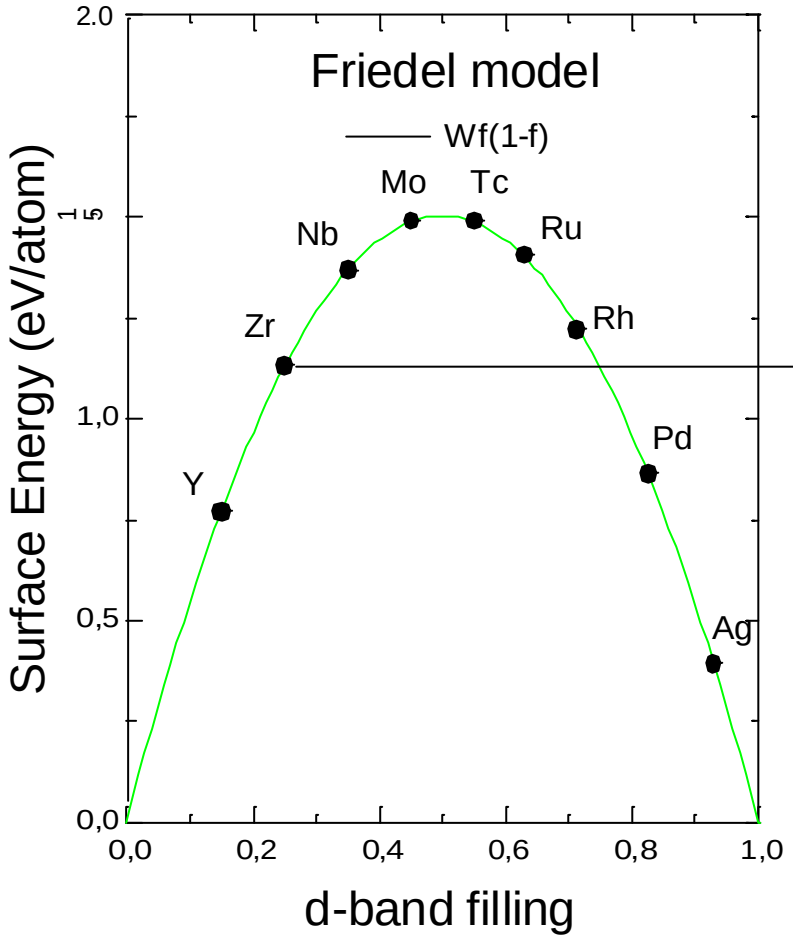
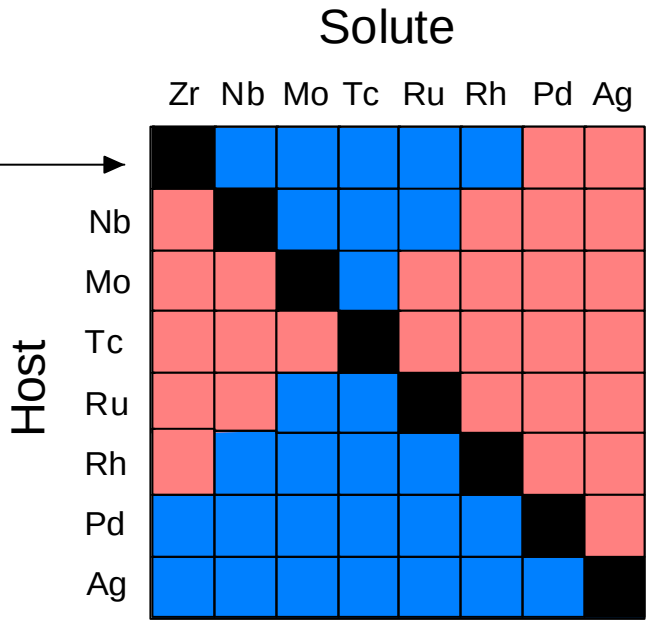
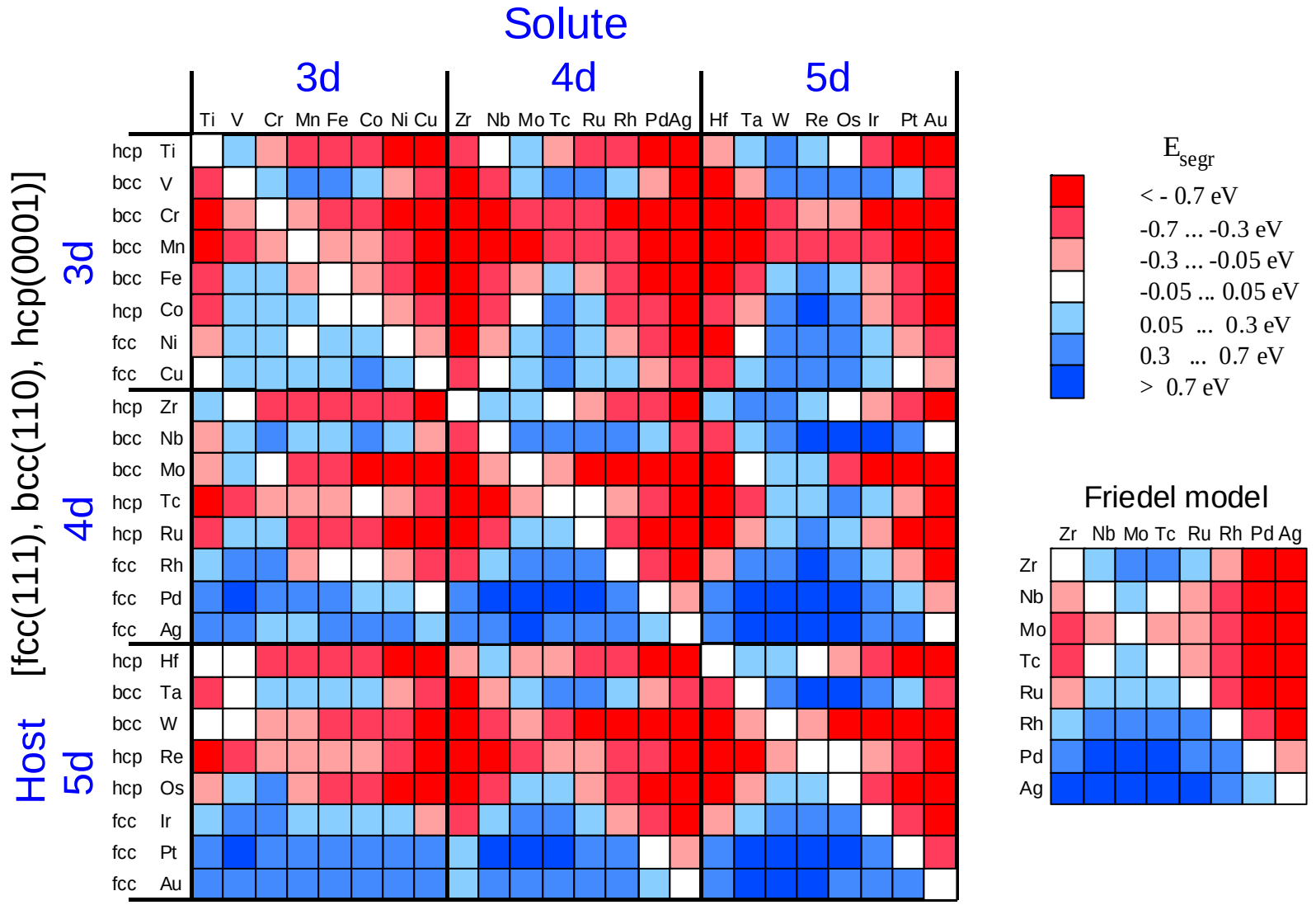


# Calculated Segregation Energy




A.V. Ruban, H.L. Skriver, J.K. Nørskov, Phys. Rev. B**59,** 15990 (1999)

# Surface Core Level Shift

Thermodynamical model of a fully screened core-hole

B. Johansson and N. Mårtensson,
Phys. Rev. B**21,** 4427 (1980)

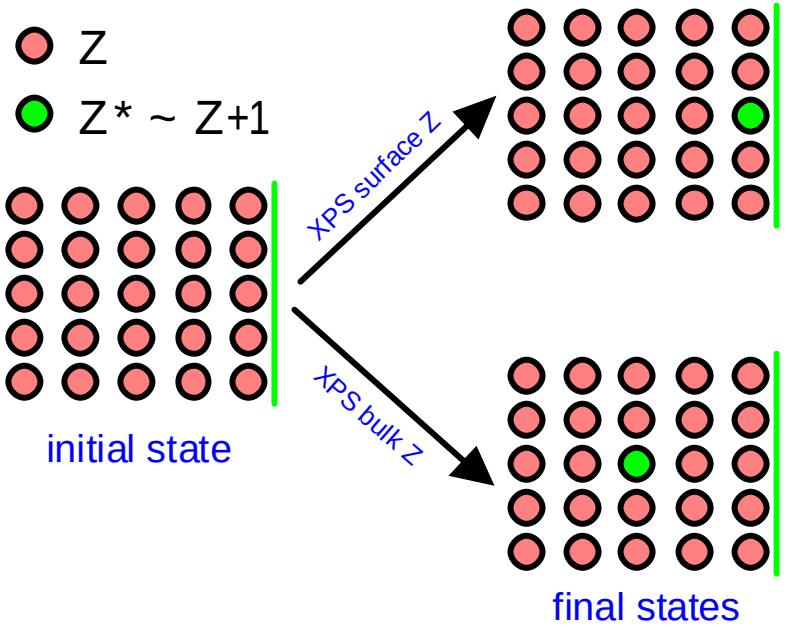
$$Ç^{SB} = E_{sol}^{bulk}(Z^*) - E_{sol}^{surf}(Z^*)$$

$$\sim E_{segr}^{Z+1 \rightarrow Z}$$

Friedel model, *d* -band filling f

$$E_{segr}^{Z+1 \rightarrow Z} = E_{surf}^{Z+1} - E_{surf}^{Z}$$

$$\sim \frac{dE_{surf}}{df} \sim \frac{W}{10}(1 - 2f)$$



# Calculated Surface Core Level Shift

## Thermodynamical model

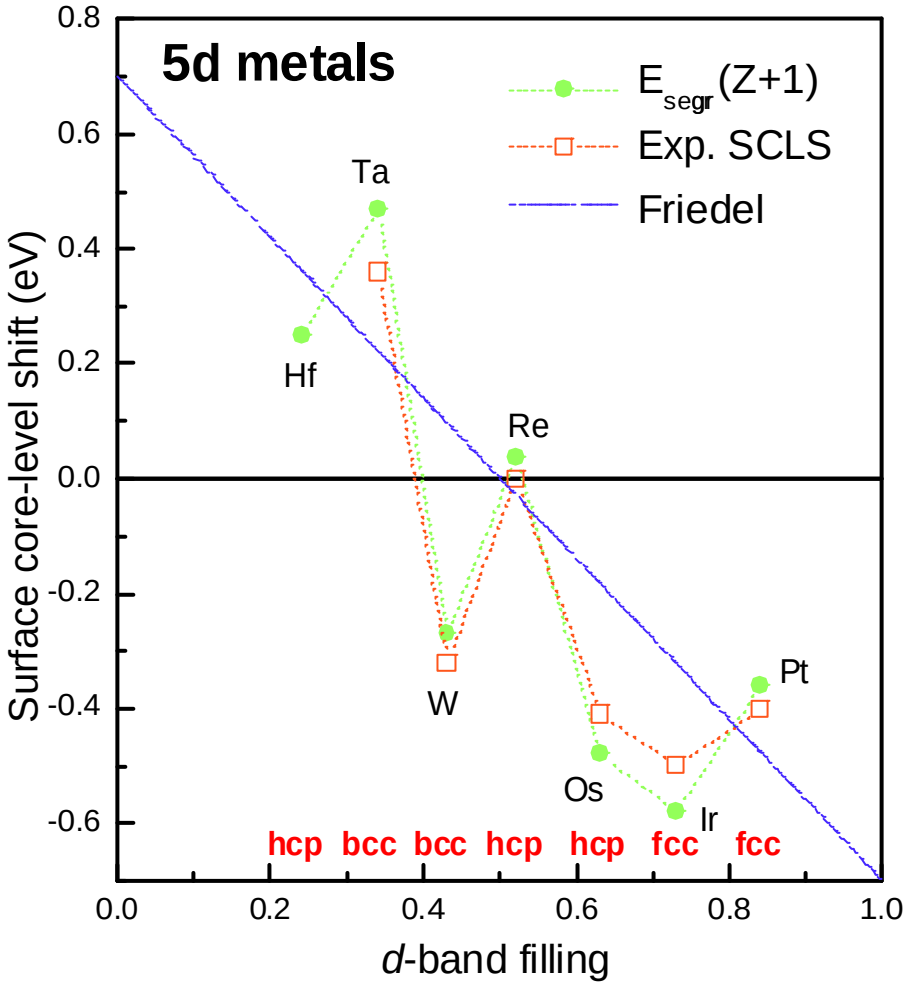
B. Johansson and N. Mårtensson,
Phys. Rev. B**21,** 4427 (1980)

$$Ç^{SB} = E_{segr}^{Z+1 \rightarrow Z}$$

## Friedel model, *d* -band filling f

$$E_{segr}^{Z+1 \rightarrow Z} \sim \frac{W}{10}(1 - 2f)$$

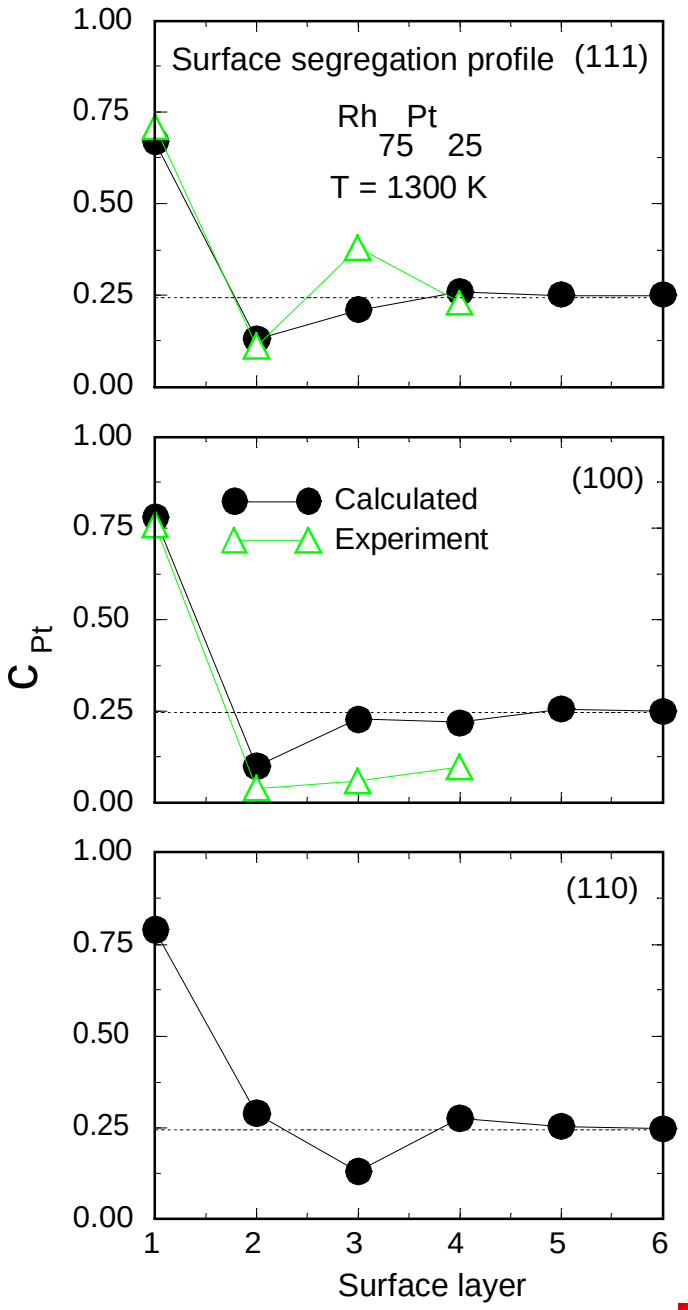
A.V. Ruban and H.L. Skriver,
Comp. Mat. Sci. **15,** 119 (1999)



# Database:

Calculated Surface segregation energy

- Transition - transition metal at calculated volume
- LMTO-ASA plus multipole correction
- Green function approach, semi-infinite geometry
- Coherent Potential Approximation CPA
- LDA: Perdew-Zunger Ceperley-Alder
- LSD: Vosko-Wilk-Nusair




A.V. Ruban, H.L. Skriver, J.K. Nørskov, Phys. Rev. B**59,** 15 990 (1999)

A.V. Ruban, H.L. Skriver, Comp.Mat. Sci. **15,** 119 (1999)

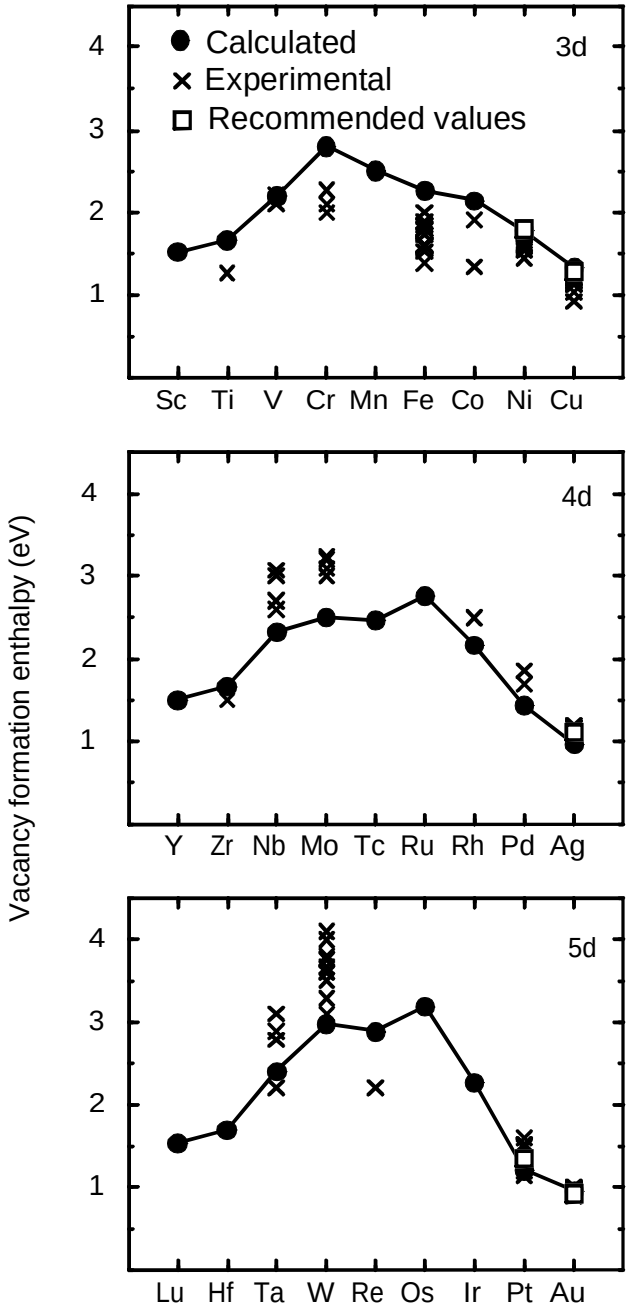
# Database:

Calculated Vacancy formation energy

- Transition metals
- Supercell approach: Order-N Locally Self-consistent Greens Funtion LSGF method

$$H^{F}_{1V}(P=0) = E(1,\tilde{V}) - \frac{N-1}{N} E(0,V)$$

- s,p,d,f LMTO-ASA plus multipole correction
- Perdew, Burke, Ernzerhof GGA





P.A. Korzhavyi, I.A. Abrikosov, B. Johansson,
A.V. Ruban, H.L. Skriver, Phys. Rev. B**59,** 11 693 (1999)

# Vacancy Formation Energy

Empirically

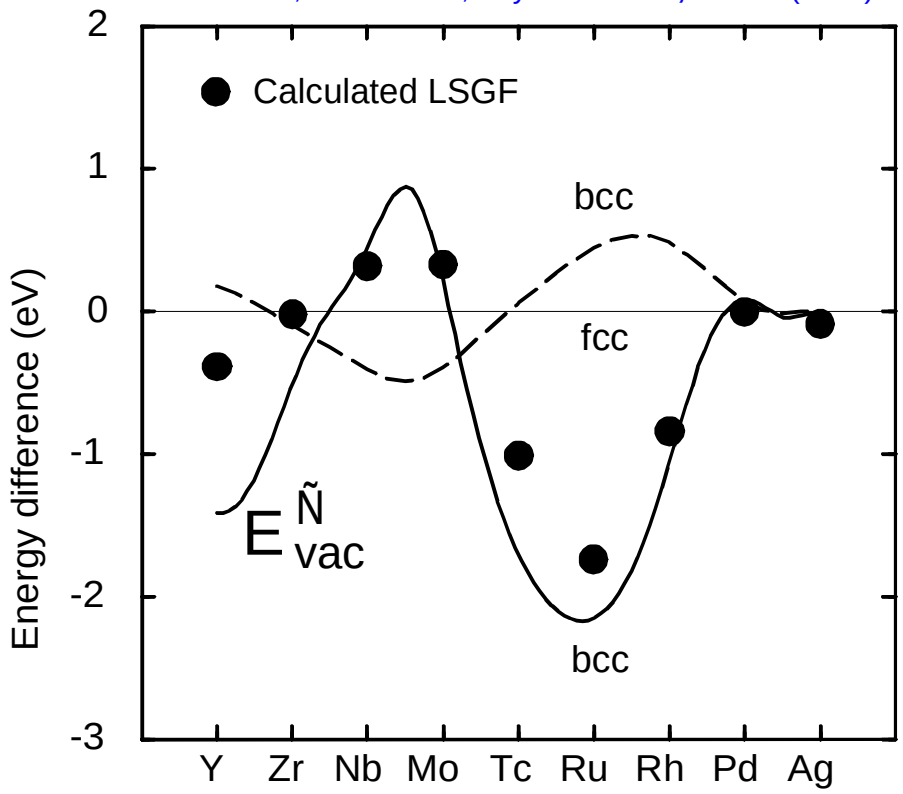
$$E^{F}_{1V} \sim \frac{1}{3} E_{coh}$$

Structural contribution, i.e., beyond Friedel, to the vacancy formation energy

$$E^{\tilde{N}}_{coh} = E^{Friedel}_{coh} + E^{\tilde{N}}_{str}$$

$$E^{\tilde{N}}_{vac} \sim z\left(1 - \left[\frac{z-1}{z}\right]^{1/2}\right) E^{\tilde{N}}_{coh} - z\left[\frac{z-1}{z}\right]^{1/2} E^{\tilde{N}}_{str}$$

P.A. Korzhavyi, I.A. Abrikosov, B. Johansson, A.V. Ruban, H.L. Skriver, Phys. Rev. B**59,** 11 693 (1999)



# Database:

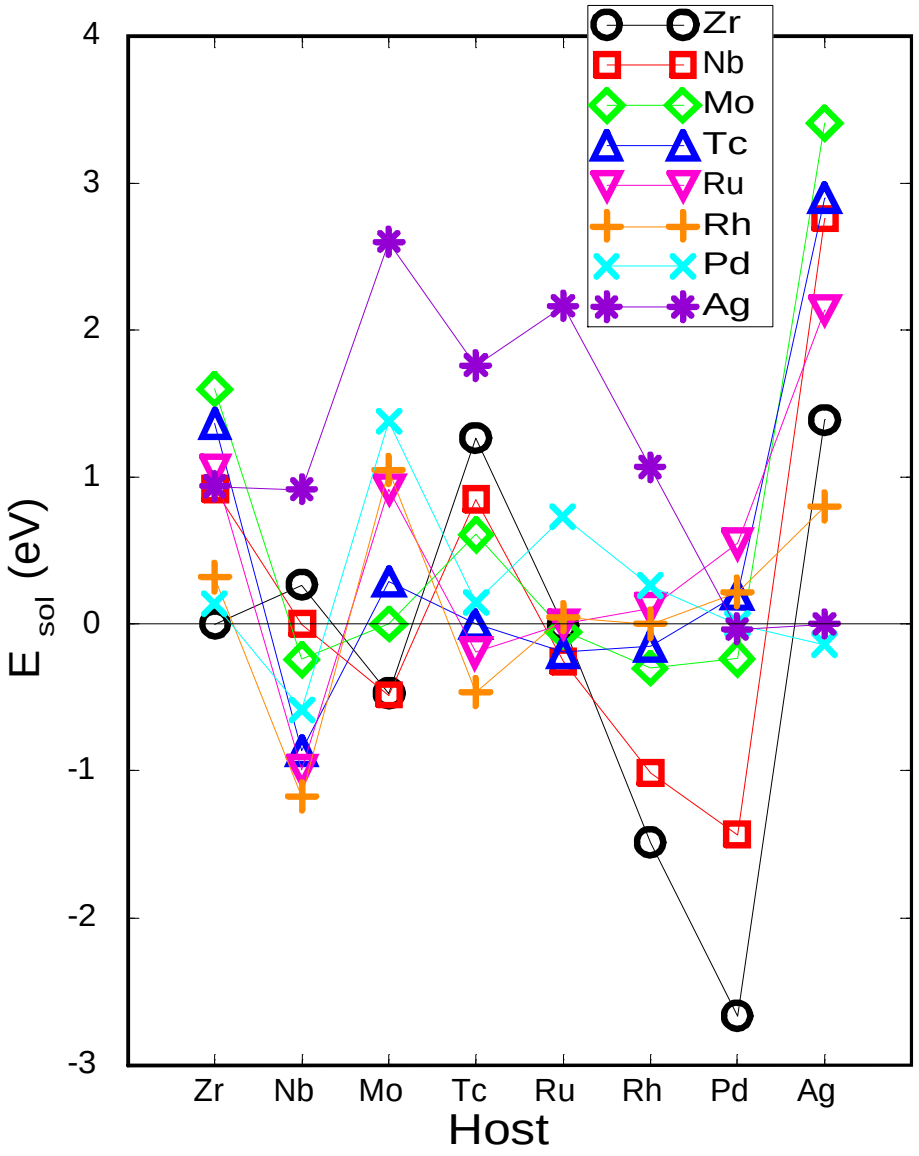
Calculated impurity solution energy

- 4*d* transition metals at calculated volume
- LMTO-ASA
- Coherent Potential Approximation
- Perdew-Zunger Ceperley-Alder XC

Solution of B -> A

$$E_{sol}^{\tilde{N}} = \left.\frac{dE_{A_{1-c}B_c}}{dc}\right|_{c=0} + E_A^{\tilde{N}} - E_B^{\grave{O}}$$

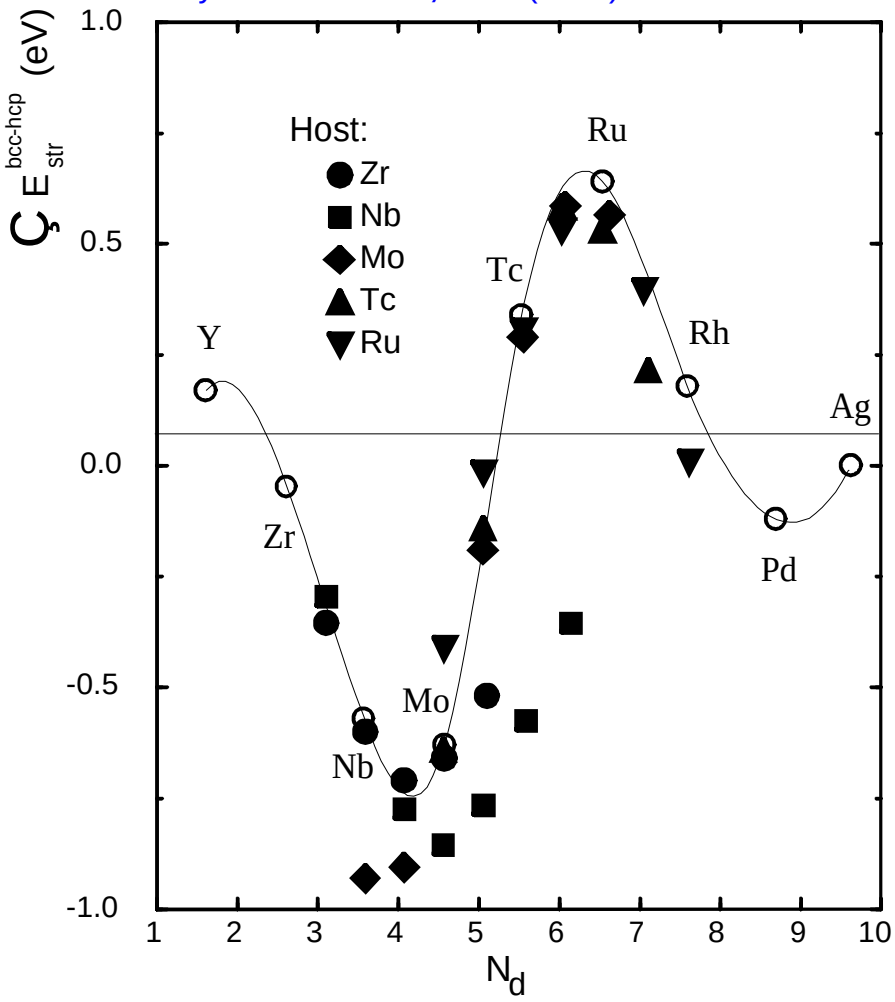
A.V. Ruban, H.L. Skriver, J.K. Nørskov,
Phys. Rev. Lett. **80,** 1240 (1998)



# Impurity Solution Energy

Crystal structure contribution to the solid solubility in transition metal alloys

$$\Delta E_{sol}^{A\text{-}B} = 2\Delta E_{str}^{A\text{-}B}(N_d^C) - \Delta E_{str}^{A\text{-}B}(N_d^A)$$

$$N_d^C = \frac{1}{2}(N_d^A + N_d^B)$$

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