Computational Materials Physics

narrated by

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thanks to

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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


![Graph showing measured cohesive energies vs. d-occupation.](image-url)
Cohesive Energy

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

$$E_{\text{coh}} = E_{\text{bond}} - \ll E_{\text{atom}}$$

$$\ll E_{\text{atom}} = E_{\text{pro}} + \ll E$$

$$\ll E : \text{Calculated from local exchange integrals}$$

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

Cohesive Energy

The Friedel Model


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

**D-band occupation:**

**Bonding energy:**

\[ E_{\text{bond}} = -\int_0^{E_F} D(E) \left( E - E_a \right) \, dE \]

\[ = - \left( \bar{E} - E_a \right) n_d \]

\[ = \frac{W}{20} n_d \left( 10 - n_d \right) \]
Local Density Theory of Metallic Cohesion

Calculations by

using

DFT
P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964)

LDA

LSD

and fast KKR

Figure 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

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fcc, bcc, hcp
Canonical Band Theory

Calculated Structural Energy


4d metals

- Theory
- "Exp."

Calculated Structural Energy

[Graph showing energy levels for different elements and crystal structures]
Database:
Calculated Structural energy differences

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

Database:
Calculated Stacking fault energy

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

Surface Energy

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

Friedel:

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

\[ E_{surf} = \frac{W}{20} n_d (10 - n_d) \]

Tight-Binding:

\[ 'W = 1 - (8/12)^{1/2} \approx 0.19 \]
Experimental Surface Tension

Eötvös Law

Surface tension (energy) is linear in temperature.

Discontinuity at melting is approximately 20%.

\[ "(T) = "(T_m) + "(T_m - T) \]
"Experimental" Surface Energy

Surfactants 4d

Surface tension at the melting temperature

atomic number

Surface energy (J/m²)

4d metals

Calc. fcc111

De Boer

: 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

![Graph showing calculated surface energies for 4d metals](image)

**Graph Details**
- **4d metals**: Mo, Tc, Ru, Rh, Pd, Ag, Zr, Nb, Y, Sr, Rb
- **Surface energy (J/m²)**
- **Number of valence electrons**
- **Surface energy (eV/atom)**
- **d-band filling**

**Sources**
- 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

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**Legend**
- **: 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

Surface Segregation Energy

Bulk \( A_{1-c}B_c \)

\[
< = \frac{dE_{\text{bulk}}}{dc} \bigg|_{c=0}
\]

Surface \( A_{1-c\epsilon}B_{c\epsilon} \)

\[
E_{\text{surf}} = \bar{\lambda} \left( E_{\epsilon} - E_{\text{bulk}} \right) - < c_{\epsilon}
\]

\[
E^{B \rightarrow A}_{\text{segr}, \epsilon} = \frac{dE_{\text{surf}}}{dc_{\epsilon}} \bigg|_{c_{\epsilon}=0}
\]

Friedel model

\[
E^{B \rightarrow A}_{\text{segr}} \sim E^{B}_{\text{surf}} - E^{A}_{\text{surf}}
\]
Surface Segregation Energy

\[ W_f(1-f) \]

Friedel model

Surface Energy (eV/atom)

\[ d\text{-band filling} \]

Solute

Host

- Zr
- Nb
- Mo
- Tc
- Ru
- Rh
- Pd
- Ag

Y
Calculated Segregation Energy

Surface Core Level Shift

Thermodynamical model of a fully screened core-hole


\[ \langle S_B \rangle = E_{\text{sol}}^{\text{bulk}} (Z^*) - E_{\text{surf}}^{\text{surf}} (Z^*) \]

\[ \sim E_{\text{segr}}^{Z+1 \rightarrow Z} \]

Friedel model, d-band filling \( f \)

\[ E_{\text{segr}}^{Z+1 \rightarrow Z} = E_{\text{surf}}^{Z+1} - E_{\text{surf}}^{Z} \]

\[ \sim \frac{dE_{\text{surf}}}{df} \sim \frac{W}{10} (1 - 2f) \]
Calculated Surface Core Level Shift

Thermodynamical model

\[ \langle S_B \rangle = E_{segr}^{Z+1 \rightarrow Z} \]

Friedel model, d-band filling f

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

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

Database:

Calculated Vacancy formation energy

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

\[ H_{1V}^F(P=0) = E(1,\tilde{V}) - \frac{N-1}{N} E(0,V) \]

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

Vacancy Formation Energy

Empirically

\[ E_{1V}^F \sim \frac{1}{3} E_{coh} \]

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

\[ E_{coh} = E_{coh}^{\text{Friedel}} + E_{str} \]

\[ E_{vac} \sim z \left( 1 - \left[ \frac{z-1}{z} \right]^{1/2} \right) E_{coh} \]

\[ - z \left[ \frac{z-1}{z} \right]^{1/2} E_{str} \]

Database:

Calculated impurity solution energy

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

Solution of $B \rightarrow A$

$$E_{sol} = \frac{dE_{A_{1-c}B_c}}{dc} \bigg|_{c=0} + E_{A} - E_{B}$$

Impurity Solution Energy

Crystal structure contribution to the solid solubility in transition metal alloys

\[ \ll E_{\text{sol}} = 2 \ll E_{\text{str}}(N^C_d) - \ll E_{\text{str}}(N^A_d) \]

\[ N^C_d = \frac{1}{2} (N^A_d + N^B_d) \]