

Structural phase transitions

Some materials make a transition from one crystal structure to another.

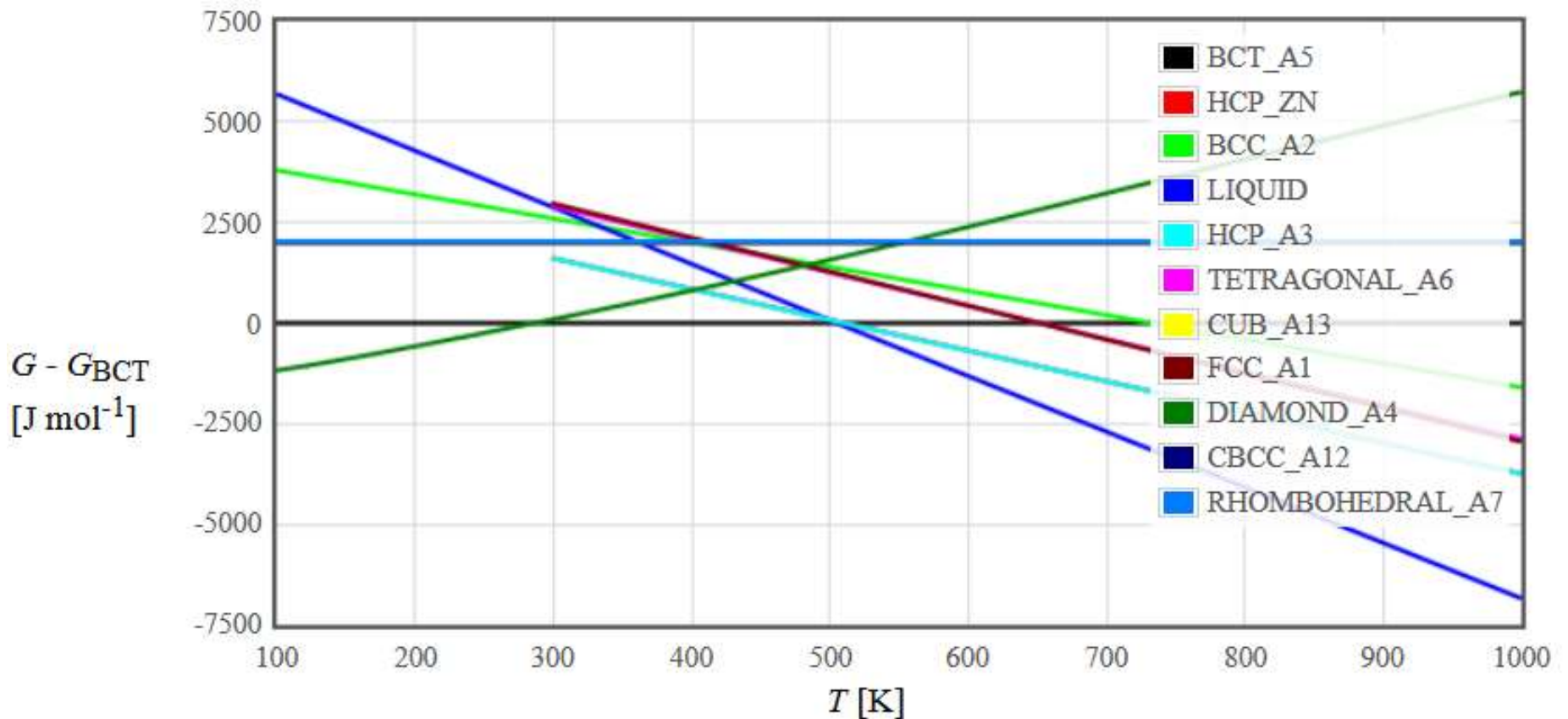
Two allotropes of tin: gray tin (α -Sn) is stable at temperatures below 13.2°C and white tin (β -Sn) is stable above.

The phase with the lowest free energy prevails. (White tin can be stabilized below 13.2 C by adding impurities.)

$$F = U - TS$$

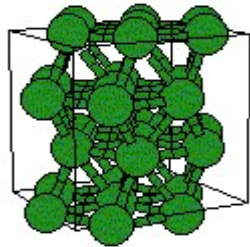
Structural phase transition in Sn

metal β Sn = A5



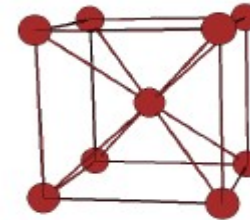
<http://lampx.tugraz.at/~hadley/ss1/materials/sgte/SGTE.html>

Structural phase transitions

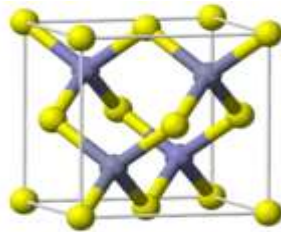


α -Ti, hcp

transition at 890 C



β -Ti, bcc



Zincblende, ZnS

transition at 1020 C



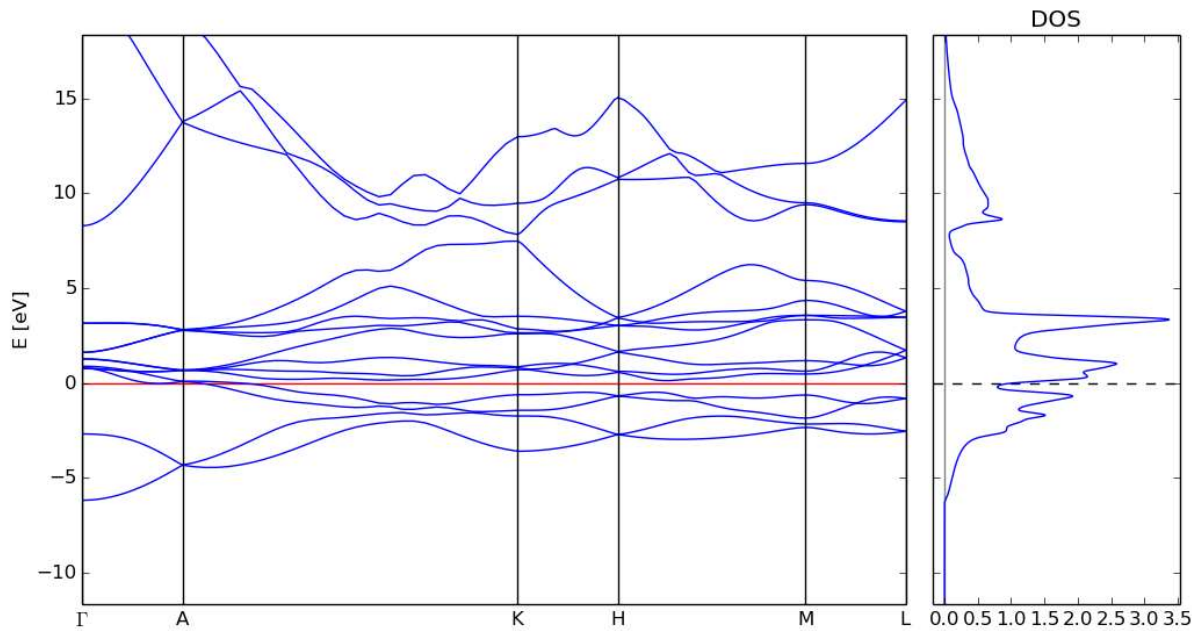
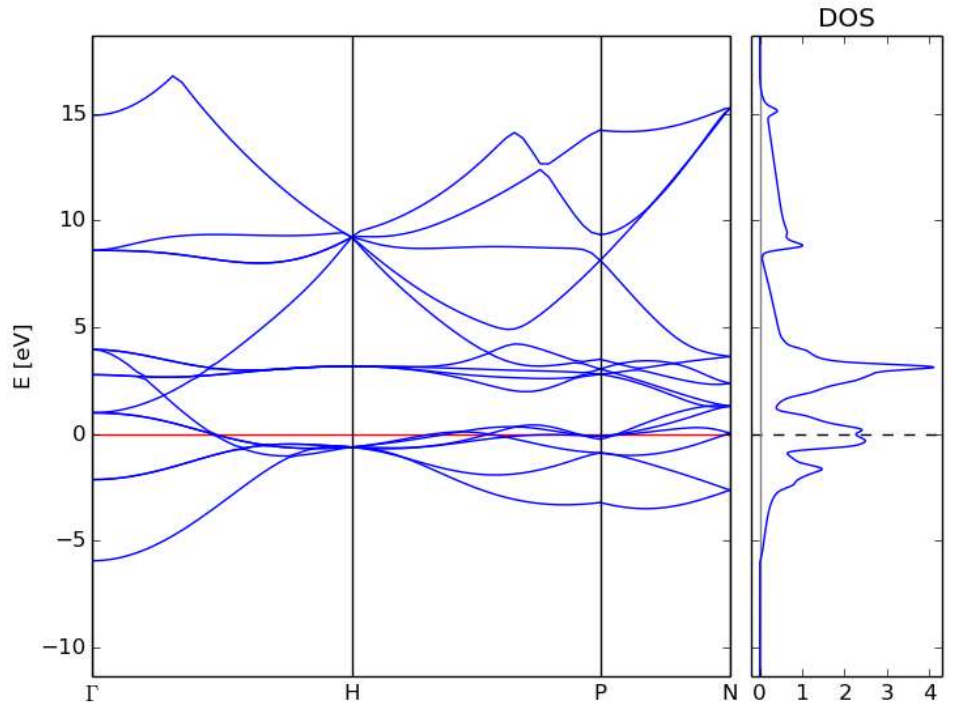
Wurtzite, ZnS

The crystal structure with the lowest free energy will be observed.
Softer phonons >> lower Debye frequency >> more modes occupied >> higher entropy

Titanium



bcc →

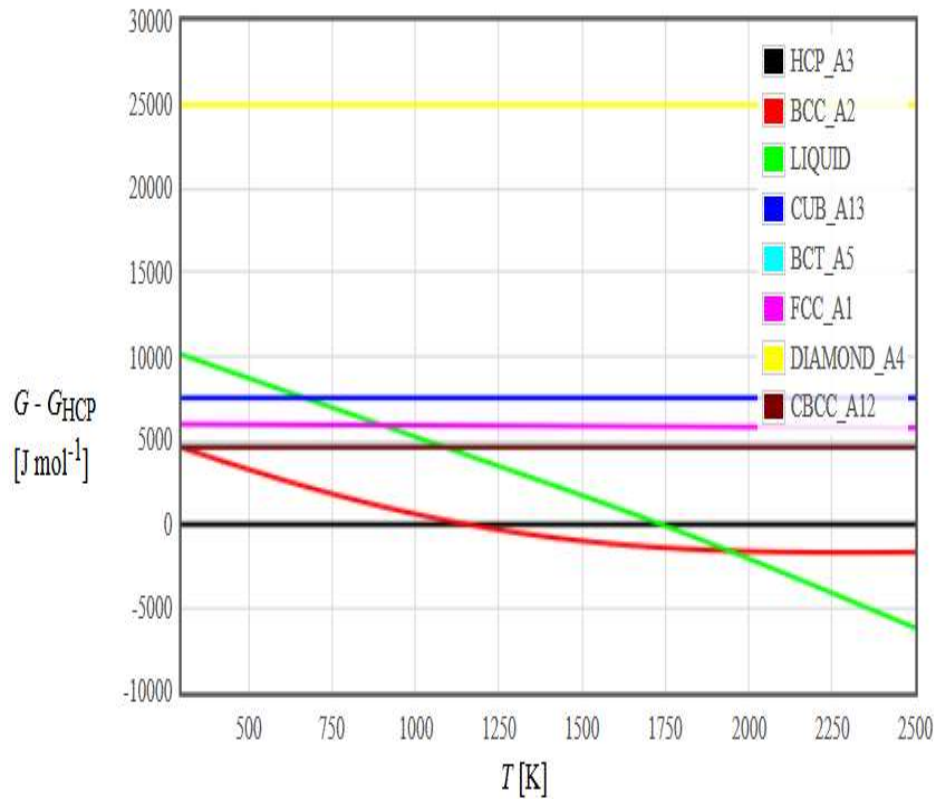


← hcp

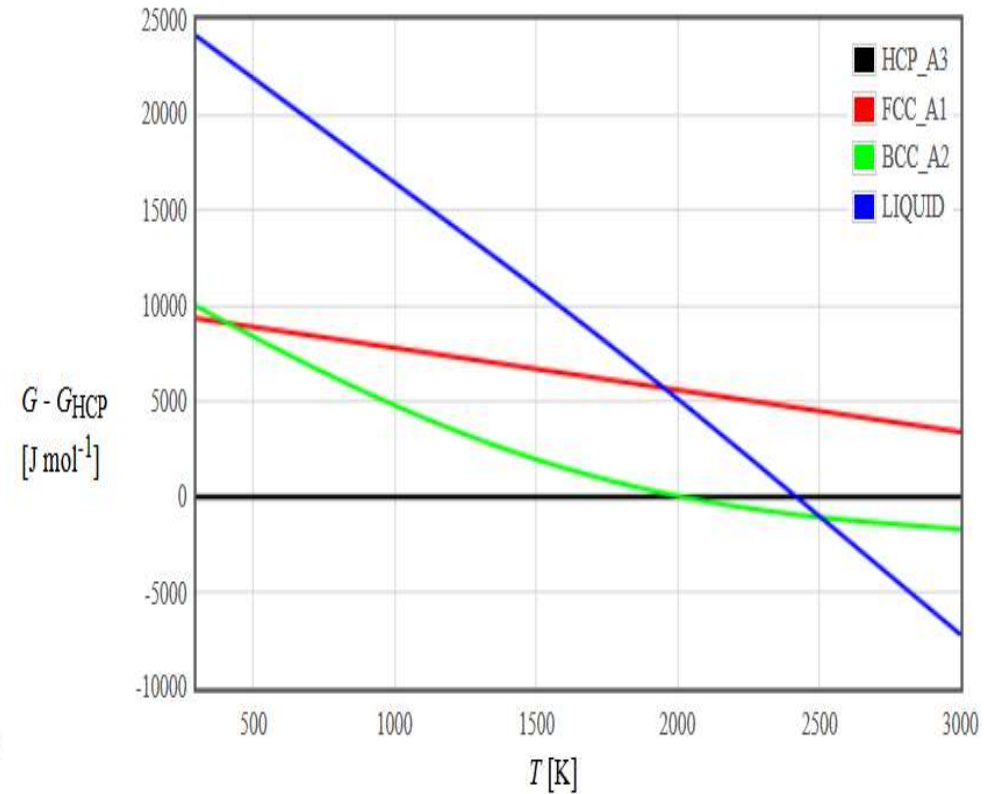
Calculated using FHI-aims by Lydia Nemec

Close packed → bcc

Ti



Hf



Close packed → bcc: Am, Be, Ca, Gd, Nd, Pr, Hf, Sc, Sm, Sr, Ti, Tb, Th, Tl, Y, Yb, Zr

<http://lampx.tugraz.at/~hadley/ss1/materials/sgte/SGTE.html>

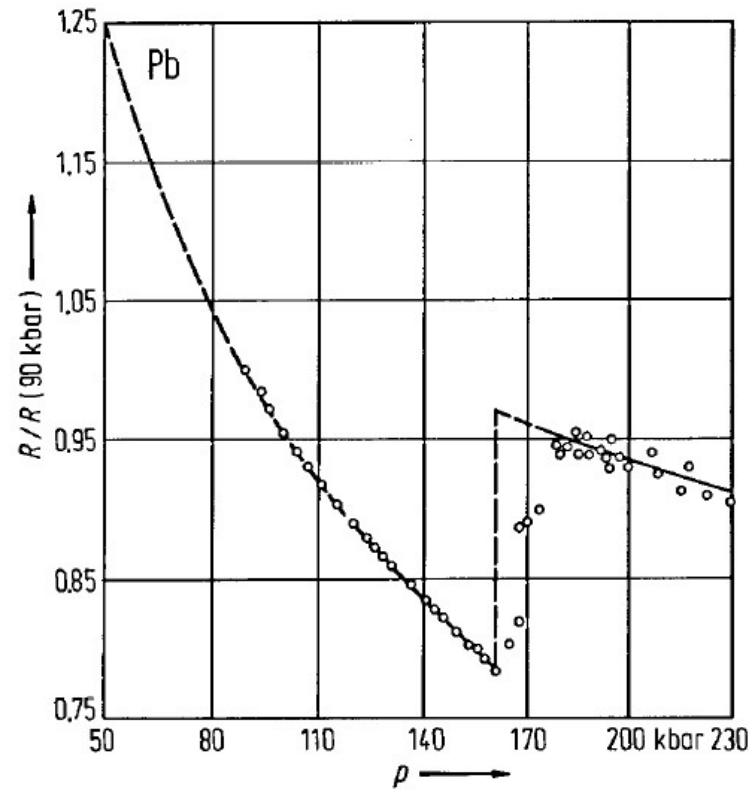
Strain

Strain displaces the atoms and the band structure needs to be recalculated.

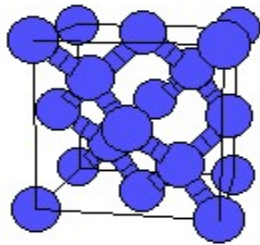
This changes the density of states and the thermodynamic properties.

Make Legendre transformations from the internal energy to the enthalpy that has temperature and pressure as independent variables. The crystal structure with lowest enthalpy will be observed.

Enthalpy is calculated from the microscopic states of electrons and phonons.

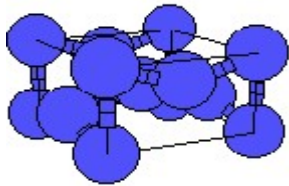


Structural phase transitions



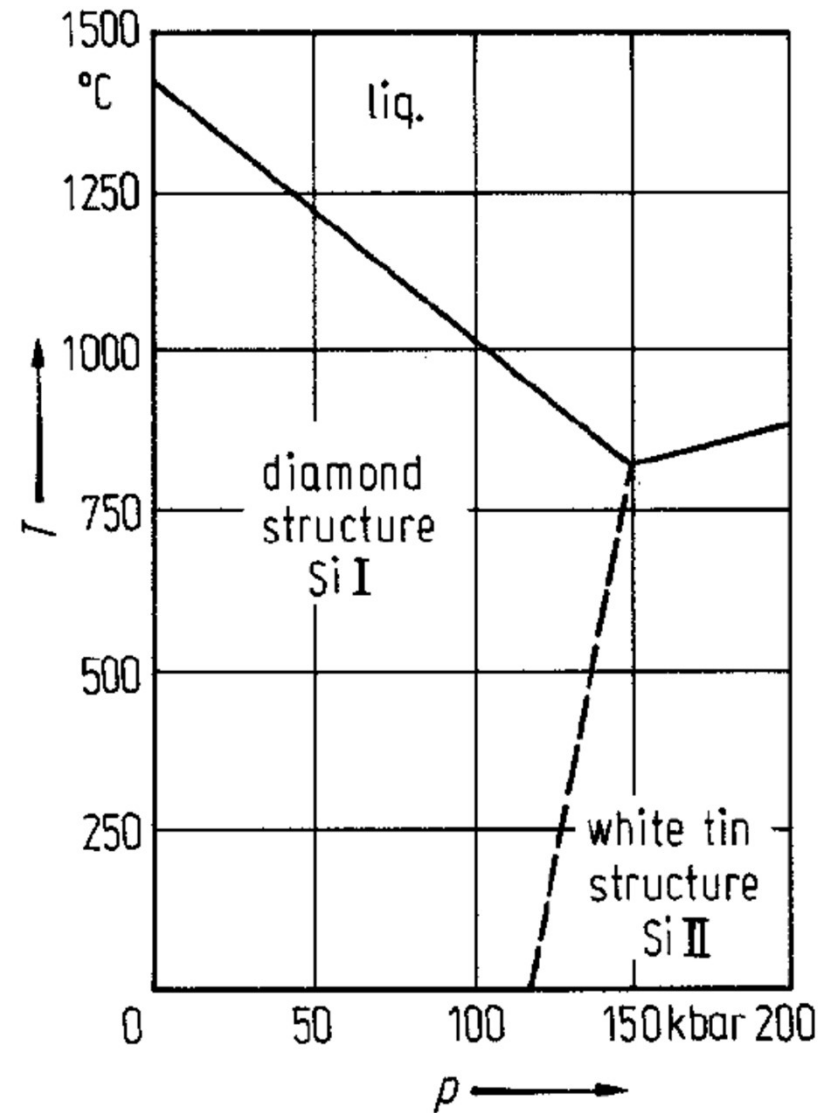
α -Sn, gray tin, diamond

transition at 13 C

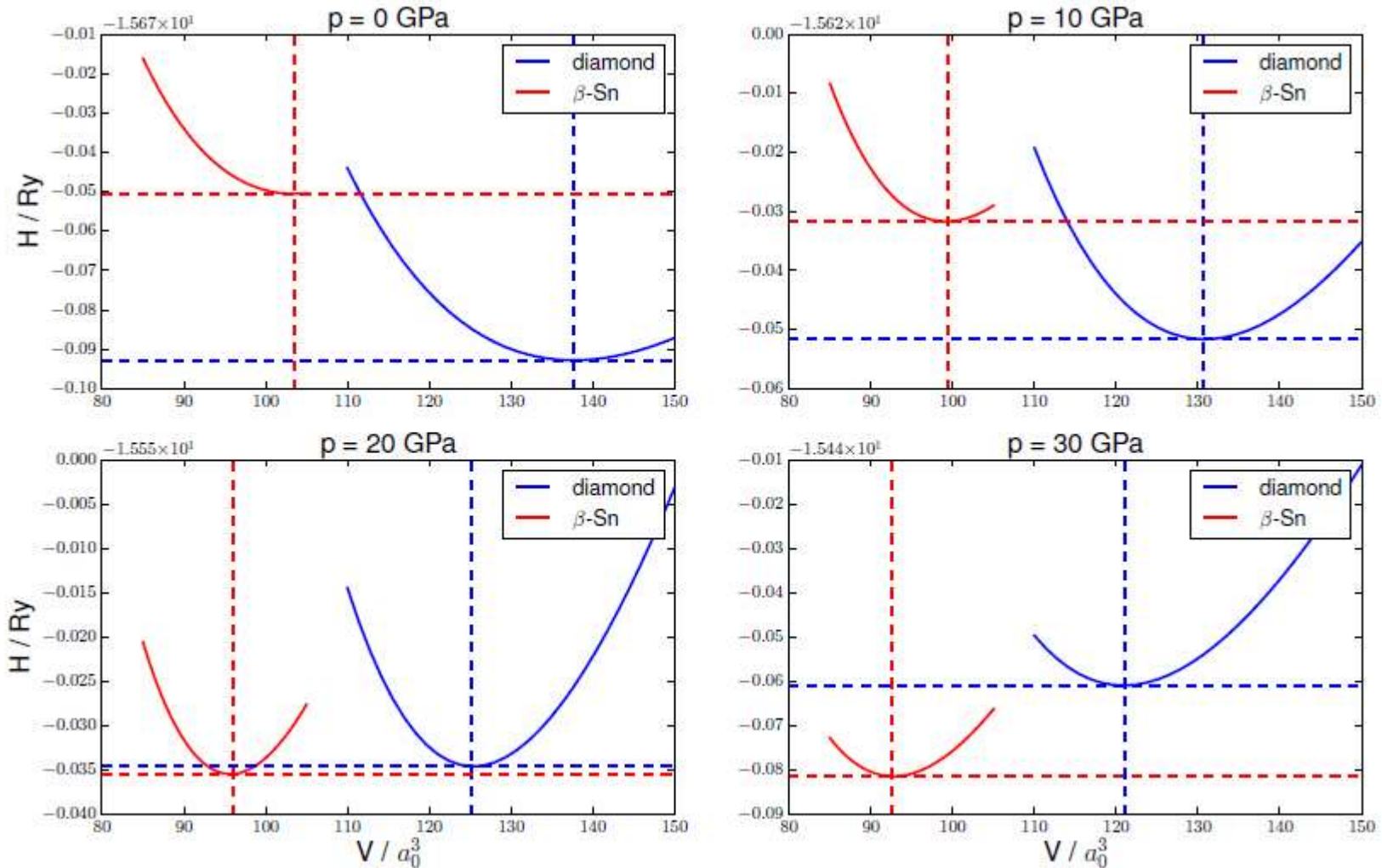


β -Sn, white tin, tetragonal

silicon makes a diamond to β -Sn transition under pressure



Structural phase transition in Si



Michael Scherbela 2015

Structural phase transition in Si

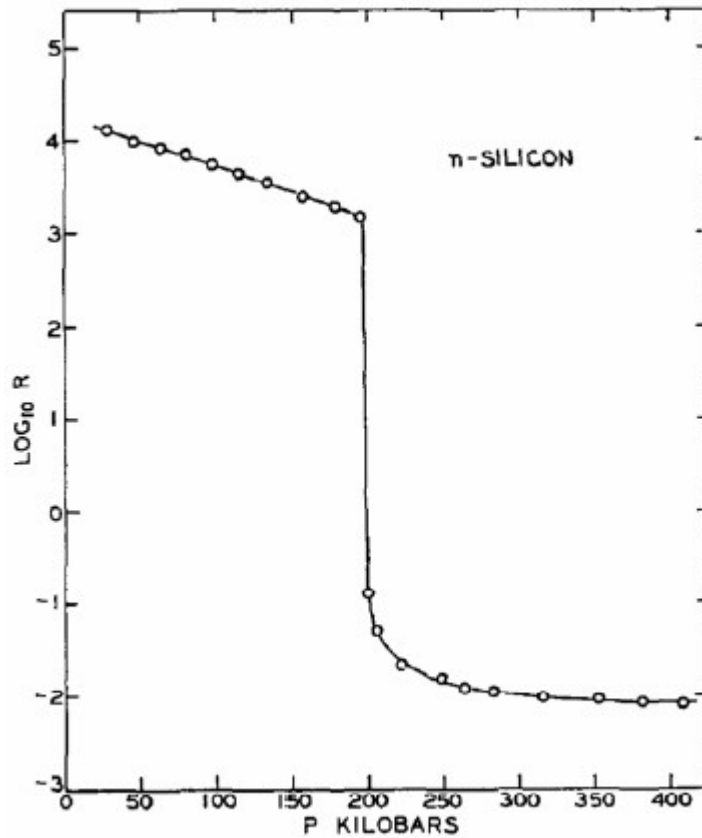
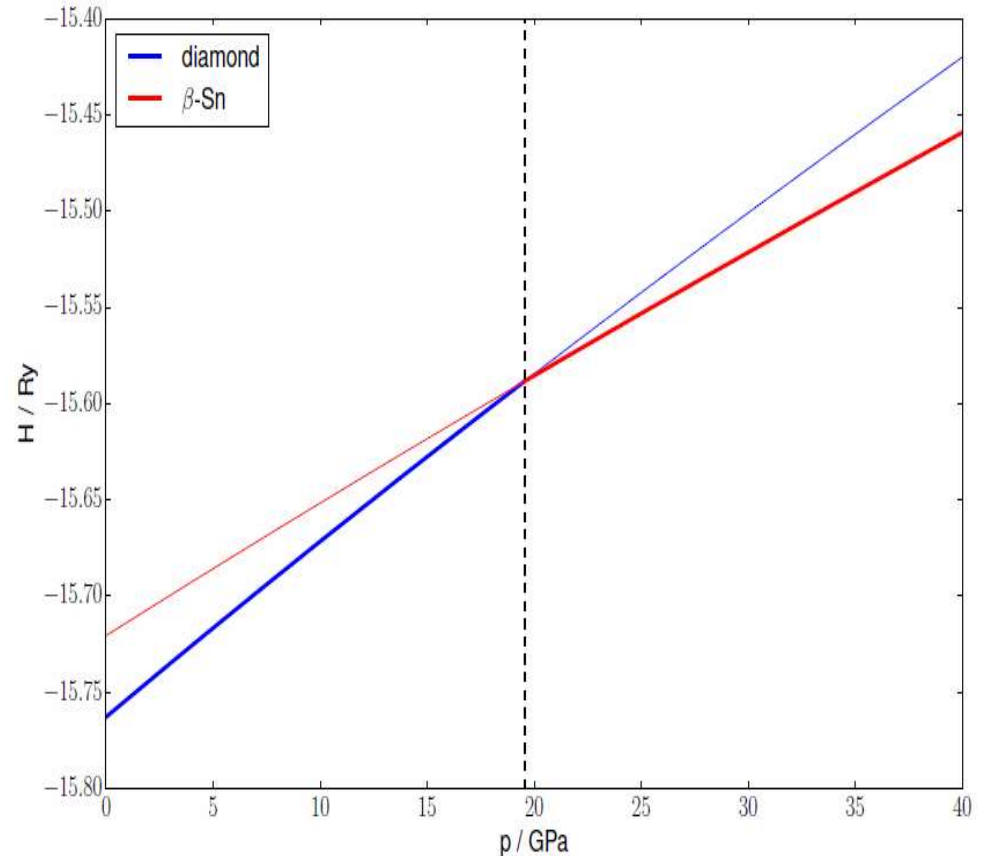


FIG. 1. Resistance vs. pressure—*n*-Silicon.



200 kbar = 20 GPa

Michael Scherbela 2015

H. G. D. S. Minomura, "Pressure induced phase transitions in silicon, germanium and some iii-v compounds," *J. Phys. Chem. Solids Pergamon Press*, vol. 23, pp. 451–456, 1962.

The surprising role of magnetism on the phase stability of Fe (Ferro)

1. Introduction

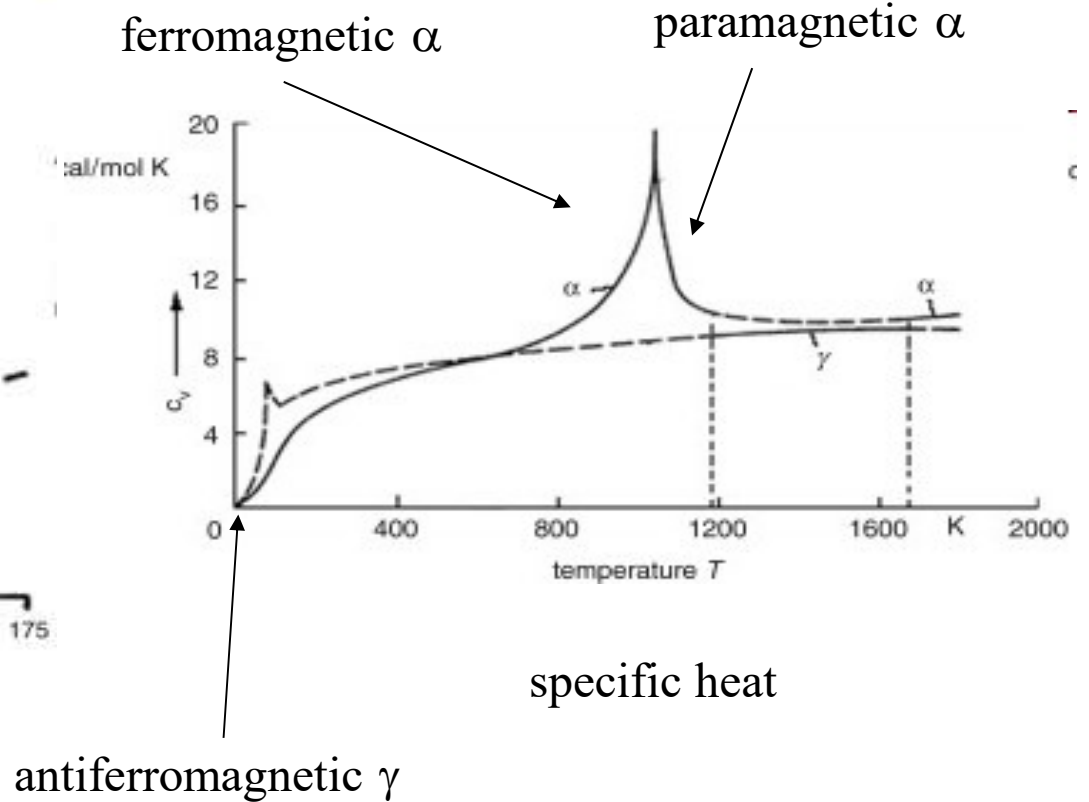
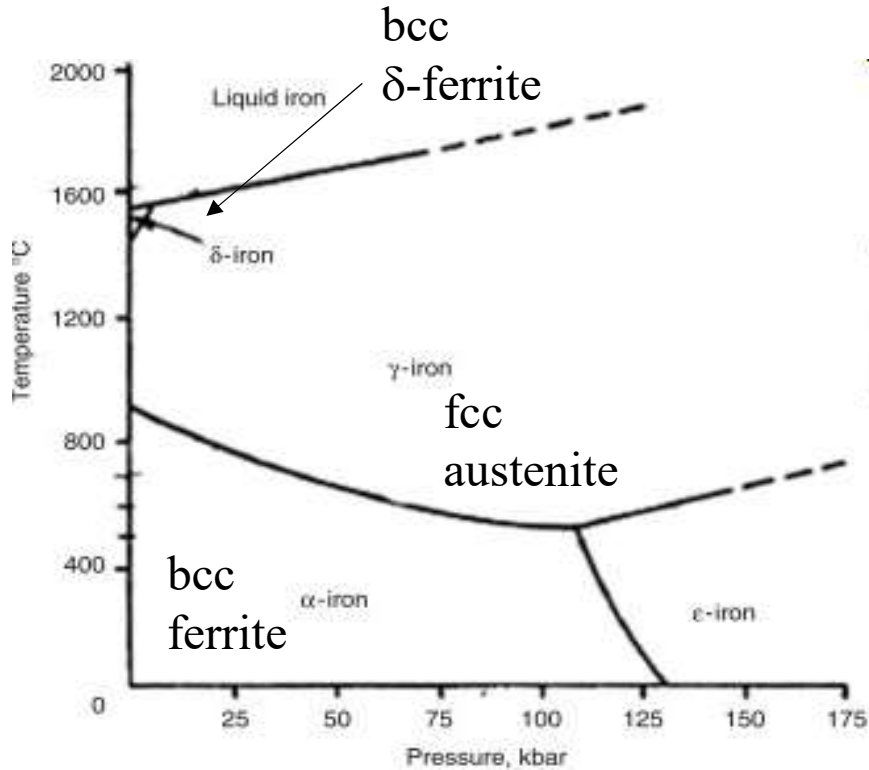
The phase stability of many elements shows the following pattern:

1. A low enthalpy is mainly responsible for the choice of structure at low temperatures.
2. At higher temperatures, structures (phases) are stable which have higher entropies.

This often translates into the low temperature phase being a close packed one and the high temperature phase having a more open structure, that is, a less close packed structure. For example, the low temperature phase of Ti is close packed hexagonal (HCP) while the high temperature phase is BCC.

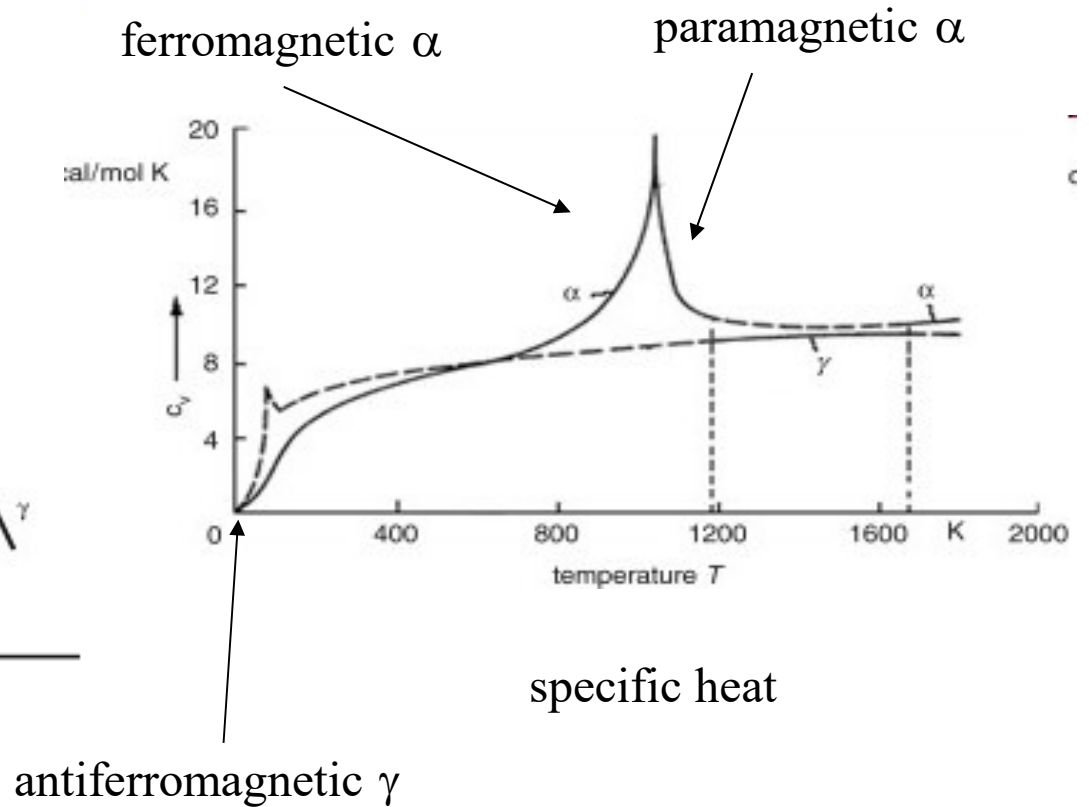
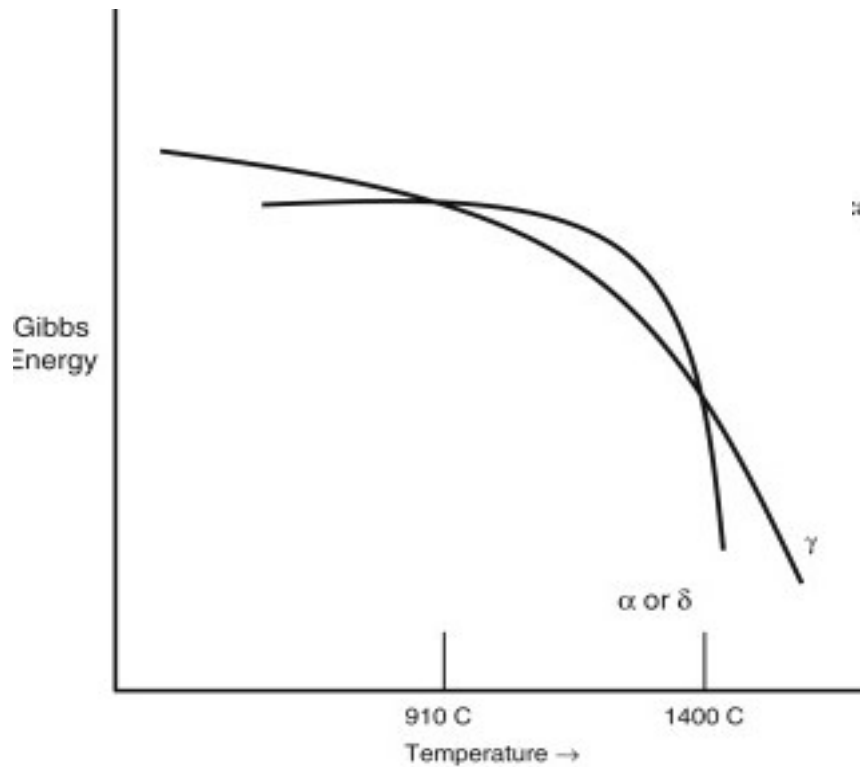
$$G = U + pV - TS$$

Structural phase transitions in iron



doi:10.1016/j.calphad.2008.07.009

Structural phase transitions in iron



doi:10.1016/j.calphad.2008.07.009

Iron alloy phases

Ferrite (α -iron, δ -iron)

Austenite (γ -iron)

Pearlite (88% ferrite, 12% cementite)

Martensite

Bainite

Ledeburite (austenite-cementite eutectic, 4.3% carbon)

Cementite (iron carbide, Fe_3C)

Beta ferrite (β -iron)

Hexaferrum (ϵ -iron)

Steel classes

Crucible steel

Carbon steel ($\leq 2.1\%$ carbon; low alloy)

Spring steel (low or no alloy)

Alloy steel (contains non-carbon elements)

Maraging steel (contains nickel)

Stainless steel (contains $\geq 10.5\%$ chromium)

Weathering steel

Tool steel (alloy steel for tools)

Other iron-based materials

Cast iron ($> 2.1\%$ carbon)

Ductile iron

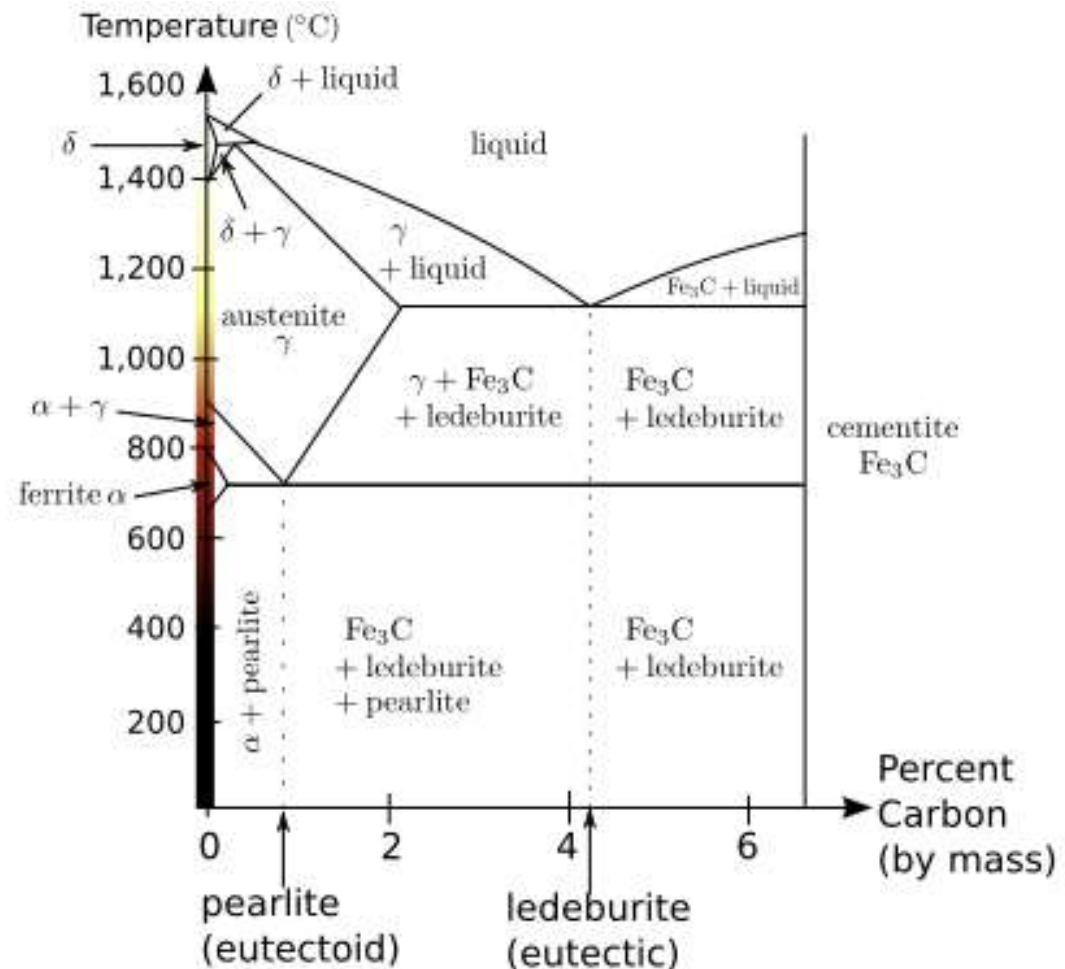
Gray iron

Malleable iron

White iron

Wrought iron (contains slag)

v · d · e



Electron-electron interactions

Including electron-electron interactions into the description of solids is very, very difficult.

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

One of the simplest approximation is to say that the electron-electron interactions screen the nuclei-electron interactions.

Screening = Abschirmung

Electron screening (Abschirmung)

$$\nabla \cdot \vec{E} = \frac{e\delta(r)}{\epsilon_0} \quad \vec{E} = -\nabla V$$

Poisson equation

$$\nabla^2 V = -\frac{e\delta(r)}{\epsilon_0} \quad V = \frac{e}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}$$

If a charge is put in a metal, the other charges will move

$$\nabla^2 V = -\frac{e\delta(r)}{\epsilon_0} - \frac{\rho_{ind}}{\epsilon_0}$$

If ρ_{ind} is proportional to $-V$,

$$\frac{\rho_{ind}}{\epsilon_0} = -k_s^2 V$$

The Helmholtz equation in 3-d

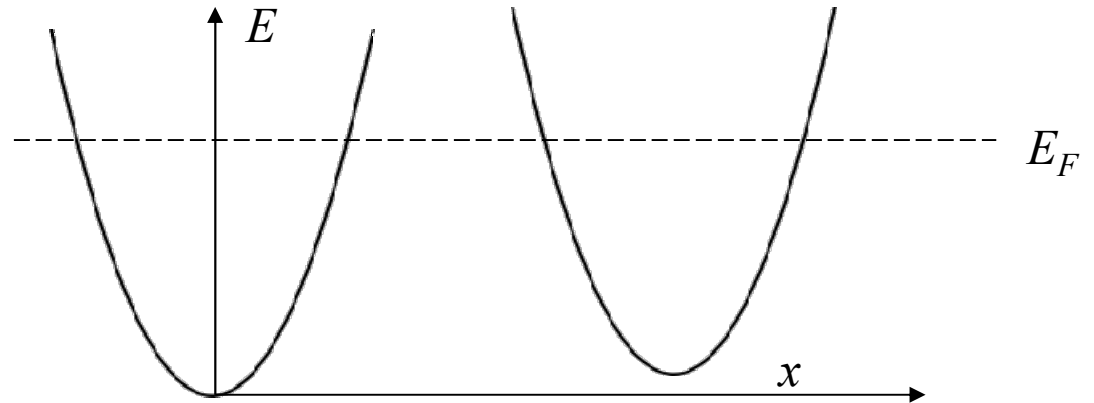
$$\nabla^2 V - k_s^2 V = -\frac{e\delta(r)}{\epsilon_0} \quad V = \frac{e \exp(-k_s |\vec{r} - \vec{r}'|)}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}$$

Thomas-Fermi screening

$$\Delta n = -D(E_F)eV$$

$$\rho_{ind} = e\Delta n = -e^2 D(E_F)V$$

$$D(E_F) = \frac{3n}{2E_F}$$



$$\nabla^2 V = -\frac{e\delta(r)}{\epsilon_0} - \frac{\rho_{ind}}{\epsilon_0} = -\frac{e\delta(r)}{\epsilon_0} + \frac{3e^2 n}{2\epsilon_0 E_F} V$$

$$\nabla^2 V - \frac{3e^2 n}{2\epsilon_0 E_F} V = -\frac{e\delta(r)}{\epsilon_0}$$

Thomas - Fermi screening length

$$k_s^2 = \frac{3e^2 n}{2\epsilon_0 E_F} = \frac{3^{1/3} m e^2 n^{1/3}}{\epsilon_0 \hbar^2 \pi^{4/3}}$$

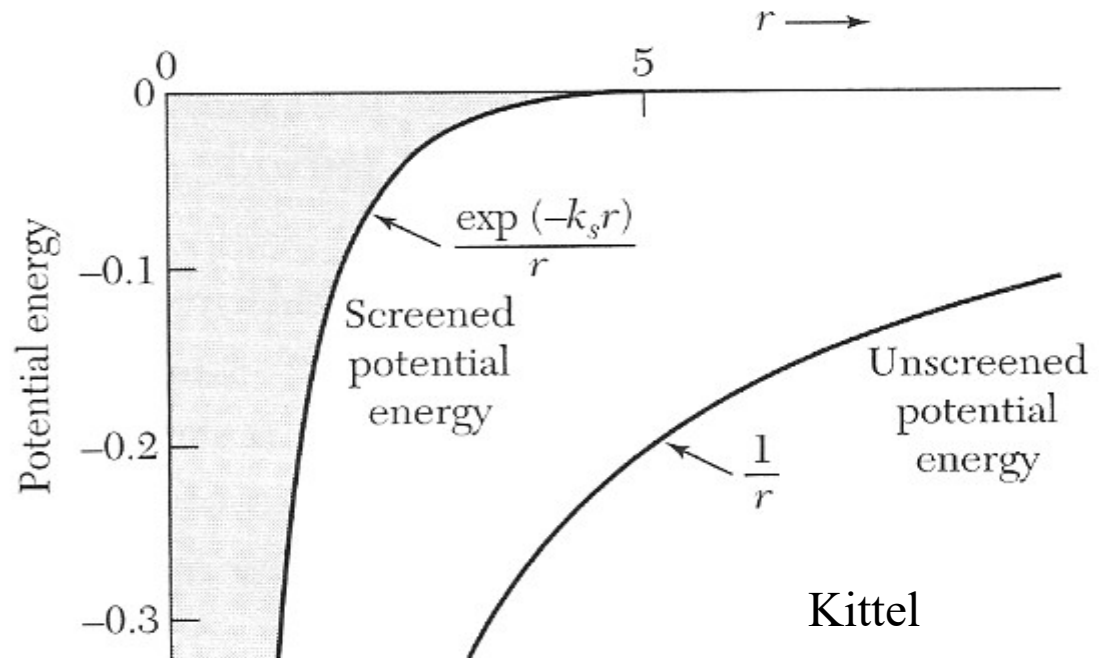
$$V = \frac{-e \exp(-k_s |\vec{r} - \vec{r}'|)}{4\pi\epsilon |\vec{r} - \vec{r}'|}$$

Electron screening

$$V = \frac{-\exp(-k_s |\vec{r} - \vec{r}'|)}{4\pi\epsilon |\vec{r} - \vec{r}'|}$$

$$k_s^2 = \frac{3e^2 n}{2\epsilon_0 E_F} = \frac{3^{1/3} m e^2 n^{1/3}}{\epsilon_0 \hbar^2 \pi^{4/3}}$$

Thomas - Fermi screening length



$$k_s^2 \propto n^{1/3}$$

Screening length depends on the electron density