Phase transitions

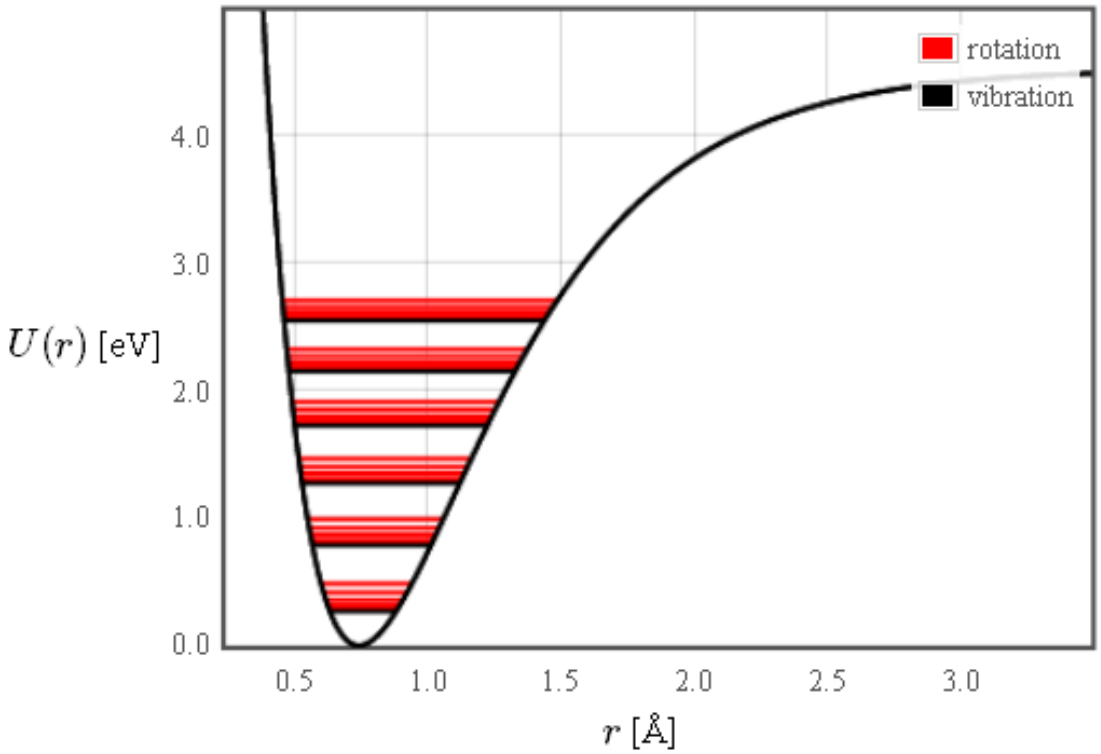
Anharmonic terms

Expand the energy in terms of the normal modes of the linearized problem u_k

$$U = U_0 + \frac{\partial U}{\partial u_k} u_k + \frac{1}{2} \frac{\partial^2 U}{\partial u_j \partial u_k} u_j u_k + \frac{1}{6} \frac{\partial^3 U}{\partial u_i \partial u_j \partial u_k} u_i u_j u_k + \frac{1}{24} \frac{\partial^4 U}{\partial u_h \partial u_i \partial u_j \partial u_k} u_h u_i u_j u_k + \cdots$$

Thermal expansion
Thermal conductivity limited by Umklapp scattering
High temperature limit of specific heat does not approach the Dulong-Petit law

Nonlinear effects



Thermal expansion

Thermal conductivity limited by Umklapp scattering

High temperature limit of specific heat does not approach the Dulong-Petit law

Structural phase transitions

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

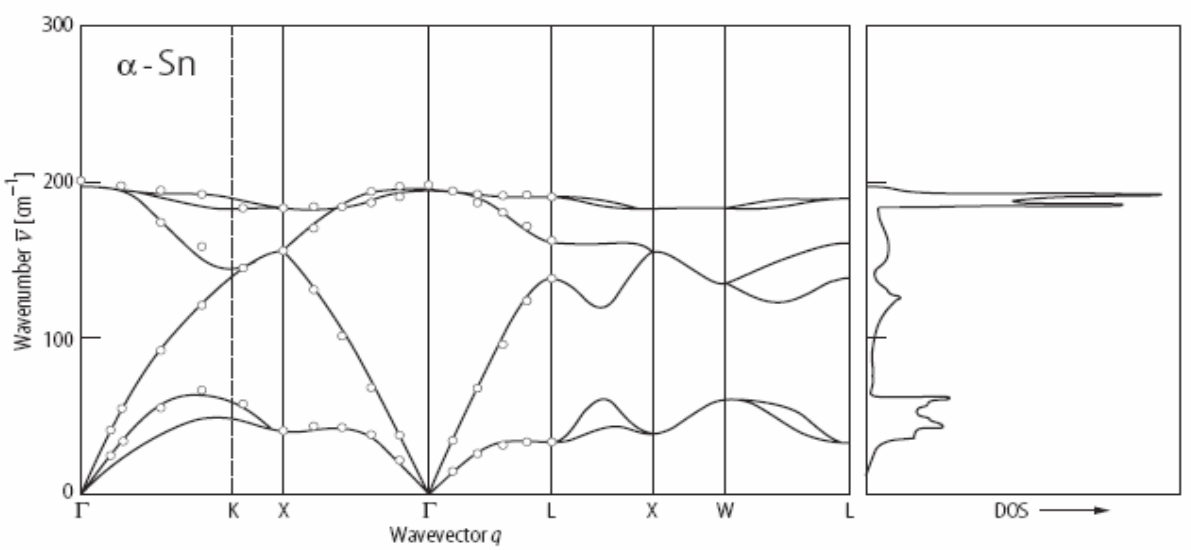
Two allotropes of tin: gray tin (α-Sn) is stable at temperatures below 13.2°C and white tin (β-Sn) is stable above.

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

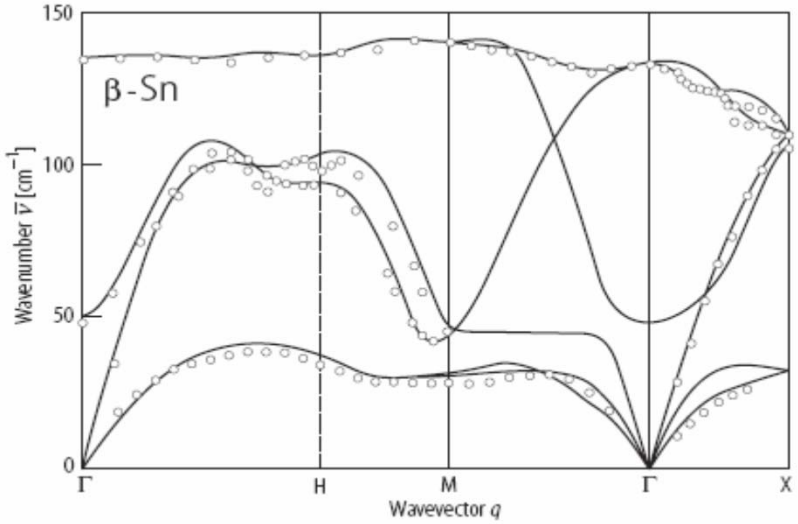
$$F = U - TS$$

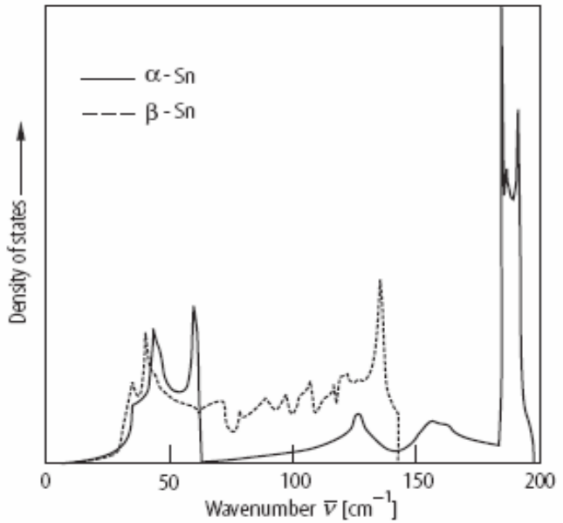
Structural phase transition in Sn

semiconductor
diamond crystal
structure

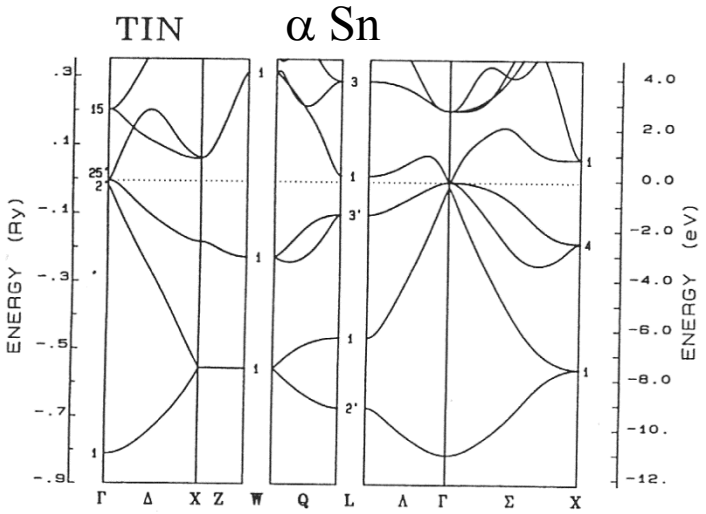


metal
tetragonal
crystal structure

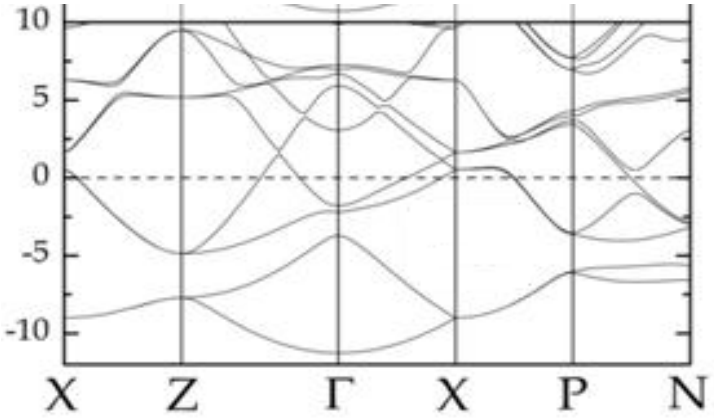




Structural phase transition in Sn



metal β Sn



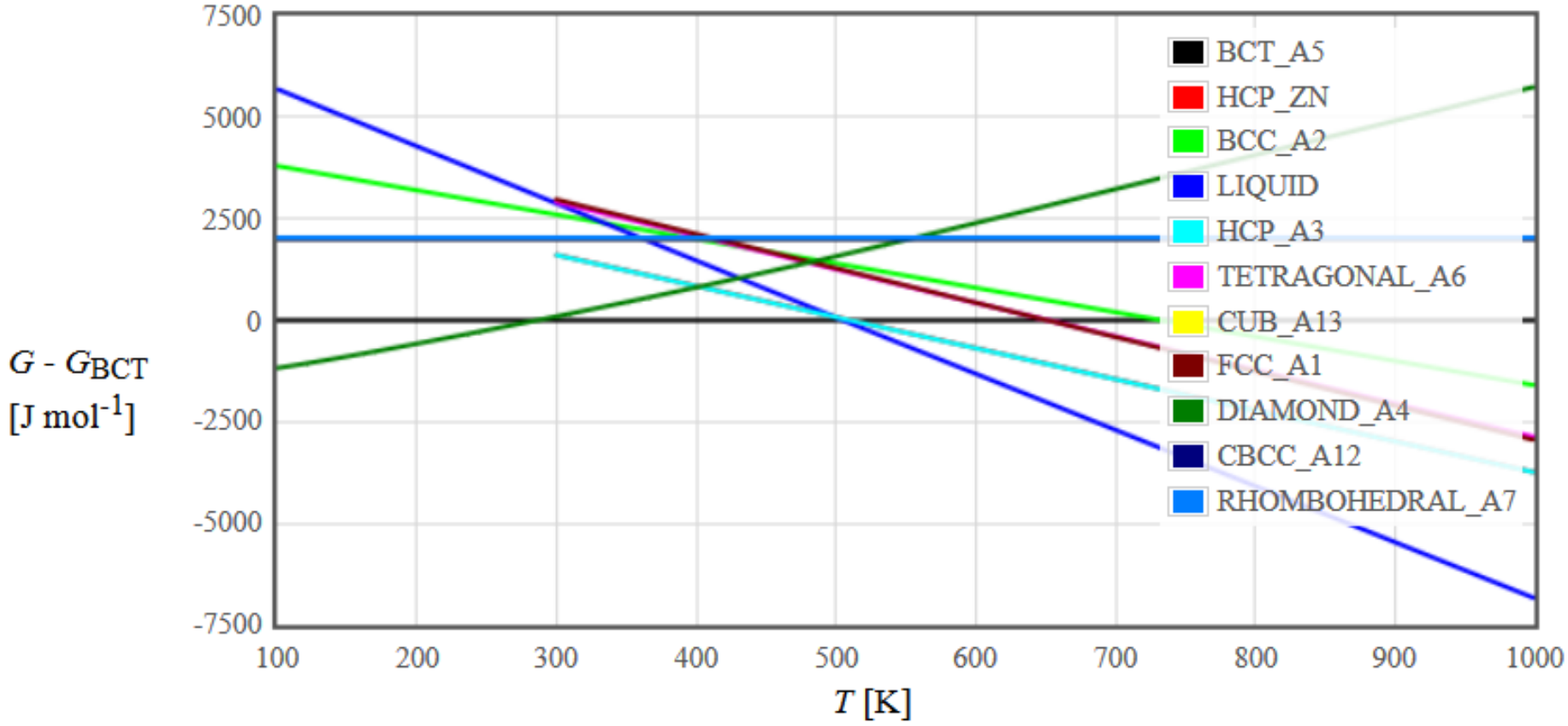
$$s \approx \frac{\pi^2 D(E_F)}{3} k_B^2 T$$

semiconductor: electrons make a negligible contribution to the entropy

$$s = \frac{\sqrt{2\pi}}{2\pi^2\hbar^3}\left(m_e^* m_h^*\right)^{3/4} \exp\left(\frac{-E_g}{2k_B T}\right)\left(k_B T\right)^{3/2}\left(5k_B + \frac{E_g}{T}\right),$$

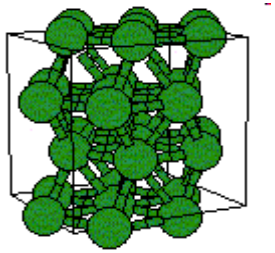
Structural phase transition in Sn

metal β Sn = A5



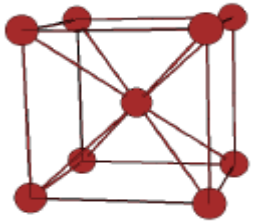
http://lampx.tugraz.at/~hadley/ss1/materials/sgte/SGTE.html

Structural phase transitions

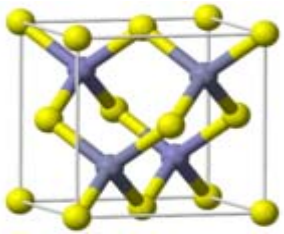


α-Ti, hcp

transition at 890 C



β-Ti, bcc



Zincblende, ZnS

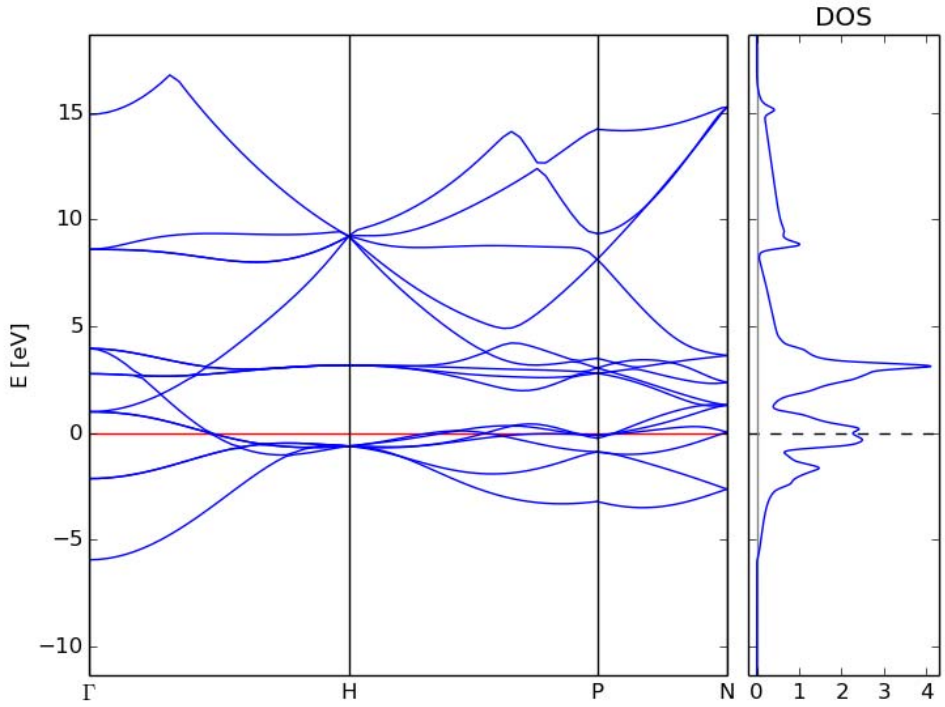
transition at 1020 C

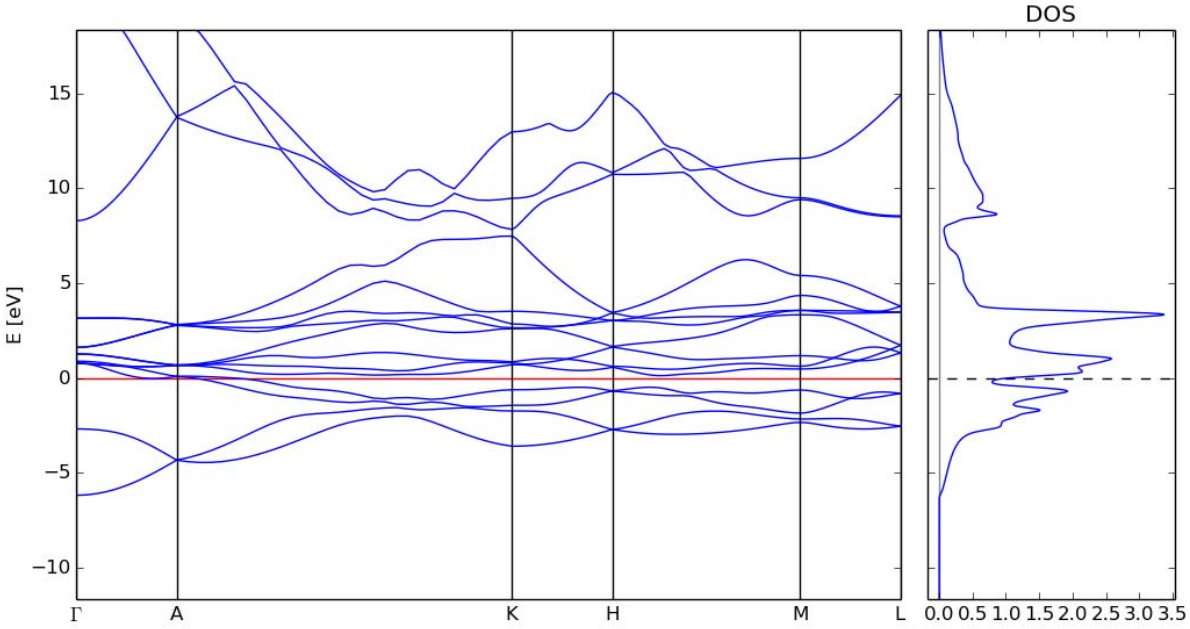
Wurtzite, ZnS

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

Titanium

bcc →



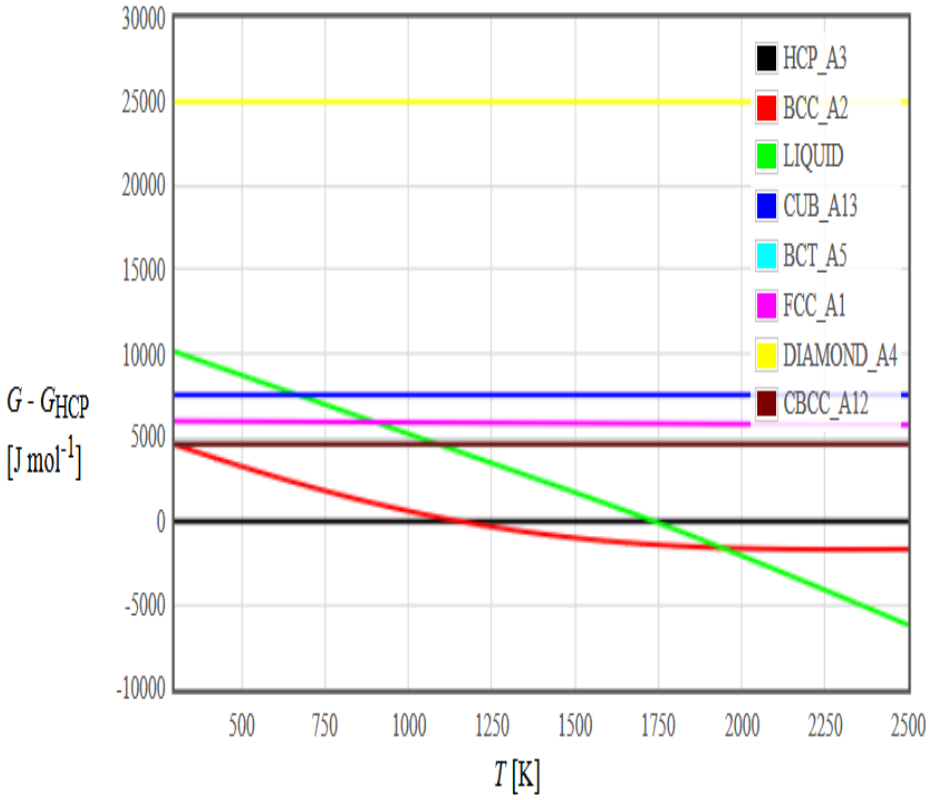


← hcp

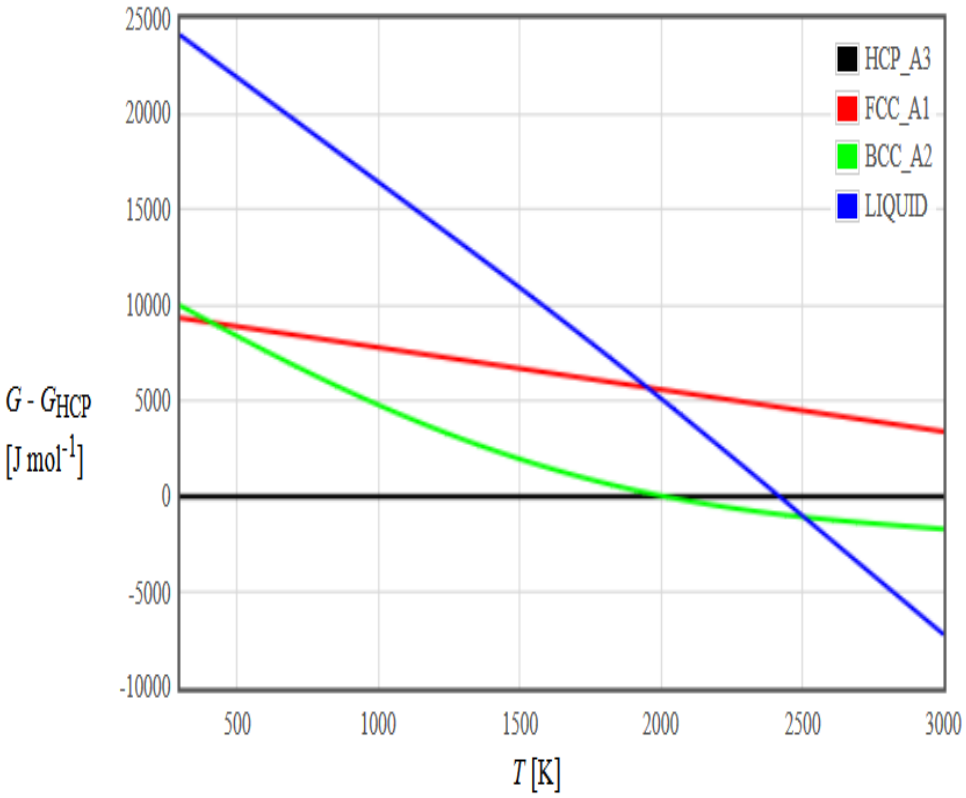
Calculated using FHI-aims by Lydia Nemec

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

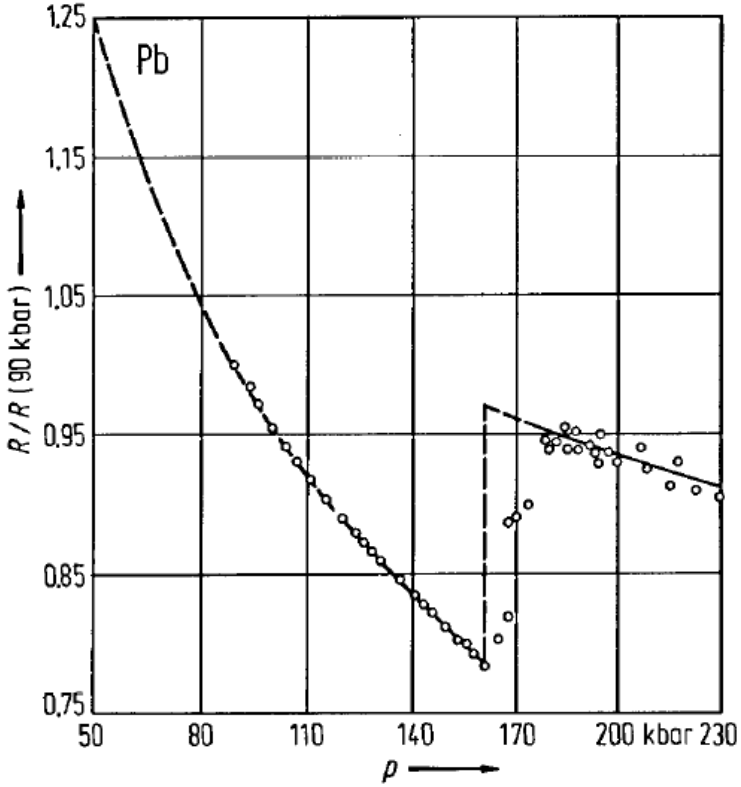
Strain

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

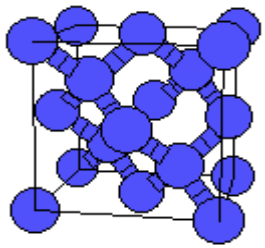
This changes the density of states and the thermodynamic properties.

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.

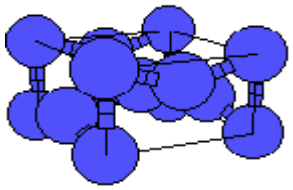


Structural phase transitions



α-Sn, gray tin, diamond

transition at 13 C



β-Sn, white tin, tetragonal

silicon makes a diamond to β-Sn transition under pressure