

# 26. Phase Transitions

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Physical properties of crystals  
Edited by A. Authier

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## Chapter 1.6. Classical linear crystal optics<sup>1</sup>

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## Chapter 1.7. Nonlinear optical properties

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# Rank 4 Tensors

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Stiffness tensor

Compliance tensor

Piezoconductivity

Electrostriction

Magnetostriction

How the Seebeck effect depends on stress

How the electric susceptibility depends on stress

How the magnetic susceptibility depends on stress

Nonlinear electric susceptibility

Nonlinear magnetic susceptibility

# Symmetric and asymmetric tensors

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$$-\left(\frac{\partial^2 G}{\partial E_j \partial E_k}\right) = \frac{\partial P_k}{\partial E_j} = \chi_{kj} = -\left(\frac{\partial^2 G}{\partial E_k \partial E_j}\right) = \frac{\partial P_j}{\partial E_k} = \chi_{jk}$$

## Symmetric

electric susceptibility  
magnetic susceptibility  
electrical conductivity  
thermal conductivity  
stiffness tensor

## Asymmetric

Seebeck effect  
Peltier effect  
piezoconductivity

# Anharmonic terms

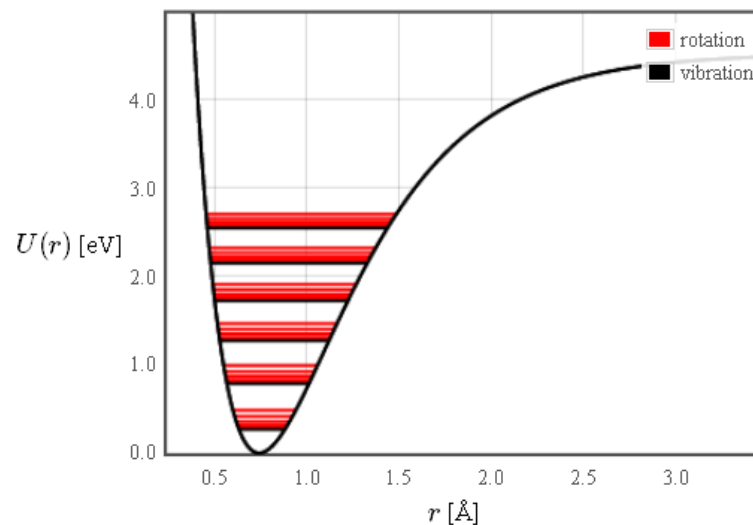
Expand the energy in terms of the normal modes of the linearized problem  $u_k$

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

Thermal expansion

Thermal conductivity limited by Umklapp scattering

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



# Phase transitions

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# Structural phase transitions

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

Two allotropes of tin: gray tin ( $\alpha$ -Sn) is stable at temperatures below 13.2°C and white tin ( $\beta$ -Sn) is stable above.

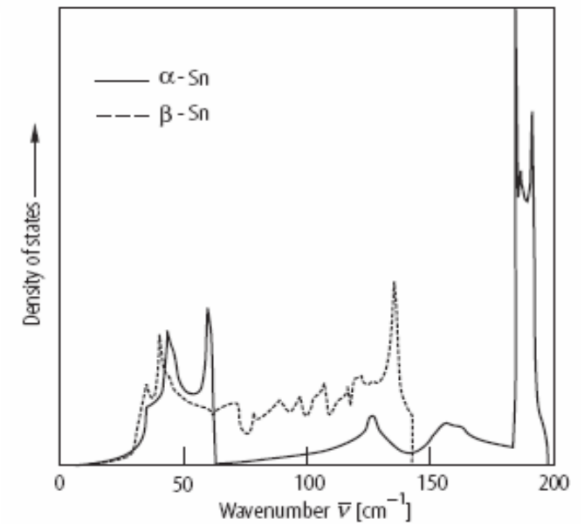
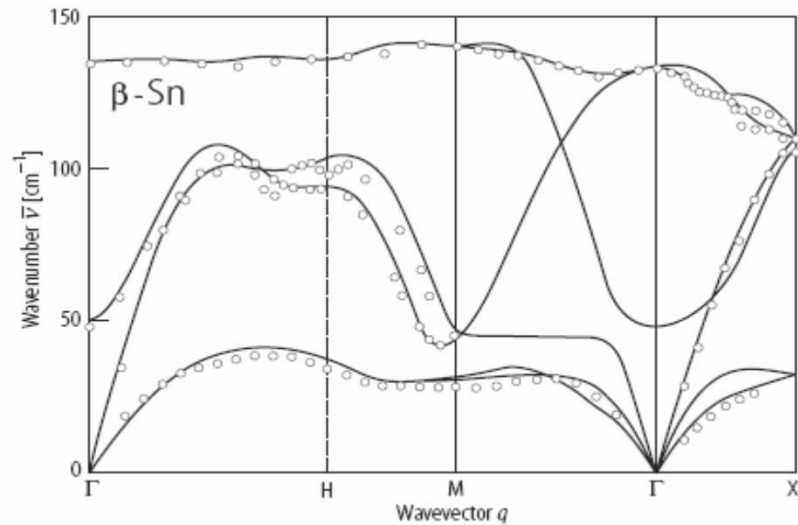
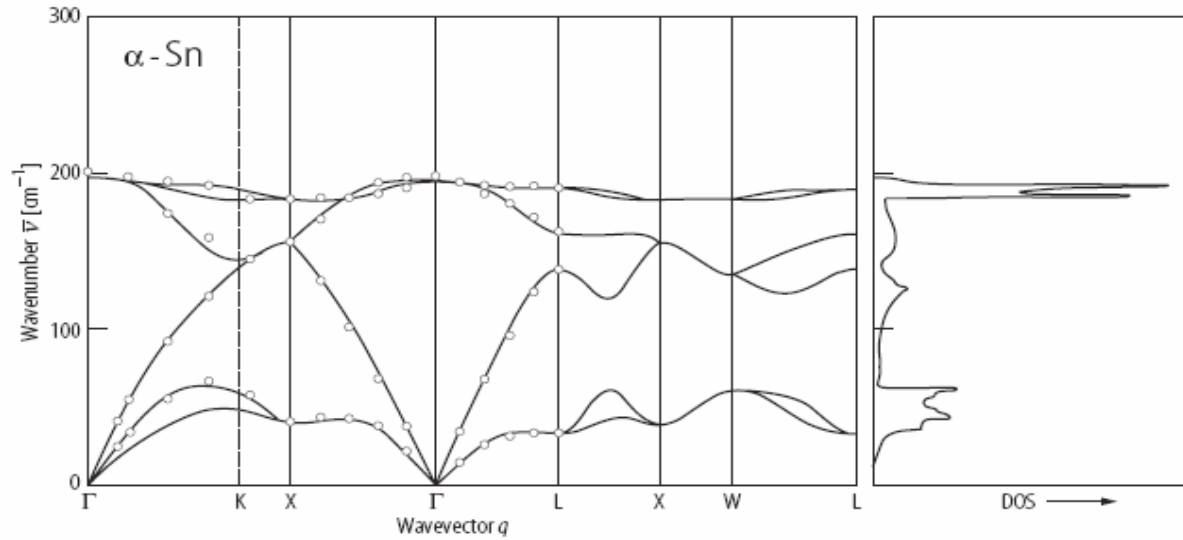
The phase with the lowest free energy prevails. (White tin can be stabilized below 13.2 C by adding impurities.)

$$F = U - TS$$

# Structural phase transition in Sn

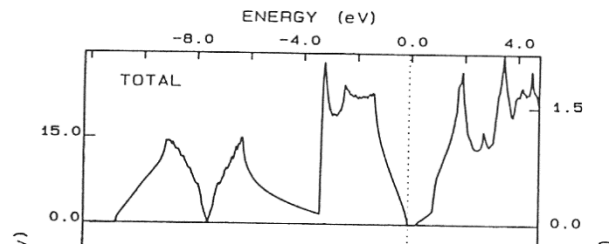
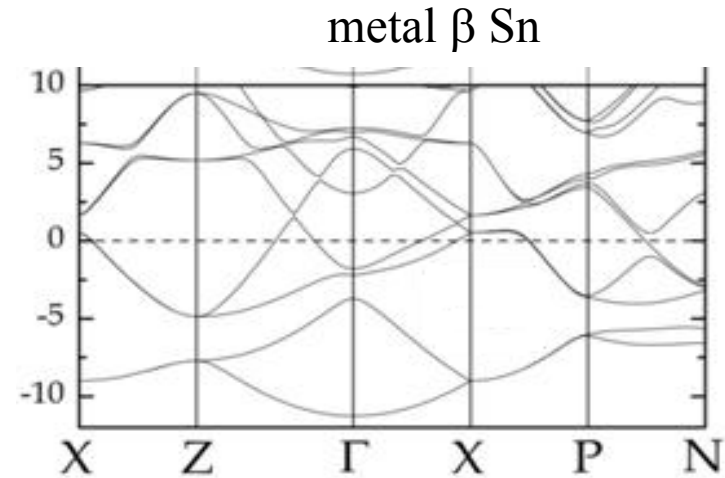
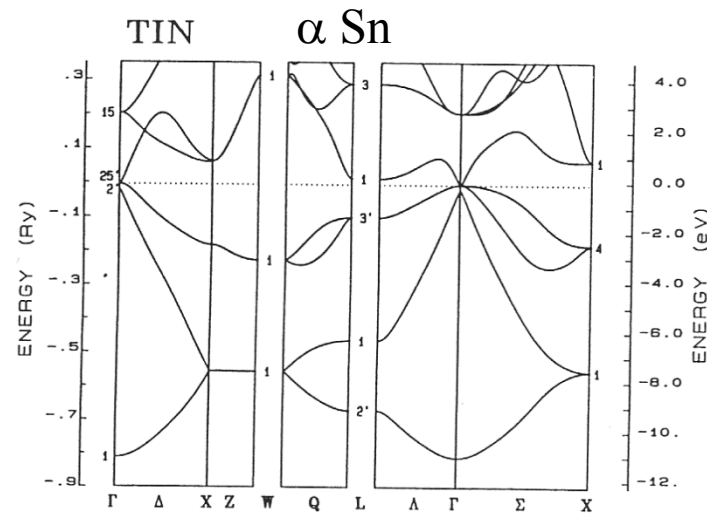
semiconductor  
diamond crystal  
structure

metal  
tetragonal  
crystal structure





# Structural phase transition in Sn



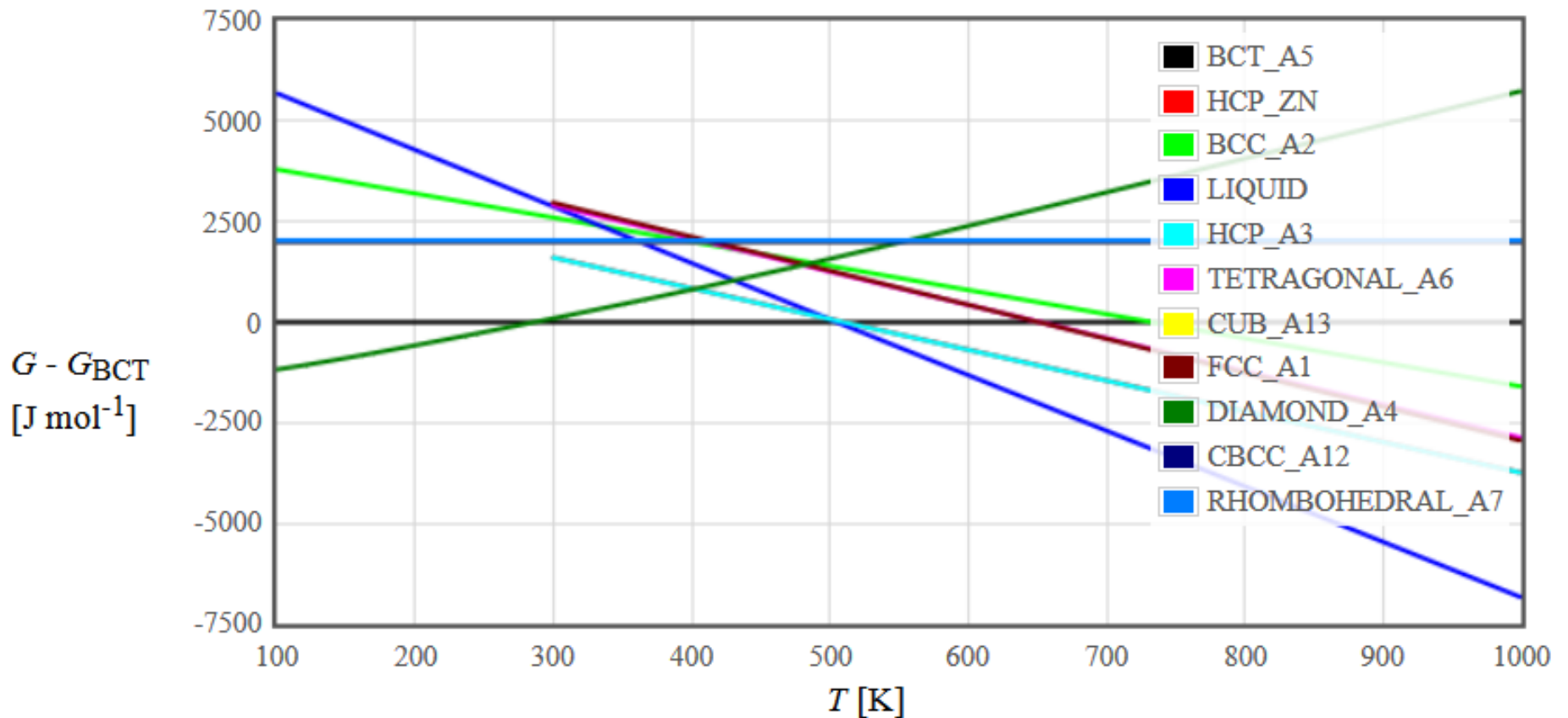
semiconductor: electrons make a negligible contribution to the entropy

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

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

# Structural phase transition in Sn

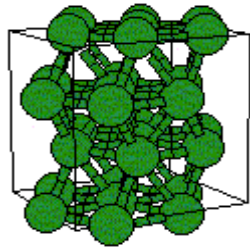
metal  $\beta$  Sn = A5



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

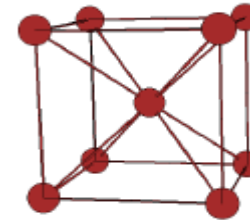
# Structural phase transitions

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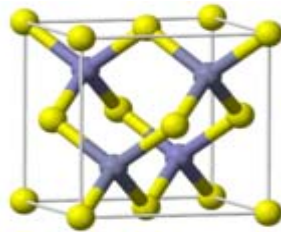


$\alpha$ -Ti, hcp

transition at 890 C

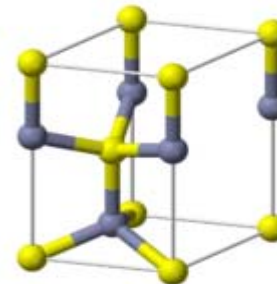


$\beta$ -Ti, bcc



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

# Ti phonon dispersion

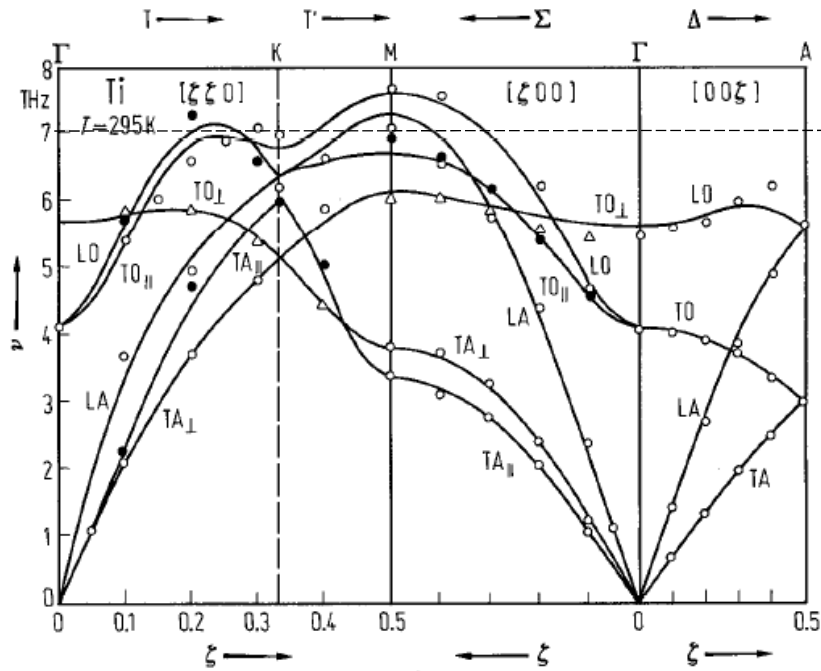


Fig. 1. Ti. Measured phonon dispersion curves at 295 K. The solid lines were obtained from the sixth neighbour Born-von Karman model of Table 3 Ti [79St2].

Springer Materials

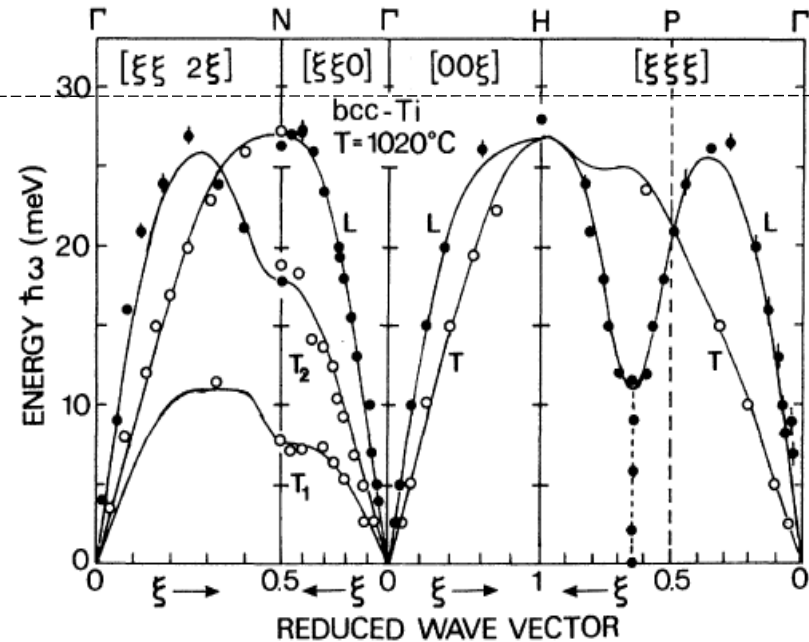


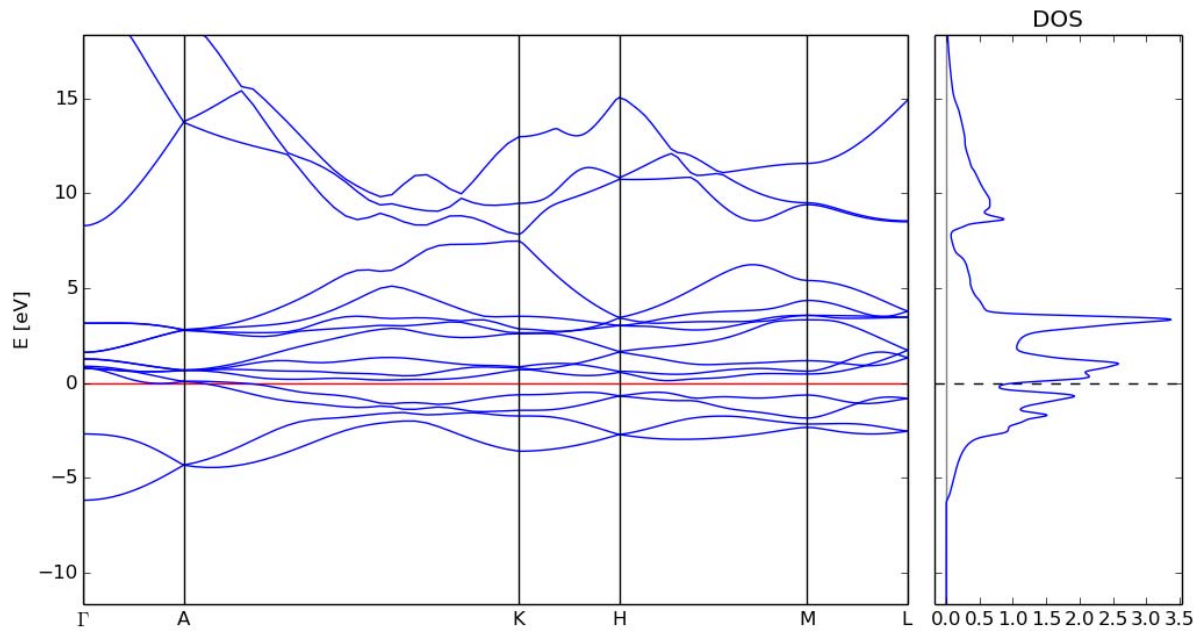
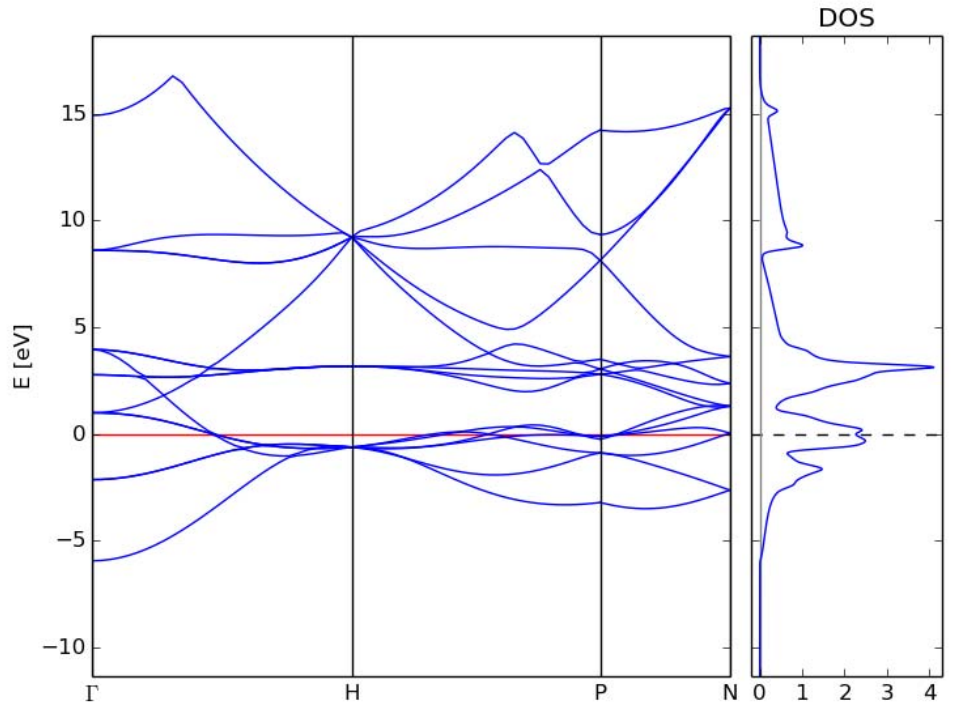
FIG. 2. Phonon dispersion for bcc Ti measured at 1020°C. (The  $T_1[\xi\xi0]$  branch has been measured at 965°C). The solid line shows a Born-von Kármán fit with force constants up to the fifth nearest-neighbor shell.

Phonon dispersion of the bcc phase of group-IV metals. I. bcc titanium, W. Petry, A. Heiming, J. Trampenau, M. Alba, C. Herzig, H. R. Schober, and G. Vogl, Phys. Rev. B 43, 10933 – (1991)

# Titanium



bcc →

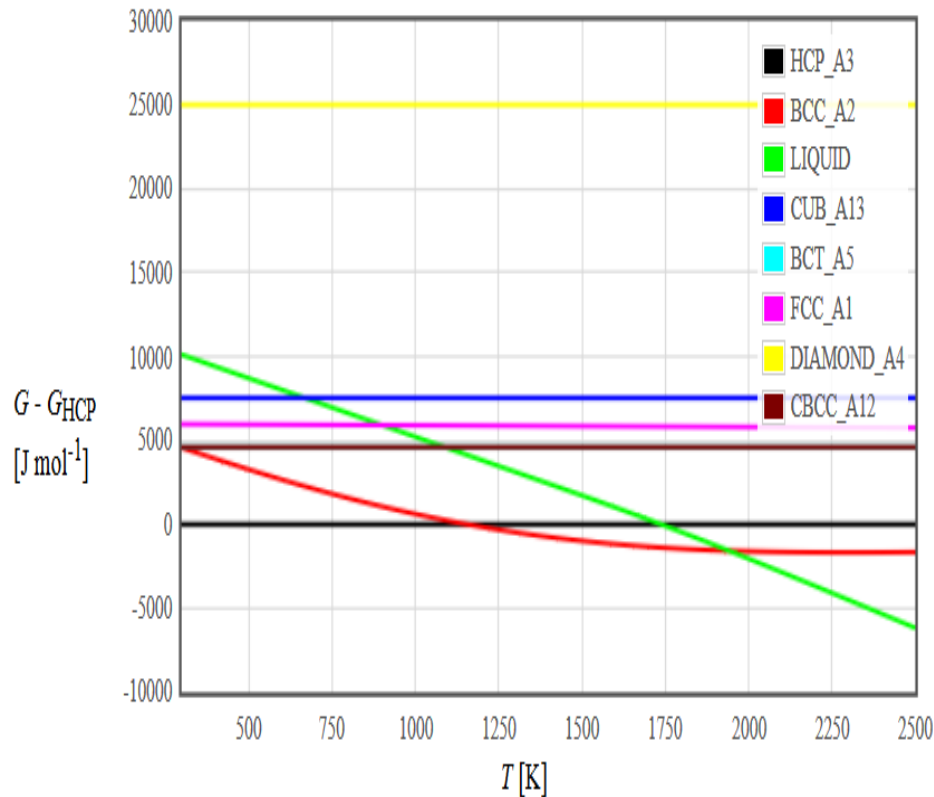


← hcp

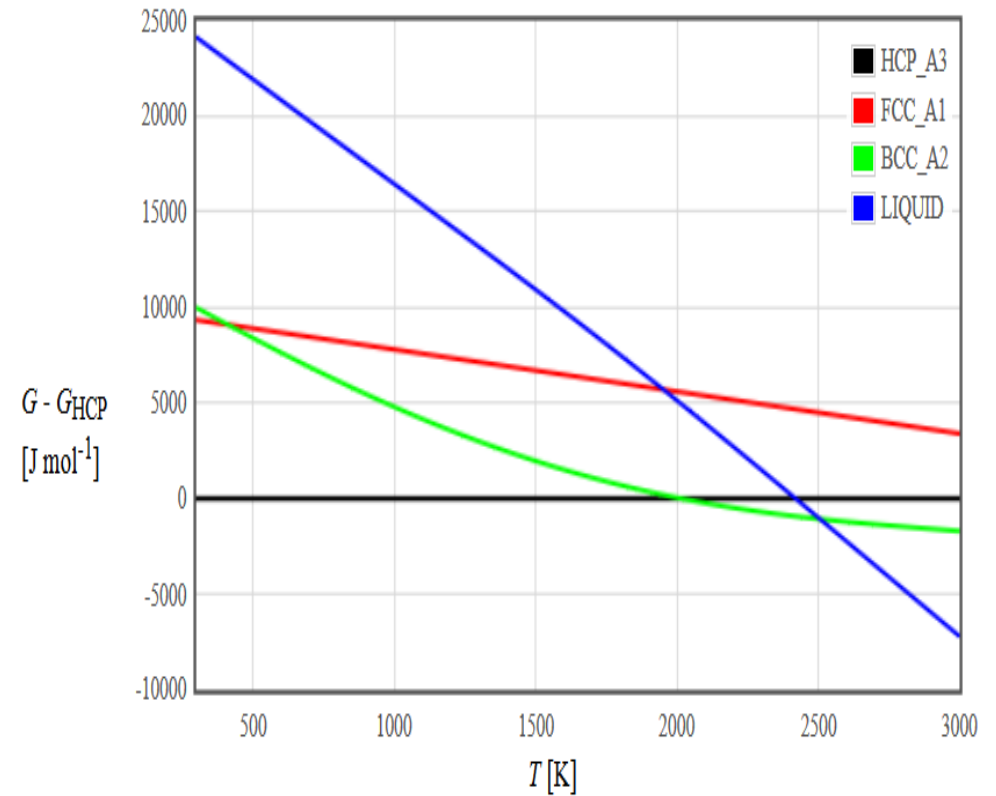
Calculated using FHI-aims by Lydia Nemec

# Close packed $\rightarrow$ bcc

Ti



Hf



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

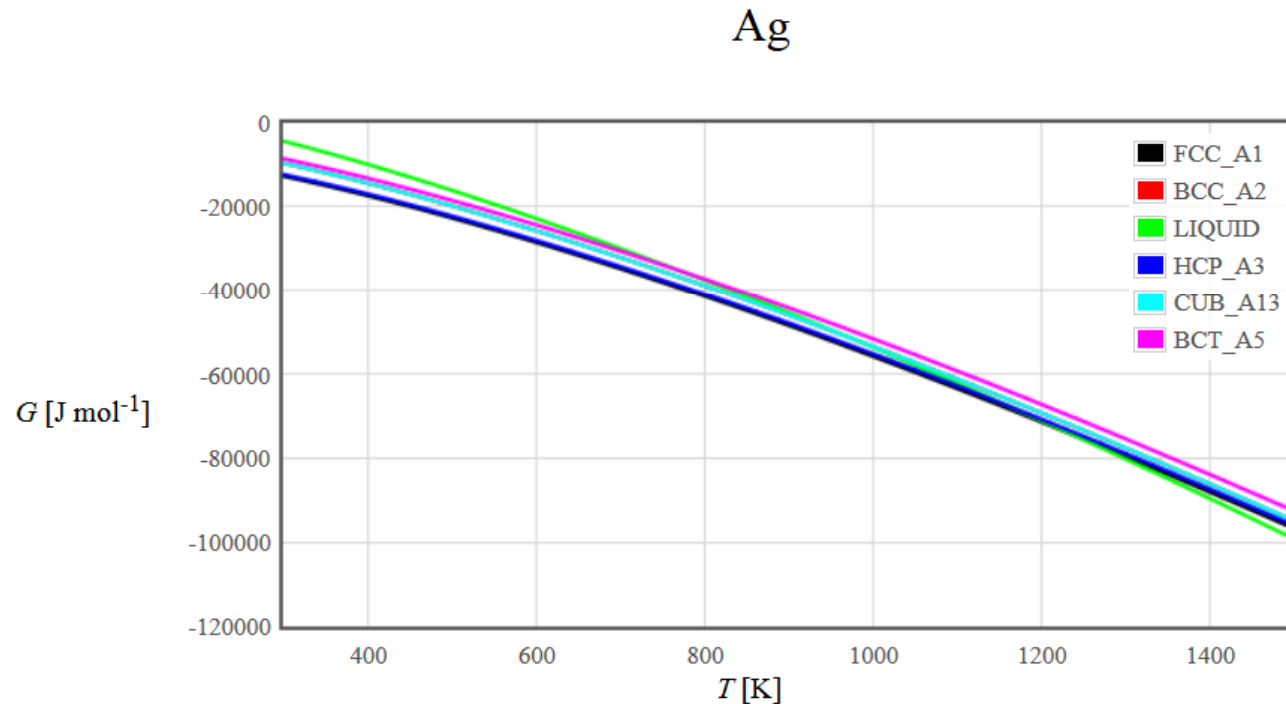
<http://lampx.tugraz.at/~hadley/ss1/materials/sgte/SGTE.html>

## SGTE thermodynamic data

The [Scientific Group Thermodata Europe SGTE](http://www.sgte.org) maintains [thermodynamic databanks for inorganic and metallurgical systems](http://www.sgte.org). Data from their 'pure element database' is plotted below.

Typically, experiments are performed at constant pressure  $p$ , temperature  $T$ , and number  $N$ . Under these conditions, the system will go to the minimum of the Gibbs energy  $G = U + pV - TS$ . Here  $U$  is the internal energy,  $V$  is the volume, and  $S$  is the entropy. The top plot is the Gibbs energy per mole.

Ag	Al	Am	As
Au	B	Ba	Be
Bi	C	Ca	Cd
Ce	Co	Cr	Cs
Cu	Dy	Er	Eu
Fe	Ga	Gd	Ge
Hf	Hg	Ho	In
Ir	K	La	Li
Lu	Mg	Mn	Mo
N	Na	Nb	Nd
Ni	Np	O	Os
P	Pa	Pb	Pd
Pr	Pt	Pu	Rb
Re	Rh	Ru	S
Sb	Sc	Se	Si
Sm	Sn	Sr	Ta
Tb	Tc	Te	Th
Ti	Tl	Tm	U
V	W	Y	Yb
Zn	Zr		



Since the Gibbs energies of the different phases fall almost on top of each other, it is convenient to plot them relative to the phase that has the lowest Gibbs energy at low temperature.

<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.

