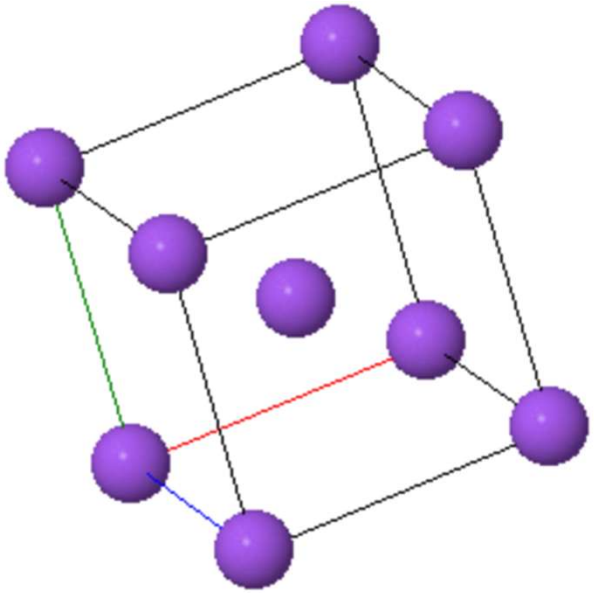
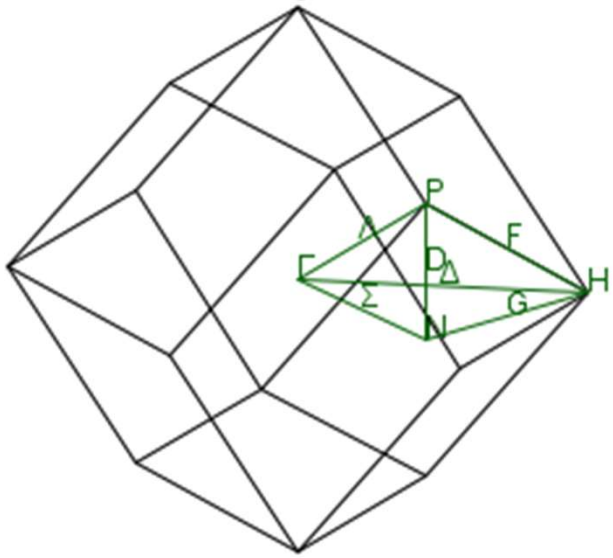
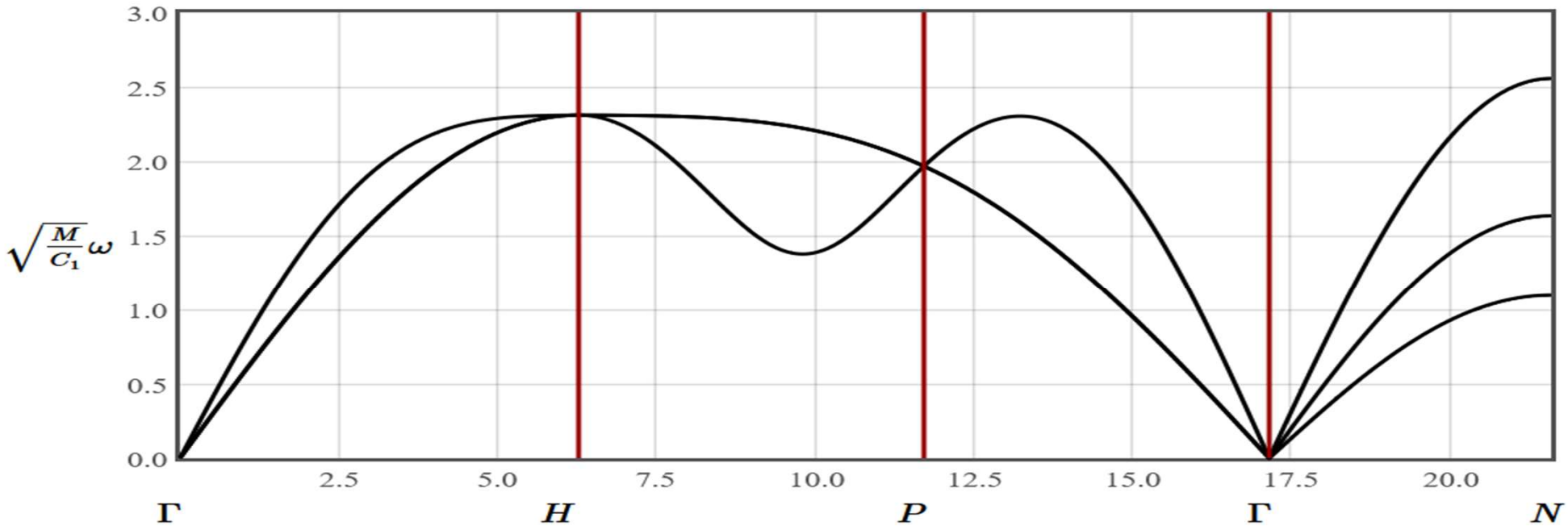
Phonons
Thermal properties

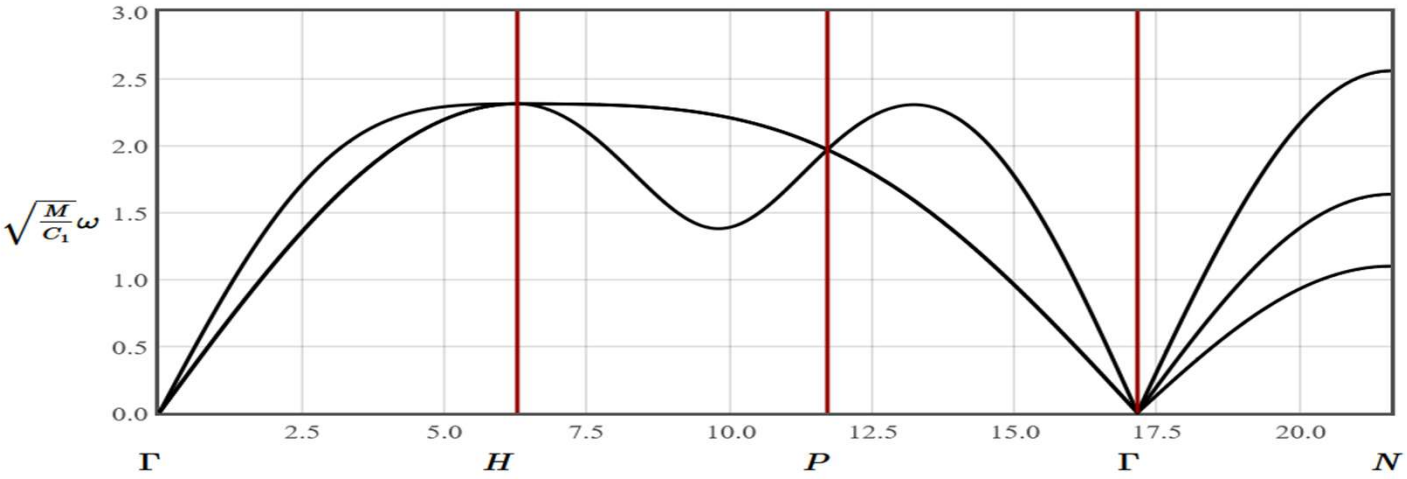
Phonon dispersion bcc

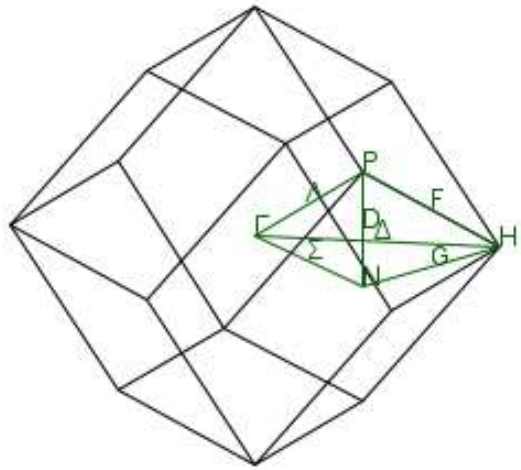






Phonon dispersion Fe





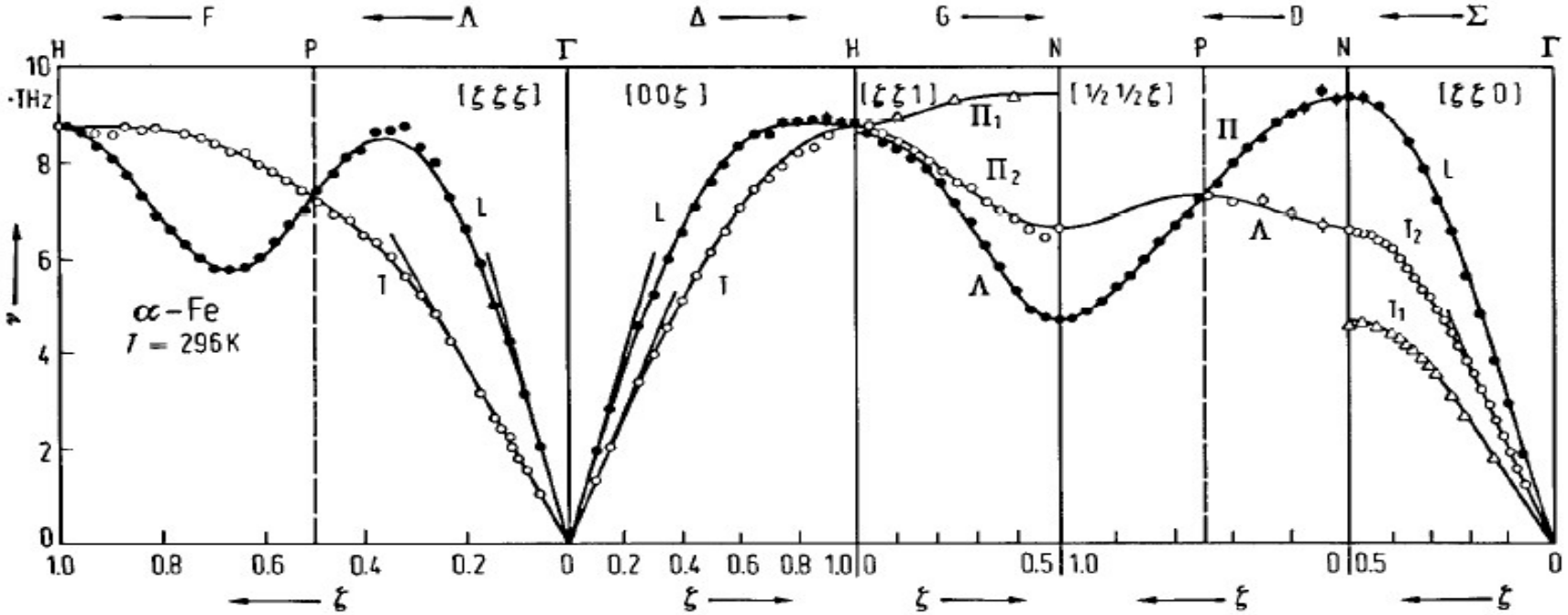
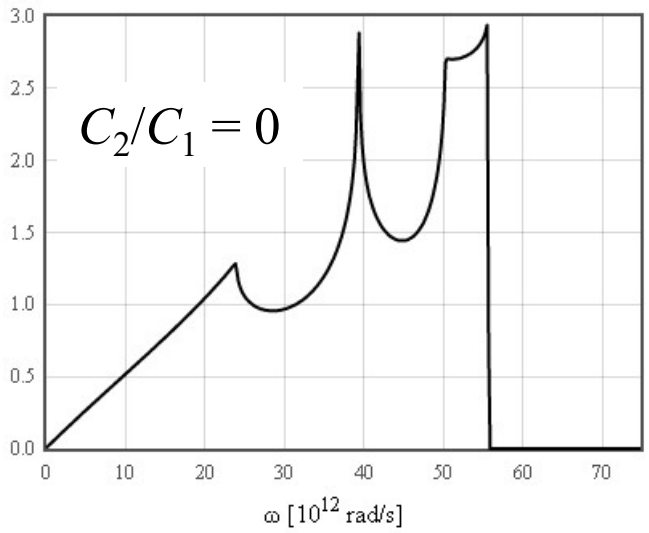
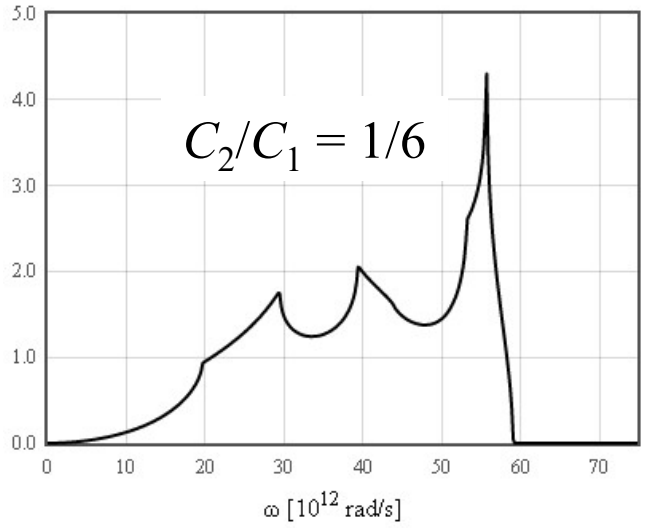


Fig. 2. Fe. Phonon dispersion curves in α-iron at 296 K. Experimental points: [68Va2]. Solid curve: fifth neighbour Born-von Karman model (Table 3 Fe [68Va2]).

From Springer Materials: Landholt Boernstein Database

Phonon DOS Fe





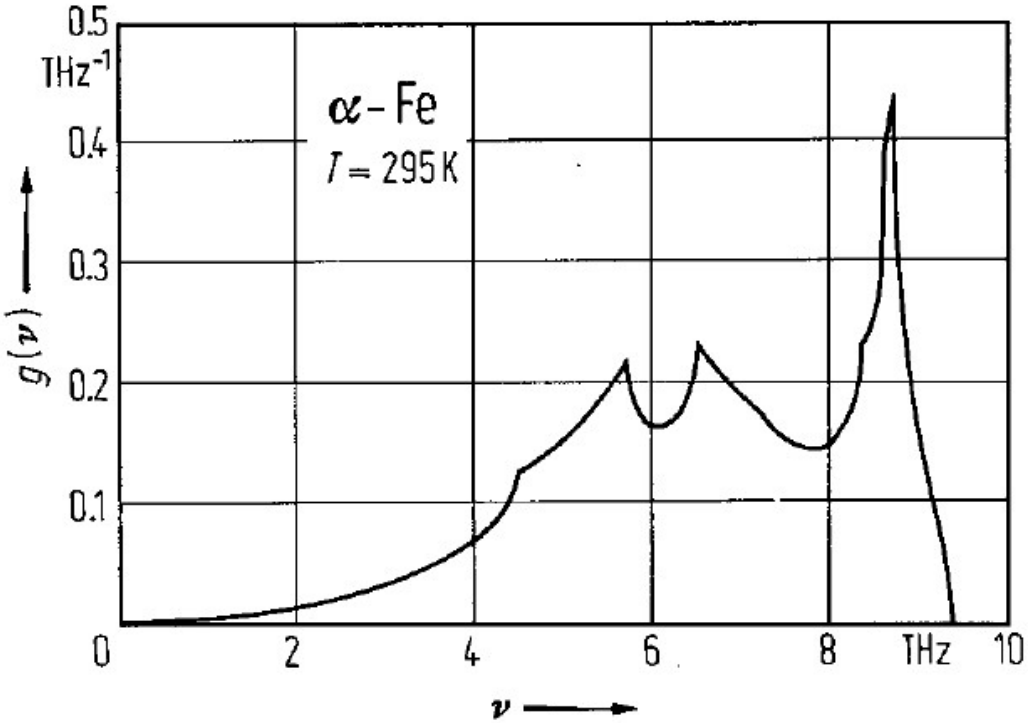
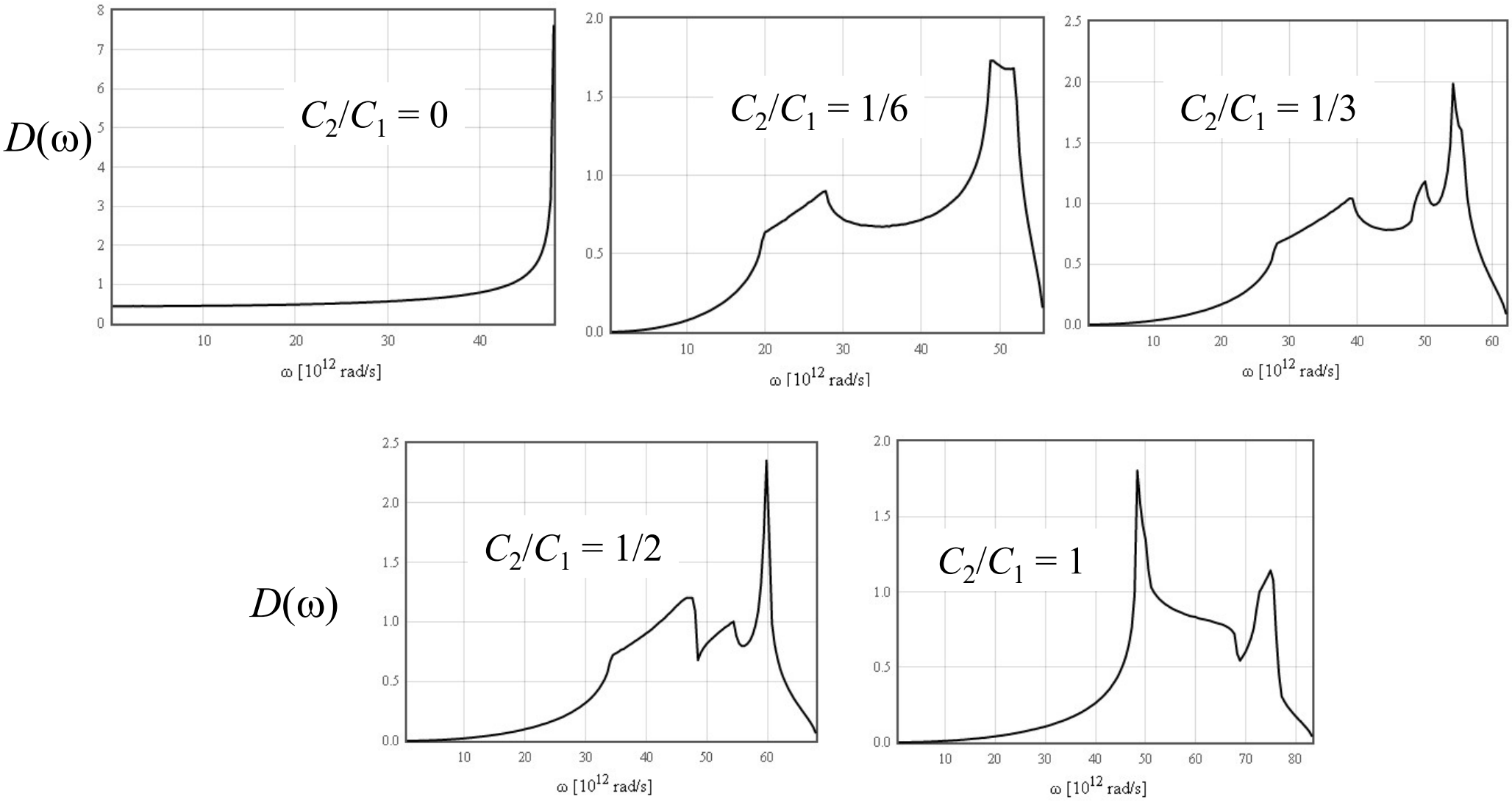


Fig. 3. Fe. Frequency spectrum of α-iron at 295 K calculated from the Born-von Karman force constants of Table 3 Fe [67Mi1].

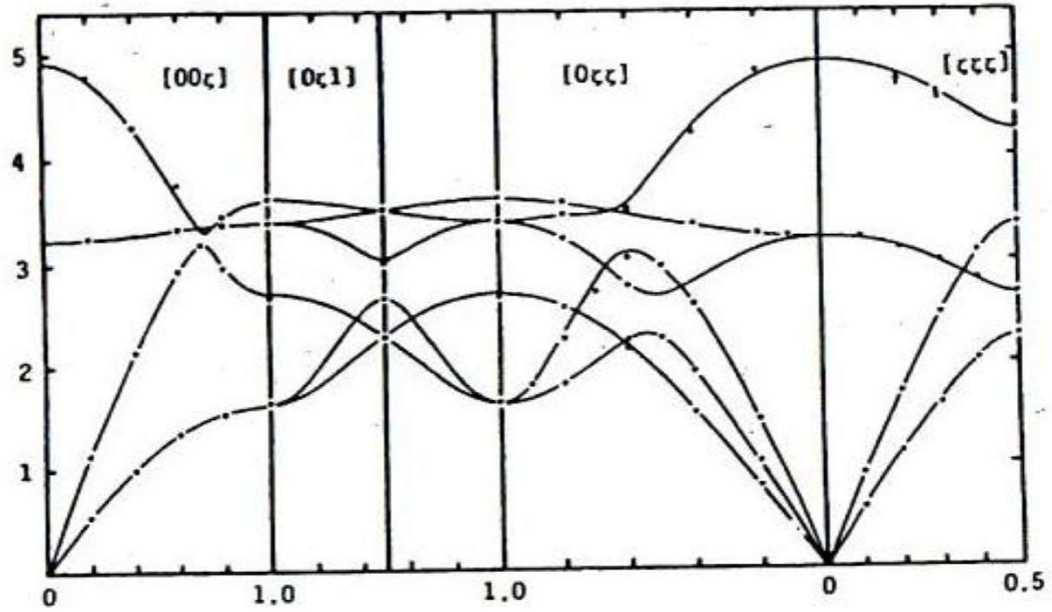
From Springer Materials: Landholt Boernstein Database

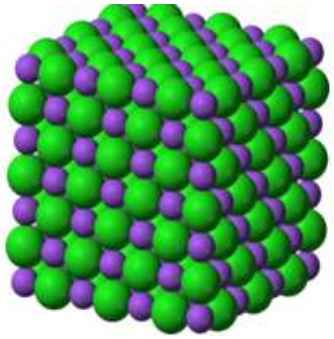
Next nearest neighbors (simple cubic)



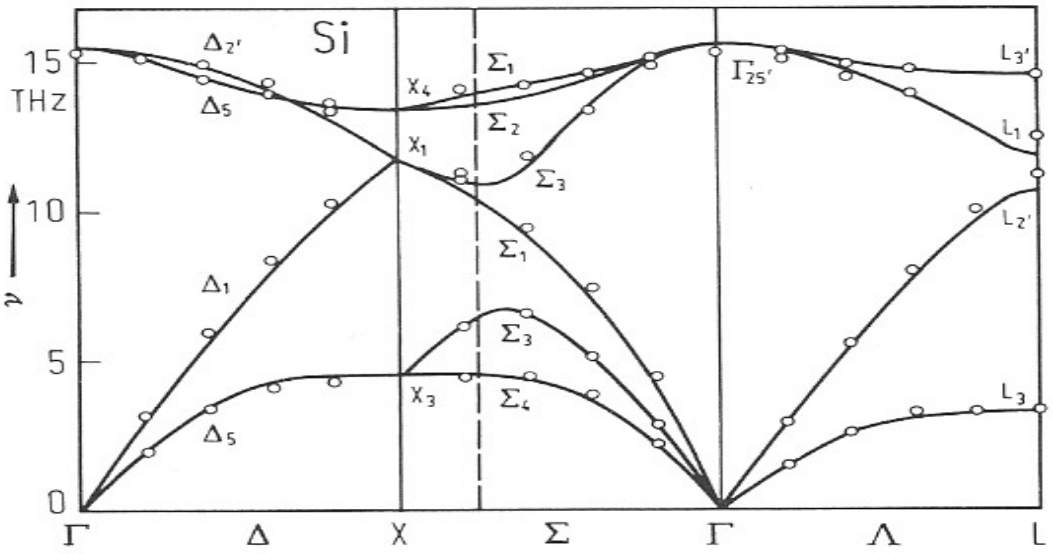
Sometimes the 5th neighbors are included.

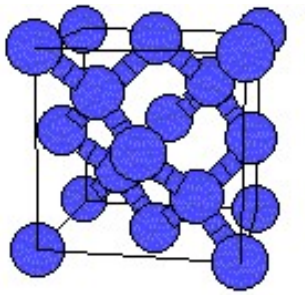
Two atoms per primitive unit cell





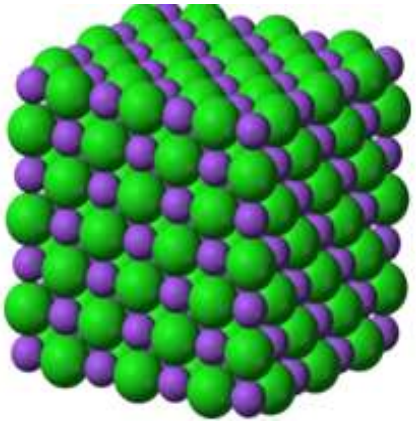
NaCl





Si

NaCl



2 atoms/unit cell

6 equations

3 acoustic and
3 optical branches

$$M_{\mathrm{Na}}\frac{d^2u^x_{lmn}}{dt^2} = \frac{C_{\mathrm{Na\text{-}Na}}}{2}\Big[(u^x_{(l+1)mn}-u^x_{lmn})+(u^x_{(l-1)mn}-u^x_{lmn})+(u^x_{l(m+1)n}-u^x_{lmn})+(u^x_{l(m-1)n}-u^x_{lmn})$$
$$+(u^x_{(l+1)m(n-1)}-u^x_{lmn})+(u^x_{(l-1)m(n+1)}-u^x_{lmn})+(u^x_{l(m+1)(n-1)}-u^x_{lmn})+(u^x_{l(m-1)(n+1)}-u^x_{lmn})$$
$$+(u^y_{l(m+1)n}-u^y_{lmn})+(u^y_{l(m-1)n}-u^y_{lmn})-(u^y_{(l+1)m(n-1)}-u^y_{lmn})-(u^y_{(l-1)m(n+1)}-u^y_{lmn})$$
$$+(u^z_{(l+1)mn}-u^z_{lmn})+(u^z_{(l-1)mn}-u^z_{lmn})-(u^z_{l(m+1)(n-1)}-u^z_{lmn})-(u^z_{l(m-1)(n+1)}-u^z_{lmn})\Big]$$
$$+C_{\mathrm{Na\text{-}Cl}}\left(-2u^x_{lmn}+v^x_{lmn}+v^x_{(l-1)(m-1)(n+1)}\right),$$

$$M_{\mathrm{Na}}\frac{d^2u^y_{lmn}}{dt^2} = \frac{C_{\mathrm{Na\text{-}Na}}}{2}\Big[(u^y_{l(m+1)n}-u^y_{lmn})+(u^y_{l(m-1)n}-u^y_{lmn})+(u^y_{(l+1)m(n-1)}-u^y_{lmn})+(u^y_{(l-1)m(n+1)}-u^y_{lmn})$$
$$+(u^y_{(l-1)(m+1)n}-u^y_{lmn})+(u^y_{lm(n-1)}-u^y_{lmn})+(u^y_{(l+1)(m-1)n}-u^y_{lmn})+(u^y_{lm(n+1)}-u^y_{lmn})$$
$$+(u^x_{l(m+1)n}-u^x_{lmn})+(u^x_{l(m-1)n}-u^x_{lmn})-(u^x_{(l-1)m(n+1)}-u^x_{lmn})-(u^x_{(l+1)m(n-1)}-u^x_{lmn})$$
$$+(u^z_{lm(n-1)}-u^z_{lmn})+(u^z_{lm(n+1)}-u^z_{lmn})-(u^z_{(l+1)(m-1)n}-u^z_{lmn})-(u^z_{(l-1)(m+1)n}-u^z_{lmn})\Big]$$
$$+C_{\mathrm{Na\text{-}Cl}}\left(-2u^y_{lmn}+v^y_{(l-1)m(n+1)}+v^y_{l(m-1)n}\right),$$

$$M_{\mathrm{Na}}\frac{d^2u^z_{lmn}}{dt^2} = \frac{C_{\mathrm{Na\text{-}Na}}}{2}\Big[(u^z_{(l-1)mn}-u^z_{lmn})+(u^z_{(l-1)l(m+1)n}-u^z_{lmn})+(u^z_{l(m+1)(n-1)}-u^z_{lmn})+(u^z_{lm(n-1)}-u^z_{lmn})$$
$$+(u^z_{lm(n+1)}-u^z_{lmn})+(u^z_{(l+1)mn}-u^z_{lmn})+(u^z_{(l+1)(m-1)n}-u^z_{lmn})+(u^z_{l(m-1)(n+1)}-u^z_{lmn})$$
$$+(u^x_{(l+1)mn}-u^x_{lmn})+(u^x_{(l-1)mn}-u^x_{lmn})-(u^x_{l(m-1)(n+1)}-u^x_{lmn})-(u^x_{l(m+1)(n-1)}-u^x_{lmn})$$
$$+(u^y_{lm(n+1)}-u^y_{lmn})+(u^y_{lm(n-1)}-u^y_{lmn})-(u^y_{(l-1)(m+1)n}-u^y_{lmn})-(u^y_{(l+1)(m-1)n}-u^y_{lmn})\Big]$$
$$+C_{\mathrm{Na\text{-}Cl}}\left(-2u^z_{lmn}+v^z_{(l-1)mn}+v^z_{l(m-1)(n+1)}\right),$$

$$M_{\mathrm{Cl}}\frac{d^2v^x_{lmn}}{dt^2} = \frac{C_{\mathrm{Cl\text{-}Cl}}}{2}\Big[(v^x_{(l+1)mn}-v^x_{lmn})+(v^x_{(l-1)mn}-v^x_{lmn})+(v^x_{l(m+1)n}-v^x_{lmn})+(v^x_{l(m-1)n}-v^x_{lmn})$$
$$+(v^x_{(l+1)m(n-1)}-v^x_{lmn})+(v^x_{(l-1)m(n+1)}-v^x_{lmn})+(v^x_{l(m+1)(n-1)}-v^x_{lmn})+(v^x_{l(m-1)(n+1)}-v^x_{lmn})$$
$$+(v^y_{l(m+1)n}-v^y_{lmn})+(v^y_{l(m-1)n}-v^y_{lmn})-(v^y_{(l+1)m(n-1)}-v^y_{lmn})-(v^y_{(l-1)m(n+1)}-v^y_{lmn})$$
$$+(v^z_{(l+1)mn}-v^z_{lmn})+(v^z_{(l-1)mn}-v^z_{lmn})-(v^z_{l(m+1)(n-1)}-v^z_{lmn})-(v^z_{l(m-1)(n+1)}-v^z_{lmn})\Big]$$
$$+C_{\mathrm{Na\text{-}Cl}}\left(-2v^x_{lmn}+u^x_{lmn}+u^x_{(l+1)(m+1)(n-1)}\right),$$

$$M_{\mathrm{Cl}}\frac{d^2v^y_{lmn}}{dt^2} = \frac{C_{\mathrm{Cl\text{-}Cl}}}{2}\Big[(v^y_{l(m+1)n}-v^y_{lmn})+(v^y_{l(m-1)n}-v^y_{lmn})+(v^y_{(l+1)m(n-1)}-v^y_{lmn})+(v^y_{(l-1)m(n+1)}-v^y_{lmn})$$
$$+(v^y_{(l-1)(m+1)n}-v^y_{lmn})+(v^y_{lm(n-1)}-v^y_{lmn})+(v^y_{(l+1)(m-1)n}-v^y_{lmn})+(v^y_{lm(n+1)}-v^y_{lmn})$$
$$+(v^x_{l(m+1)n}-v^x_{lmn})+(v^x_{l(m-1)n}-v^x_{lmn})-(v^x_{(l-1)m(n+1)}-v^x_{lmn})-(v^x_{(l+1)m(n-1)}-v^x_{lmn})$$
$$+(v^z_{lm(n-1)}-v^z_{lmn})+(v^z_{lm(n+1)}-v^z_{lmn})-(v^z_{(l+1)(m-1)n}-v^z_{lmn})-(v^z_{(l-1)(m+1)n}-v^z_{lmn})\Big]$$
$$+C_{\mathrm{Na\text{-}Cl}}\left(-2v^y_{lmn}+u^y_{l(m+1)n}+u^y_{(l+1)m(n-1)}\right),$$

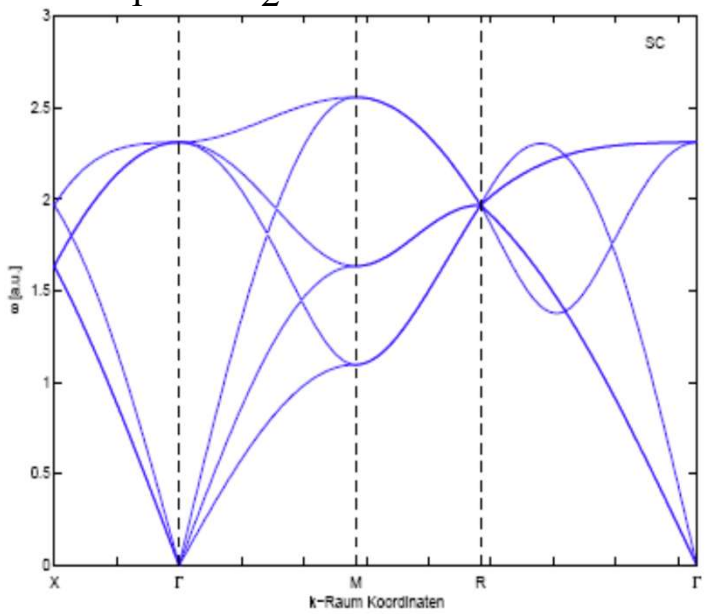
$$M_{\mathrm{Cl}}\frac{d^2v^z_{lmn}}{dt^2} = \frac{C_{\mathrm{Cl\text{-}Cl}}}{2}\Big[(v^z_{(l-1)mn}-v^z_{lmn})+(v^z_{(l-1)l(m+1)n}-v^z_{lmn})+(v^z_{l(m+1)(n-1)}-v^z_{lmn})+(v^z_{lm(n-1)}-v^z_{lmn})$$
$$+(v^z_{lm(n+1)}-v^z_{lmn})+(v^z_{(l+1)mn}-v^z_{lmn})+(v^z_{(l+1)(m-1)n}-v^z_{lmn})+(v^z_{l(m-1)(n+1)}-v^z_{lmn})$$
$$+(v^x_{(l+1)mn}-v^x_{lmn})+(v^x_{(l-1)mn}-v^x_{lmn})-(v^x_{l(m-1)(n+1)}-v^x_{lmn})-(v^x_{l(m+1)(n-1)}-v^x_{lmn})$$
$$+(v^y_{lm(n+1)}-v^y_{lmn})+(v^y_{lm(n-1)}-v^y_{lmn})-(v^y_{(l-1)(m+1)n}-v^y_{lmn})-(v^y_{(l+1)(m-1)n}-v^y_{lmn})\Big]$$
$$+C_{\mathrm{Na\text{-}Cl}}\left(-2v^z_{lmn}+u^z_{l(m+1)(n-1)}+u^z_{(l+1)mn}\right).$$

$$u^x_{nml}=u^x_{\vec{k}}\exp\left(i\left(\vec{k}\cdot\vec{a}_1+\vec{k}\cdot\vec{a}_2+\vec{k}\cdot\vec{a}_3-\omega t\right)\right) \qquad v^x_{nml}=v^x_{\vec{k}}\exp\left(i\left(\vec{k}\cdot\vec{a}_1+\vec{k}\cdot\vec{a}_2+\vec{k}\cdot\vec{a}_3-\omega t\right)\right)$$

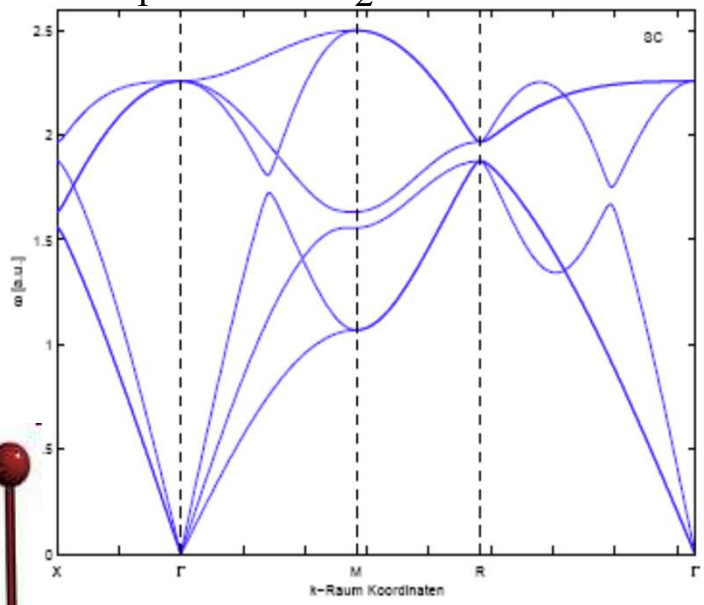
CsCl

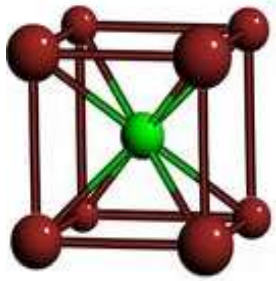
Hannes Brandner

$M_1 = M_2$

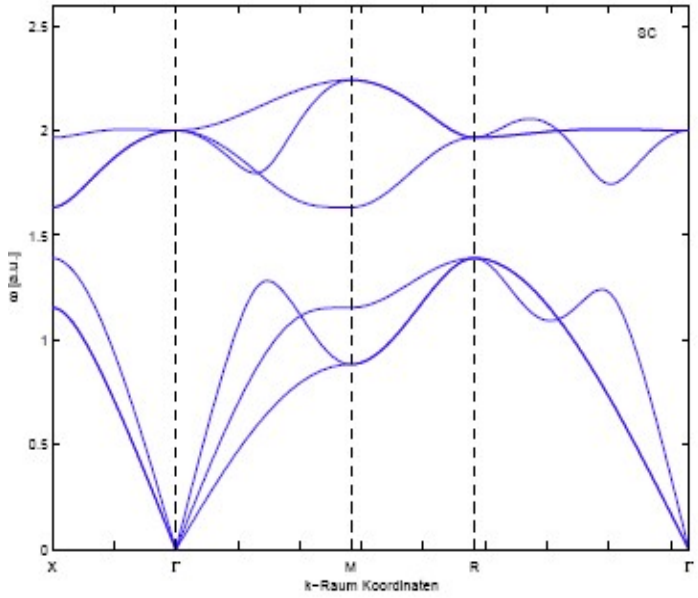


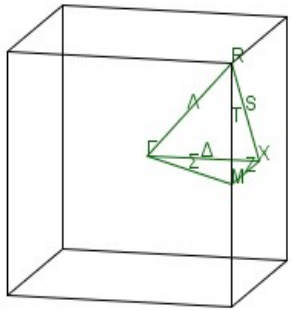
$M_1 = 1.1\ M_2$



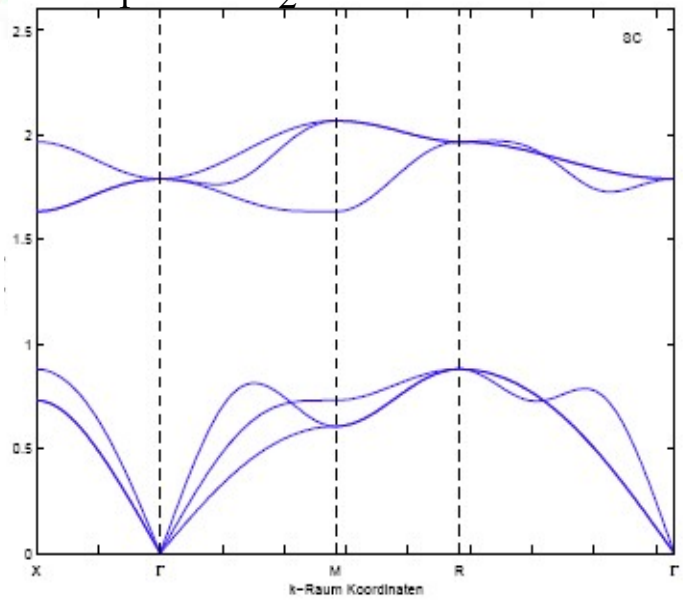


$M_1 = 2M_2$





$M_1 = 5M_2$



3 dimensions

N atoms

3*N* normal modes

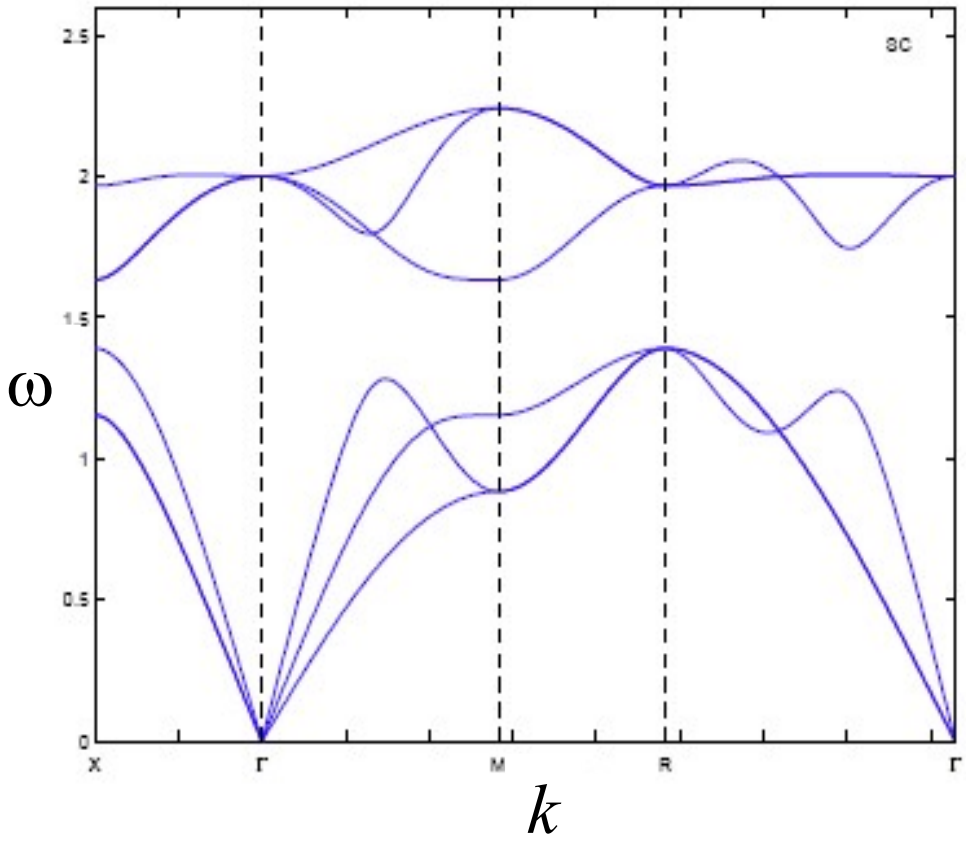
p atoms per unit cell

N/p unit cells = *k* vectors

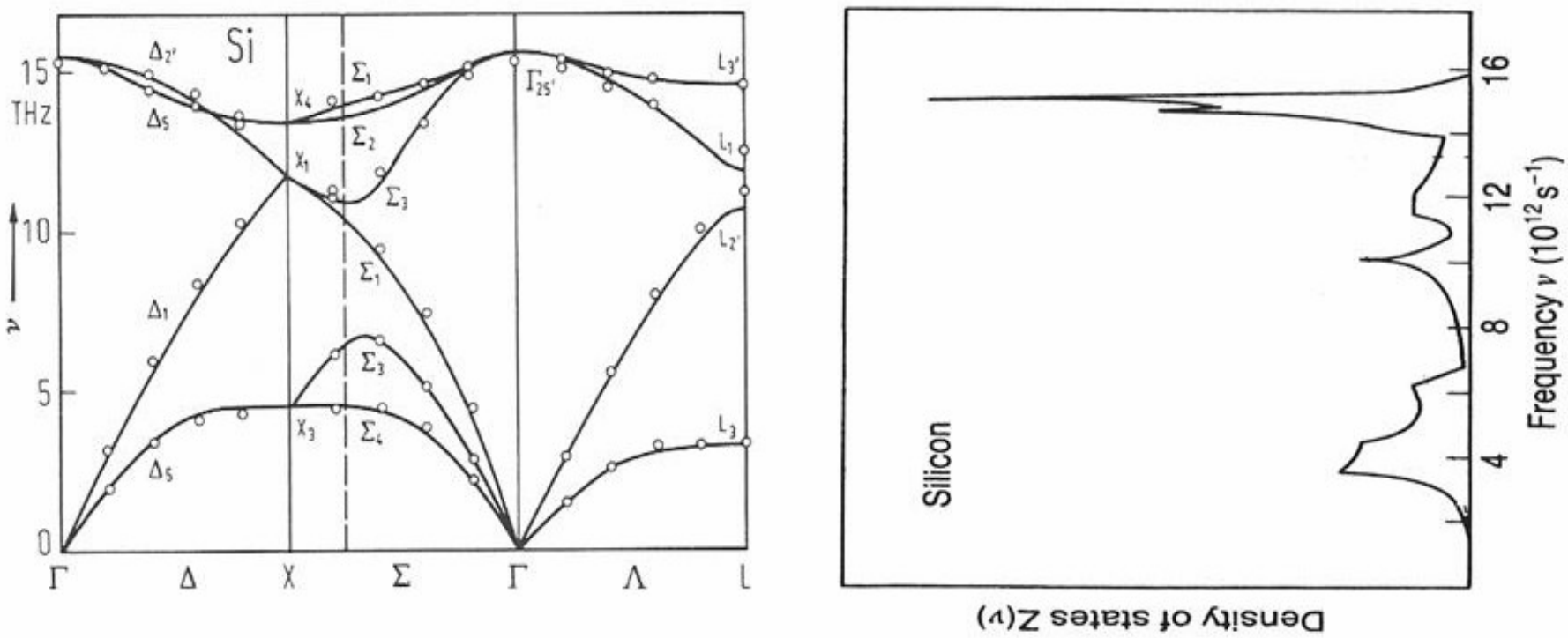
3*p* branches to the dispersion relation

3 acoustic modes (1 longitudinal, 2 transverse)

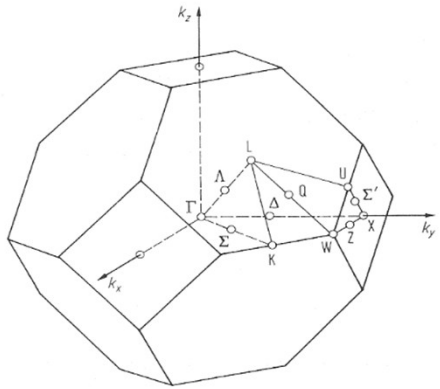
3*p* - 3 optical modes



Silicon phonon dispersion, DOS

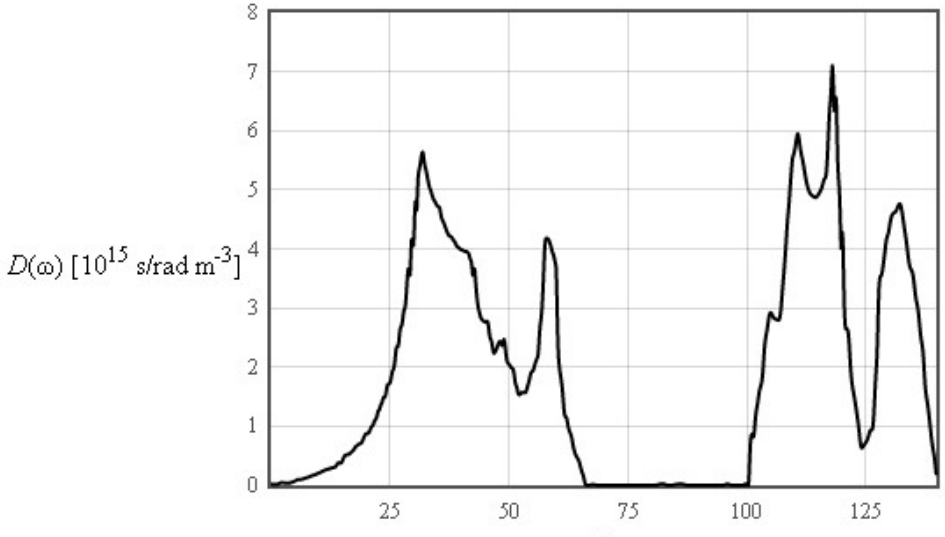


Different speeds of sound for different directions and polarizations causes dispersion of pulses.

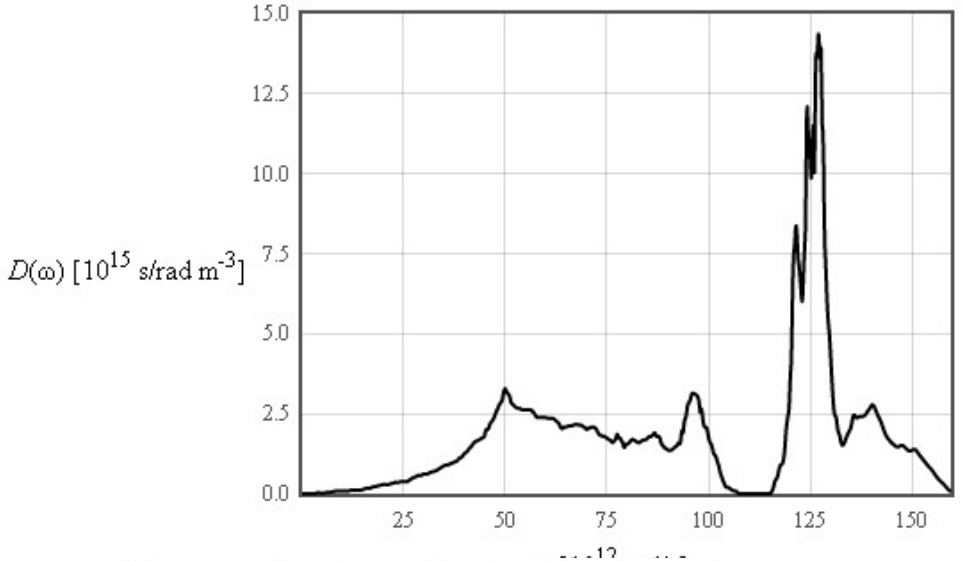


Two atoms per primitive unit cell

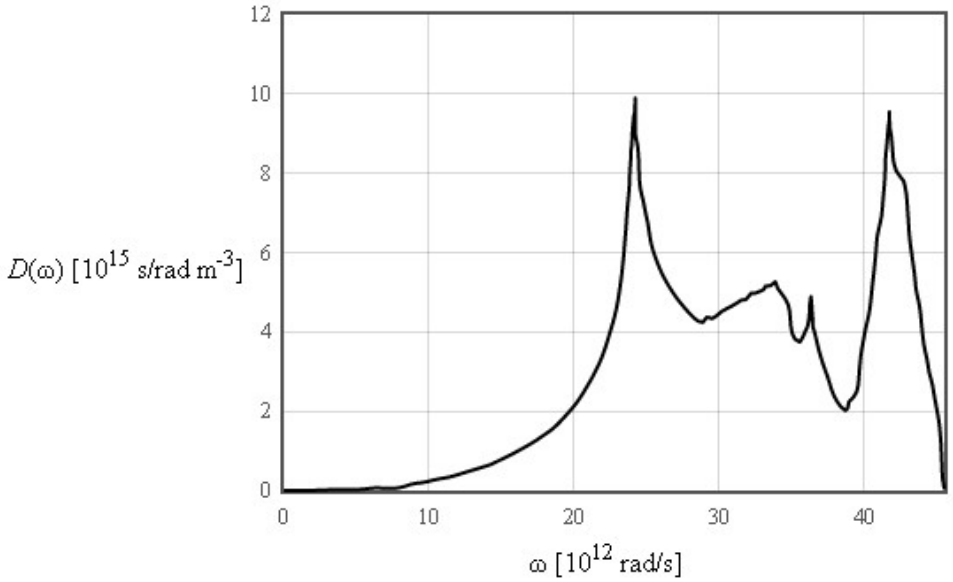
Phonon density of states for GaN



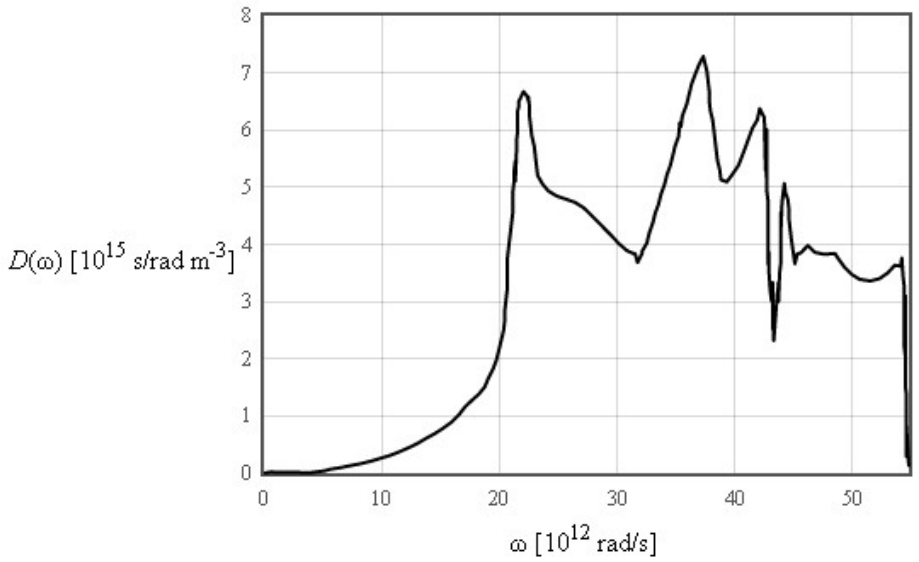
Phonon density of states for AlN

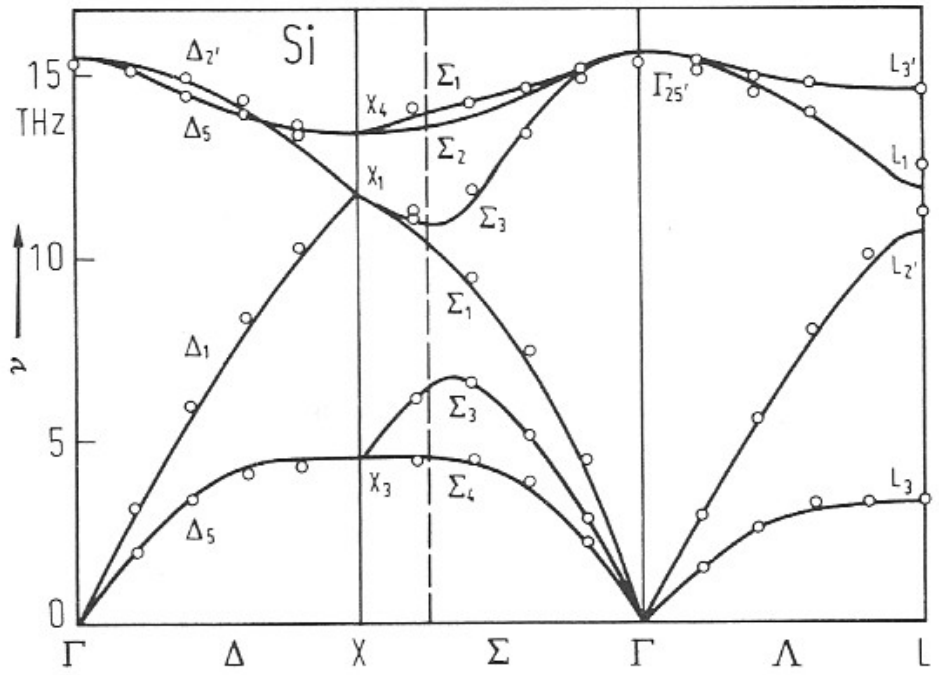


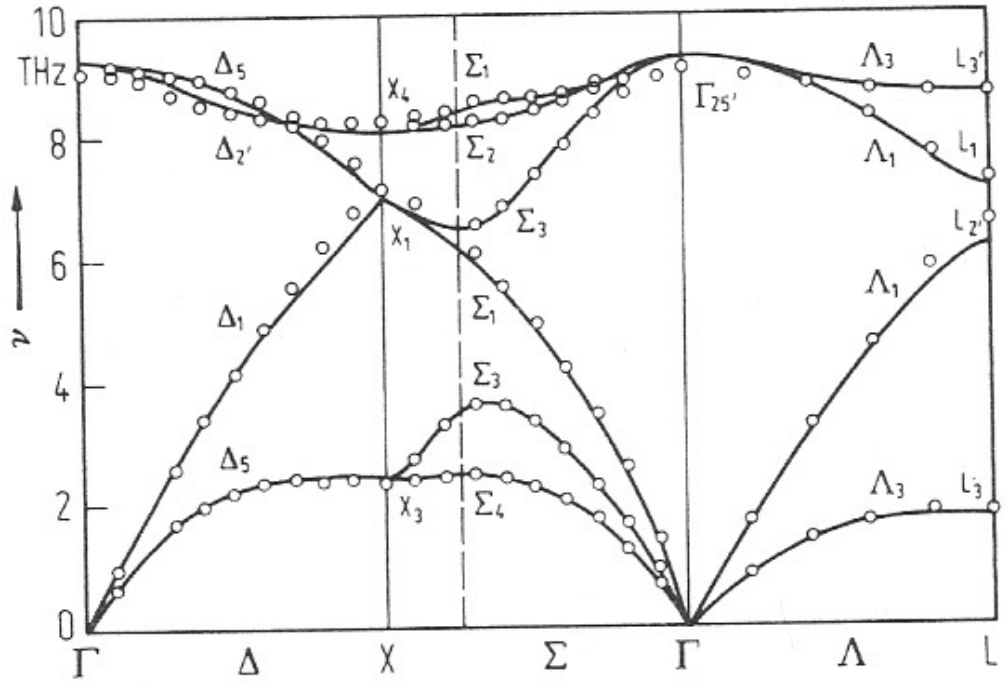
Phonon density of states for hcp magnesium



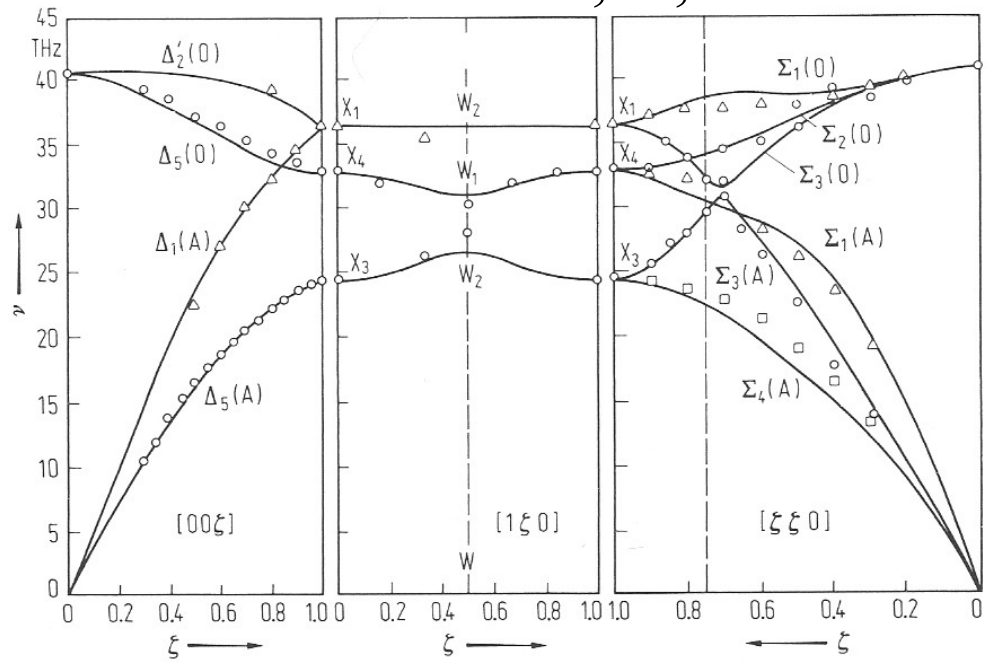
Phonon density of states for hcp titanium

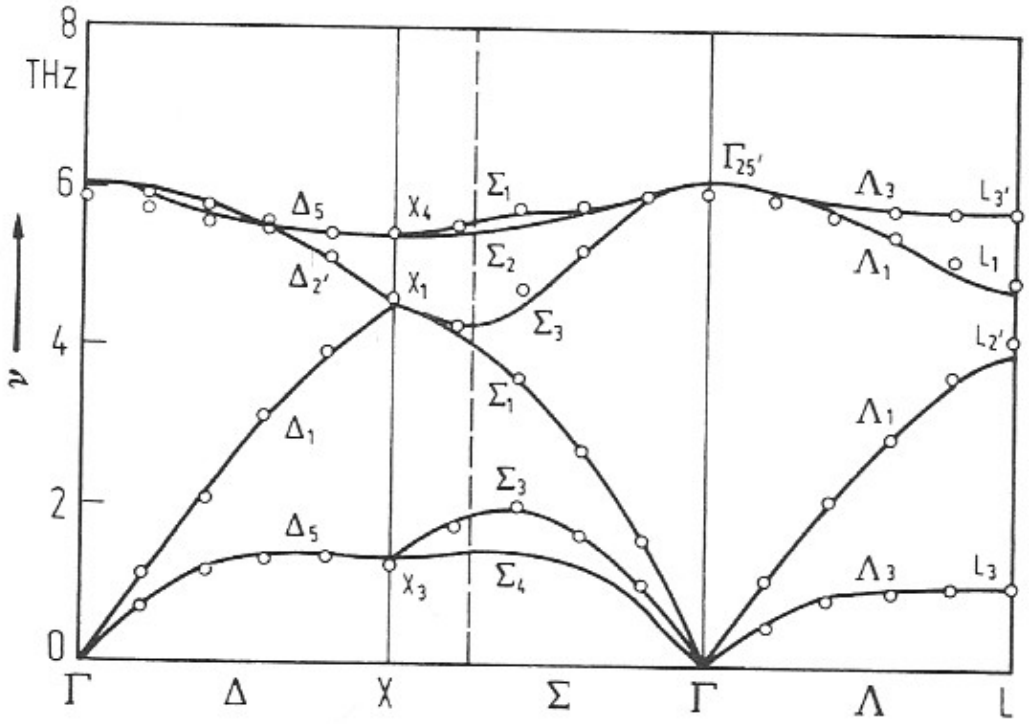



Si
15
THz
10
5
0
ν
Γ
Δ
X
Σ
Γ
Λ
L
Δ2'
Δ5
Δ1
X4
X1
X3
Σ1
Σ2
Σ3
Σ4
Γ25'
L3'
L1
L2'
L3


10
THz
8
6
4
2
0
ν
Γ
Δ
X
Σ
Γ
Λ
L
Δ5
Δ2'
Δ1
X4
X1
X3
Σ1
Σ2
Σ3
Σ4
Γ25'
Λ3
L3'
Λ1
L1
L2'
L3

Ge, C, α-Sn ?


45
THz
40
35
30
25
20
15
10
5
0
ν
Δ2'(0)
Δ5(0)
Δ1(A)
Δ5(A)
[00ζ]
[1ζ0]
[ζζ0]
X1
X4
X3
W2
W1
W
Σ1(0)
Σ2(0)
Σ3(0)
Σ1(A)
Σ3(A)
Σ4(A)
0 0.2 0.4 0.6 0.8 1.0
1.0 0.8 0.6 0.4 0.2 0
ζ


8
THz
6
4
2
0
ν
Γ
Δ
X
Σ
Γ
Λ
L
Δ5
Δ2'
Δ1
X4
X1
X3
Σ1
Σ2
Σ3
Σ4
Γ25'
Λ3
L3'
Λ1
L1
L2'
L3

Si

mp-149

TABLE OF CONTENTS

doi 10.17188/1190959

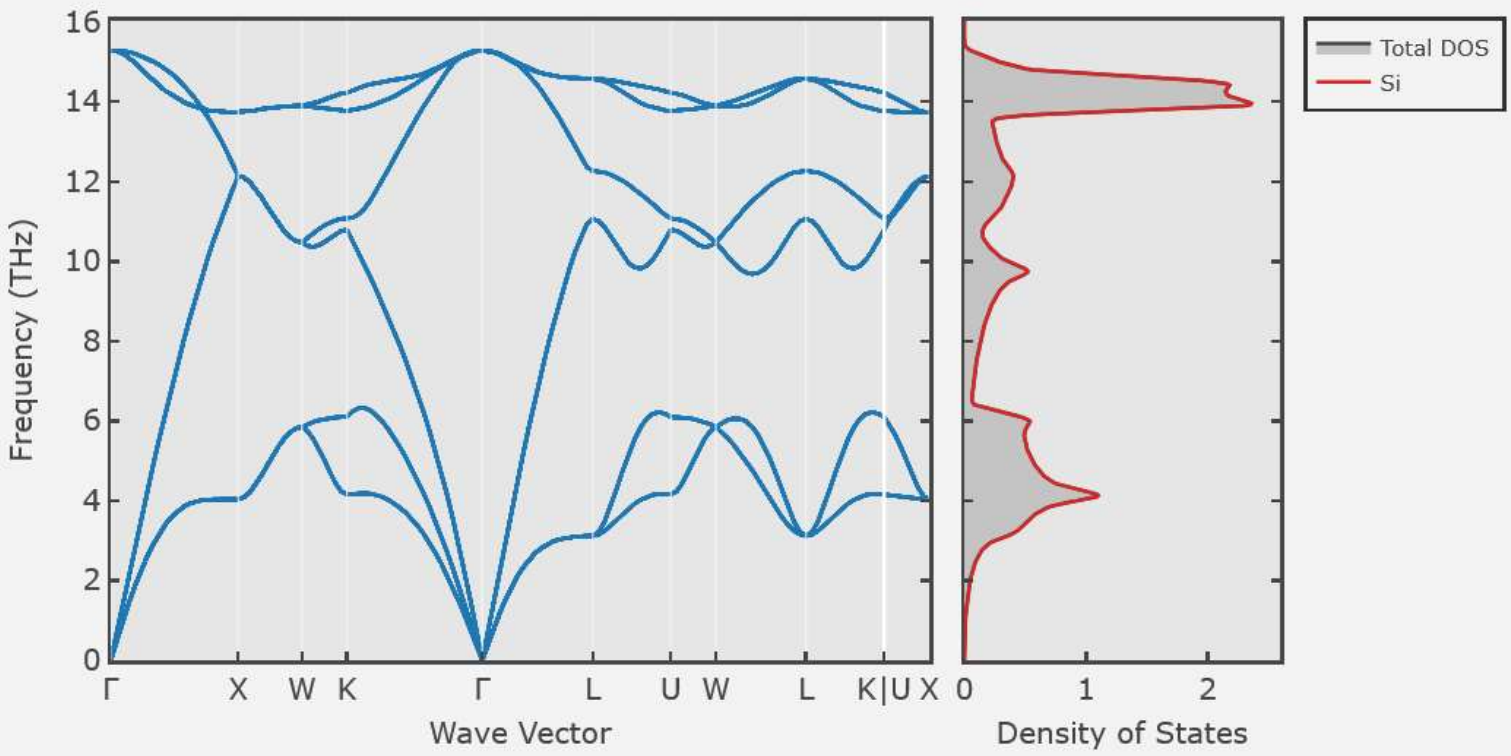
Properties

Phase Stability | Electronic Structure | **Phonon** | Spectra | Mechanical | Heterostructures | Surface

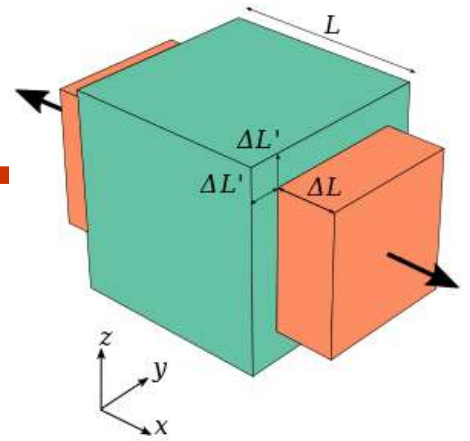
Phonon Dispersion

Phonon Dispersion

Data | Methods | API



Poisson's ratio



Wikipedia

For an isotropic solid

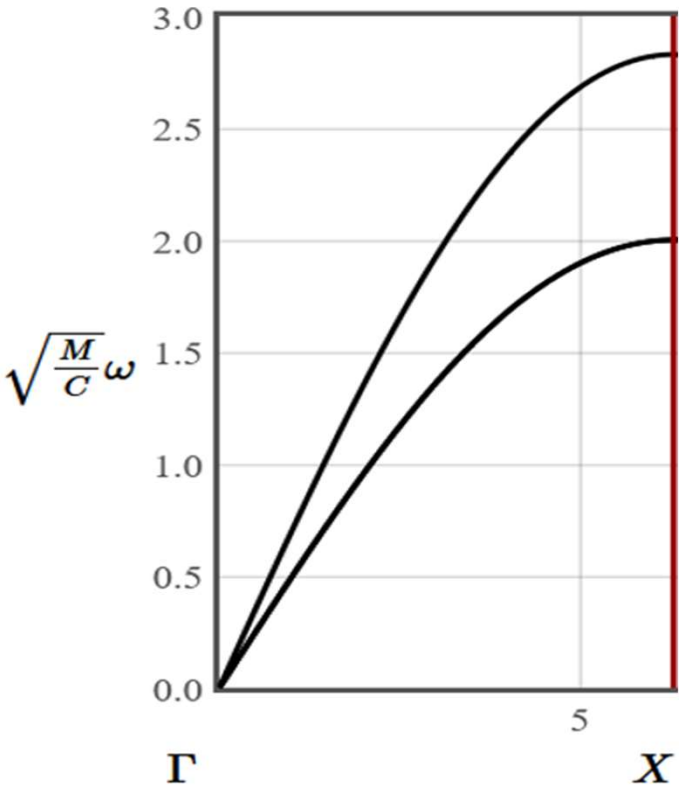
E - Elastic constant

ν - Poisson's ratio

ρ - density

$$c_T = \sqrt{\frac{E(1-\nu)}{\rho(1-\upsilon-2\upsilon^2)}}$$

$$c_L = \sqrt{\frac{E}{2\rho(1+\upsilon)}}$$



If the density is known, you can determine E and ν.

Inelastic phonon scattering

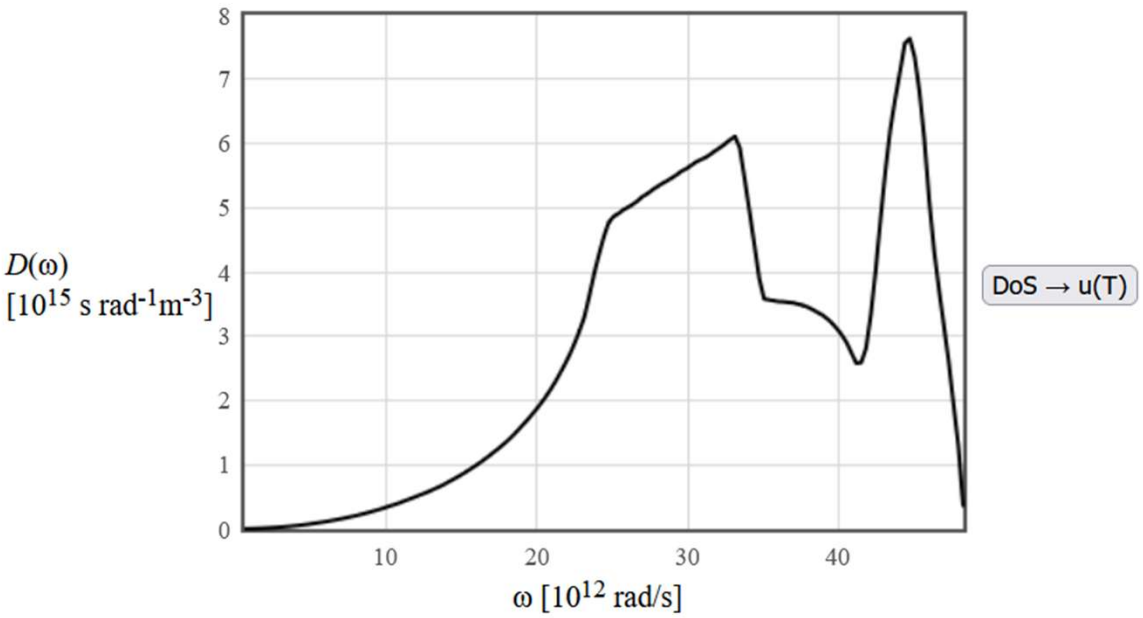
$$\hbar\vec{k} = \hbar\vec{k}' + \hbar\vec{G} \pm \hbar\vec{K}_{ph}$$

neutrons $$\hbar\omega_{ph} = \frac{\hbar^2(k')^2}{2m_n} - \frac{\hbar^2 k^2}{2m_n}$$

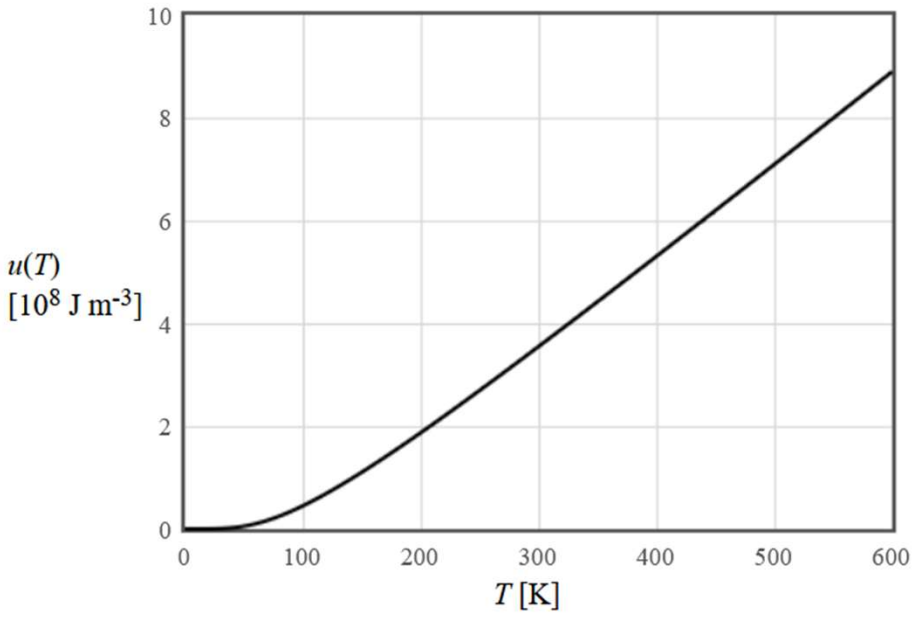
x-rays $$\hbar\omega_{ph} = \hbar ck' - \hbar ck$$

Density of states → Internal energy density

$$u(T) = \int_0^\infty \frac{\hbar\omega D(\omega)}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}\, d\omega$$



DoS → u(T)



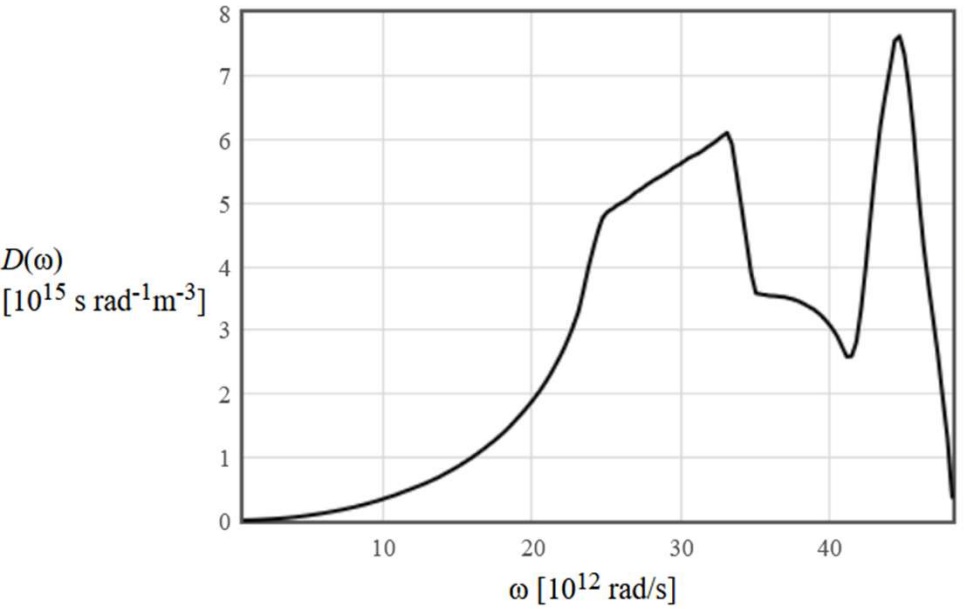
http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2ut.html

Specific Heat

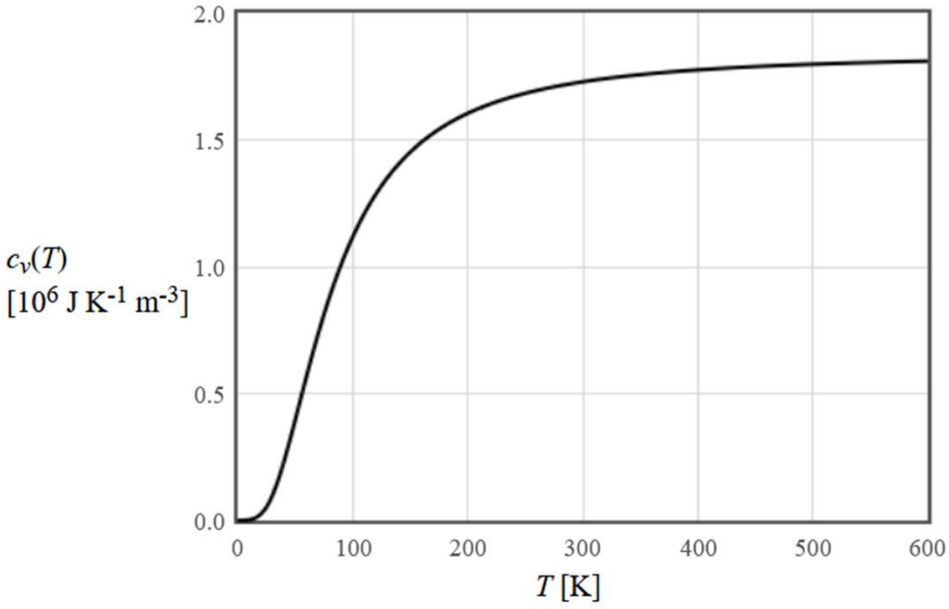
$$c_v = \left(\frac{\partial u}{\partial T}\right)_{N,V}$$

$$c_v = \int \hbar\omega D(\omega) \frac{\partial}{\partial T}\left(\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}\right) d\omega$$

$$c_v = \int \left(\frac{\hbar\omega}{T}\right)^2 \frac{D(\omega) e^{\frac{\hbar\omega}{k_B T}}}{k_B \left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^2} d\omega$$



DoS → cv(T)



http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2cv.html

Heat capacity / specific heat

Heat capacity is the measure of the heat energy required to increase the temperature of an object by a certain temperature interval.

Specific heat is the measure of the heat energy required to increase the temperature of a unit quantity of a substance by a certain temperature interval.

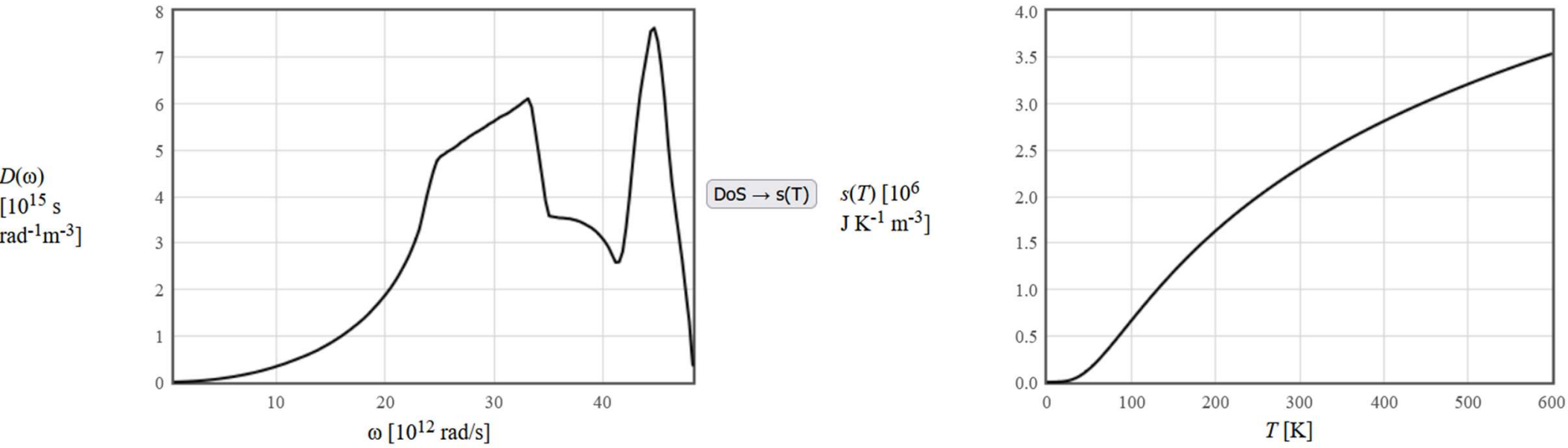
For solids, the heat capacity at constant volume and heat capacity at constant pressure are almost the same.

The heat capacity was historically important for understanding solids.

Density of states → entropy density

$$s = \int \frac{c_v}{T} dT$$

$$s = -\frac{\partial f}{\partial T} = -k_B \int_0^\infty D(\omega) \left(\ln\left(1 - e^{-\hbar\omega / k_B T}\right) + \frac{\hbar\omega}{k_B T \left(1 - e^{\hbar\omega / k_B T}\right)} \right) d\omega$$

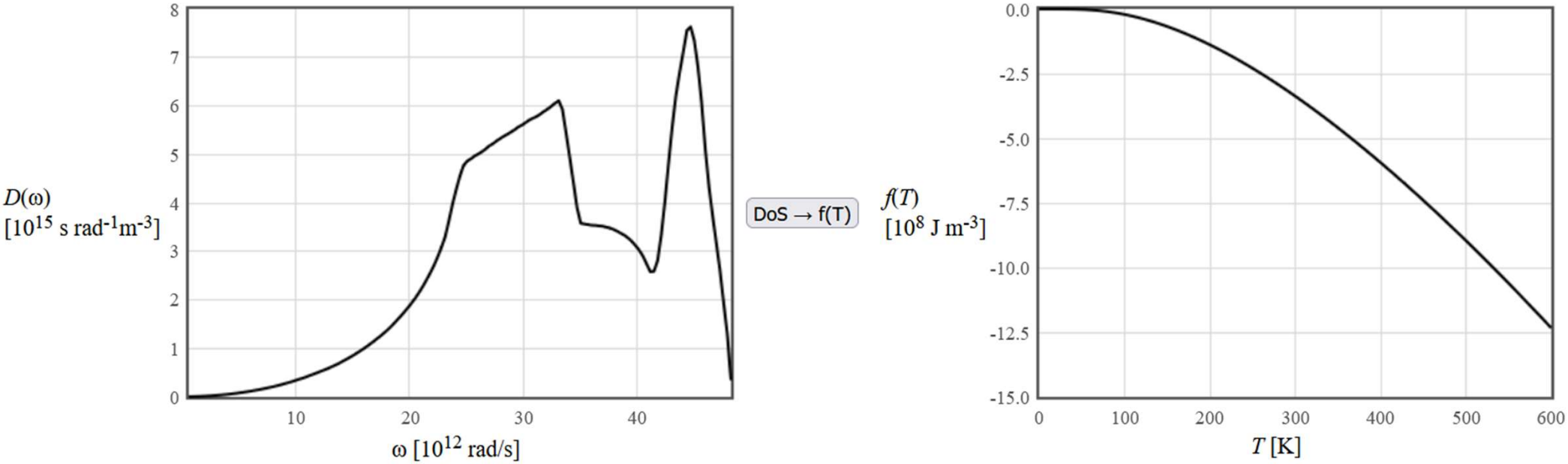


http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2s.htmll

Density of states → Helmholtz free energy density

$$f(T) = k_B T \int_0^\infty D(\omega) \ln\left(1 - \exp\left(\frac{-\hbar\omega}{k_B T}\right)\right) d\omega$$

$$f = u - Ts$$



http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2h.html

Thermal properties

internal energy density $u = \int_0^\infty u(\omega) d\omega = \int_0^\infty \frac{\hbar\omega D(\omega)}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega$ $\left[\ \mathrm{J/m^3}\ \right]$

specific heat $c_v = \frac{du}{dT} = \int \left(\frac{\hbar\omega}{T}\right)^2 \frac{D(\omega)\exp\left(\frac{\hbar\omega}{k_B T}\right)}{k_B \left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^2} d\omega$ $[\mathrm{J\ K^{-1}\ m^{-3}}]$

entropy density $s(T) = \int \frac{c_v}{T} dT = \frac{1}{T} \int_0^\infty \frac{\hbar\omega D(\omega)}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega$ $[\mathrm{J\ K^{-1}\ m^{-3}}]$

Helmholtz free energy density

$$f(T) = u - Ts = k_B T \int_0^\infty D(\omega) \ln\left(1 - \exp\left(\frac{-\hbar\omega}{k_B T}\right)\right) d\omega \quad \left[\mathrm{J/m^3}\right]$$

Quartz

α-Quartz
trigonal
2.65 g/cm^3

573°C ⟹

β-Quartz
hexagonal
2.53 g/cm3

870°C ⟹

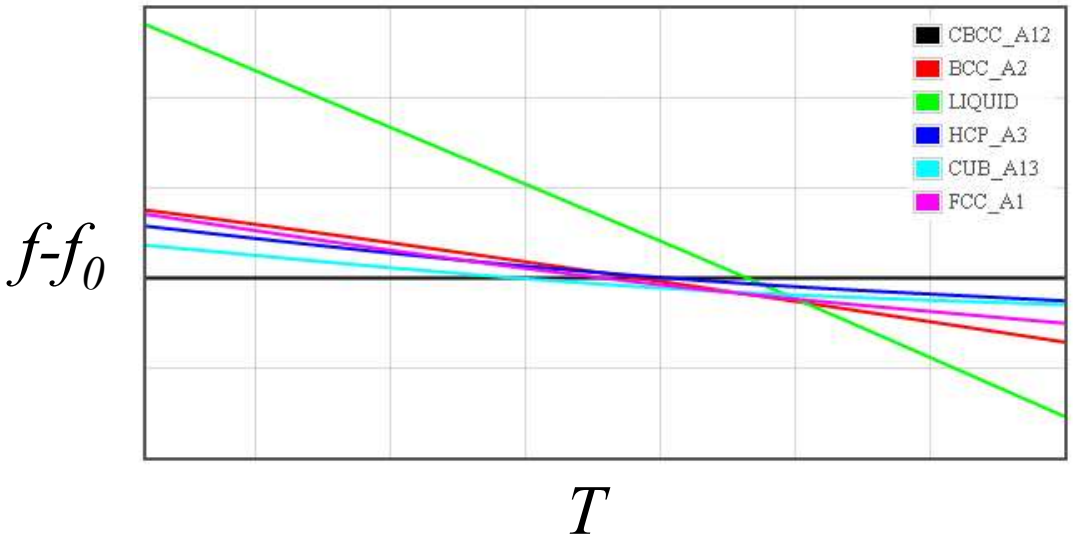
β-Tridymite
hexagonal
2.25 g/cm^3

1470°C ⇓

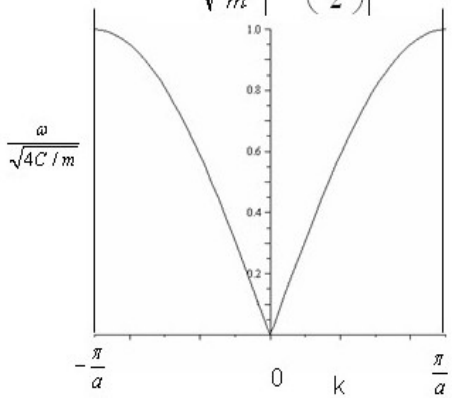
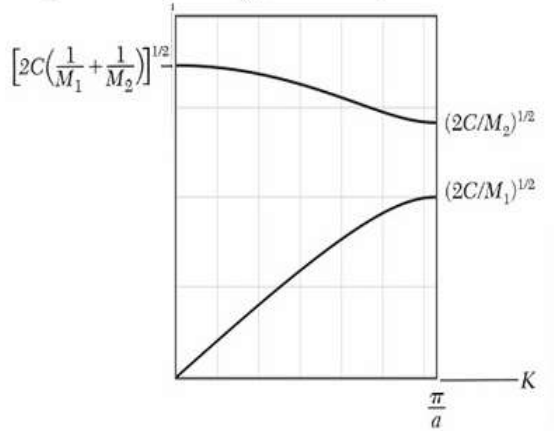
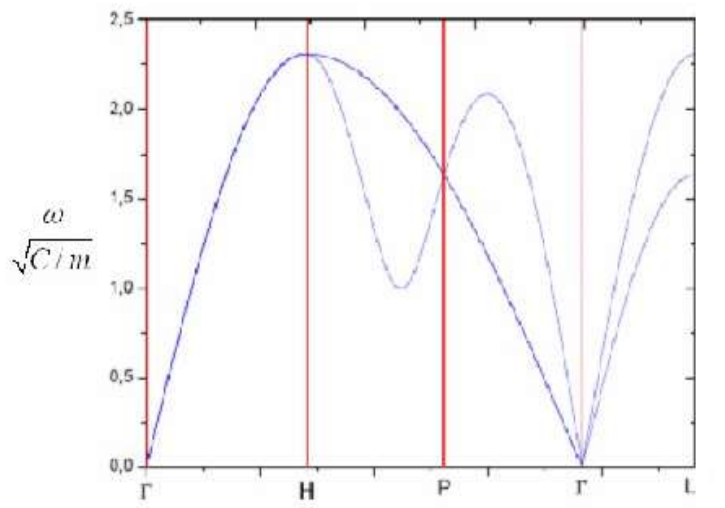
β-Cristobalite
cubic
2.20 g/cm3

1705°C ⟸

Silica Melt



Phonons

	Linear Chain	Linear chain 2 masses	body centered cubic
	$$m\frac{d^2u_s}{dt^2} = C(u_{s+1} - 2u_s + u_{s-1})$$	$$M_1\frac{d^2u_s}{dt^2} = C(v_{s-1} - 2u_s + v_s)$$ $$M_2\frac{d^2v_s}{dt^2} = C(u_s - 2v_s + u_{s+1})$$	$$\frac{d^2u^x_{lmn}}{dt^2} = \frac{C}{\sqrt{3}\,m}[(u^x_{l+1m+1n+1} - u^x_{lmn}) + (u^x_{l-1m+1n+1} - u^x_{lmn}) + (u^x_{l+1m-1n+1} - u^x_{lmn}) + (u^x_{l+1m+1n-1} - u^x_{lmn}) + (u^x_{l+1m-1n-1} - u^x_{lmn}) + (u^y_{l+1m+1n+1} - u^y_{lmn}) - (u^y_{l-1m+1n+1} - u^y_{lmn}) + (u^y_{l+1m-1n+1} - u^y_{lmn}) - (u^y_{l+1m+1n-1} - u^y_{lmn}) + (u^y_{l+1m-1n-1} - u^y_{lmn}) + (u^z_{l+1m+1n+1} - u^z_{lmn}) - (u^z_{l-1m+1n+1} - u^z_{lmn}) + (u^z_{l+1m-1n+1} - u^z_{lmn}) - (u^z_{l+1m+1n-1} - u^z_{lmn}) + (u^z_{l-1m+1n-1} - u^z_{lmn}) - (u^z_{l+1m-1n-1} - u^z_{lmn})]$$ And similar expressions for the y and z
Eigenfunction solutions	$$u_s = A_k e^{i(ksa-\omega t)}$$	$$u_s = ue^{i(ksa-\omega t)}$$ $$v_s = ve^{i(ksa-\omega t)}$$	$$u^x_{lmn} = u^x_{\vec{k}} e^{i(l\vec{k}\cdot\vec{a_1}+m\vec{k}\cdot\vec{a_2}+n\vec{k}\cdot\vec{a_3})} = u^x_{\vec{k}} e^{i(\frac{(-l-}$$ And similar expressions for the y and z
Dispersion relation	$$\omega = \sqrt{\frac{4C}{m}}\left\lvert\sin\left(\frac{ka}{2}\right)\right\rvert$$ 	$$\omega^2 = C\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4\sin^2\left(\frac{ka}{2}\right)}{M_1M_2}}$$  Calculate ω(k)	The dispersio $$\begin{bmatrix} 4-\cos(\frac{a}{2}(k_x+k_y+k_z))-\cos(\frac{a}{2}(3k_x-k_y-k_z)) & -\cos(\frac{a}{2}(k_x+k_y \\ -\cos(\frac{a}{2}(-k_x+3k_y-k_z))-\cos(\frac{a}{2}(-k_x-k_y+3k_z))-\frac{m\omega^2}{\sqrt{3}C} & +\cos(\frac{a}{2}(-k_x+3 \\ -\cos(\frac{a}{2}(k_x+k_y+k_z))+\cos(\frac{a}{2}(3k_x-k_y-k_z)) & 4-\cos(\frac{a}{2}(k_x+ \\ +\cos(\frac{a}{2}(-k_x+3k_y-k_z))-\cos(\frac{a}{2}(-k_x-k_y+3k_z)) & -\cos(\frac{a}{2}(-k_x+3 \\ -\cos(\frac{a}{2}(k_x+k_y+k_z))+\cos(\frac{a}{2}(3k_x-k_y-k_z)) & -\cos(\frac{a}{2}(k_x+k_y \\ -\cos(\frac{a}{2}(-k_x+3k_y-k_z))+\cos(\frac{a}{2}(-k_x-k_y+3k_z)) & +\cos(\frac{a}{2}(-k_x+3 \end{bmatrix}$$ 
Density of states $D(k)$	$$D(k) = \frac{1}{\pi}$$	$$D(k) = \frac{1}{\pi}$$	$$D(k) = \frac{3k^2}{2\pi^2}$$

For the exam

- Know that the motion of atoms in a crystal can be described in terms of the normal modes. There are 3 times as many normal modes as there are atoms in a crystal.
- In a normal mode, all of the atoms in a crystal oscillate with the same frequency. Each of the normal modes has a wave-like solution that can be associated with one of the $\vec{k}$ vectors in the first Brillouin zone.
- There are as many $\vec{k}$ vectors in the first Brillouin zone as there are primitive unit cells in the crystal.
- Be able to describe how the phonon dispersion relation ω vs. k is calculated: (1) Write the $3p$ differential equations for the motion of the atomic masses connected by linear springs, where p is the number of atoms in the primitive unit cell. (2) Insert normal mode solution into the equations, which result in $3p$ coupled algebraic equations. (3) Solve the algebraic equations for the normal mode frequencies.
- Know that for a 3-D crystal, there are always three acoustic branches. and $3p$ - 3 optical branches. One third of the branches are longitudinal modes and two thirds are transverse modes.
- The acoustic branches are linear near $\vec{k} = 0$ while the optical branches have zero slope at $\vec{k} = 0$. The phonon dispersion relation has zero slope at the Brillouin zone boundaries.
- Know how to calculate the density states from the dispersion relation.
- The integral of the density of states over all frequencies is 3 times the atomic density.
- Know how to find a phonon dispersion relation or density of states for some material.
- Be able to describe how the phonon dispersion relation can be measured with inelastic phonon scattering.
- The total internal energy density stored in the phonons is the energy of a phonon mode $\hbar\omega$ times the density of states $D(\omega)$ times the Bose-Einstein factor integrated over all frequencies.

$$u = \int_0^{\omega_{\max}} \frac{\hbar\omega D(\omega)}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega \quad [\mathrm{J/m^3}].$$

- From the internal energy density know how to calculate tthe specific heat $c_v = \frac{du}{dT}$, the entropy $s = \int \frac{C_v}{T} dT$, and the Helmholtz free energy $f = u - Ts$.
- Be able to describe how to measure the specific heat and how the Helmholtz free energy determines the temperature of phase transitions.