Phonon-II: thermal properties

Masatsugu Sei Suzuki

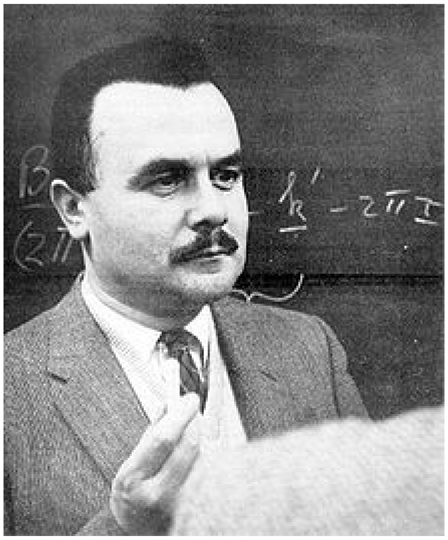
Department of Physics, SUNY at Binghamton

(Date: February 19, 2018)

Peter Joseph William Debye FRS (March 24, 1884 – November 2, 1966) was a Dutch physicist and physical chemist, and Nobel laureate in Chemistry.

http://en.wikipedia.org/wiki/Peter_Debye

Bertram Neville Brockhouse, CC, FRSC (July 15, 1918 – October 13, 2003) was a Canadian physicist. He was awarded the Nobel Prize in Physics (1994, shared with Clifford Shull) "for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter", in particular "for the development of neutron spectroscopy".



http://en.wikipedia.org/wiki/Bertram_Brockhouse

Clifford Glenwood Shull (Pittsburgh, Pennsylvania, September 23, 1915 – March 31, 2001) was a Nobel Prize-winning American physicist.
http://en.wikipedia.org/wiki/Clifford_Shull

1. Heat capacity

C_V = heat capacity at constant volume
C_p = heat capacity at constant pressure.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V ,$$

Where U is the energy and T is the temperature. The contribution of the phonons to the heat capacity of a crystal is called the lattice heat capacity.

((**Note**))
Gitter: lattice (in German)

The total energy of the phonons at T in a crystal may be written as

$$U = \sum_{\mathbf{k},\lambda} U_{\mathbf{k},\lambda} = \sum_{\mathbf{k},\lambda} \langle n_{\mathbf{k},\lambda} \rangle \hbar \omega_{\mathbf{k},\lambda} ,$$

where $\langle n_{\mathbf{k},\lambda} \rangle$ is the thermal equilibrium occupancy of phonons of wavevector ***k*** and polarization λ. $\langle n_{\mathbf{k},\lambda} \rangle$ is the Planck distribution function given by

$$\langle n \rangle = \frac{1}{e^{\beta\hbar\omega} - 1},$$

with $\beta = \frac{1}{k_B T}$, and k_B is the Boltzmann constant.

2. Planck's distribution

We consider a set of identical harmonic oscillators

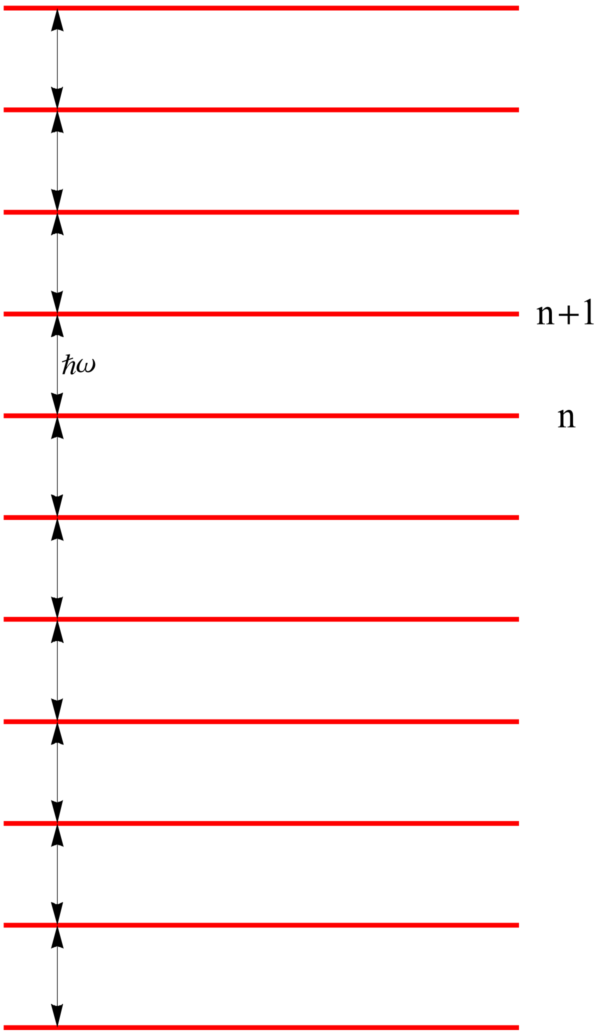


Fig. States of an oscillator that represents a mode of angular frequency ω. *When the oscillator is in the state of energy $n\hbar\omega$, the state is equivalent to n photons in the mode.* The zero point energy ($\hbar\omega/2$) is omitted for simplicity.

The ratio of the number of states $|n+1\rangle$ (n+1 photons in the mode) to the number of states in $|n\rangle$ (n photons in the mode) is

$$\frac{N_{n+1}}{N_n} = \exp(-\beta\hbar\omega),$$

by the use of the Boltzmann factorm. Note that

$$N_n = \langle n\rangle,$$

$$N_n = (e^{-\beta\hbar\omega})^{n-1} N_1 = (e^{-\beta\hbar\omega})^n N_0,$$

$$P_n = \frac{N_n}{\sum\limits_{s=0} N_s} = \frac{e^{-n\beta\hbar\omega} N_0}{\sum\limits_{s=0} e^{-s\beta\hbar\omega} N_0} = \frac{e^{-n\beta\hbar\omega}}{\sum\limits_{s=0} e^{-s\beta\hbar\omega}}.$$

We see that

$$< n^p >= \sum_s s^p P_s = \frac{\sum\limits_{s=0} s^p e^{-s\beta\hbar\omega}}{\sum\limits_{s=0} e^{-s\beta\hbar\omega}},$$

where p = 0, 1, 2, ... (integer). For p = 1, we have

$$\langle n\rangle = \frac{1}{e^{\beta\hbar\omega} - 1} = \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \frac{x}{1-x}.$$

where

$$x = e^{-\beta\hbar\omega}.$$

We also have

$$(\Delta n)^2 = \langle n^2 \rangle - \langle n \rangle^2 = \frac{x}{(1-x)^4}.$$

Using the Mathematica, we get the table of $\langle n^p \rangle$ vs p

Table $\langle n^p \rangle$ vs p, (p = 1, 2, 3, 4, and 5), where $x = e^{-\beta\hbar\omega}$.

p	<n^p>)
0	1
1	$\frac{x}{1-x}$
2	$\frac{x(1+x)}{(-1+x)^2}$
3	$-\frac{x(1+4x+x^2)}{(-1+x)^3}$
4	$\frac{x(1+11x+11x^2+x^3)}{(-1+x)^4}$
5	$-\frac{x(1+26x+66x^2+26x^3+x^4)}{(-1+x)^5}$

---

3. Normal mode enumeration

The total energy U is given by

$$U = \sum_{\mathbf{k},\lambda} U_{\mathbf{k},\lambda} = \sum_{\mathbf{k},\lambda} \langle n_{\mathbf{k},\lambda} \rangle \hbar\omega_{\mathbf{k},\lambda} = \sum_{\mathbf{k},\lambda} \frac{\hbar\omega_{\mathbf{k},\lambda}}{e^{\beta\hbar\omega_{\mathbf{k},\lambda}} - 1}.$$

Suppose that the crystal has $D_\lambda(\omega)d\omega$ modes of a given polarization λ in the frequency range ω- $\omega + d\omega$

$$U = \sum_{\lambda} \int d\omega D_\lambda(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

The lattice heat capacity is

$$C_{lat} = \frac{\partial U}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial U}{\partial \beta},$$

where

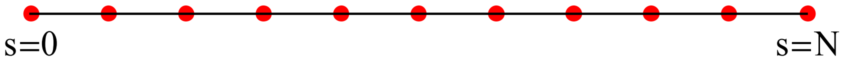
$$\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}.$$

Then we have

$$C_{latt} = k_B \sum_{\lambda} \int d\omega D_{\lambda}(\omega) \frac{(\beta\hbar\omega)^2 e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}.$$

4. Density of states in one dimension

We consider the boundary value problem for vibrations of a 1D line of length L carrying (N+1) particles at separation a.



Suppose that the particles $s = 0$ and $s = N$ at the end of lines are held fixed. Each normal mode of the polarization l has the form of a standing wave,

$$u_s = u(0)e^{-i\omega_{k,\lambda} t} \sin(ska),$$

where u_s is the displacement of the particle s; $\omega = \omega_{k,\lambda}$ (dispersion relation).

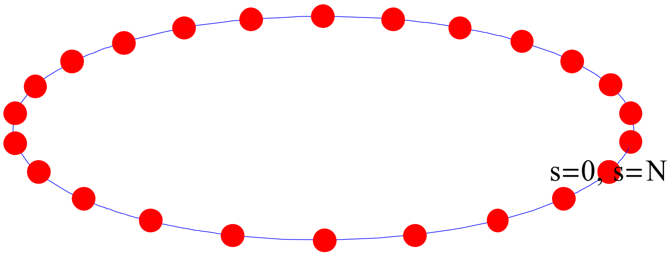
Since $u_s = 0$ at $s = 0$ and $s = N$.

$$\sin(Nka) = 0,$$

or

$$Nka = \pi,\ 2\pi, \qquad ,\ (N\text{-}1)\pi.$$

5. The method of periodic boundary conditions



$$u_s = u(0)e^{i(ska-\omega_k t)}.$$

From the periodic boundary condition, we have

$$u_s = u_{s+N},$$

$$e^{iNka} = 1.$$

where $L = N$a. The allowed values of k are

$$k = \frac{2\pi}{L}n = \frac{2\pi}{a}\frac{n}{N}, \qquad \text{(first Brillouin zone)}$$

where n is integers, n = -N/2, ..-1, 0, 1, 2, , N/2, ...

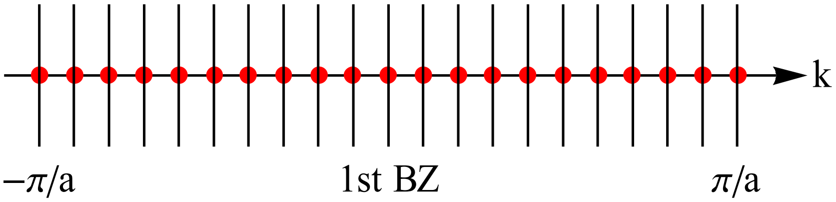


Fig. First Brillouin zone. There are N state for $|k| \leq \pi/a$.

6. Density of states for 1D system

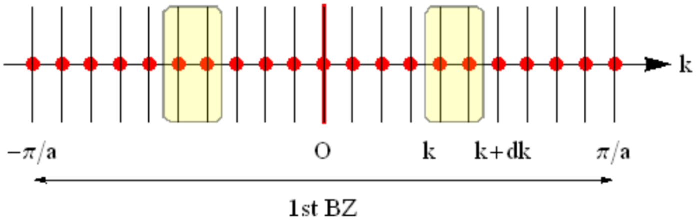


Fig. Density of states for the 1D k-space. The factor 2 arises from the even function of the dispersion relation (ω vs k) in the expression of the density of states (1D case).

There is one allowed state per ($2\pi/L$) in k-space. Or

$$\frac{1}{\left(\frac{2\pi}{L}\right)} = \frac{L}{2\pi} \quad \text{states per unit length of k-space,}$$

for each polarization and for each branch. The density of states (ω - ω + dω),

$$D(\omega)d\omega = \frac{L}{2\pi}2dk = \frac{L}{\pi}\frac{dk}{d\omega}d\omega,$$

where the factor 2 comes from the even function of the dispersion relation (ω vs k). Then we have

$$D(\omega) = \frac{L}{\pi} \frac{1}{\left(\frac{d\omega}{dk}\right)}.$$

When $\omega = vk$, we get

$$D(\omega) = \frac{L}{\pi v}.$$

Note that this is independent of ω.

---

7. Density of states for 2D system

There is one allowed states per $(2\pi/L)^2$ in 2D ***k***-space. In other words, there are

$$\frac{1}{(2\pi)^2 / L^2},$$

states per unit area of 2D ***k*** space, for each polarization and for each branch

The density of states is defined by

$$D(\omega)d\omega = \frac{dk_x dk_y}{(2\pi)^2 / L^2} = \frac{2\pi k dk}{(2\pi)^2 / L^2} = \frac{L^2 k dk}{2\pi},$$

using the linear dispersion relation, $\omega = vk$,

$$D(\omega) = \frac{L^2 \omega}{2\pi v^2}$$

which is proportional to ω.

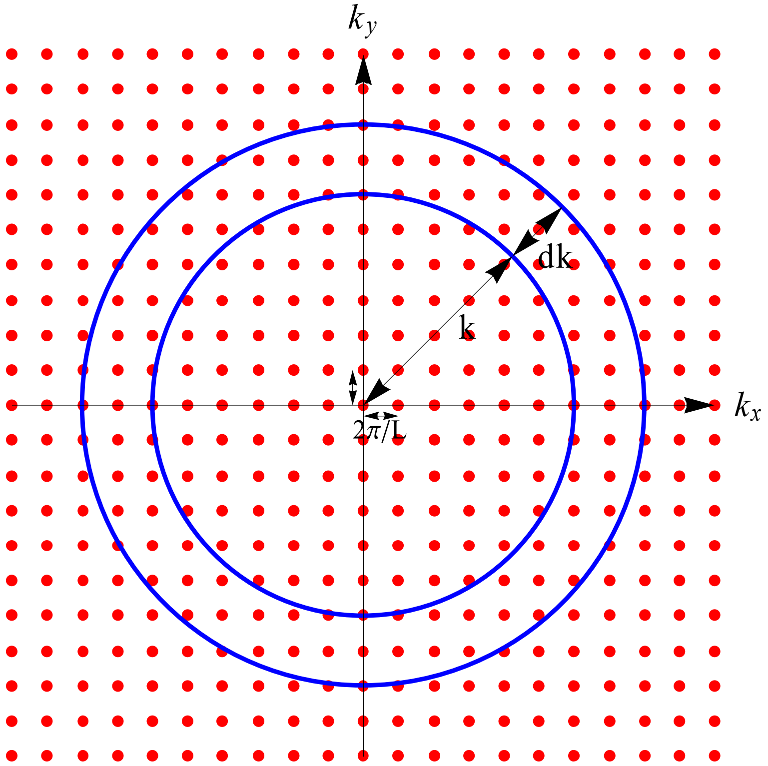


Fig. Density of states for the 2D ***k***-space. There is one state per area $\left(\frac{2\pi}{L}\right)^2$ of the reciprocal lattice plane.

8. Density of states for the 3D system

The total number of modes with wave number less than *k*,

$$N = \frac{L^3}{(2\pi)^3}\frac{4\pi}{3}k^3.$$

for each polarization type (*L* or *T*).

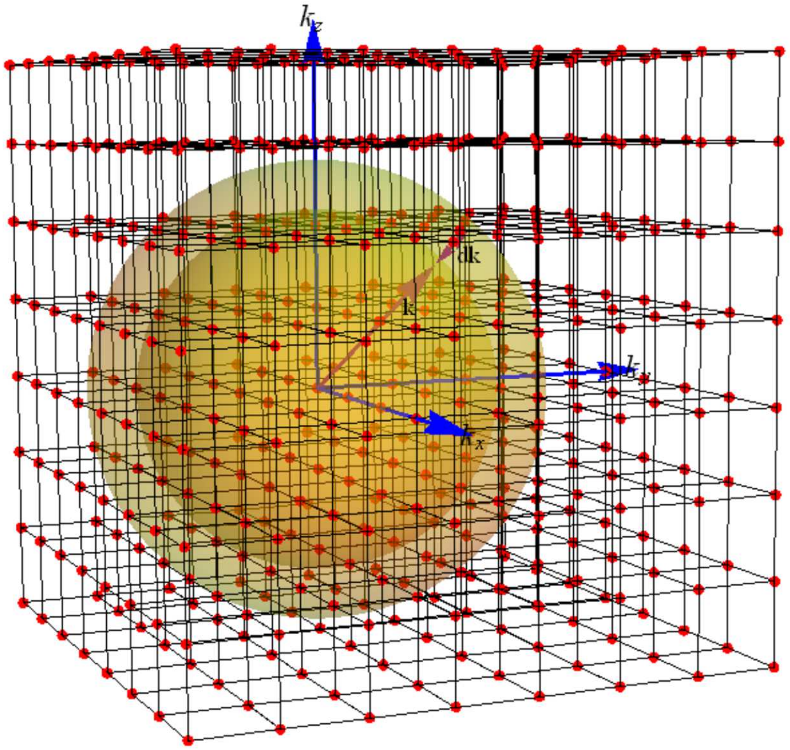


Fig. Density of states in the 3D ***k***-space.

For k - k + dk (corresponding to ω - ω + dω)

$$D(\omega)d\omega = \frac{L^3}{(2\pi)^3}4\pi k^2 dk = \frac{L^3}{2\pi^2}k^2\frac{dk}{d\omega}d\omega,$$

Then the density of states for each polarization (L or T) is

$$D(\omega) = \frac{Vk^2}{2\pi^2}\frac{dk}{d\omega}.$$

When $\omega = vk$, we have

$$D(\omega) = \frac{V\omega^2}{2\pi^2 v^3},$$

for the density of states for the 3D system.

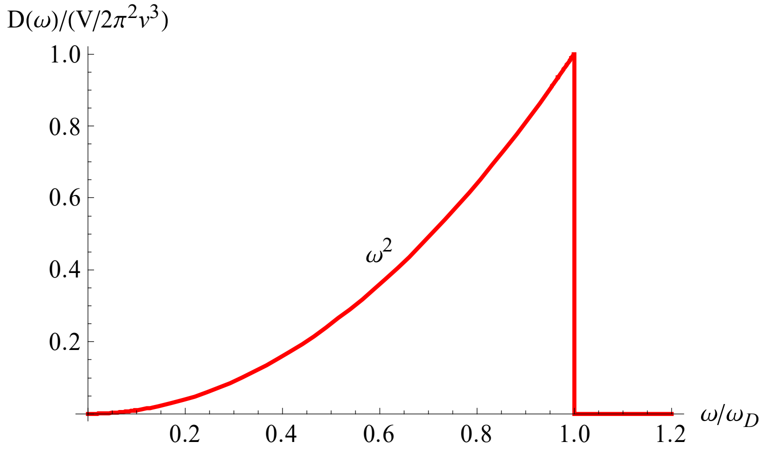


Fig. Density of states in the Debye model.

---

9. Heat capacity of 1D system

$$\omega = vk$$

$$D(\omega)d\omega = \frac{L}{\pi}\frac{dk}{d\omega}d\omega = \frac{L}{\pi v}d\omega$$

$$N = \int_0^{\omega_D} D(\omega)d\omega = \frac{L}{\pi v}\int_0^{\omega_D} d\omega = \frac{L\omega_D}{\pi v}$$ for each polarization.

Then we have

$$\omega_D = \frac{\pi v N}{L}$$

The total energy

$$U = 3\int_0^{\omega_D} d\omega D(\omega)\hbar\omega < n(\omega) > = 3\int_0^{\omega_D} d\omega \frac{L}{\pi v}\left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right)$$

where the factor 3 denotes the number of polarization. We introduce a new variable *x* as

$$x = \beta\hbar\omega\,, \qquad x_D = \frac{\hbar\omega_D}{k_B T} = \frac{k_B\Theta}{k_B T} = \frac{\Theta}{T}$$

Then we get

$$U = 3\frac{L}{\pi v}\int_0^{\omega_D} d\omega\left(\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right) = 3\frac{L}{\pi v}\int_0^{\Theta/T} d\omega\left(\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right) = 3\frac{L}{\pi v\hbar}(k_B T)^2\int_0^{\Theta/T} dx\left(\frac{x}{e^x-1}\right)$$

or

$$U = 3\frac{L{k_B}^2\Theta}{\pi v\hbar}(\frac{T}{\Theta})T\int_0^{\Theta/T} dx\left(\frac{x}{e^x-1}\right)$$

Since

$$\frac{L{k_B}^2\Theta}{\pi v\hbar} = k_B\frac{Lk_B\Theta}{\pi v\hbar} = k_B\frac{L\hbar\omega_D}{\pi v\hbar} = k_B\frac{L\hbar}{\pi v\hbar}\frac{\pi vN}{L} = Nk_B\,,$$

we have

$$U = 3Nk_B(\frac{T}{\Theta})T\int_0^{\Theta/T} dx\left(\frac{x}{e^x-1}\right).$$

At low temperatures where $T \ll \Theta$,

$$\int_0^{\Theta/T} dx\left(\frac{x}{e^x-1}\right) = \int_0^{\infty} dx\frac{x}{e^x-1} = \frac{\pi^2}{6}\,,$$

using the Mathematica. Then we have

$$U \approx 3Nk_B(\frac{T}{\Theta})T\frac{\pi^2}{6} = \frac{\pi^2}{2}Nk_B\frac{T^2}{\Theta}\,.$$

The heat capacity is

$$C = \frac{\partial U}{\partial T} = \pi^2 N k_B \frac{T}{\Theta}$$

which is proportional to T.

## 10.	Heat capacity of 2D system

((Problem 5-4 , Kittel)) Hint.

We calculate the heat capacity of 2D systems in the Debye approximation. The ther mal energy is given by

$$U = \int d\omega D(\omega)\hbar\omega < n(\omega) > = \int_0^{\omega_D} d\omega \left(\frac{L^2}{2\pi}\right)\frac{\omega}{v^2}\hbar\omega\left(\frac{1}{e^{\beta\hbar\omega}-1}\right)$$

for each polarization type (2 TA, 1 LA). For simplicity, we assume that the phonon velocity is independent of the polarization ($v_t = v_l = v$). Then we get

$$U = 3\left(\frac{\hbar L^2}{2\pi v^2}\right)\int_0^{\omega_D} d\omega \left(\frac{\omega^2}{e^{\beta\hbar\omega}-1}\right)$$

The heat capacity is

$$C = \frac{\partial U}{\partial T} = 3\left(\frac{\hbar L^2}{2\pi v^2}\right)\frac{d\beta}{dT}\int_0^{\omega_D} d\omega \frac{d}{d\beta}\left(\frac{\omega^2}{e^{\beta\hbar\omega}-1}\right)$$

or

$$C = \frac{\partial U}{\partial T} = 3\left(\frac{\hbar L^2}{2\pi v^2}\right)\frac{\hbar}{k_B T^2}\int_0^{\omega_D} d\omega \frac{\omega^3 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

Here we note that

$$N = \int_0^{\omega_D} d\omega D(\omega) = \int_0^{\omega_D} d\omega \frac{L^2}{2\pi}\frac{\omega}{v^2} = \frac{L^2 \omega_D{}^2}{4\pi v^2},$$

or

$$\omega_D{}^2 = 4\pi v^2 \frac{N}{L^2} = \frac{k_B{}^2}{\hbar^2}\Theta^2 ,$$

Then we have

$$C = \frac{\partial U}{\partial T} = 6Nk_B\left(\frac{T}{\Theta}\right)^2 \int_0^{\Theta/T} dx \frac{x^3 e^x}{\left(e^x - 1\right)^2} .$$

For $T << \Theta$,

$$C = 6Nk_B\left(\frac{T}{\Theta}\right)^2 \int_0^{\infty} dx \frac{x^3 e^x}{\left(e^x - 1\right)^2} = 6\varsigma(3)Nk_B\left(\frac{T}{\Theta}\right)^2 = 43.274Nk_B\left(\frac{T}{\Theta}\right)^2 ,$$

where

$$\int_0^{\infty} dx \frac{x^3 e^x}{\left(e^x - 1\right)^2} = 6\varsigma(3) = 7.21234 ,$$

where

$$\varsigma(3) = 1.2020569032 \;.$$

---

11. Heat capacity of 3D system

In the Debye model approximation, the velocity of sound is taken constant

$$\omega = vk ,$$

where v is the constant velocity of sound. The density of states becomes

$$D(\omega) = \frac{V\omega^2}{2\pi^2 v^3} ,$$

where $V = L^3$. The dimension of $D(\omega)$ is $[\frac{cm^3/s^2}{cm^3/s^3} = s]$. If there is N primitive cell, the total number of modes is N. A cut-off frequency ω_D is defined by

$$N = \int_0^{\omega_D} D(\omega)d\omega = \frac{V}{2\pi^2 v^3}\int_0^{\omega_D} \omega^2 d\omega = \frac{V{\omega_D}^3}{6\pi^2 v^3},$$

or

$${\omega_D}^3 = 6\pi^2 v^3 \frac{N}{V}.$$

Since $\omega_L = vk_D$ (k_D: cut-off wave vector),

$$k_D = \left(6\pi^2 \frac{N}{V}\right)^{1/3}.$$

In the Debye model, we do not allowed modes of wavenumber larger than k_D.

((**Note**))

$V = Na^3$ for sc crystal.

$$k_D = \left(6\pi^2 a^{-3}\right)^{1/3} = \left(6\pi^2\right)^{1/3} a^{-1} = \frac{3.89778}{a}.$$

Θ is the Debye temperature, and is defined by

$$\Theta = \frac{\hbar v}{k_B} k_D = \frac{\hbar v}{k_B}\left(6\pi^2 \frac{N}{V}\right)^{1/3}.$$

We introduce a new variable x defined by

$$x = \beta\hbar\omega = \frac{\hbar\omega}{k_B T},$$

where

$$x_D = \frac{\hbar\omega_D}{k_B T} = \frac{k_B\Theta}{k_B T} = \frac{\Theta}{T}.$$

We now consider the contribution of one longitudinal acoustic (LA) mode and the two transverse acoustic (TA) mode. Here for simplicity, we assume that

$$\frac{3}{v^3} = \frac{1}{{v_L}^3} + \frac{2}{{v_T}^3}.$$

where v_L and v_T are the velocities for the LA and TA modes. Note that we use

$$1\frac{V\omega^2}{2\pi^2 {v_L}^3} + 2\frac{V\omega^2}{2\pi^2 {v_T}^3} = \frac{V\omega^2}{2\pi^2}(\frac{1}{{v_L}^3} + \frac{2}{{v_T}^3}) = 3\frac{V\omega^2}{2\pi^2 v^3}.$$

Then we have

$$U = 3\int d\omega D(\omega)\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} = \frac{3\hbar V}{2\pi^2 v^3}\left(\frac{k_B T}{\hbar}\right)^4 \int_0^{\Theta/T} \frac{x^3}{e^x - 1}dx, \qquad (1)$$

or

$$\begin{aligned} U &= 3\frac{\hbar V}{2\pi^2 v^3}\frac{{k_B}^4}{\hbar^4} T^4 \int_0^{\Theta/T} \frac{x^3}{e^x - 1}dx \\ &= 3\frac{\hbar V}{2\pi^2 v^3}\frac{{k_B}^4}{\hbar^4}\Theta^3 T\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^3}{e^x - 1}dx \\ &= 9Nk_B T\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^3}{e^x - 1}dx \end{aligned}$$

The heat capacity is evaluated from the direct derivative of U given by Eq.(1),

$$C = \frac{\partial U}{\partial T} = 3\int d\omega D(\omega)\frac{d}{dT}\frac{\hbar\omega}{e^{\beta\hbar\omega}-1} = 3\int d\omega D(\omega)\frac{(\hbar\omega)^2(-e^{\beta\hbar\omega})}{\left(e^{\beta\hbar\omega}-1\right)^2}(-\frac{1}{k_BT^2}),$$

or

$$C = 3k_B\int d\omega D(\omega)\frac{e^{\beta\hbar\omega}(\beta\hbar\omega)^2}{\left(e^{\beta\hbar\omega}-1\right)^2} = 9Nk_B\left(\frac{T}{\theta}\right)^3\int_0^{\Theta/T}\frac{x^4e^x}{\left(e^x-1\right)^2}dx.$$

It is clear that C is derived by a scaling function of a reduced temperature T/Θ. In other words, C depends only on the variable T/Θ.

(a) For $\frac{\Theta}{T} << 1$ (the high temperature limit)

$$U = 9Nk_BT\left(\frac{T}{\Theta}\right)^3\int_0^{\Theta/T}\frac{x^3}{e^x-1}dx \approx 9Nk_BT\left(\frac{T}{\Theta}\right)^3\frac{1}{3}\left(\frac{\Theta}{T}\right)^3 = 3Nk_BT,$$

$$C = 9Nk_B\left(\frac{T}{\theta}\right)^3\int_0^{\Theta/T}\frac{x^4e^x}{\left(e^x-1\right)^2}dx \approx 9Nk_B\left(\frac{T}{\theta}\right)^3\int_0^{\Theta/T}x^2dx = 3Nk_B.$$

The heat capacity is independent of T as

$C = 3Nk_B$. (Dulong-Petit law).

(b) For $\frac{\Theta}{T} >> 1$ (the low temperature limit)

The upper limit of the integral may be taken to be infinite for all practical purposes. The integral then tends to be a constant. The total energy is evaluated as

$$U \approx 9Nk_BT\left(\frac{T}{\Theta}\right)^3\int_0^{\infty}\frac{x^3}{e^x-1}dx = 9Nk_BT\left(\frac{T}{\Theta}\right)^3\frac{\pi^4}{15},$$ Debye T^3 law

where

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}.$$

Then the heat C is obtained as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\Theta}\right)^3 = 233.782 N k_B \left(\frac{T}{\Theta}\right)^3,$$

which is well-known T^3 law of specific heat, valid at low temperatures. The heat capacity can be evaluated directly as

$$\begin{aligned} C &= 9 N k_B \left(\frac{T}{\theta}\right)^3 \int_0^{\Theta/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx \\ &= 9 N k_B \left(\frac{T}{\theta}\right)^3 \int_0^{\infty} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx \\ &= 9 N k_B \left(\frac{T}{\theta}\right)^3 \frac{4\pi^4}{15} = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta}\right)^3 \end{aligned}$$

where

$$\int_0^\infty \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx = \frac{4\pi^4}{15}.$$

12. Physical meaning of $C_V \approx T^3$ at low temperatures.

$$\hbar\omega_D = \hbar v k_D = k_B \Theta, \qquad \hbar v k_T = k_B T.$$

Only those lattice modes having $\hbar\omega < k_B T$ will be excited to any appreciable extent at T,

The fraction occupied by the excited modes is

$$\frac{\left(\frac{L}{2\pi}\right)^3 \frac{4\pi}{3} k_T{}^3}{\left(\frac{L}{2\pi}\right)^3 \frac{4\pi}{3} k_D{}^3} = \left(\frac{k_T}{k_D}\right)^3 = \left(\frac{T}{\Theta}\right)^3 .$$

The total number of states is $3N$ for 1 TA and 2 LA modes (N for each branch). Then there are of the order of

$$3N(\frac{T}{\Theta})^3 ,$$

excited modes, each having $k_B T$. The energy is

$$3Nk_B T(\frac{T}{\Theta})^3 ,$$

and the heat capacity is

$$C \approx 12Nk_B \left(\frac{T}{\Theta}\right)^3 .$$

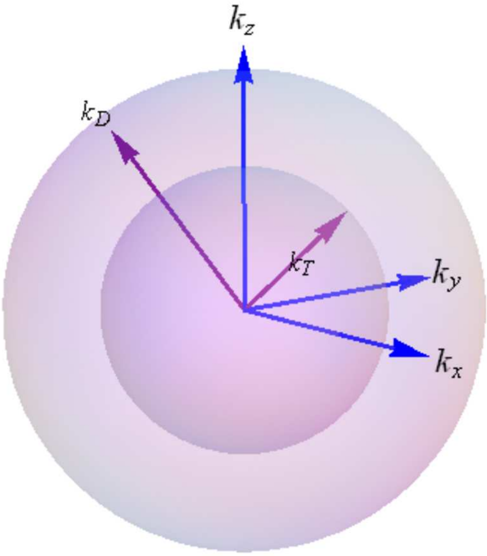


Fig. Definition of k_T and k_D (the Debye model) for the 3D spherical ***k***-space.

13. Numerical calculation of the heat capacity

$$\frac{C_M}{3R} = 3\left(\frac{T}{\theta}\right)^3 \int_0^{\Theta/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx \,,$$

where N_A is the Avogadro number, and R is the gas constant and $R = N_A k_B$.

R = 8.3144621 J/(mol K),

or

R = 1.9858775 cal/(mol K).

Note that

$$\int_0^{\infty} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx = \frac{4\pi^4}{15}$$

At low temperature ($T<<\Theta$),

$$\frac{C_M}{3R}=\frac{4\pi^4}{5}\left(\frac{T}{\theta}\right)^3.$$

At low temperature ($T>>\Theta$),

$$\frac{C_M}{3R}=1.$$

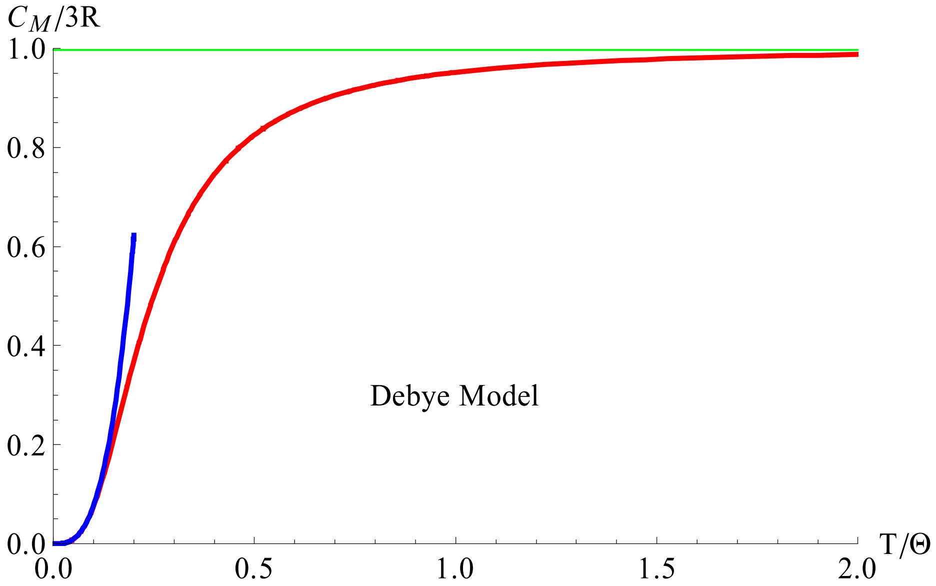


Fig. Scaling relation of $C_M/3R$ vs T/Θ, which is predicted from the Debye model. C_M is the molar specific heat. R is the gas constant. The blue line denotes the approximation valid for low temperatures ($T/\Theta<<1$). The green line denotes the Dulong Petit law at high temperatures ($T/\Theta>>1$)

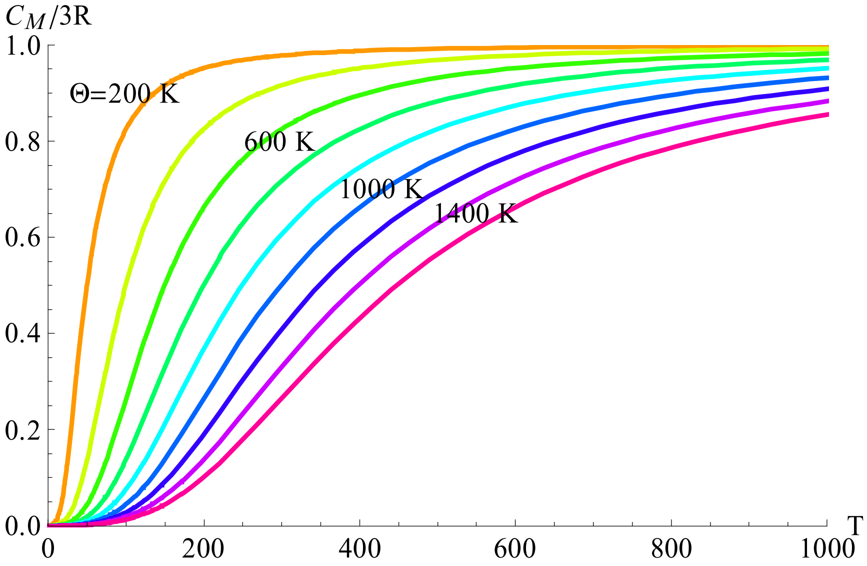


Fig. Specific heat $C_M/3R$ as s function of T, where Θ is changed as a parameter.

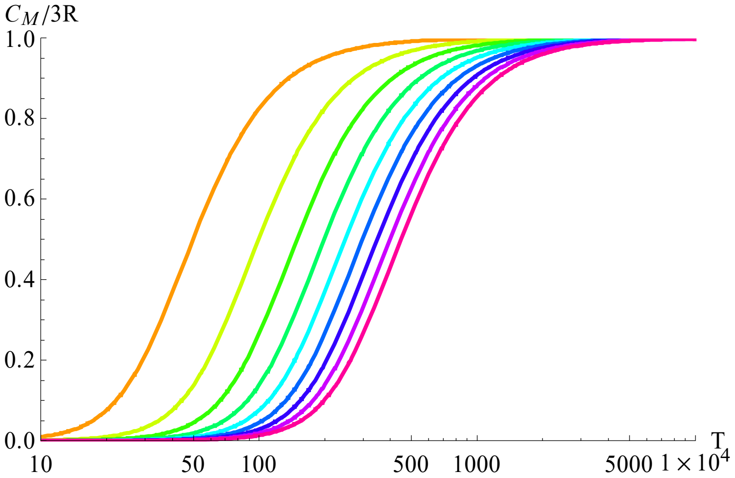


Fig. Specific heat $C_M/3R$ as s function of T (a logarithmic scale of the T axis).

14. Einstein model of the heat capacity

In the Einstein model, only the optical mode contributes to the specific heat. In this case, there exists only the optical phone: $3N$ states at ω. In the case of diatomic model, there are 2 branches (acoustic and optical branches). For the optical branch, there are 3N states (N for longitudinal modes and 2N for transverse modes).

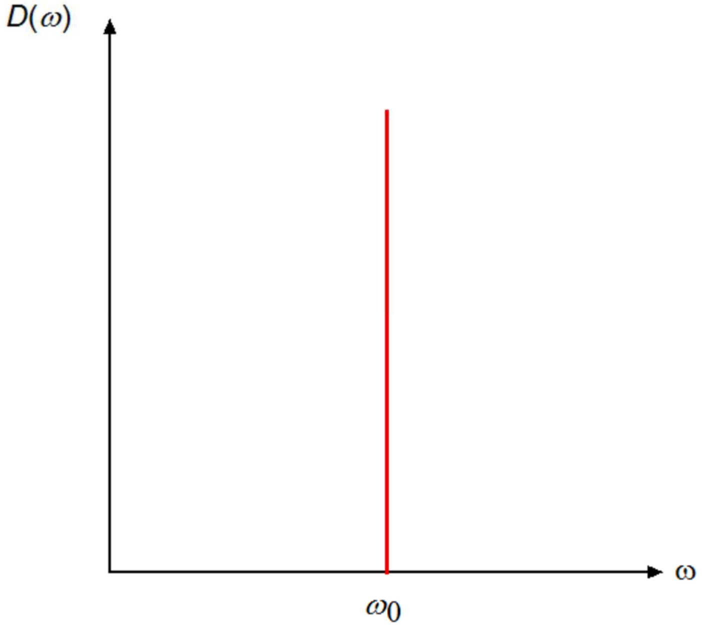


Fig. Density of states in the Einstein model.

$$D(\omega') = 3N\delta(\omega' - \omega) .$$

$$U = \int D(\omega')\hbar\omega' < n(\omega') > = 3N\hbar\omega < n(\omega) > = \frac{3N\hbar\omega}{e^{\beta\hbar\omega} - 1} .$$

The heat capacity of the oscillators is

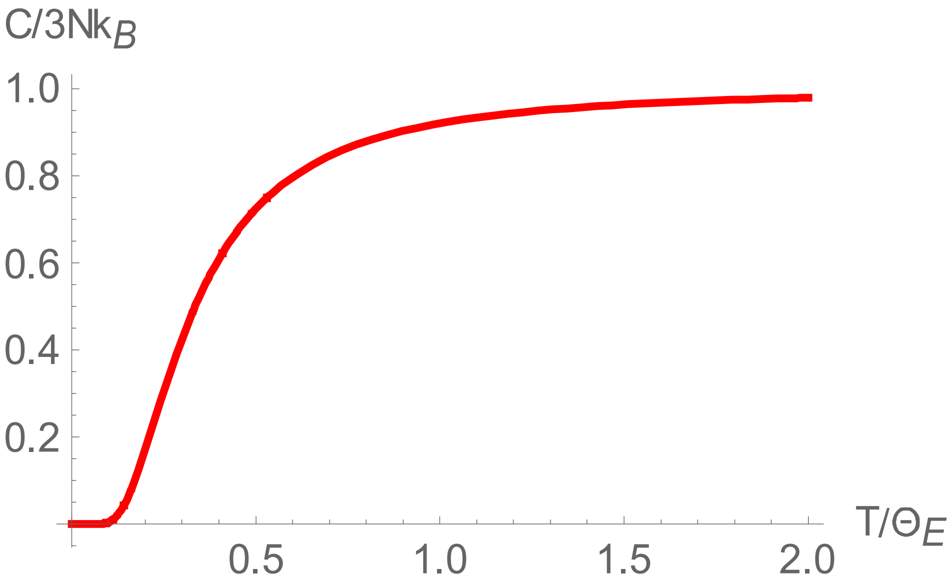
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2} .$$

The characteristic temperature Θ_E is defined by

$$\Theta_E = \frac{\hbar\omega}{k_B} .$$

Then

$$C_V = 3Nk_B(\frac{\Theta_E}{T})^2 \frac{e^{\frac{\Theta_E}{T}}}{\left(e^{\frac{\Theta_E}{T}}-1\right)^2}$$



Type equation here.

Fig. Heat capacity for the Einstein model.

((Note)) Specific heat in the Debye model

Table: Calculation of $C_M/3R$ vs T/Θ.

T/Θ	C_M/3R
0.	0.
0.05	0.00974076
0.1	0.075821
0.15	0.212992
0.2	0.368635
0.25	0.503059
0.3	0.607703
0.35	0.686573
0.4	0.745853
0.45	0.790823
0.5	0.825408
0.55	0.852407
0.6	0.873796
0.65	0.890976
0.7	0.904954
0.75	0.91646
0.8	0.926033
0.85	0.934076
0.9	0.940893
0.95	0.946718
1.	0.951732

15. General result for *D*(*ω*)

In general, the density of states can be expressed as

$$D(\omega)d\omega = \frac{L^3}{(2\pi)^3}\int_{shell} d^3\mathbf{k} = \frac{L^3}{(2\pi)^3}\int_{shell} dS_\omega dk_\perp ,$$

where

$$dk_\perp = dk_n ,$$

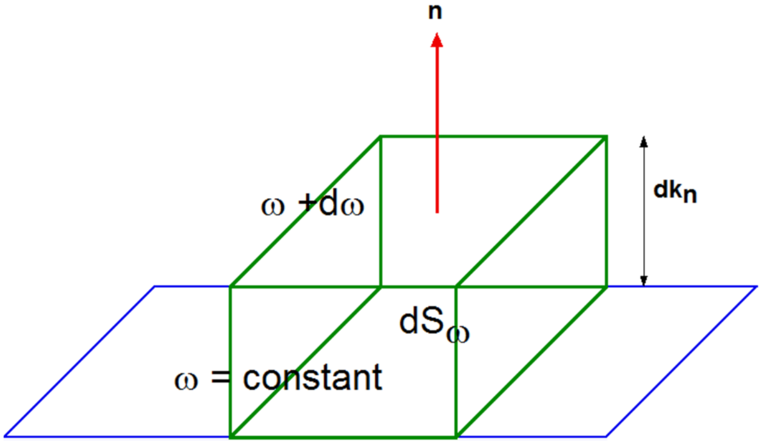


Fig. The volume element in the k space. $dk_n = dk_\perp$. $d^3k = dS_\omega dk_n = dS_\omega dk_\perp$

The group velocity is defined by

$$\mathbf{v}_k = \nabla_k \omega,$$

which is normal to the surface of ω = constant. We note that from the definition, we have

$$d\omega = \nabla_k \omega \cdot d\mathbf{k} = \mathbf{v}_k \cdot d\mathbf{k}.$$

When $d\omega = 0$ (ω = constant surface), $\nabla_k \omega$ is perpendicular to any vector on the surface (ω = constant). In other words, the group velocity $\mathbf{v}_k = \nabla_k \omega$ is normal to the surface with ω = constant.

Since the magnitude of the group velocity is given by

$$v_g = |\mathbf{v}_k| = \frac{\partial \omega}{\partial k_\perp},$$

or

$$d\omega = |\mathbf{v}_k| dk_\perp,$$

we have the k-space volume element as

$$dS_\omega dk_\perp = dS_\omega \frac{d\omega}{|\mathbf{v}_k|} = dS_\omega \frac{d\omega}{v_g}.$$

Then we get

$$D(\omega)d\omega = \frac{L^3}{(2\pi)^3} \int_{shell} \frac{dS_\omega d\omega}{v_g},$$

or

$$D(\omega) = \frac{V}{(2\pi)^3} \int_{shell} \frac{dS_\omega}{v_g}.$$

The integral is taken over the area of the surface with constant ω, in the ***k*** space.

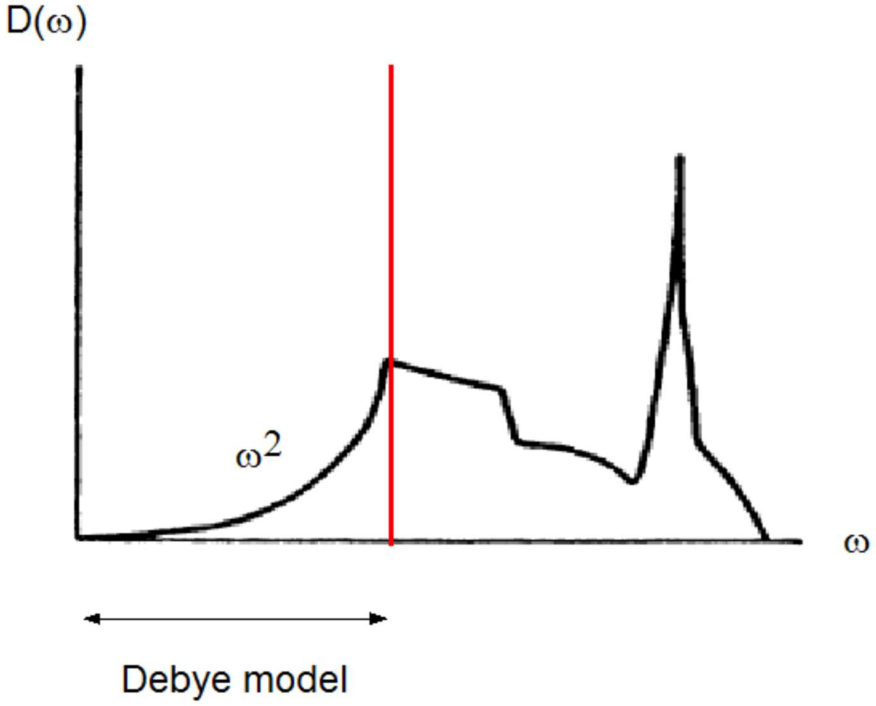


Fig. Actual lattice spectrum.

The spectrum for the crystal starts as ω^2 for small ω, but discontinuities develop at singular points.

---

16. Melting criterion for the 3D case

((**Lindeman criterion**))

Solid melts because the vibrations of the atoms about their equilibrium positions becomes too large.

The mean squares amplitude of vibration is defined as

$$\left\langle u_x{}^2 \right\rangle = \left\langle \left| u(\mathbf{q}) \right|^2 \right\rangle = \sum_{\mathbf{q}} \frac{\hbar\omega_q (< n_q > + \frac{1}{2})}{NM\omega_q{}^2} = \frac{1}{NM} \sum_{\mathbf{q}} \frac{\left\langle E_{\mathbf{q}} \right\rangle}{\omega_{\mathbf{q}}{}^2} .$$

The solid melts where $\left\langle \delta R_i{}^2 \right\rangle$ becomes comparable to a^2, where a is the lattice constant. Here we use the Debye model;

$$M\left\langle u_x{}^2 \right\rangle = \frac{1}{N} \sum_{\mathbf{q}} \frac{\left\langle E_{\mathbf{q}} \right\rangle}{\omega_{\mathbf{q}}{}^2} = \frac{\int_0^{\omega_D} D_3(\omega) d\omega \frac{\hbar\omega}{\omega^2} [n(\omega) + \frac{1}{2}]}{\int_0^{\omega_D} D_3(\omega) d\omega}$$

where $D_3(\omega)$ is the density of states for the 3D system,

$$D_3(\omega) = \frac{V\omega^2}{2\pi^2 v^3} ,$$

and

$$x = \frac{\hbar\omega}{k_B T} , \qquad \frac{\hbar\omega_D}{k_B T} = \frac{\Theta}{T} .$$

Note that Θ is defined by.

$$k_B\Theta = \hbar\omega_D = \hbar v q_D = \hbar v(\frac{6\pi^2 N}{V})^{1/3}.$$

Since $V = Na^3$, we get

$$q_D = \left(\frac{6\pi^2}{a^3}\right)^{1/3}.$$

Then we have

$$\langle u_x{}^2\rangle = \frac{3\hbar^2}{Mk_B\Theta}\left(\frac{T}{\Theta}\right)^2 \int_0^{\Theta/T} x dx(\frac{1}{e^x - 1} + \frac{1}{2}).$$

For $T << \Theta$,

$$\langle u_x{}^2\rangle \approx \frac{3\hbar^2}{4Mk_B\Theta}.$$

For $T >> \Theta$,

$$\langle u_x{}^2\rangle = \frac{3\hbar^2}{Mk_B\Theta}\left(\frac{T}{\Theta}\right).$$

which is proportional to *T*.

((Melting criterion)) Lindemann criterion

We define the parameter *f*

$$f = \frac{\sqrt{\langle u_x{}^2\rangle + \langle u_y{}^2\rangle + \langle u_z{}^2\rangle}}{a} = \sqrt{\frac{9\hbar^2 T}{Ma^2 k_B \Theta^2}} \qquad \text{for } T >> \Theta.$$

When $f = f_c$, the melting occurs at $T = T_m$;

$$T_m = \frac{f_c^{\ 2}}{9\hbar^2} M k_B \Theta^2 a^2 ,$$

where f_c = 0.2 - 0.3 (typically).

((**Example**))

Al (aluminium)

Θ = 428 K. a = 4.05 Å (fcc). Density ρ = 2.375 g/cm^3.

T_m = 933.47 K. Molar mass = 26.9815386 g.

Then we have

$$T_m = 185696 f_c^{\ 2}$$

leading to

f_c = 0.07.

Rb (rubidium)

Θ = 56 K. a = 5.585 Å, (bcc). Density ρ = 1.532 g/cm^3.

T_m = 312.46 K. Molar mass = 85.4678 g.

$$T_m = 19149.7 f_c^{\ 2} ,$$

leading to

f_c = 0.128.

17. Stability of the 2D system: Lindemann criterion

Let us calculate

$$M\left\langle u_x^{\ 2}\right\rangle = \frac{1}{N}\sum_{\mathbf{q}} \frac{\left\langle E_{\mathbf{q}}\right\rangle}{\omega_{\mathbf{q}}^{\ 2}} = \frac{\int_0^{\omega_D} D_2(\omega)d\omega \frac{\hbar\omega}{\omega^2}[n(\omega)+\frac{1}{2}]}{\int_0^{\omega_D} D_2(\omega)d\omega}$$

for the 2D system,where

$$D_2(\omega) = \frac{L^2\omega}{2\pi v^2}, \qquad x = \frac{\hbar\omega}{k_B T}, \qquad \frac{\hbar\omega_D}{k_B T} = \frac{\Theta}{T}$$

Note that Θ is defined as follows.

$$N = \int_0^{\omega_D} D_2(\omega) d\omega = \int_0^{\omega_D} \frac{L^2\omega}{2\pi v^2} d\omega = \frac{L^2 {\omega_D}^2}{4\pi v^2},$$

or

$$\hbar\omega_D = k_B\Theta = \hbar\left(\frac{4\pi v^2 N}{L^2}\right)^{1/2}$$

Then we get

$$\langle {u_x}^2 \rangle = \frac{2\hbar^2}{Mk_B\Theta}\left(\frac{T}{\Theta}\right)\int_0^{\Theta/T}\left(\frac{1}{e^x - 1} + \frac{1}{2}\right)dx .$$

The integral does not converge

$$\lim_{x\to 0}\frac{1}{e^x - 1} = \infty .$$

The calculation of the mean quadratic displacement in the plane (or in the chain) leads to a divergent value at any temperature. Thus 2D crystals are unstable in the harmonic approximation. Some 3D interaction (whatever small with respect to intralayer or interchain interaction is necessary to stabilize the low dimensional system.

18. Summary

((Density of states))

In d-dimensional harmonic crystal, the low frequency density of states varies as ω^{d-1}.

For the 1D system

$$D(\omega) = \frac{L}{\pi v}.$$

For the 2D system

$$D(\omega) = \frac{A\omega}{2\pi v^2}.$$

For the 3D system

$$D(\omega) = \frac{V\omega^2}{2\pi^2 v^3}.$$

where A is the area for the 2D system and V is the volume of the 3D system.

((**Heat capacity**))

For the 1D system

$$C = \pi^2 N k_B (\frac{T}{\Theta}).$$

For the 2D system

$$C = 43.3 N k_B (\frac{T}{\Theta})^2.$$

For the 3D system

$$C = \frac{12\pi^4}{5} N k_B (\frac{T}{\Theta})^3.$$

19. Debye-Waller factor in the x-ray scattered intensity

As the temperature of the crystal is increases, the intensity of Bragg reflection decreases. This result can be explained as follows. Suppose that the position of atom depends on time *t* as

$$\boldsymbol{R}_j(t) = \boldsymbol{R}_j + \boldsymbol{u}(t).$$

Then the structure factor is given by

$$S_G = \sum_j f_j \left\langle \exp[-i\mathbf{G}\cdot\mathbf{R}_j(t)] \right\rangle = \sum_j f_j \exp[-i\mathbf{G}\cdot\mathbf{R}_j] \left\langle \exp[-i\mathbf{G}\cdot\mathbf{u}(t)] \right\rangle,$$

where <··> denotes thermal average, $\boldsymbol{R}_j$ is the position vector of *j*-th atom in the unit cell in thermal equilibrium, and f_j is the atomic form factor. Using the series expansion, we get

$$\begin{aligned}\left\langle \exp[-i\boldsymbol{G}\cdot\boldsymbol{u}(t)] \right\rangle &= 1 - \frac{i}{1!}\left\langle [\boldsymbol{G}\cdot\boldsymbol{u}(t)] \right\rangle - \frac{1}{2!}\left\langle [\boldsymbol{G}\cdot\boldsymbol{u}(t)]^2 \right\rangle + \frac{i}{3!}\left\langle [\boldsymbol{G}\cdot\boldsymbol{u}(t)]^3 \right\rangle + ... \\ &= 1 - \frac{i}{1!}G\left\langle u \right\rangle \left\langle \cos\theta \right\rangle - \frac{1}{2!}G^2\left\langle u^2 \right\rangle \left\langle \cos^2\theta \right\rangle + \frac{i}{3!}G^3\left\langle u^3 \right\rangle \left\langle \cos^3\theta \right\rangle + .\end{aligned}$$

where θ is the angle between $\boldsymbol{G}$ and $\boldsymbol{u}$. Note that $\boldsymbol{u}$ is a random thermal displacement uncorrelated with the direction of $\boldsymbol{G}$. Then we have

$$\left\langle [\boldsymbol{G}\cdot\boldsymbol{u}(t)]^p \right\rangle = G^p\left\langle u^p \right\rangle \left\langle \cos^p\theta \right\rangle = \frac{1}{2}[\frac{1+(-1)^p}{1+p}]G^p\left\langle u^p \right\rangle,$$

for the isotropic system;

$$\begin{aligned}\left\langle \cos^p\theta \right\rangle &= \frac{1}{4\pi}\int \cos^p\theta d\Omega \\ &= \frac{1}{4\pi}\int_0^\pi \cos^p\theta(2\pi\sin\theta)d\theta. \\ &= \frac{1}{2}\frac{1+(-1)^p}{1+p}\end{aligned}$$

Then

$$S_G = \sum_j f_j \exp[-i\mathbf{G}\cdot\mathbf{R}_j]\{1 - \frac{1}{6}G^2\left\langle u^2 \right\rangle + ...\} = \exp[-\frac{1}{6}G^2\left\langle u^2 \right\rangle]\sum_j f_j \exp[-i\mathbf{G}\cdot\mathbf{R}_j].$$

The scattered intensity is

$$I_G = S_G S_G^* = I_0 \exp[-\frac{1}{3} G^2 \langle u^2 \rangle] = I_0 \exp[-2W],$$

where I_0 is the scattered intensity from the rigid lattice. The exponential factor W is the Debye-Waller factor. Here $\langle u^2 \rangle$ is the mean square displacement of an atom. The thermal average potential energy of a simple harmonics in the 3D system is

$$\frac{1}{2} M\omega^2 \langle u^2 \rangle = \langle U \rangle = \langle K \rangle = \frac{3}{2} k_B T \ ,$$

where $\langle U \rangle$ and $\langle K \rangle$ are the average of the potential energy and the average of the kinetic energy. Then we have

$$\langle u^2 \rangle = \frac{3k_B T}{M\omega^2} .$$

Then the intensity is evaluated as

$$I_G = I_0 \exp[-\frac{k_B T}{M\omega^2} G^2] .$$

The intensity exponentially decreases with increasing temperature.

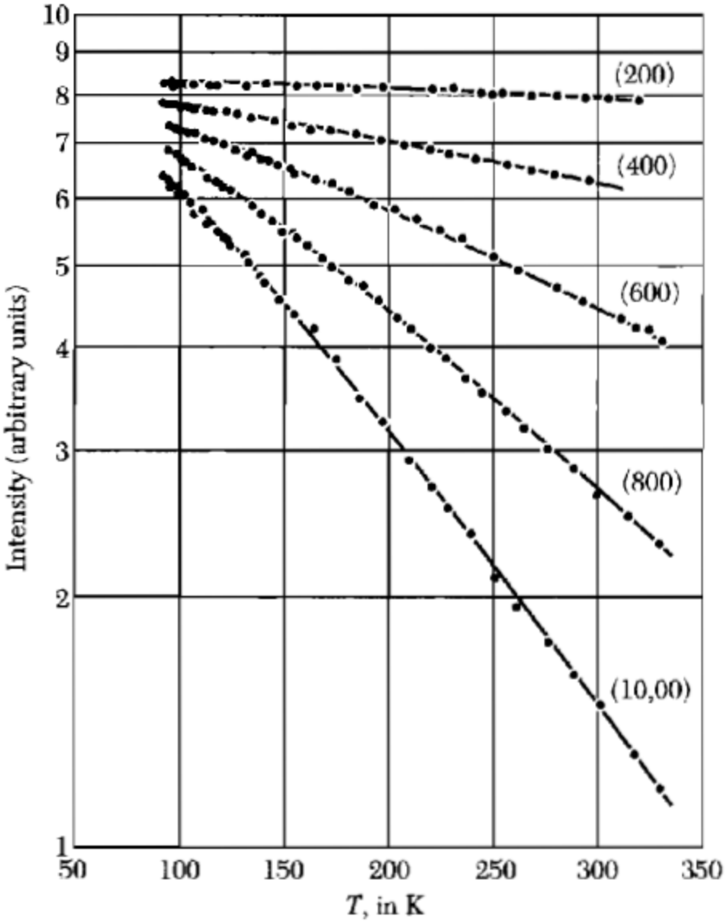


Fig. The dependence of intensity on temperature for the (h00) x-ray reflections of Al. Reflections (h00) with h odd are forbidden for a fcc structure (R.M. Nicklow and R.A. Young, Phys. Rev. 152, 591 (1966).). [This figure is obtained from the book of "Introduction to Solid State Physics, by C. Kittel 8-th edition].

20. Debye-Waller factor (quantum mechanical treatment)

Here we calculate the Debye-Waller factor calculation based on the quantum mechanical treatment. First we define the Debye temperature *Θ*.

$$N = \sum_q 1 = \frac{L^3}{(2\pi)^3}\int_0^{q_D} 4\pi q^2 dq = \frac{L^3}{(2\pi)^3} 4\pi \frac{q_D{}^3}{3} = \frac{L^3 q_D{}^3}{6\pi^2},$$

or

$$q_D = \left(\frac{6\pi^2 N}{L^3}\right)^{1/3},$$

or

$$\Theta = \frac{\hbar v}{k_B} q_D = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{L^3}\right)^{1/3}.$$

The Debye-Waller factor is given by

$$W = \frac{1}{6}G^2 \sum_q \left\langle u_q{}^2 \right\rangle = \frac{1}{6}G^2 \sum_q \frac{\hbar^2 (n_q + 1)}{\hbar N M \omega_q} = \frac{\hbar^2 G^2}{6NM} \sum_q \frac{(n_q + \frac{1}{2})}{\hbar \omega_q},$$

or

$$W = \frac{\hbar^2 G^2}{6NM} \frac{3L^3}{(2\pi)^3} \int_0^{q_D} 4\pi q^2 dq \frac{(n_q + \frac{1}{2})}{\hbar \omega_q} = \frac{\hbar^2 G^2}{2NM} \frac{4\pi L^3}{(2\pi)^3} \int_0^{q_D} q^2 dq \frac{(n_q + \frac{1}{2})}{\hbar \omega_q}.$$

We assume that $\omega = vq$. Then we get

$$W = \frac{\hbar G^2 L^3}{4\pi^2 v^3 NM} \int_0^{q_D} \omega d\omega (n_q + \frac{1}{2}) = \frac{\hbar G^2 L^3}{4\pi^2 v^3 NM} \left(\frac{k_B T}{\hbar}\right)^2 \int_0^{\Theta/T} x dx (\frac{1}{e^x - 1} + \frac{1}{2}),$$

or

$$\begin{aligned} W &= \frac{\hbar G^2 L^3}{4\pi^2 v^3 NM} \frac{\hbar}{k_B \Theta} \left(\frac{k_B \Theta}{\hbar}\right)^3 \left(\frac{T}{\Theta}\right)^2 \int_0^{\Theta/T} x dx (\frac{1}{e^x - 1} + \frac{1}{2}) \\ &= \frac{G^2 L^3}{4\pi^2 v^3 NM} \frac{1}{\Theta} \frac{k_B{}^2}{\hbar} \Theta^3 \left(\frac{T}{\Theta}\right)^2 \int_0^{\Theta/T} x dx (\frac{1}{e^x - 1} + \frac{1}{2}) \\ &= \frac{3\hbar^2 G^2}{2M k_B \Theta} \left(\frac{T}{\Theta}\right)^2 \int_0^{\Theta/T} x dx (\frac{1}{e^x - 1} + \frac{1}{2}) \end{aligned}$$

When $\Theta/T << 1$ (high temperatures), we get

$$2W = \frac{3\hbar^2 G^2}{Mk_B\Theta}\left(\frac{T}{\Theta}\right)^2 \int_0^{\Theta/T} dx = \frac{3\hbar^2 G^2 T}{Mk_B\Theta^2}.$$

where we use the approximation

$$x(\frac{1}{e^x - 1} + \frac{1}{2}) = 1 + \frac{x^2}{12} + O(x^3)$$

21. Neutron inelastic scattering

Thermal neutrons interact with matter through the interaction with nucleus via the so-called strong force. The interaction is strong, but extends only over a distance of the order of 10 fm (femtometers), the size of the atomic nucleus.

1 fm = 10^{-15}m = 10^{-13} cm.

It can have the effect of the neutron being scattered by the nucleus. In this sense, the form factor b_j is independent of the related wavevectors, unlike the case of x-ray scattering.

Now we consider the case when the incoming neutron (wavevector $\boldsymbol{k}_i = \boldsymbol{k}$, energy E_k) is scattered by a system. In this process, a phonon (wavevector $\boldsymbol{q}$, energy $\hbar\omega_q$) are absorbed or emitted. After that, the outgoing neutron has a wavevector $\boldsymbol{k}_f = \boldsymbol{k}'$, energy $E_{k'}$. where $\boldsymbol{k}$ is the wavevector of the incoming neutron,

$$\hbar\omega_k = \frac{\hbar^2 k^2}{2M_n},$$ (the energy of incoming neutron with mass M_n)

$$\hbar\omega_{k'} = \frac{\hbar^2 k'^2}{2M_n}.$$ (the energy of outgoing neutron)

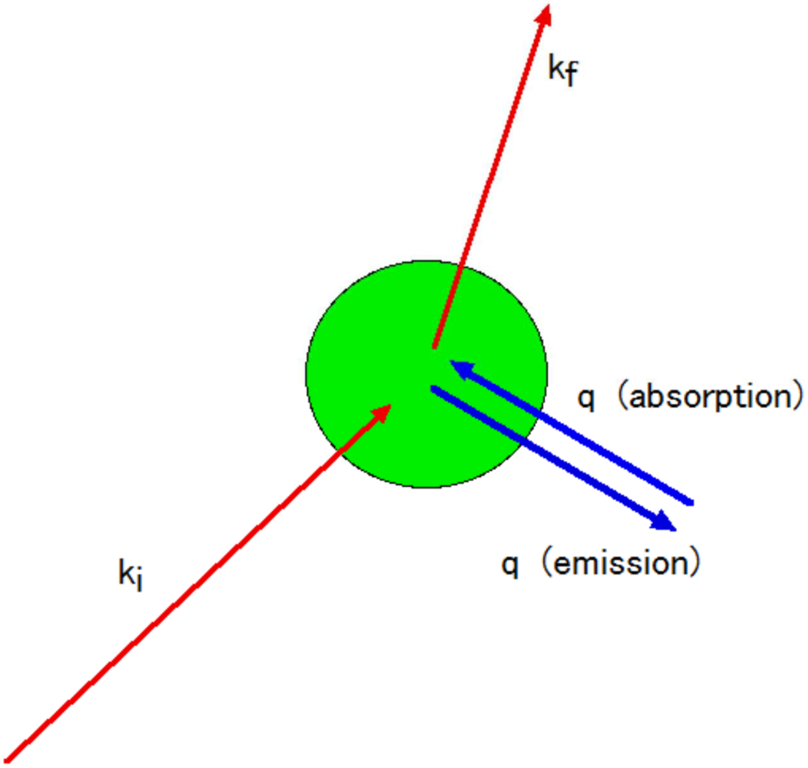


Fig. Schematic diagram of the inelastic neutron scattering. $\boldsymbol{k}_\mathrm{i} = \boldsymbol{k}$. $\boldsymbol{k}_\mathrm{f} = \boldsymbol{k}'$.

We consider the scattering amplitude defined by

$$S(t) = e^{i\omega_0 t} \int d\boldsymbol{r} e^{-i\boldsymbol{Q}\cdot\boldsymbol{r}} V(\boldsymbol{r},t),$$

where

$$V(\boldsymbol{r},t) = \sum_j b_j \delta[\boldsymbol{r} - \boldsymbol{R}_j - \boldsymbol{u}_j(t)],$$

is the interaction potential [for simplicity we neglect the term) $(2\pi\hbar^2/m)$ and b_j is the scattering length for atoms for neutron scattering. We note that the potential

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{G}} V_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}} = \sum_j b_j \delta(\boldsymbol{r} - \boldsymbol{R}_j)$$

satisfies the periodic condition such that

$$V(\boldsymbol{r}+\boldsymbol{T}) = V(\boldsymbol{r}).$$

The Fourier component V_G is calculated as

$$\begin{aligned} V_{\boldsymbol{G}} &= \int d\boldsymbol{r} e^{-i\boldsymbol{G}\cdot\boldsymbol{r}} V(\boldsymbol{r}) \\ &= \int d\boldsymbol{r} e^{-i\boldsymbol{G}\cdot\boldsymbol{r}} \sum_j b_j \delta(\boldsymbol{r}-\boldsymbol{R}_j) \\ &= \sum_j b_j e^{-i\boldsymbol{G}\cdot\boldsymbol{R}_j} \end{aligned}$$

which is similar to the structure factor when b_j is equal to the atomic form factor f_j for the *x*-ray diffraction. Thus we get

$$\begin{aligned} S(t) &= e^{i\omega_0 t} \int d\boldsymbol{r} e^{-i\boldsymbol{Q}.\boldsymbol{r}} V(\boldsymbol{r},t) \\ &= \sum_j b_j \int e^{-i(\boldsymbol{Q}\cdot\boldsymbol{r}-\omega_0 t)} \delta[\boldsymbol{r}-\boldsymbol{R}_j-\boldsymbol{u}_j(t)] d\boldsymbol{r} \\ &= \sum_j b_j e^{i\omega_0 t} e^{-i[\boldsymbol{Q}\cdot\{\boldsymbol{R}_j+\boldsymbol{u}_j(t)\}]} \end{aligned}$$

where $\boldsymbol{Q}$ is the scattering vector and is defined by

$$\boldsymbol{Q} = \boldsymbol{k}' - \boldsymbol{k},$$

and

$$\omega_0 = \omega_{k'} - \omega_k.$$

((**Note**)) In typical textbooks of neutron scattering, $\boldsymbol{Q}$ and ω_0 are defined as

$$\boldsymbol{Q} = \boldsymbol{k} - \boldsymbol{k}',$$

and

$$\omega_0 = \omega_k - \omega_{k'} .$$

Using the Taylor expansion, we get

$$S(t) = e^{i\omega_0 t} \sum_j b_j e^{-i\mathbf{Q}\cdot\mathbf{R}_j} [1 - i\mathbf{Q}\cdot\mathbf{u}_j(t) + ...] .$$

Here we note that

$$\mathbf{u}_j(t) = u\mathbf{e}_q e^{i(\mathbf{q}\cdot\mathbf{R}_j - \omega_q t)} ,$$

where $\boldsymbol{e}_\mathrm{q}$ is the polarization vector of phonon (LA, TA, LO, TO branches of phonon), and *u* is the amplitude of oscillation in the displacement. So we have

$$\begin{aligned} S(t) &= e^{i\omega_0 t} \sum_j b_j e^{-i\boldsymbol{Q}\cdot\boldsymbol{R}_j} \{1 + (\boldsymbol{Q}\cdot\boldsymbol{e}_q) u e^{i(\boldsymbol{q}\cdot\boldsymbol{R}_j - \omega_q t)}\} \\ &= e^{i\omega_0 t} \sum_j b_j e^{-i\boldsymbol{Q}\cdot\boldsymbol{R}_j} + \sum_j b_j (\boldsymbol{Q}\cdot\boldsymbol{e}_q) u e^{-i(\boldsymbol{Q}-\boldsymbol{q})\cdot\boldsymbol{R}_j} e^{i(\omega_0 - \omega_q)t} \end{aligned}$$

The first term is the elastic scattering (time-independent term except for $e^{i\omega_0 t}$). We use

$$S_{elastic} = \sum_j b_j e^{-i\mathbf{Q}\cdot\mathbf{R}_j} ,$$

where the Bragg condition

$$\boldsymbol{k}' = \boldsymbol{k}_\mathrm{Bragg}, \qquad \boldsymbol{Q} = \boldsymbol{k}_\mathrm{Bragg} - \boldsymbol{k} = \boldsymbol{G}.$$

is satisfied and

$$\boldsymbol{k}_\mathrm{Bragg} = \boldsymbol{k} + \boldsymbol{G}$$

which lies on the Ewald sphere;

$$|\mathbf{k}_{Bragg}| = |\mathbf{k}| = k = \frac{2\pi}{\lambda} .$$

The second term is the inelastic scattering (time-dependent term),

$$S_{inelatic}(t) = \sum_j b_j(\boldsymbol{Q}\cdot\boldsymbol{e}_q)ue^{-i(\boldsymbol{Q}-\boldsymbol{q})\cdot\boldsymbol{R}_j}e^{i(\omega_0-\omega_q)t} ,$$

where

$$\boldsymbol{Q}-\boldsymbol{q}=\boldsymbol{G},$$

with

$$\boldsymbol{Q}=\boldsymbol{k}'-\boldsymbol{k} .$$

Note that ***k***' is no longer equal to ***k***$_{\text{Bragg}}$ on the Ewald sphere,

$$\boldsymbol{k}'=\boldsymbol{k}_{Bragg}+\boldsymbol{q} .$$

Using these relations, we get the momentum conservation,

$$\boldsymbol{Q}=\boldsymbol{k}'-\boldsymbol{k}=(\boldsymbol{k}_{Bragg}+\boldsymbol{q})-\boldsymbol{k}=(\boldsymbol{k}_{Bragg}-\boldsymbol{k})+\boldsymbol{q}=\boldsymbol{G}+\boldsymbol{q} ,$$

We note that the wavevector ***q*** of the phonon is in the first Brillouin zone centered around ***G*** in the reciprocal lattice space.

From the integral over time *t*, we get

$$\int dte^{i(\omega_0-\omega_q)t}=2\pi\delta(\omega_0-\omega_q) ,$$

leading to the energy conservation law

$$\omega_0=\omega_{k'}-\omega_k=\omega_q .$$

where ω_q is the angular frequency of the phonon with the wavevector ***q***.

22. The absorption and emission of phonon

We assume that the displacement vector ***u***$_{\text{j}}$ is given by

$$\boldsymbol{u}_j = \boldsymbol{e}_q[u_q e^{i(\boldsymbol{q}\cdot\boldsymbol{R}_j - \omega_q t)} + u_q^{\,*} e^{-i(\boldsymbol{q}\cdot\boldsymbol{R}_j - \omega_q t)}],$$

where $\boldsymbol{q}$ is the wavevector of phonon, $\mathbf{e}_q$ is the polarization vector, and u_q is the displacement amplitude (in general, a complex number). Then the inelastic scattering term is rewritten as

$$S_{inelastic}(t) = -i(\mathbf{Q}\cdot\mathbf{e}_q)\sum_j b_j\{u_q e^{i(\omega_0-\omega_q)t} e^{-i(\mathbf{Q}-\mathbf{q})\cdot\mathbf{R}_j} + u_q e^{i(\omega_0+\omega_q)t} e^{-i(\mathbf{Q}+\mathbf{q})\cdot\mathbf{R}_j}\}.$$

Taking the integral over time t, we have

$$S_{inelastic}(\mathbf{Q},\omega_0) = -i2\pi(\mathbf{Q}\cdot\mathbf{e}_q)\sum_j b_j\{u_q\delta(\omega_0-\omega_q)e^{-i(\mathbf{Q}-\mathbf{q})\cdot\mathbf{R}_j} + u_q^{\,*}\delta(\omega_0+\omega_q)e^{-i(\mathbf{Q}+\mathbf{q})\cdot\mathbf{R}_j}\}.$$

The first term corresponds to the absorption of phonon and the second term corresponds to the emission of phonon. For simplicity, b_j is independent of j. Then we get

$$\begin{aligned} S_{inelastic}(\mathbf{Q},\omega_0) = -i2\pi bN(\mathbf{Q}\cdot\mathbf{e}_q)\{&u_q\delta(\omega_0-\omega_q)\delta(Q-\mathbf{q}-\mathbf{G}) \\ &+ u_q^{\,*}\delta(\omega_0+\omega_q)\delta(Q+\mathbf{q}-\mathbf{G})\} \end{aligned}$$

Here we use the notation

$$|u_q|^2 = \frac{\hbar\left(\langle n_q\rangle + \frac{1}{2}\right)}{NM\omega_q},$$

from the previous chapter and the consideration from the quantum mechanics of the simple harmonics,

$$\hat{a}_\mathbf{q}^{\,+}|n_\mathbf{q}\rangle = \sqrt{n_\mathbf{q}+1}\,|n_\mathbf{q}+1\rangle, \qquad \text{for the creation of phonon,}$$

$$\hat{a}_\mathbf{q}|n_\mathbf{q}\rangle = \sqrt{n_\mathbf{q}}\,|n_\mathbf{q}-1\rangle. \qquad \text{for the destruction of phonon.}$$

Finally we get the scattering intensity which is proportional to

$$I(\mathbf{Q},\omega_0) = b^2 \frac{(\mathbf{Q}\cdot\mathbf{e}_q)^2}{M\omega_{\mathbf{q}}}[(\langle n_{\mathbf{q}}\rangle + 1)\delta(\omega_0 - \omega_{\mathbf{q}})\delta(\mathbf{Q}-\mathbf{q}-\mathbf{G}) \\ + \langle n_{\mathbf{q}}\rangle \delta(\omega_0 + \omega_q)\delta(\mathbf{Q}+\mathbf{q}-\mathbf{G})\}] .$$

Using the factor $(\mathbf{Q}\cdot\mathbf{e}_q)^2$, we can select the branch. if $\mathbf{Q}\perp\mathbf{e}_q$, the branch does not contribute to the inelastic neutron scattering.

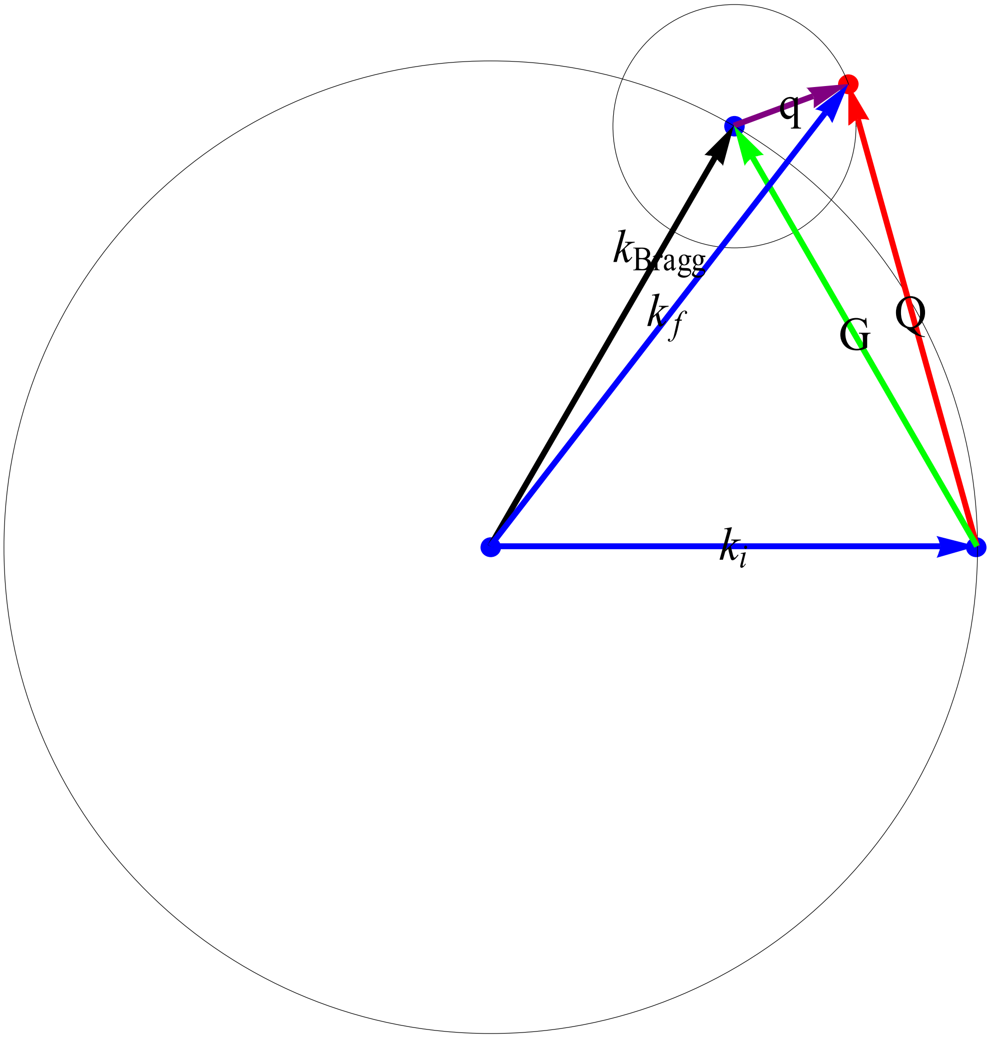


Fig. **Selection rule**. The transverse phone mode (***e***$_{\text{q}}$//***q***). The longitudinal mode (***e***$_{\text{q}}$⊥***q***). In this configuration, the scattering vector ***Q*** is nearly perpendicular to the vector ***q***. Thus the transverse phonon mode can be observed mainly. The first Brillouin zone is the smallest square region surrounding around the point (***q*** = 0).

23. Ewald sphere for the inelastic neutron scattering

We rewrite the energy and momentum conservation laws for neutrons

$$\Delta E = E_{k'} - E_k = \hbar\omega_0 = \hbar\omega_q ,$$

$$\Delta \mathbf{k} = \mathbf{k}' - \mathbf{k} = \mathbf{Q} = \mathbf{G} + \mathbf{q} ,$$

where $\hbar\omega_q$ and ***q*** are the energy and momentum, lost (or gained) by a lattice vibration (phonon). ***q*** is the wavevector of phonon and is in the first Brillouin zone centered at the reciprocal lattice vector ***G*** in the reciprocal lattice. If we know E_{k} and ***k*** and measure $E_{\mathrm{k'}}$ and ***k'***, we can obtain $\hbar\omega_q$ and ***q***, which give us a point on the dispersion curve of the phonon.

The modified Ewald sphere is given below. We note that $\boldsymbol{k}_{\mathrm{Bragg}}$ and ***k*** lie on the Ewald sphere and

$$\left|\mathbf{k}_{Bragg}\right| = \left|\mathbf{k}\right| = k = \frac{2\pi}{\lambda} .$$

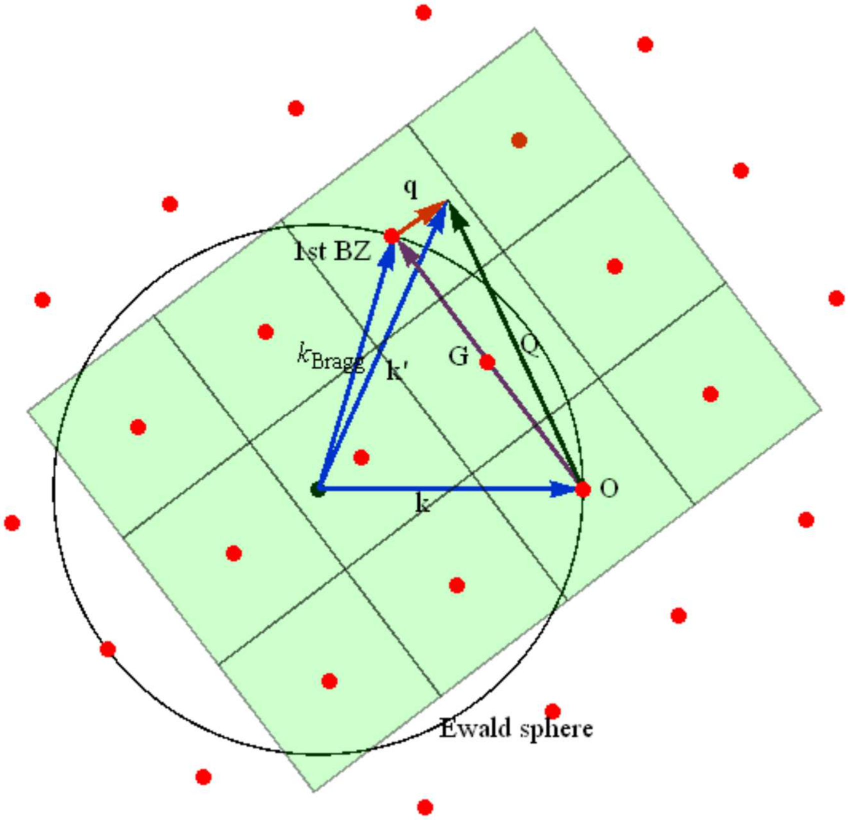
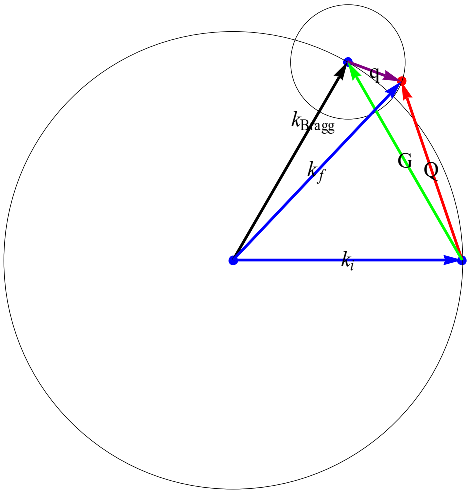
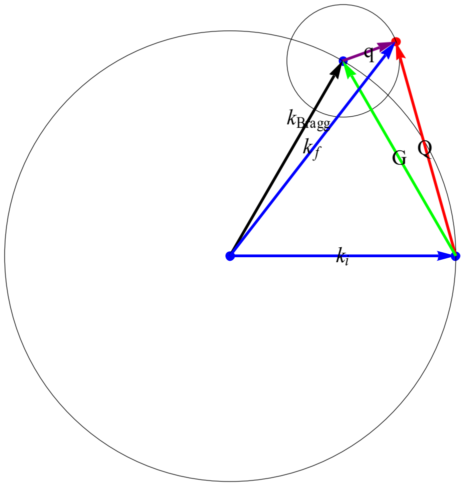


Fig. Modified Ewald construction for inelastic neutron scattering measurement. $\boldsymbol{k}$ and $\mathbf{k}_{Bragg} = \mathbf{k} + \mathbf{G}$ lie on the Ewald sphere. The angle between $\boldsymbol{k}_{\text{Bragg}}$ and $\boldsymbol{k}$, is the angle $2\theta_{\text{Bragg}}$. The Bragg reflection occurs at $\boldsymbol{k}_{\text{Bragg}}$ on the Ewald sphere. $\mathbf{k}_{Bragg} = \mathbf{k} + \mathbf{G} = \mathbf{k}' - \mathbf{q}$. $\Delta E = \hbar\omega' - \hbar\omega = E_{k'} - E_{k} = \hbar\omega_{q}$. $\boldsymbol{Q}$ = $\boldsymbol{k}'$ - $\boldsymbol{k}$ (the scattering vector). The phonon dispersion curve can be obtained from the relation between $\hbar\omega_{q}$ and $\boldsymbol{q}$ in the first Brillouin zone around the reciprocal lattice vector G (the $\boldsymbol{q} = 0$ point). O is the origin of the reciprocal lattice space.

((**Scattering diagrams**))

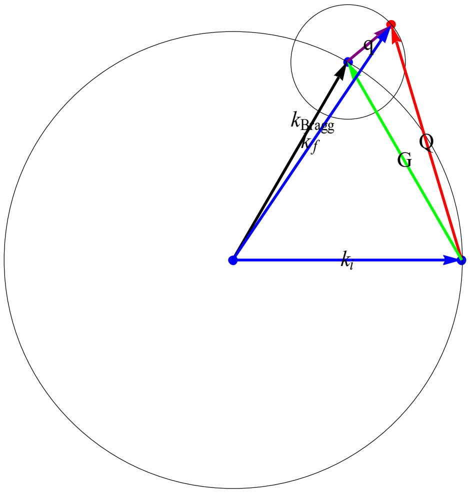


Energy gain

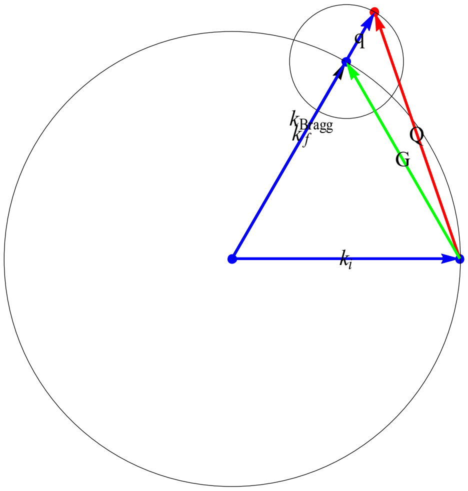


Energy gain

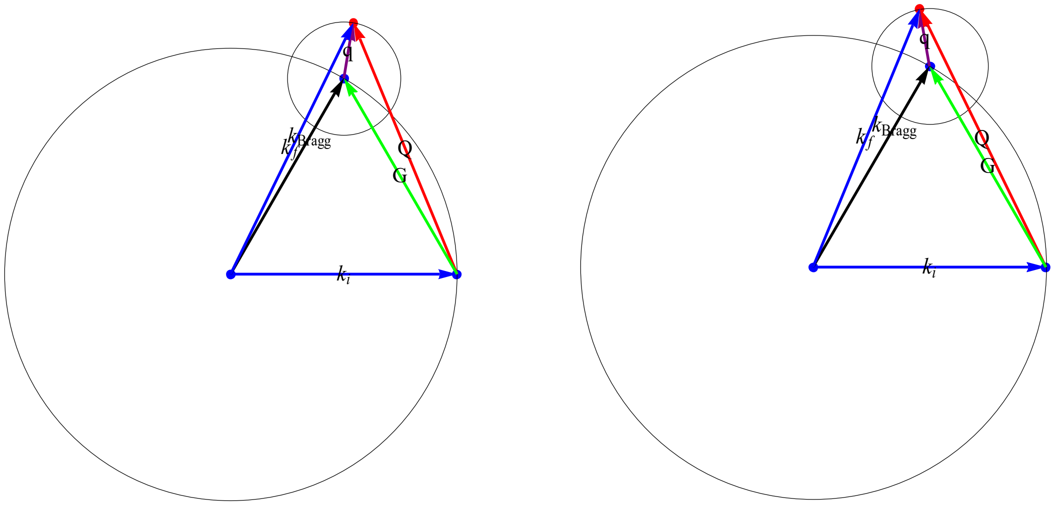
Fig. $\boldsymbol{k}_{Bragg} = \boldsymbol{k}_i + \boldsymbol{G}$. $\boldsymbol{k}_f - \boldsymbol{k}_i = \boldsymbol{Q}$. $\boldsymbol{Q} = \boldsymbol{G} + \boldsymbol{q}$. $k_i > k_f$ (energy loss). $k_i < k_f$ (energy gain). In the configuration (the right side), $\boldsymbol{q}$ is perpendicular to $\boldsymbol{Q}$. No longitudinal mode can be measured.



Energy gain

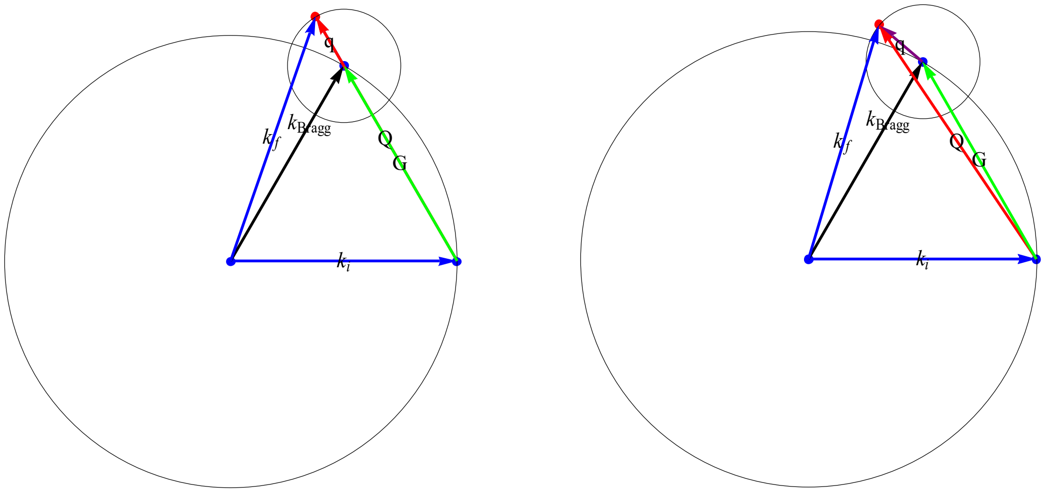


Energy gain



Energy gain

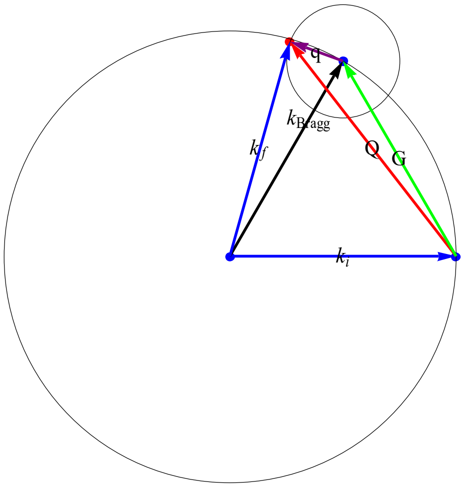
Energy gain



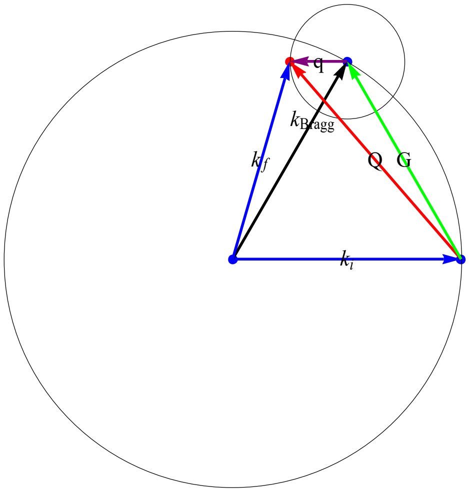
Energy gain

Energy gain

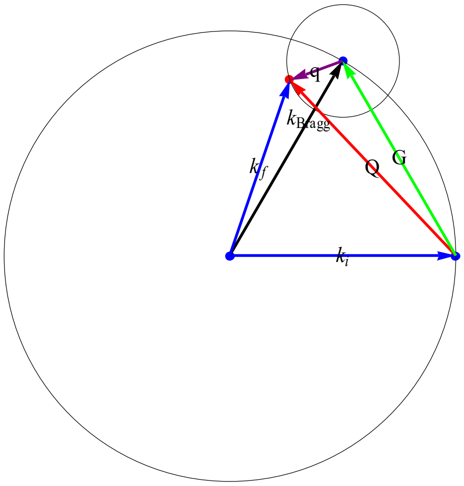
Fig. ***q***//***Q***. No transverse mode can be observed.



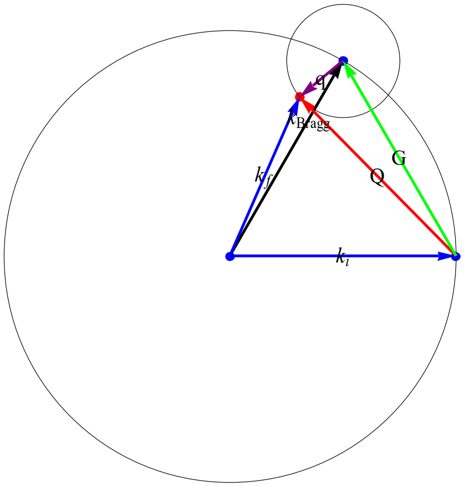
Energy is conserved



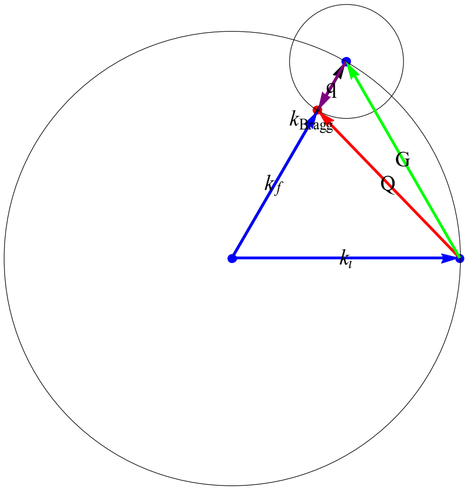
Energy loss



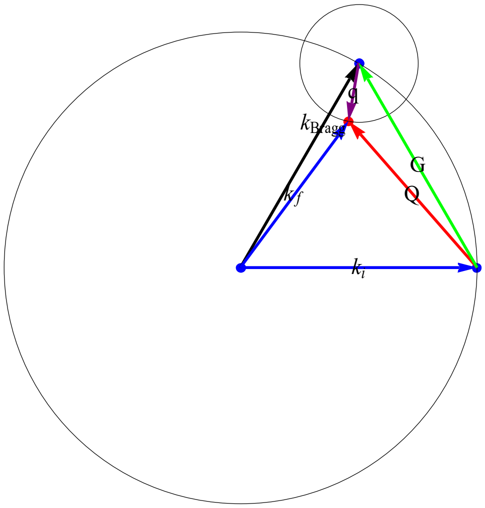
Energy loss



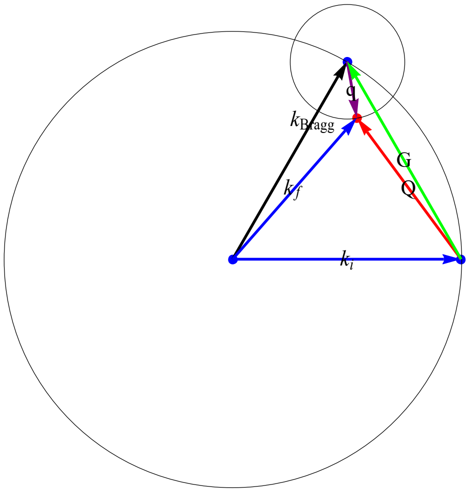
Energy loss



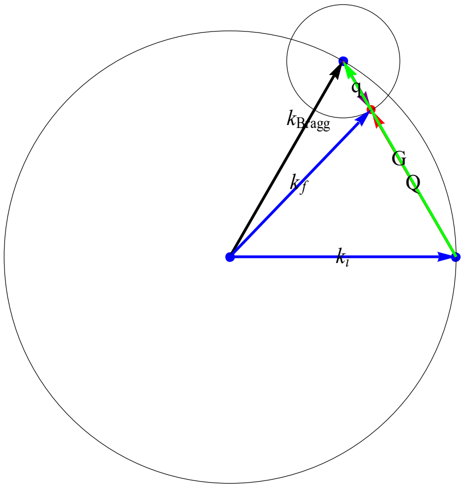
Energy loss



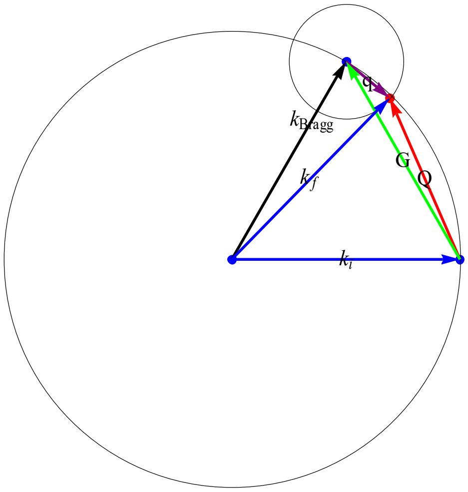
Energy loss



Energy loss



Energy loss



24. Triple axis spectrometer for the inelastic neutron scattering.

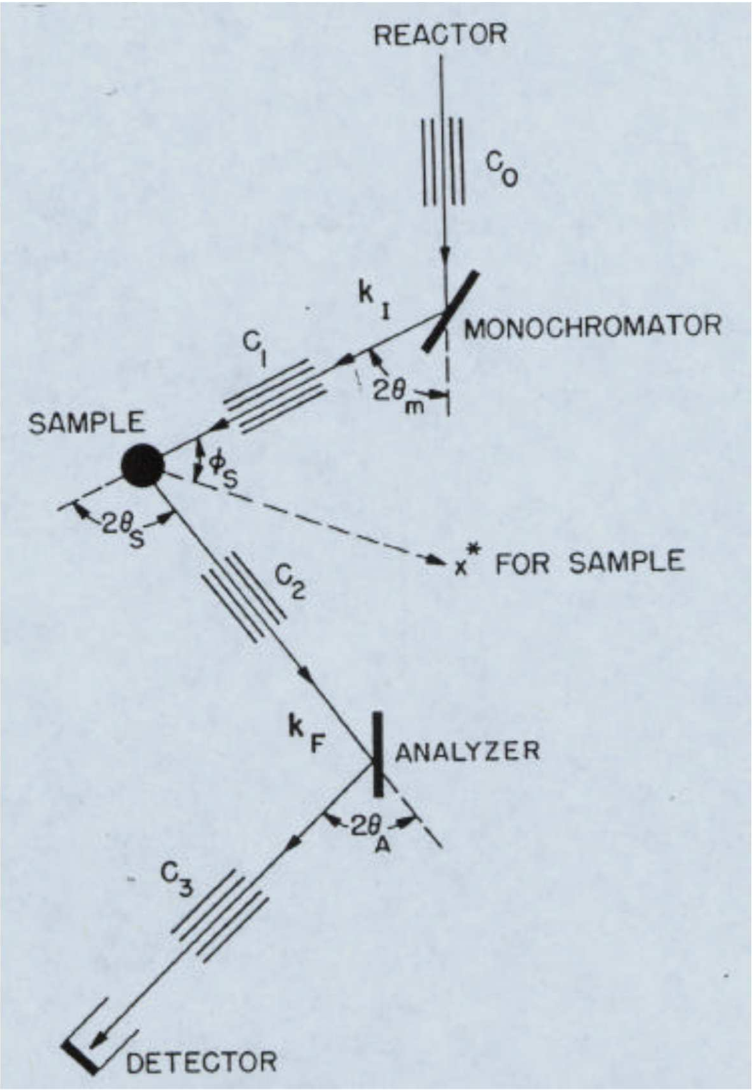


Fig. Schematic diagram for the triple-axis spectrometer for the measurement of inelastic neutron scattering.

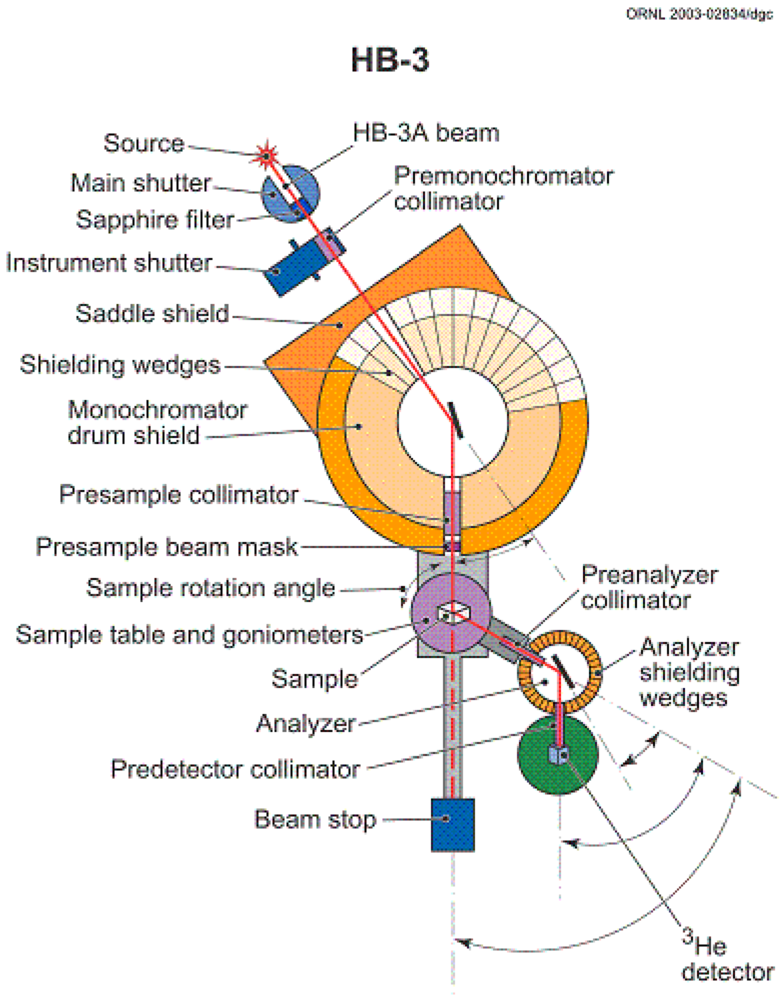


Fig. Triple-Axis Spectrometer (HB-3). Oak Ridge National Laboratory. The triple-axis spectrometer is one of the most versatile instruments for measuring excitations in solids via neutron scattering. HB-3 is a colossal flux thermal neutron three-axis spectrometer designed for inelastic measurements on single crystals over a wide range of energy and momentum transfers. While the energy and momentum range for measurements is quite large at HB-3, the instrument is the ideal location to perform experiments at high energy transfers. This is due to a combination of its location directly at the end of the beam tube and the availability of a beryllium monochromator.
http://neutrons.ornl.gov/instruments/HFIR/HB3/

((**Example-1**)) **Inelastic neutron scattering of NaI**

Phonon dispersion determined from the inelastic neutron scattering experiment.

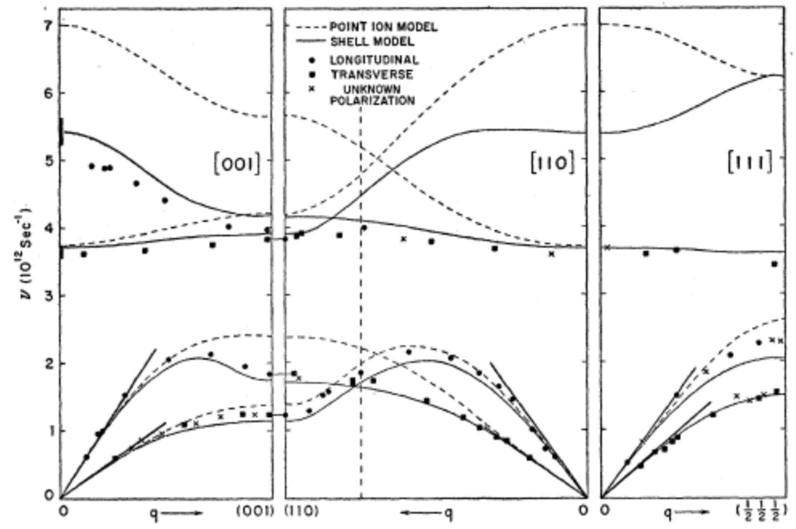


FIG. 2. The dispersion relations for sodium iodide in the [001], [110], and [111] directions. The points were determined by experiment at 110°K. Some points in the [001] direction are not independent of corresponding points in the [110] direction. Such points have been joined by a thin horizontal line. The solid curves have been calculated from the shell model and the dashed curves from the point ion model. These curves coincide for the transverse branches in the [111] direction. The slopes of the heavy solid lines indicate the appropriate velocities of sound as calculated from the elastic constants. The thick vertical bars represent the uncertainties in $(\nu_{TO})_{q=0}$ and $(\nu_{LO})_{q=0}$ deduced from existing knowledge of ω_0, ϵ, and ϵ_0.

Fig. Phonon dispersion curve of NaI. Wood, Cochran and Brookhause, Phys. Rev. **119**, 980 (1960).

((**Example-2**)) **Inelastic neutron scattering of Si**

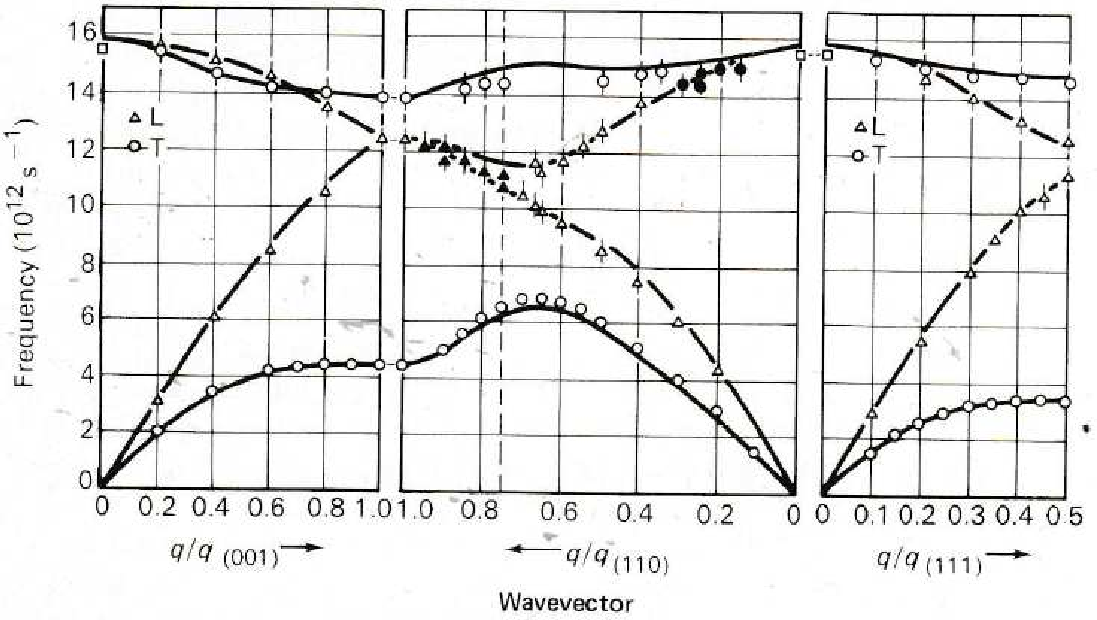


Figure 5.5 Measured frequencies in silicon for the wavevector **q** in each of three symmetry directions, as in Fig. 4.2. The lines give the results of calculations based on a shell model. (After Dolling, article in *Inelastic Scattering of Neutrons in Solids and Liquids*, International Atomic Energy Agency, Vienna, 1963.)

((**Example-3**)) **Inelastic neutron scattering of phonon in Cu**

G. Shirane, S.M. Shapiro, and J.M. Tranquanda, Neutron Scattering with a Triple-Axis Spectrometer (Cambridge, 2004).

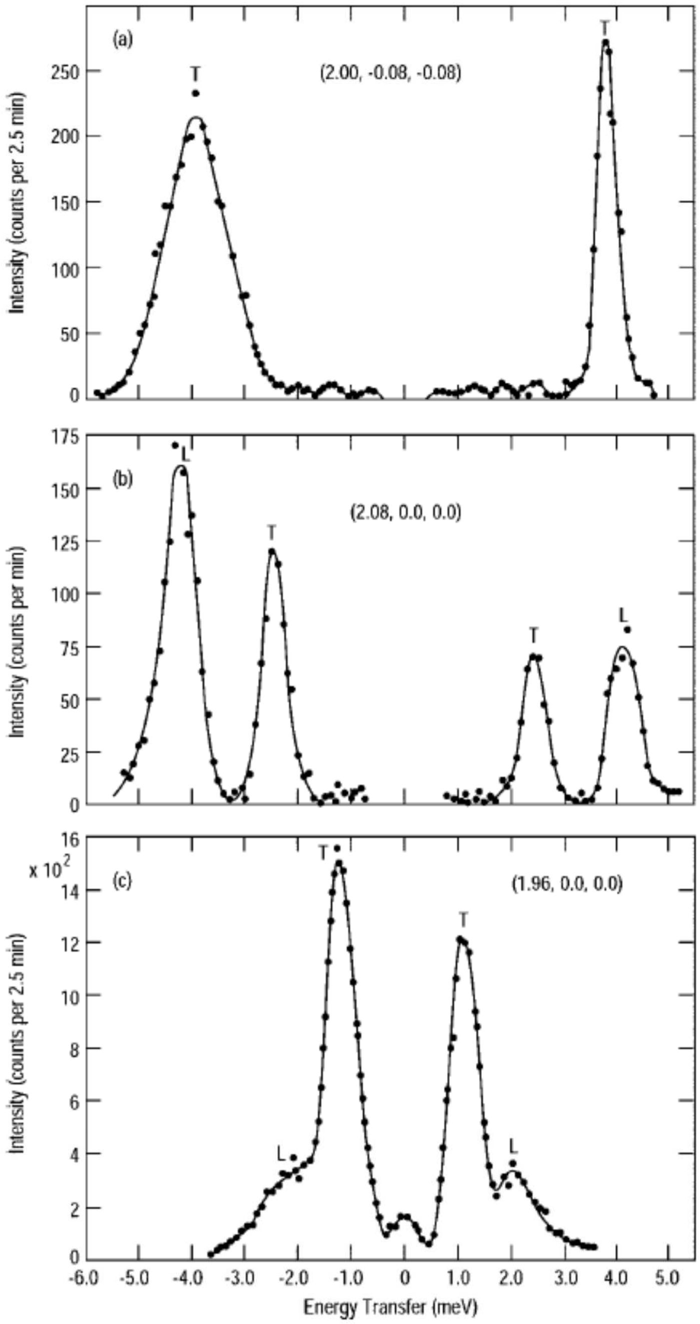


Fig. 4.13. Three typical phonon scans in copper. (a) Measurement of [110]T mode where only one phonon branch is observed for both phonon annihilation and creation. (b) Nominal measurement of [100]L mode. The peaks marked T are due to the large vertical resolution. (c) Nominal measurement of [100]L mode where the desired longitudinal response is obscured (from Skalyo and Lurie, 1973).

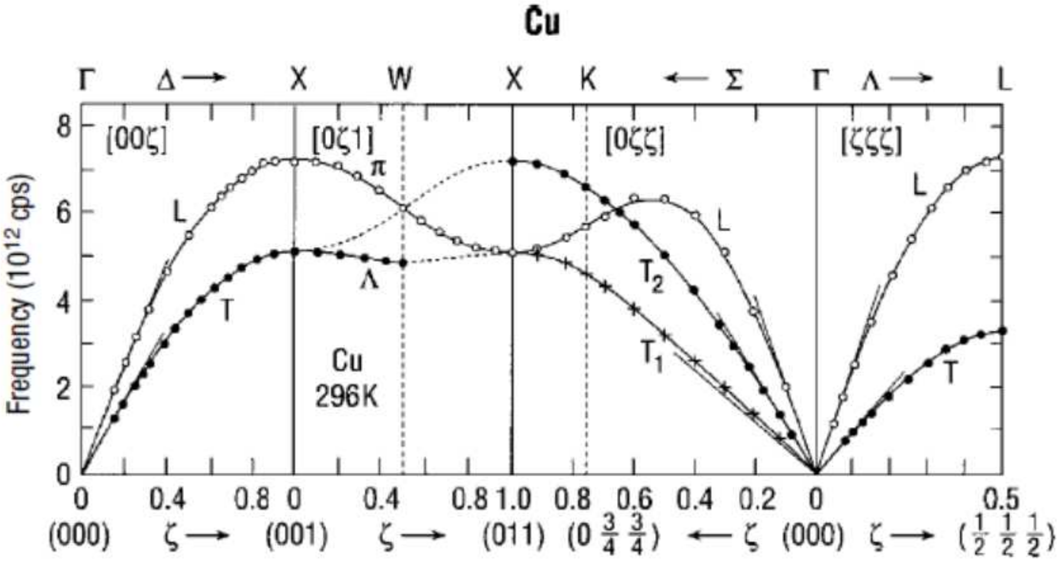


Fig. Phonon dispersion curves for fcc Cu at 296 K as measured by Svensson, Brookhouse, and Rowe (1967).

1 THz = 4.13567 meV.

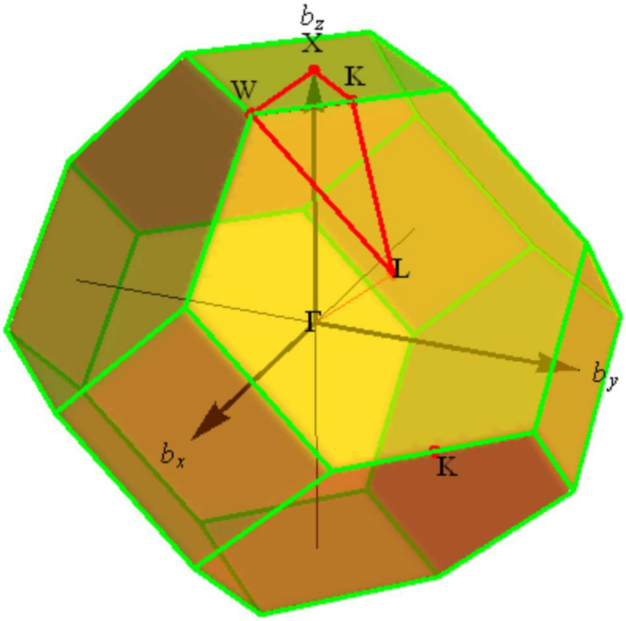
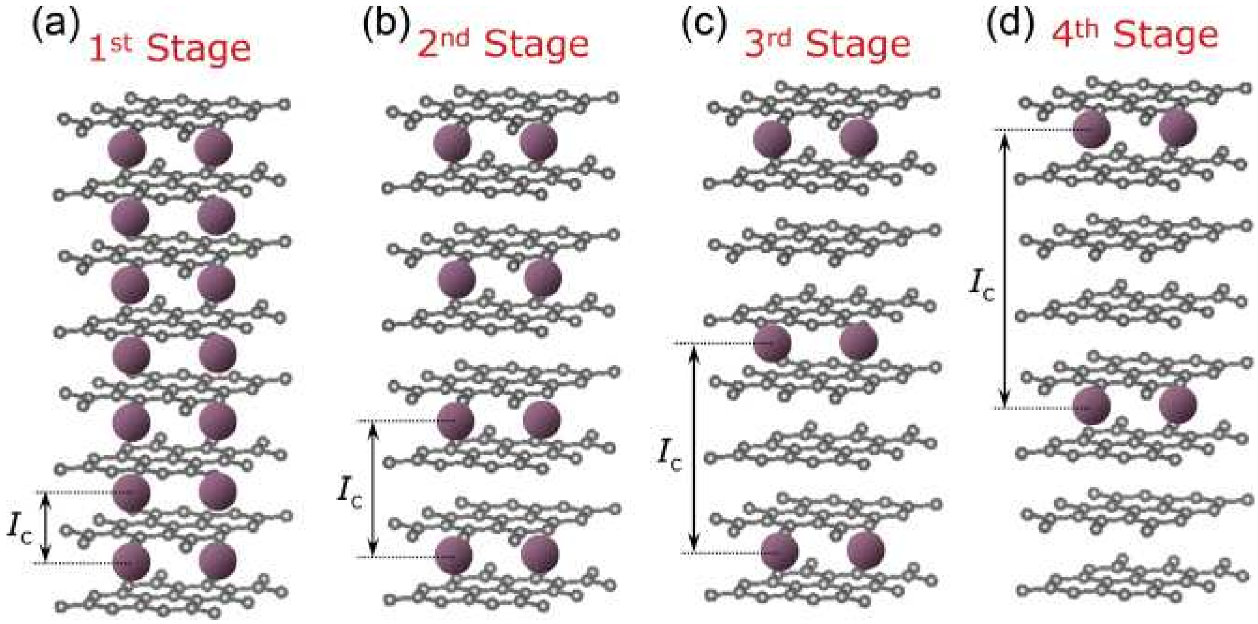


Fig. Brillouin zone of fcc Cu

((**Example-4**)) Inelastic neutron scattering of alkali-metal graphite intercalation compounds

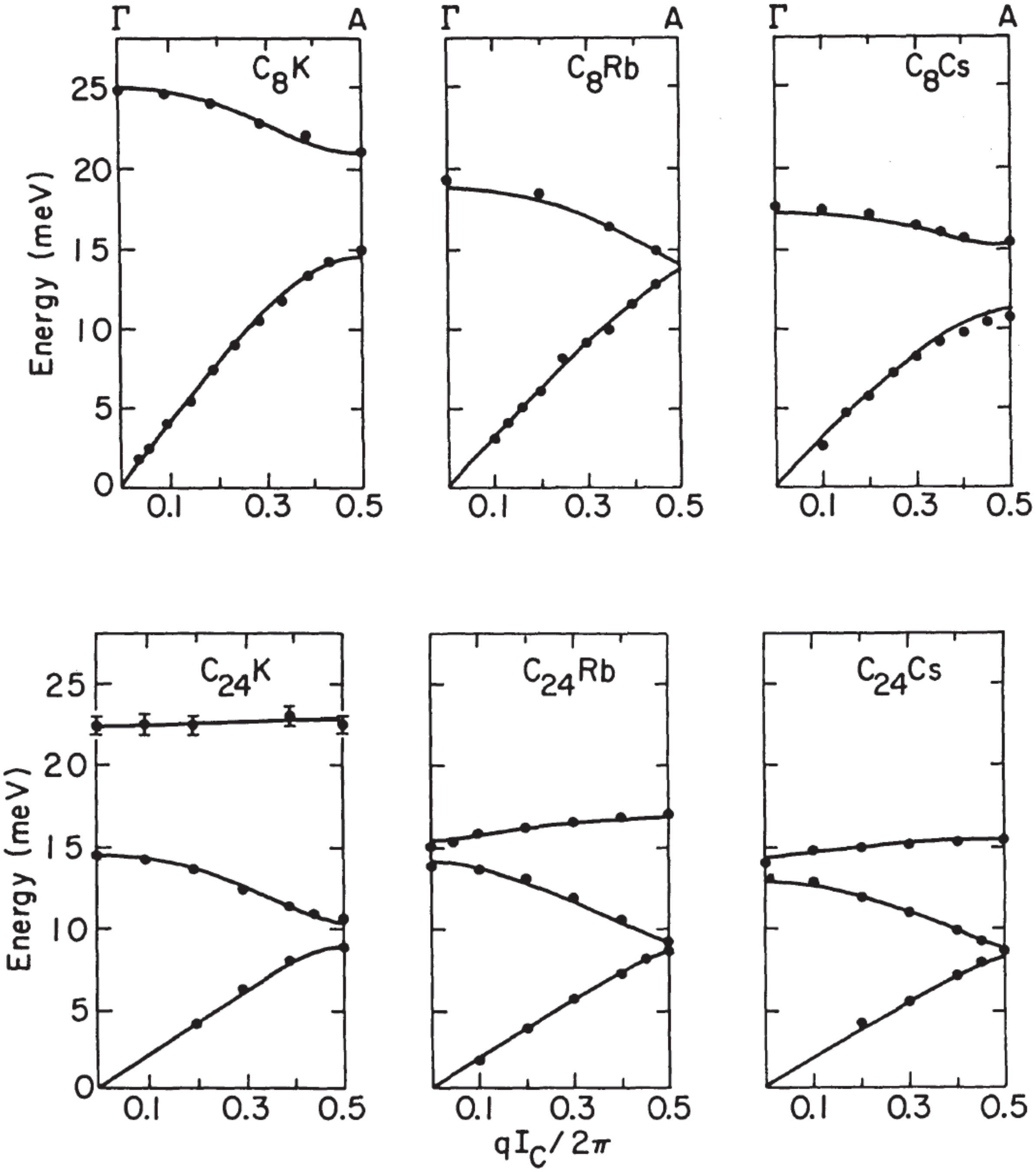
Measured phonon energies of [00q] L modes in alkali-metal graphite intercalation compounds at room temperature. KC_8, RbC_8, CsC_8 (stage-1). KC_{24}, RbC_{24}, CsC_{24} (stage-2). KC_{36}, CsC_{36} (stage-3).

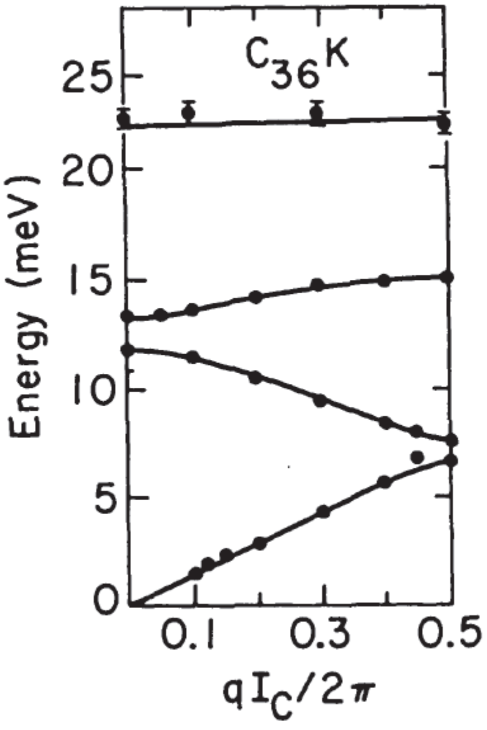
(i) Staging structure of alkali-metal graphite intercalation compounds

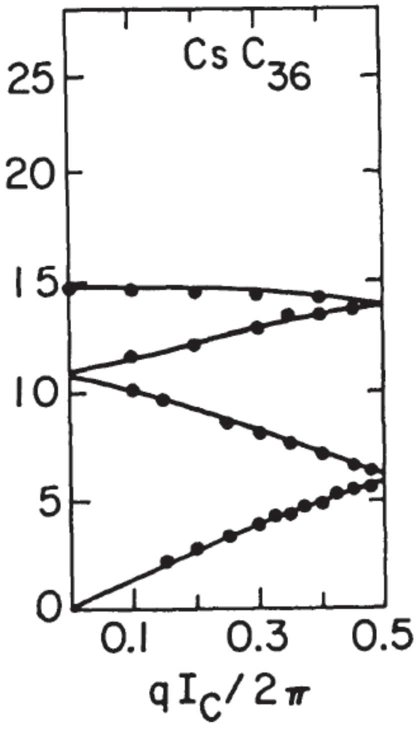


(ii) Phonon dispersion of the (00q) *L* modes in alkali-metal graphite intercalation compounds at room temperature.

KC_8, RbC_8, CsC_8 (stage-1). KC_{24}, RbC_{24}, CsC_{24} (stage-2). KC_{36}, CsC_{36} (stage-3).


Γ
A
C8K
C8Rb
C8Cs
C24K
C24Rb
C24Cs
Energy (meV)
0
5
10
15
20
25
0.1
0.3
0.5
qIC/2π





26. Raman scattering and Brillouin scattering

We consider the acoustic phonon. The velocity of acoustic phonon v is on the order of 10^5 cm/s. The wavenumber k is on the order of 10^8/cm. Then the angular frequency ω is

$$f = \frac{\omega}{2\pi} = \frac{vk}{2\pi} = \frac{10^8 10^5}{2\pi} Hz = 1\,\text{THz}.$$

When $k = 0$, ω is equal to zero. Therefore ω changes from 0 to 10 THz as the wavenumber changes. The wavelength of the laser is

$$\lambda = 633 nm\,.$$

for typical He-Ne laser. If the excitation is an acoustic phonon, the inelastic light scattering process is called Brillouin scattering, while light scattering by optical phonons is called Raman scattering.

27. Brillouin scattering (acoustic phonon)

The light scattering experimental technique is an exceedingly valuable tool for the study of fundamental excitations in solids, such as phonons. We now consider the Brillouin scattering when the incident light interacts with phonon (acoustic phonon).

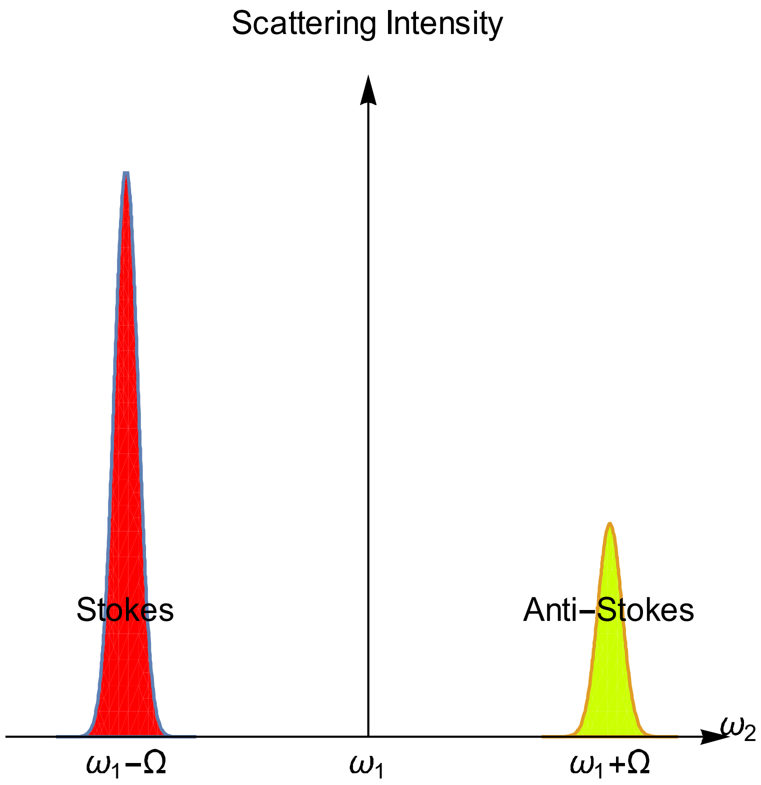


Fig. Brillouin scattering. Stokes line at $\omega_2 = \omega_1 - \Omega$. Anti-Stokes line at $\omega_2 = \omega_1 + \Omega$

The Brillouin scatterings are schematically shown in the above figure, in which ω_1 and ω_2 is the frequency of the incident and outgoing light.

$$\omega_2 = \omega_1 \pm \Omega(\boldsymbol{q}) . \qquad \text{(energy conservation)}$$

$$\boldsymbol{k}_1 - \boldsymbol{k}_2 = \pm \boldsymbol{q} \qquad \text{(momentum conservation)}$$

$\Omega(\boldsymbol{q})$ is the angular frequency of phonon at the wave vector $\boldsymbol{q}$. The photon at $\omega_2 = \omega_1 - \Omega$ is called the Stokes line and that at $\omega_2 = \omega_1 + \Omega$ is called the anti-Stokes line. The intensity of the Stokes line involves the matrix element for phonon creation,

$$I(\omega_2 = \omega_1 - \Omega) \propto \left|\langle n_q | \hat{u} | n_q + 1\rangle\right|^2 \propto (n_q + 1)$$

where n_q is the initial population of phonon mode $\boldsymbol{q}$.

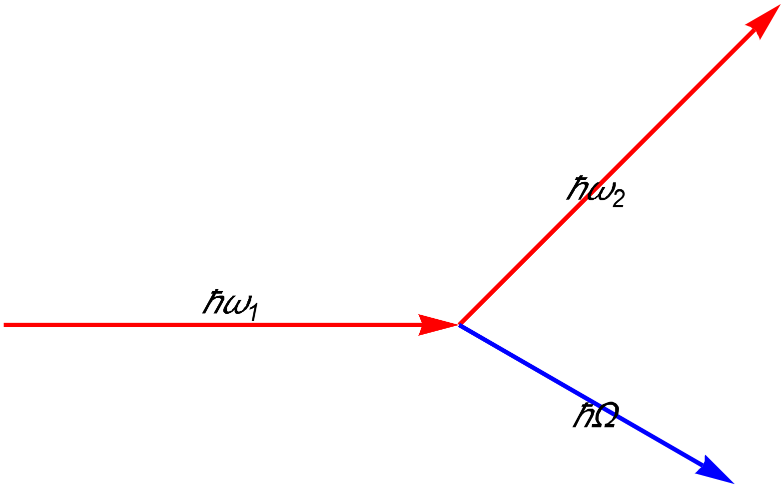


Fig. Brillouin scattering. Stokes line. Creation of phonon. Red (photon). Blue (phonon).

The intensity of the anti-Stokes line involve the matrix element for phonon annihilation,

$$I(\omega_2 = \omega_1 + \Omega) \propto \left|\langle n_q - 1 | \hat{u} | n_q\rangle\right|^2 \propto n_q$$

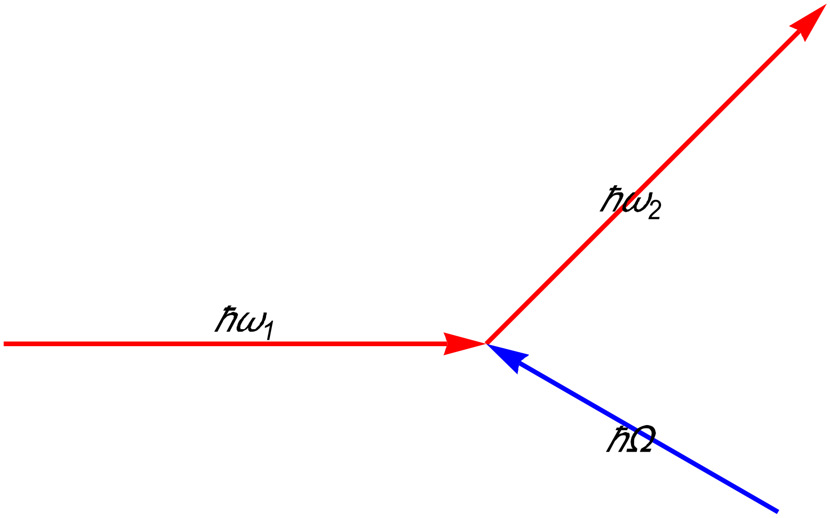


Fig. Brillouin scattering. Anti-Stokes line. Annihilation of phonon. Red (photon). Blue (phonon).

If the phonon population is initially in thermal equilibrium at temperature *T*, the intensity ratio of the two lines is

$$\frac{I(\omega_1+\Omega)}{I(\omega_1-\Omega)} = \frac{\langle n_q\rangle}{\langle n_q\rangle + 1} = \frac{\dfrac{1}{e^{\beta\hbar\Omega}-1}}{1+\dfrac{1}{e^{\beta\hbar\Omega}-1}} = e^{-\beta\hbar\Omega} < 1$$

where $\langle n_q\rangle$ is the Planck's distribution function

$$\langle n_q\rangle = \frac{1}{e^{\beta\hbar\Omega}-1}.$$

Note that the intensity of the Stokes line is stronger than that of the anti-Stokes line.

28. Determination of the velocity of acoustic phonon: Brillouin scattering

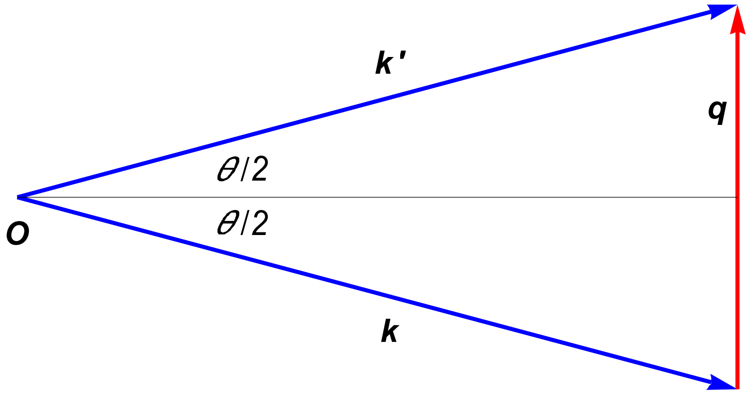


Fig. Brillouin scattering configuration. The wavevectors of incident light and scattered light, ***k*** and ***k***'. $\boldsymbol{k}' - \boldsymbol{k} = \boldsymbol{q}$.

In the Brillouin scattering (due to the acoustic phonon), we have

$$q = 2k \sin\frac{\theta}{2} = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

The maximum of the wavenumber q for phonon is $\frac{4\pi}{\lambda}$. Since $\omega = vq$, ω_{max} is on the order of $2\pi\times 10^{10}$ (1/s). From the experimental results of the dispersion relation

$$\omega = vq = v\frac{4\pi}{\lambda}\sin\frac{\theta}{2},$$

the phonon velocity v can be determined. The measurement of $\Delta\omega$ vs the angle θ yields the value of the velocity v. Note that

$$\begin{aligned}\Delta f &= \frac{4\pi 10^5}{(2\pi)6\times 10^{-5}}\sin\frac{\theta}{2} \approx \frac{1}{3}\times 10^{10}\sin\frac{\theta}{2}\\ &= \frac{1}{300}\sin\frac{\theta}{2}[THz] = \frac{33.3565}{300}\sin\frac{\theta}{2}[cm^{-1}]\\ &= 0.11\sin\frac{\theta}{2}[cm^{-1}]\end{aligned}$$

Therefore the measurement of Δf can be measured using the Brillouin Scattering.

29. Classical model for the Brillouin scattering

The polarizability of atom is dependent on the displacement of atom, u. The dipole moment p is

$$p = (\alpha + \alpha' u)E$$

where

$$u = u_0 \cos[\omega(q)\, t], \qquad E = E_0 \cos(\omega_0\, t),$$

Where E is the electric field. Thus the electric dipole moment can be calculated as

$$\begin{aligned}p &= \alpha E_0 \cos(\omega_0\, t), + \alpha' u_0\, E_0 \cos[\omega(q)\, t]\cos(\omega_0\, t)\\ &= \alpha E_0 \cos(\omega_0\, t), + \frac{1}{2}\alpha' u_0 E_0\, \{\cos[(\omega_0 + \omega(q))t] + \cos[(\omega_0 - \omega(q))t]\}\end{aligned}$$

So the scattered light has the frequency of

$$\omega_1 = \omega_0 \pm \omega(q).$$

30. Experimental result (Brillouin scattering)

W. Cochran, The Structures and Properties of Solids 3, The Dynamics of Atoms in Crystals (Edward Arnold, 1973).

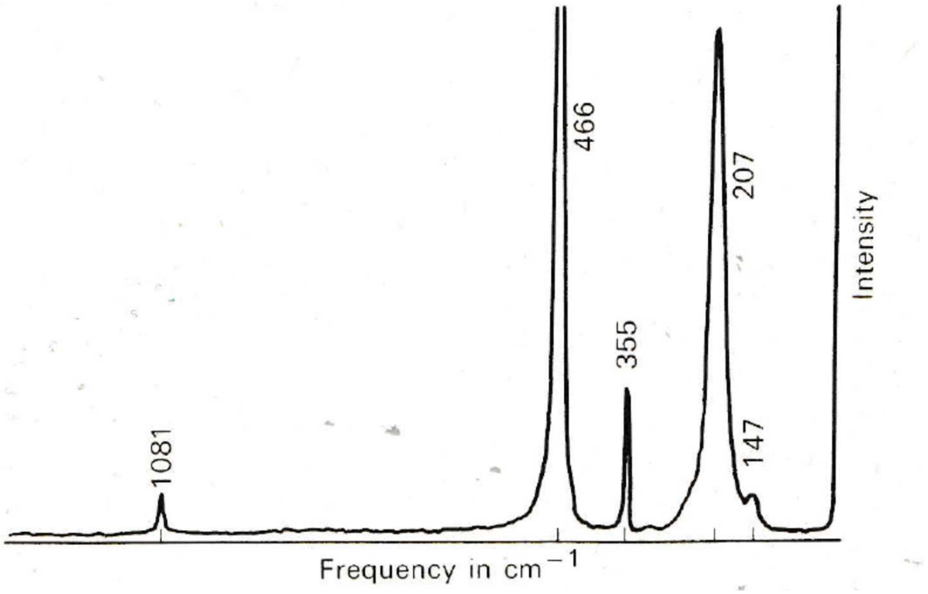


Fig. Raman spectrum of quartz. The intensity vs frequency (in the units of cm^{-1}). A small peak at 147 cm^{-1} is considered to arise from a non-harmonic term. 1 cm^{-1} = 29.9792458 GHz=0.0299792458 THz. [Shapiro, O'Shea, and Cummins, Phys. Rev. Lett. 19, 361 (1967).]

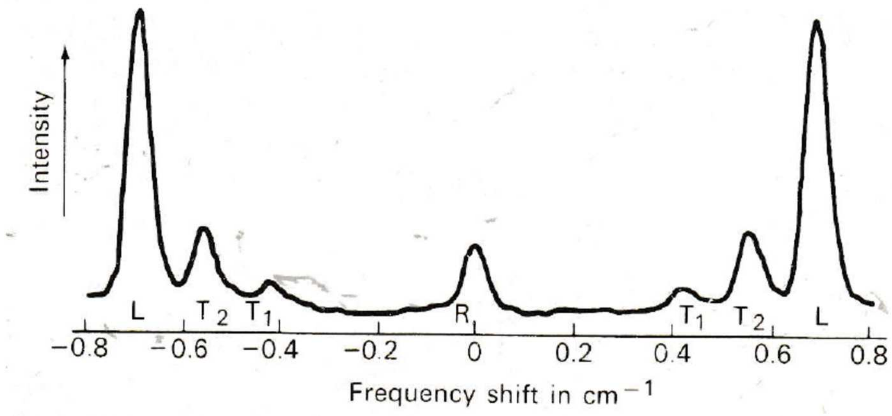


Fig. Brillouin spectrum of quartz. The scattering from all three acoustic modes is observed. The horizontal axis is the change of frequency (in units of cm^{-1}). 1 cm^{-1} = 29.9792458 GHz=0.0299792458 THz [Shapiro, O'Shea, and Cummins, Phys. Rev. Lett. **19**, 361 (1967)].

31. Raman scattering (optical phonon)

((Introduction))

Like inelastic neutron scattering, Raman scattering involves the scattering of photons from phonons with change in energy and wave vector. However the fact that the wave vector of light is small means that the changes in the wave vector through the scattering process must also be small. In effect, this means that measurements are restricted to phonons with wave vectors that are barely different from zero when compared with the range of wave vectors within the Brillouin zone. To illustrate this, consider an incident light beam from an Ar laser with wavelength and frequency

$$\lambda_i = 514.5 \text{ nm}, \qquad \nu_i = 582.686 \text{ THz}$$

The wave vector of the incident laser beam is

$$k_i = \frac{2\pi}{\lambda_i} = 1.22122 \times 10^{-3} \text{Å}^{-1}$$

With the precision available with optics, changes in the frequency as small as 0.01 THz can be measured (although most phonon peaks are intrinsically much broader than this, and this will limit the resolution of a measurement). We now calculate the scattering vector for a one-phonon interaction that changes the frequency by 5 THz;

$$\nu_f = 587.686 \text{ THz}, \qquad \lambda_f = 510.123 \text{ nm}$$

$$k_f = \frac{2\pi}{\lambda_f} = 1.2317 \times 10^{-3} \text{Å}^{-1}$$

This will lead to a change in the wave vector of around 1%. If this beam is scattered through 90°, the scattering vector *Q* will be close to

$$Q = \sqrt{2} k_i = 1.727 \times 10^{-3} \text{Å}^{-1}$$

When we compare this value with the typical reciprocal lattice vector, which is of order,

$$\frac{\pi}{a} \approx 1 \text{ Å}^{-1}$$

we can see that the scattering vectors for Raman scattering are very close to $Q \sim 0$. In effect, Raman scattering measures optic phonons with $k = 0$ (the corresponding processes that lead to scattering from acoustic modes give rise to Brillouin scattering. This is strikingly different from neutron scattering, which can measure phonons with wave vectors across a wide range of reciprocal space. On the other hand, Raman scattering can achieve a resolution that is virtually unattainable by single-crystal neutron inelastic scattering, whilst covering a wide range of energies that is hard to cover by neutron scattering, and on a time scale that is much faster (as well as being a much cheaper technique.

((Theory))

Optical phonon at $q = 0$ can be measured using the Raman scattering, where

$$\omega_f = \omega_i \pm \omega_q$$

and

$$\mathbf{k}_f - \mathbf{k}_i = \mathbf{q} \approx 0$$

From the measurement of $\Delta\omega$, we can determine the frequency of the optical phonon.

$$\Delta\omega = |\omega_f - \omega_i| = |\omega_q|$$

The stokes component and the anti-Stokes component are defined as

$$\omega_f = \omega_i - \omega_q, \qquad \omega_f = \omega_i + \omega_q$$

respectively.

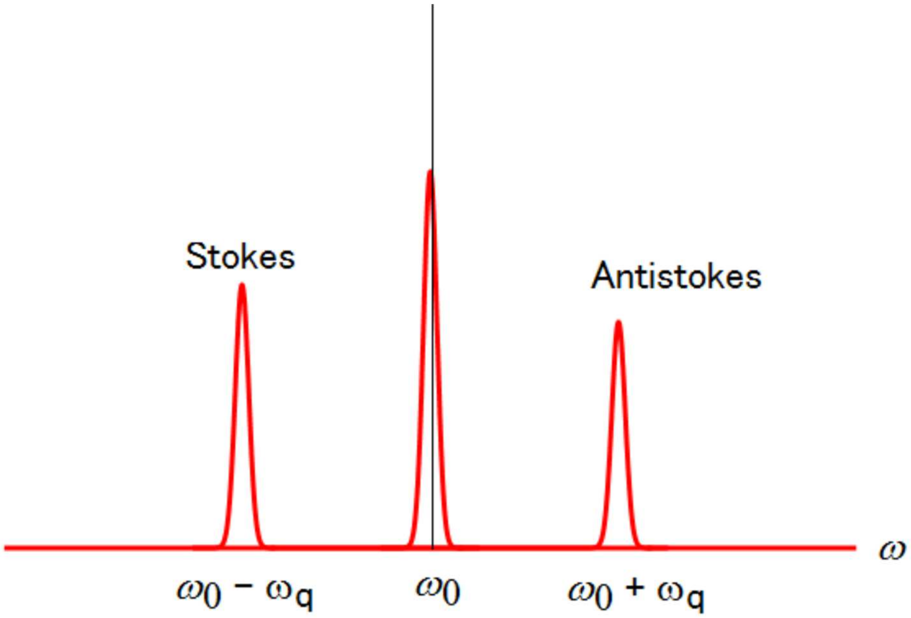


Fig. Schematic diagram of Raman scattering. Unshifted Rayleigh line (ω_0). Stokes line (emission, ω_0 - ω_q) and anti-Stokes line (absorption, ω_0 + ω_q). The ratio of the Stokes to ant-Stokes can be used to estimate the temperature of the phonon system

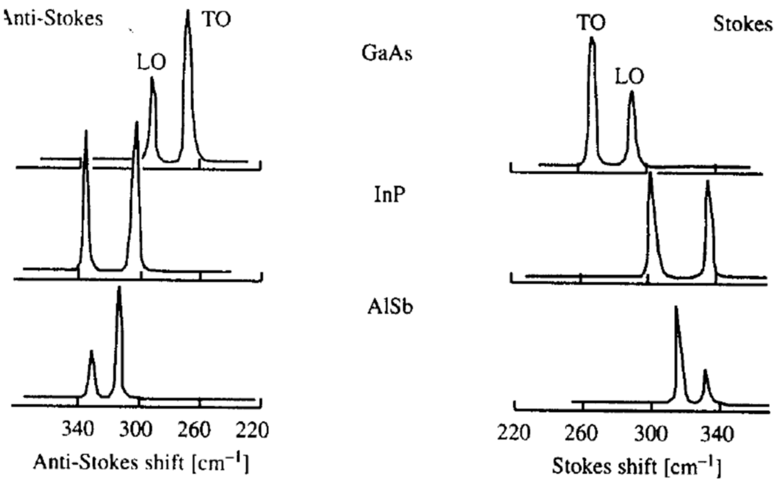


Fig. Raman spectra of three zinc-blende-type semiconductors showing the TO and LO phonons in both Stokes and ant-Stokes scattering. (M.S. Dresselhaus, Solid State Physics, Part II, Optical Properties of Solids). Note that $\nu = 10$ THz corresponds to 333.565 cm^{-1}.

((Stokes line))

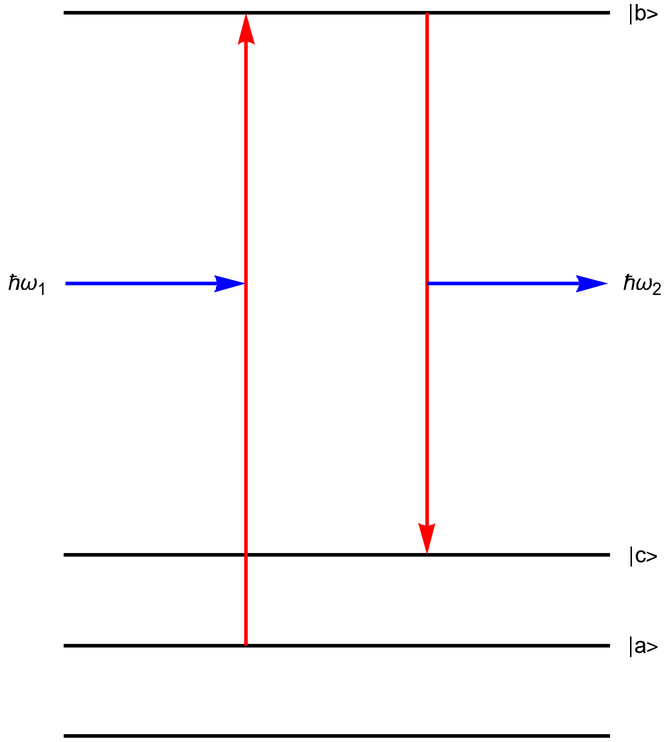


Fig. Raman scattering. Stokes' line. $E_i + \hbar\omega_1 = E_f + \hbar\omega_2$ (energy conservation). $\hbar\omega_2 = \hbar\omega_1 - (E_f - E_i) < \hbar\omega_1$ since $E_f > E_i$. A Stokes' line in atomic spectra is more reddish than that of the incident radiation. The inelastic scattering.

((**Anti Stokes-line**)

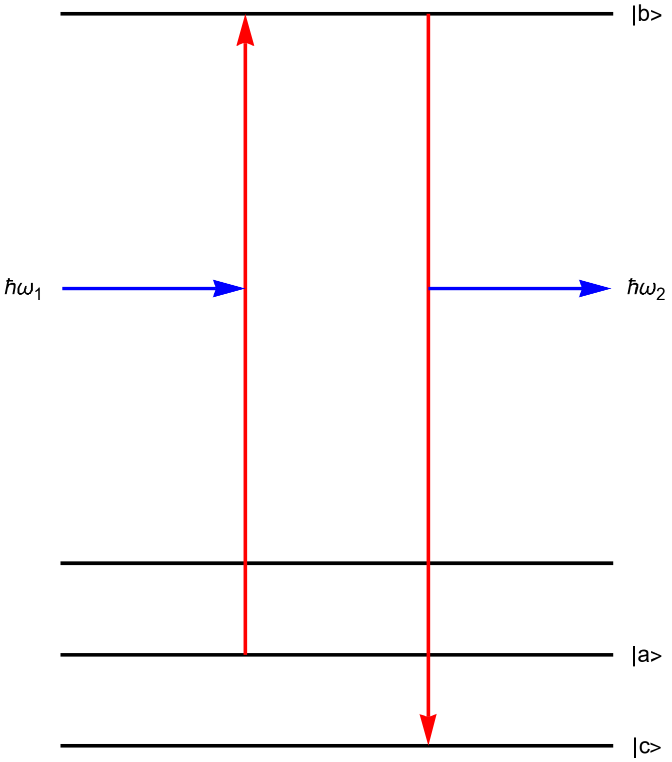


Fig. Raman scattering. Anti-Stokes' line. $E_i + \hbar\omega_1 = E_f + \hbar\omega_2$ (energy conservation). $\hbar\omega_2 = \hbar\omega_1 + (E_i - E_f) > \hbar\omega_1$ since $E_f > E_i$. A Stokes' line in atomic spectra is more violet than that of the incident radiation. The inelastic scattering.

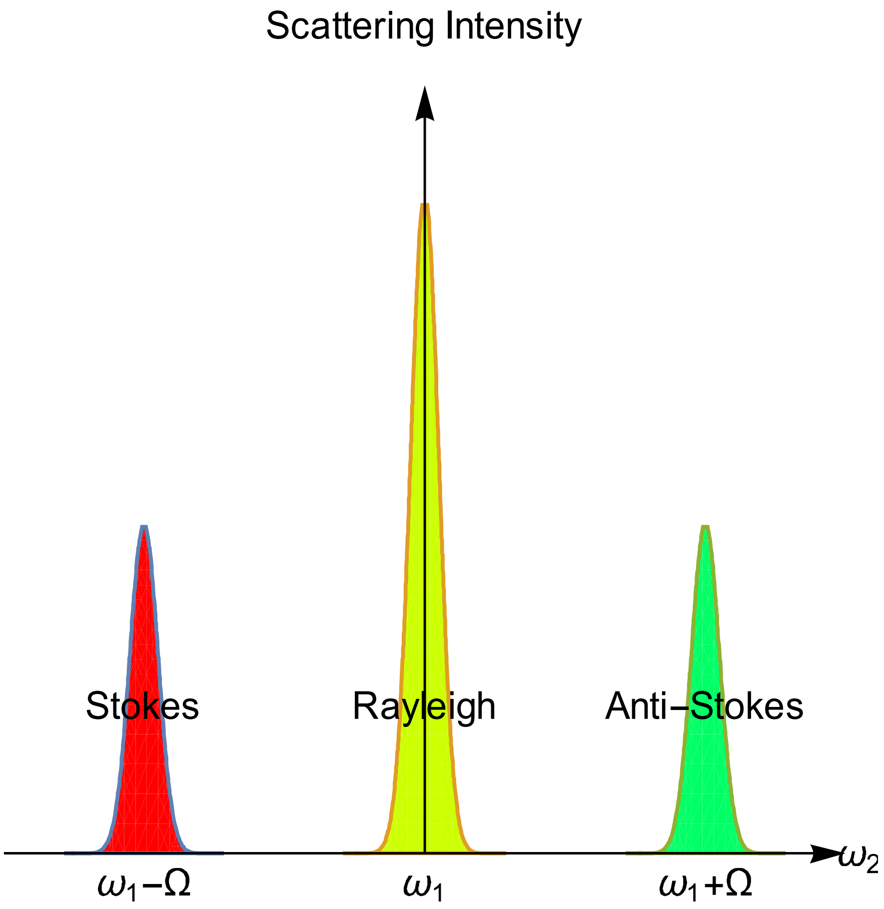


Fig. Schematic diagram for the Stokes' line, Rayleigh scattering, and anti-Stokes' line.

The intensity of the Stokes line involves the matrix element for the phonon creation, as

$$I(\omega_1-\Omega)\propto(n_{\boldsymbol{k}}+1)$$

Where $n_{\boldsymbol{k}}$ is the initial population of phonon mode $\boldsymbol{k}$. The intensity of the anti-Stokes line involves the matrix element for the phonon annihilation, as

$$I(\omega_1+\Omega)\propto n_{\boldsymbol{k}}$$

The intensity ratio of the two lines is

$$\frac{I(\omega+\Omega)}{I(\omega-\Omega)}=\frac{n_{\boldsymbol{k}}}{n_{\boldsymbol{k}}+1}=e^{-\beta\hbar\omega_{\boldsymbol{k}}}$$

32. Rayleigh scattering

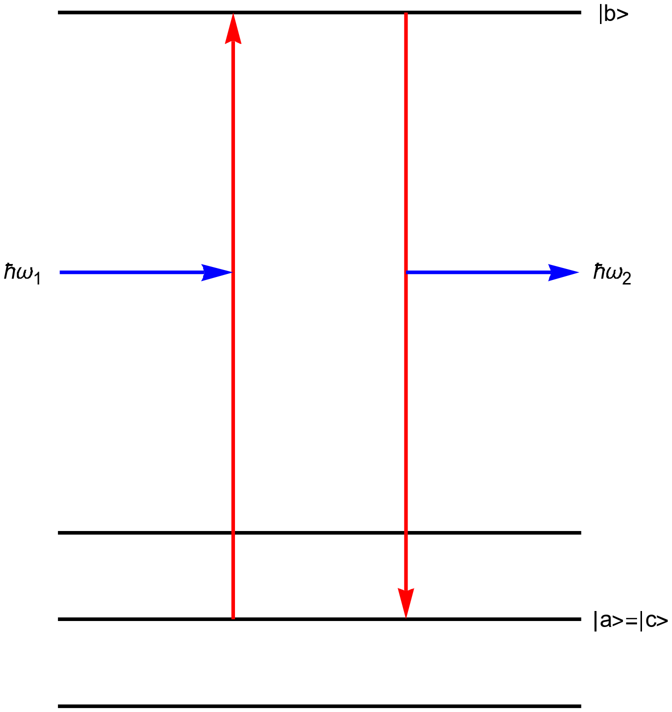


Fig. Rayleigh scattering. $\hbar\omega_1 = \hbar\omega_2$. The elastic scattering.

Why the sky is blue in daytime? That is because of the Rayleigh scattering. The wavelength of blue light is much shorter than that of red light. The Rayleigh scattering is an elastic scattering. The cross section of the Rayleigh scattering due to the small particles with diameter *d* is given by

$$\sigma_s = \frac{2\pi^5}{3}\frac{d^6}{\lambda^4}\left(\frac{n^2-1}{n^2+2}\right)^2,$$

where *n* is the refractive index *n* of particles from a beam of unpolarized light of wavelength λ. Such a strong wavelength dependence of the scattering ($\sim\lambda^{-4}$) means that shorter (blue) wavelengths are scattered more strongly than longer (red) wavelengths. This results in the indirect blue light coming from all regions of the sky. Rayleigh scattering is a good approximation of the manner in which light scattering occurs within various media for which scattering particles have a small size parameter.

Why is the sky red in sunset? The reddening of sunlight is intensified when the sun is near the horizon, because the density of air and particles near the earth's surface through which sunlight must pass is significantly greater than when the sun is high in the sky. The Rayleigh scattering effect is thus increased, removing virtually all blue light from the direct path to the observer. The remaining un-scattered light is mostly of a longer wavelength, and therefore appears to be orange.

APPENDIX

A.1 Nature of neutron

ε (meV): neutron energy in meV
ε (THz): neutron energy in THz
k (Å^{-1}): wavenumber in Å^{-1}
λ (Å): wavelength in Å
v (km/s): neutron velocity in km/s

The energy of neutron is given by

$$\varepsilon = \hbar\omega = \frac{1}{2} M_n v^2 , \qquad v = \sqrt{\frac{2\varepsilon}{M_n}} .$$

The momentum p is

$$p = \frac{h}{\lambda} = \hbar k = M_n v . \qquad \text{(de Broglie relation).}$$

The wavelength λ is

$$\lambda = \frac{h}{M_n v} = \frac{9.04457}{\sqrt{\varepsilon(meV)}} \text{ (Å),}$$

$$v(km/s) = \sqrt{\frac{\varepsilon(meV)}{5.227}} = 0.4374\sqrt{\varepsilon(meV)} \text{ [km/s],}$$

$$k = \sqrt{\frac{\varepsilon(meV)}{2.072}} = 0.6947\sqrt{\varepsilon(meV)} \text{ [Å}^{-1}\text{].}$$

((**Example**))

When $\lambda = 1$ Å,

$$\varepsilon(meV) = 81.7 \text{ meV}.$$

$$v \text{ (km/s)} = 0.4374 \sqrt{\varepsilon(meV)} = 0.4374 \sqrt{81.7} = 3.95 \text{ km/s}.$$

It takes $t = 1000/3.95$ μs = 253 μs for neutron to travel in the distance of 1 m.

((**Note**))

The energy of the x-ray is much larger than that of the lattice vibrations ($\hbar\omega = 10^5$ eV for x-ray, $\hbar\omega = 0.1$ eV). The energy of the lattice vibration is on the same order as that of neutrons. Ony the elastic scattering can be observed in the x-ray scattering, while the inelastic scattering as well as the elastic scattering can be observed in the neutron scattering.

A wavelength at the Brillouin zone edge of

$$\lambda = 2\pi/k = 2a \approx 10 \text{ Å} = 10^{-7} \text{ cm} = 1 \text{ nm}.$$

for $a = 5$ Å. The velocity of phonon would be 10^5 cm/s. Then the frequency is on the order of

$$f = \frac{v}{\lambda} = \frac{10^5}{10^{-7}} = 10^{12} \text{ Hz} = 1 \text{ THz}.$$

The corresponding energy is

$$E = \hbar\omega = \hbar(2\pi v) = 4.13567 \text{ meV for } f = 1 \text{ THz}.$$

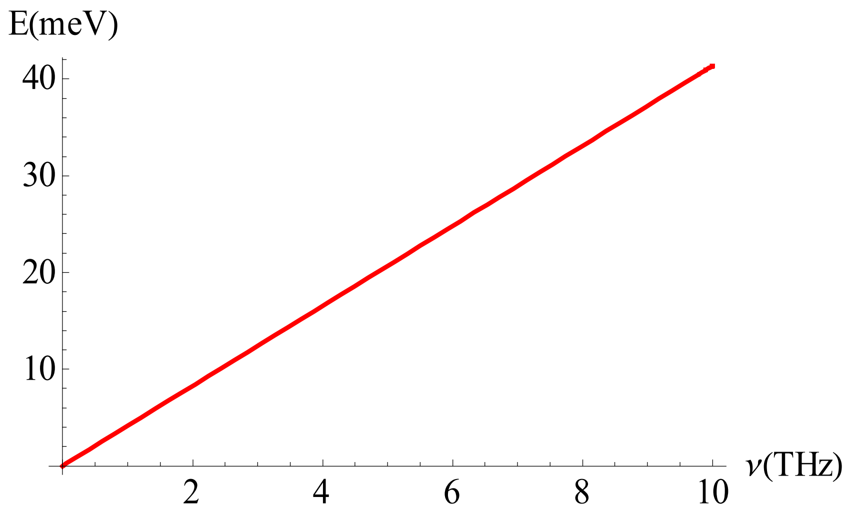


Fig. The neutron scattering by phonons in the system. $\boldsymbol{k}_i$ (= $\boldsymbol{k}$) is the wavevector of the incident neutron and $\boldsymbol{k}_f$ (= $\boldsymbol{k}'$) is the wavevector of the outgoing neutron. $\boldsymbol{Q}$ is the scattering vector. $\boldsymbol{Q} = \boldsymbol{k}_f - \boldsymbol{k}_i$. $|\boldsymbol{k}_i| = 2\pi/\lambda$, λ is the wavelength of the incoming neutron.

A.2 Unit [Kayser] in spectroscopy

The energy of light E is given by

$$c = \lambda \nu .$$

Then we have

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{10^{12}}{c}\nu[THz] = 33.3565 \quad \nu[THz] \qquad [\mathrm{cm}^{-1}]$$

$$\frac{1}{\lambda} = \frac{E}{2\pi\hbar c} = 8.06556 \quad E[meV] \qquad [\mathrm{cm}^{-1}]$$

$$\frac{1}{\lambda} = \frac{E}{2\pi\hbar c} = 5.03413 \times 10^{15} \quad E[erg] \qquad [\mathrm{cm}^{-1}]$$

$$\frac{1}{\lambda}=\frac{k_B T}{2\pi\hbar c}=0.695037\ \ T[K] \qquad\qquad [\mathrm{cm}^{-1}]$$

The unit [cm^{-1}] is called as Kayser.

A3. Units of Kayser (cm^{-1})

The energy of photon is

$$E=\hbar\omega=\hbar ck=\hbar c\frac{2\pi}{\lambda}$$

or

$$\frac{1}{\lambda}=\frac{E}{2\pi\hbar c}=\frac{\hbar\omega}{2\pi\hbar c}=\frac{\omega}{2\pi c}=\frac{f}{c}$$

When $1/_{\lambda}=1cm^{-1}$,

$$E=0.123984\ \mathrm{meV}$$

$$f=29.9792\ \mathrm{GHz}$$

A4. Bulk modulus: Hint of Kittel Problem 5-2

Charles Kittel Introduction to Solid State Physics 8-th edition

Rms, thermal dilation of crystal cell

(a) Estimate for 300 K the root mean square thermal dilation $\Delta V/V$ for a primitive cell of sodium. Take the bulk modulus as 7 x 10^{10} erg/cm^3. Note that the Debye temperature 158 K is less than 300 K, so that the thermal energy is of the order of $k_B T$.

(b) Use this result to estimate the root mean square thermal fluctuation $\Delta a/a$ of the lattice parameter.

((**Solution**))

We start from the equation

$$B = V\frac{dU^2}{dV^2}.$$

where B is the bulk modulus and U is the total internal energy.

$$\frac{dU^2}{dV^2} = \frac{B}{V}.$$

We introduce a new variable x for the volume V;

$$V = V_0(1 + x)$$

where x is very small compared to unity. Thus we get

$$\frac{1}{V_0{}^2}\frac{d^2U}{dx^2} = \frac{B}{V_0(1 + x)}$$

or

$$\frac{d^2U}{dx^2} = \frac{BV_0}{(1 + x)}.$$

This leads to

$$\frac{dU}{dx} = BV_0 \ln(1 + x)$$

In the limit of $x \to 0$,

$$\ln(1 + x) = x - \frac{x^2}{2} + ... \approx x.$$

Using this approximation, we have

$$\frac{dU}{dx} = BV_0 x,$$

or

$$U = \frac{1}{2} B V_0 x^2$$

Noting that x can be expressed as

$$x = \frac{V - V_0}{V_0} = \frac{\Delta V}{V_0},$$

we get the final form of U as

$$U = \frac{1}{2} B V_0 \left(\frac{\Delta V}{V_0} \right)^2 .$$

The total volume is given by

$$V_0 = N_{cell} a^3 ,$$

where N_{cell} is the number of unit cell and a is the conventional lattice constant. So we get the thermal energy per unit cell as

$$\frac{U}{N_{cell}} = \frac{1}{2} B \left(\frac{\Delta V}{V_0} \right)^2 \frac{V_0}{N_{cell}} = \frac{1}{2} B \left(\frac{\Delta V}{V_0} \right)^2 a^3$$

Suppose that the distortion of the lattice occurs along the x direction.

$$\frac{\Delta V}{V_0} = \frac{3a^2 \Delta a}{a^3} = \frac{3\Delta a}{a}.$$

For bcc and fcc crystals, that there are p atoms per conventional unit cell; $p = 2$ for bcc and $p = 4$ for fcc. Each atom has a thermal energy $k_B T/2$ for the thermal motion along the x-axis direction. Then

$$\frac{U}{N_{cell}} = \frac{1}{2}B\left(\frac{3\Delta a}{a}\right)^2 a^3 = \frac{p}{2}k_B T$$

$$\frac{\Delta a}{a} = \frac{1}{3}\sqrt{\frac{pk_B T}{Ba^3}}$$

Use the values of $p = 2$, $a = 4.2906$ Å for Na.