

$\omega_{ph} > \omega$ . It, therefore, follows from Eqs. (4.41) and (4.42) that

$$\omega_{ph} \approx \omega'_{ph}$$

and

$$k \approx k'$$

The wave vectors  $\mathbf{k}$ ,  $\mathbf{k}'$ , and  $\mathbf{K}$  are related to each other as shown in Fig. 4.13. It also follows from Fig. 4.13 that, for  $\mathbf{k} = \mathbf{k}'$ , the triangle becomes isosceles and we have

$$K = 2k \sin \frac{\phi}{2} \quad (4.44)$$

where  $\phi$  is the angle between  $\mathbf{k}$  and  $\mathbf{k}'$ . Thus a phonon is produced when a photon is scattered inelastically at an angle  $\frac{\phi}{2}$  from the direction of incidence.

The frequency of the phonon is given by

$$\omega = v_s K$$

$$= 2 v_s k \sin \frac{\phi}{2}$$

$$= 2 \frac{v_s \omega_{ph} n}{c} \sin \frac{\phi}{2} \quad (4.45)$$

The phonons have been generated in quartz and sapphire in the microwave frequency range by scattering the visible light produced from an intense laser source. The observed shift in frequency of the photon agrees well with the shift calculated from Eq. (4.45) using the value of the velocity of sound determined by ultrasonic methods at low frequencies.

#### 4.7 SPECIFIC HEAT

The specific heat of a substance is defined as the heat required to raise the temperature of one gram molecule of the substance through  $1^\circ\text{C}$ , i.e.,

$$C = \frac{dQ}{dT} \quad (4.46)$$

where  $dQ$  is the amount of heat added to a system to raise its temperature from  $T$  to  $T + dT$ . The quantity of heat required to increase the temperature of a body is different under different conditions; accordingly, one can have various types of specific heats. For example, the specific heat at constant pressure,  $C_p$ , is generally different from the specific heat at constant volume,  $C_v$ . The former is always greater than the latter.

According to the first law of thermodynamics, the heat added to a system is used up in two ways; firstly, to increase the internal energy of the

system, thereby raising its temperature, and secondly, to do some work on the system to increase its volume against an external pressure. It is the latter quantity which may have different values under different conditions. If the system expands against a constant pressure, then the first law can be written as

$$dQ = dE + pdV \quad (4.47)$$

The first term on the right hand side represents the change in internal energy of the system and the second one represents the work done to change the volume by an amount  $dV$  at a pressure  $p$ . If heat is added to the system at constant volume, the second term in Eq. (4.43) vanishes and the specific heat at constant volume may be expressed as

$$C_v = \left( \frac{dQ}{dT} \right)_v = \left( \frac{\partial E}{\partial T} \right)_v \quad (4.48)$$

Similarly, one can express the specific heat at constant pressure as

$$C_p = \left( \frac{dQ}{dT} \right)_p$$

In gases, there is a large difference in  $C_p$  and  $C_v$ . However, in solids, due to a small change in volume,  $C_p$  is almost the same as  $C_v$  particularly at low temperatures. For this reason, the term 'specific heat of solids' is commonly used in case of solids. However, it strictly means the specific heat at constant volume and is given by Eq. (4.48). Thus, in solids, most of the heat supplied is used up in increasing the internal energy. The increase in internal energy of a solid may occur in two ways :

- (i) The atoms, which ordinarily vibrate freely about their equilibrium positions, are set into rigorous vibrations. This is manifested by a rise in temperature.
- (ii) The free electrons in case of metals and semiconductors get thermally excited to higher energy states.

The first contribution arises from the atomic vibrations and may be called the *lattice specific heat*. The second contribution arises from the electronic system and is a relatively small contribution. Thus, in general, the specific heat of a solid may be expressed as

$$C_{\text{solid}} = C_{\text{lat}} + C_{\text{elec}} \quad (4.49)$$

For further discussion on this chapter, it is assumed that no free electrons are present and the specific heat of a crystal is only due to the excitation of thermal vibrations in the lattice. i.e., only the lattice specific heat is to be considered.

Occasionally, the term 'heat capacity' is used instead of 'specific heat' and is defined as the heat required to raise the temperature of the complete mass (or volume) of a solid through 1°C. Thus the specific heat is the heat capacity per gram (or per unit volume). The experimental facts about the heat capacity of some representative inorganic solids are given as follows:

- (i) The heat capacity of most of the solids at room temperature is close to  $3Nk_B$ , where  $N$  is the number of atoms in the solid and  $k_B$  is the Boltzmann's constant. For one mole of atoms, the heat capacity is given by  $3N_A k_B$ , where  $N_A$  is the Avogadro's number. Its value is 25 J/mole-K or 6 cal/mole-K approximately.
- (ii) At lower temperatures ( $T \rightarrow 0$  K), the heat capacity decreases sharply and follows  $T^3$ -law for insulators and  $T$ -law for metals. If metal becomes a superconductor, the decrease is even faster.
- (iii) In magnetic solids, the heat capacity increases near the Curie temperature when the magnetic moments become ordered. This is also true for alloys exhibiting order-disorder transformations.

We discuss below the theoretical explanation of the facts regarding the lattice heat capacity. The discussion is primarily applicable to insulators.

#### 4.8 CLASSICAL THEORY OF LATTICE HEAT CAPACITY

A crystal consists of atoms which are arranged in a periodic manner and are bound together by strong binding forces. Each atom is free to vibrate about its equilibrium position and constitutes a three-dimensional harmonic oscillator. The effect of imparting thermal energy to a solid is to increase its internal energy in the form of vibrational energy of these harmonic oscillators. Thus, in the classical theory, it is assumed that each atom of a crystal acts as a three-dimensional harmonic oscillator and all the atoms vibrate independent of one another. Further, a system of  $N$  vibrating atoms or  $N$  independent three-dimensional harmonic oscillators is equivalent to a system of  $3N$  identical and independent one-dimensional harmonic oscillators. This is because each vibrating atom has three independent vibrational degrees of freedom and, according to the principle of equipartition of energy, the vibrational energy is distributed equally among all the three degrees of freedom. Thus each vibrational degree of freedom can be regarded as a one-dimensional harmonic oscillator.

We assume that each harmonic oscillator vibrates with its natural frequency  $\omega_0$ . However, the energies of these oscillators may be different because they may vibrate with different amplitudes. Also, each oscillator may acquire any value of energy ranging continuously from zero to infinity. In order to determine the heat capacity of a solid, we find out the average thermal

energy of single one-dimensional harmonic oscillator, multiply it by  $3N$  and then use Eq. (4.46) or (4.48).

The energy  $\varepsilon$  of a one-dimensional harmonic oscillator of mass  $m$  and angular frequency  $\omega_0$  is given by

$$\begin{aligned}\varepsilon &= \frac{p^2}{2m} + V(x) \\ &= \frac{p^2}{2m} + \frac{1}{2} m\omega_0^2 x^2\end{aligned}\quad (4.50)$$

where  $\frac{p^2}{2m}$  represents the kinetic energy,  $p$  being the momentum, and  $V(x)$

is the potential energy at a displacement  $x$  from the mean position. Assuming that the distribution of oscillators in energy obeys the Maxwell-Boltzmann distribution law, the average energy of each harmonic oscillator is given by

$$\bar{\varepsilon} = \frac{\int \varepsilon \exp\left(-\frac{\varepsilon}{k_B T}\right) d\varepsilon}{\int \exp\left(-\frac{\varepsilon}{k_B T}\right) d\varepsilon}$$

Using Eq. (4.50), we get

$$\begin{aligned}\bar{\varepsilon} &= \frac{\iint_{px} \left( \frac{p^2}{2m} + \frac{1}{2} m\omega_0^2 x^2 \right) \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}{\iint_{px} \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx} \\ &= \frac{\iint_{px} \left( \frac{p^2}{2m} \right) \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}{\iint_{px} \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx} \\ &\quad + \frac{\iint_{px} \left( \frac{m\omega_0^2 x^2}{2} \right) \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}{\iint_{px} \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}\end{aligned}$$

$$= \frac{\int_p \left( \frac{p^2}{2m} \right) \exp \left( -\frac{p^2}{2mk_B T} \right) dp}{\int_p \exp \left( -\frac{p^2}{2mk_B T} \right) dp} + \frac{\int_x \left( \frac{m\omega_0^2 x^2}{2} \right) \exp \left( -\frac{m\omega_0^2 x^2}{2k_B T} \right) dx}{\int_x \exp \left( -\frac{m\omega_0^2 x^2}{2k_B T} \right) dx}$$

Now

$$\int_0^\infty u^2 \exp(-au^2) du = \frac{1}{4} \sqrt{\frac{\pi}{a^3}}$$

and

$$\int_0^\infty \exp(-au^2) du = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

$$\bar{\epsilon} = \frac{1}{2m} \cdot \frac{1}{2} \left[ \pi (2mk_B T)^3 \right]^{\frac{1}{2}} + \frac{1}{2} m\omega_0^2 \frac{\frac{1}{4} \left[ \pi \left( \frac{2k_B T}{m\omega_0^2} \right)^3 \right]^{\frac{1}{2}}}{\frac{1}{2} \left[ \pi \left( \frac{2k_B T}{m\omega_0^2} \right) \right]^{\frac{1}{2}}} \\ = \frac{1}{2} k_B T + \frac{1}{2} k_B T \\ = k_B T \quad (4.51)$$

Thus the total vibrational energy of a crystal containing  $N$  identical atoms or  $3N$  one-dimensional harmonic oscillators becomes

$$E = 3N\bar{\epsilon} = 3Nk_B T \quad (4.52)$$

It is important to note that the total vibrational energy of a crystal is independent of the type of frequency distribution of oscillators assumed in this model. Also, the energy  $E$  depends only on the temperature provided the volume remains constant.

Using Eq. (4.48), the heat capacity of a solid consisting of  $N$  atoms

is

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v = 3Nk_B \quad (4.53)$$

The molar heat capacity is, therefore, given by

$$C_{vm} = 3N_a k_B = 3R = 5.96 \text{ cal/mole-K} \quad (4.54)$$

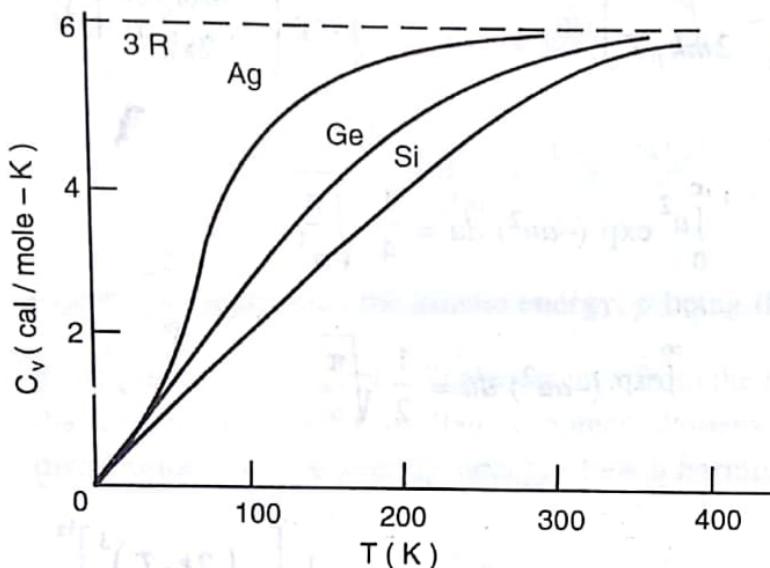


Fig. 4.14. Heat capacity of silver, germanium and silicon as a function of temperature.

temperatures and often at room temperature too. The theory, however, fails to account for the value of heat capacity at low temperatures. As shown in Fig. 4.14, the heat capacity approaches zero for Ag, Ge and Si as  $T$  approaches zero. This discrepancy was resolved first by Einstein and then by Debye by using the quantum theory.

#### 4.9 EINSTEIN'S THEORY OF LATTICE HEAT CAPACITY

Einstein, in 1911, attempted to resolve the discrepancies of the classical theory of specific heat by applying the Planck's quantum theory. Einstein retained all the assumptions of the classical theory as such except replacing the classical harmonic oscillators by quantum harmonic oscillators which can have only discrete energy values. The salient features of the Einstein's theory are listed below :

- (i) A crystal consists of atoms which may be regarded as identical and independent harmonic oscillators.
- (ii) A solid consisting of  $N$  atoms is equivalent to  $3N$  one-dimensional harmonic oscillators.
- (iii) All the oscillators vibrate with the same natural frequency due to the identical environment of each.
- (iv) The oscillators are quantum oscillators and have discrete energy

Thus, according to the classical theory, the molar heat capacity of all the solids is constant and is independent of temperature and frequency. This is called the *Dulong and Petit's law*. The result is in good agreement with the observed heat capacity for a number of solids including metals at high

spectrum rather than the continuous one as for classical oscillators.

- (v) Any number of oscillators may be present in the same quantum state.
- (vi) The atomic oscillators form an assembly of systems which are distinguishable or identifiable due to their location at separate and distinct lattice sites and hence obey the Maxwell-Boltzmann distribution of energies.

Considering the Planck's quantum theory, the discrete energy values of an oscillator with frequency  $\nu$  are given by

$$\epsilon_n = n\hbar\nu = n\hbar\omega_0 \quad (4.55)$$

where  $n = 0, 1, 2, 3, \dots$  is called the quantum number. Einstein later used the wave mechanical result which gives the energy levels of the harmonic oscillator as

$$\epsilon_n = \left(n + \frac{1}{2}\right) \hbar\nu = \left(n + \frac{1}{2}\right) \hbar\omega_0 \quad (4.56)$$

where  $\frac{1}{2}\hbar\omega_0$  is the temperature independent *zero point energy* contribution to the internal energy of the oscillator. To calculate the average energy of an oscillator, we replace integration by summation in the expression for the Maxwell-Boltzmann distribution of energy and obtain

$$\bar{\epsilon} = \frac{\sum_{n=0}^{\infty} \epsilon_n \exp\left(-\frac{\epsilon_n}{k_B T}\right)}{\sum_{n=0}^{\infty} \exp\left(-\frac{\epsilon_n}{k_B T}\right)} \quad (4.57)$$

Using Eq. (4.56), we get

$$\begin{aligned} \bar{\epsilon} &= \frac{\sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) \hbar\omega_0 \exp\left[-\left(n + \frac{1}{2}\right) \frac{\hbar\omega_0}{k_B T}\right]}{\sum_{n=0}^{\infty} \exp\left[-\left(n + \frac{1}{2}\right) \frac{\hbar\omega_0}{k_B T}\right]} \\ &= \frac{\hbar\omega_0 \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) \exp\left[\left(n + \frac{1}{2}\right) x\right]}{\sum_{n=0}^{\infty} \exp\left[\left(n + \frac{1}{2}\right) x\right]} \quad (4.58) \end{aligned}$$

where

$$x = -\frac{\hbar\omega_0}{k_B T}$$

$$\therefore \bar{\epsilon} = \frac{\hbar\omega_0 \left( \frac{1}{2} e^{x/2} + \frac{3}{2} e^{3x/2} + \frac{5}{2} e^{5x/2} + \dots \right)}{\left( e^{x/2} + e^{3x/2} + e^{5x/2} + \dots \right)}$$

$$\begin{aligned} &= \hbar\omega_0 \frac{d}{dx} \ln \left[ e^{x/2} + e^{3x/2} + e^{5x/2} + \dots \right] \\ &= \hbar\omega_0 \frac{d}{dx} \ln \left[ e^{x/2} (1 + e^x + e^{2x} + \dots) \right] \end{aligned}$$

$$\text{Now } \ln (1 + e^x + e^{2x} + \dots) = -\ln (1 - e^x)$$

$$\begin{aligned} \therefore \bar{\epsilon} &= \hbar\omega_0 \frac{d}{dx} \left[ \frac{x}{2} - \ln (1 - e^x) \right] \\ &= \hbar\omega_0 \left[ \frac{1}{2} + \frac{e^x}{1 - e^x} \right] = \hbar\omega_0 \left[ \frac{1}{2} + \frac{1}{e^{-x} - 1} \right] \\ &= \hbar\omega_0 \left[ \frac{1}{2} + \frac{1}{e^{\hbar\omega_0/k_B T} - 1} \right] \\ &= \frac{1}{2} \hbar\omega_0 + \frac{\hbar\omega_0}{\exp\left(\frac{\hbar\omega_0}{k_B T}\right) - 1} \end{aligned} \tag{4.59}$$

If Eq. (4.55) is used in Eq. (4.57), the expression for the average energy becomes

$$\bar{\epsilon} = \frac{\hbar\omega_0}{\exp\left(\frac{\hbar\omega_0}{k_B T}\right) - 1} \tag{4.60}$$

The expression (4.59) is identical to (4.60) except with the difference of the energy  $\frac{1}{2} \hbar\omega_0$  which is the temperature independent zero point energy as, for

$T = 0$ ,  $\bar{\epsilon} = \frac{1}{2} \hbar\omega_0$ . Thus, according to quantum mechanics, the atoms are not

at rest even at 0 K and each atom possesses the vibrational energy of  $\frac{1}{2} \hbar \omega_0$ . This energy, however, has no contribution to  $C_v$ . It may be noted that the expression (4.59) also contains the frequency of the oscillator, in contrast to the corresponding expression (4.51) of the classical theory.

The expression for the internal energy of the crystal becomes

$$E = 3N\bar{\epsilon}$$

$$= \frac{3}{2} N\hbar\omega_0 + \frac{3N\hbar\omega_0}{e^{\hbar\omega_0/k_B T} - 1} \quad (4.61)$$

$$\therefore C_v = \left( \frac{\partial E}{\partial T} \right)_v = 3Nk_B \left( \frac{\hbar\omega_0}{k_B T} \right)^2 \frac{e^{\hbar\omega_0/k_B T}}{\left( e^{\hbar\omega_0/k_B T} - 1 \right)^2} \quad (4.62)$$

Let

$$\theta_E = \frac{\hbar\omega_0}{k_B} \quad (4.63)$$

where  $\theta_E$  is the characteristic temperature known as the *Einstein temperature*

$$\therefore C_v = 3Nk_B \left( \frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{\left( e^{\theta_E/T} - 1 \right)^2} \quad (4.64)$$

We now consider the following cases :

(i) *High temperature behaviour*

For temperatures such that

$$k_B T \gg \hbar\omega_0 \quad \text{or} \quad T \gg \theta_E,$$

we can write

$$e^{\hbar\omega_0/k_B T} - 1 \approx 1 + \frac{\hbar\omega_0}{k_B T} + \dots - 1 = \frac{\hbar\omega_0}{k_B T} \quad (4.65)$$

and from Eq. (4.59), we get

$$\bar{\epsilon} = \frac{1}{2} \hbar\omega_0 + k_B T \approx k_B T$$

Thus at high temperatures, the average vibrational energy is the same as that obtained from the classical theory. Also, the Eq. (4.62) becomes

$$C_v = 3Nk_B \left( \frac{\hbar\omega_0}{k_B T} \right)^2 \frac{\left( 1 + \frac{\hbar\omega_0}{k_B T} \right)}{\left( \frac{\hbar\omega_0}{k_B T} \right)^2} \quad [\text{Using Eq. (4.65)}]$$

$$= 3Nk_B \left( 1 + \frac{\hbar\omega_0}{k_B T} \right)$$

For large  $T$ ,  $\frac{\hbar\omega_0}{k_B T} \rightarrow 0$  and we get

$$C_v = 3Nk_B = 3R \quad (\text{for } N = N_a)$$

which is the Dulong and Petits's law as obtained from classical theory.

(ii) *Low temperature behaviour*

For temperatures such that

$$k_B T \ll \hbar\omega_0 \text{ or } T \ll \theta_E,$$

we can write

$$e^{\hbar\omega_0/k_B T} - 1 \approx e^{\hbar\omega_0/k_B T}$$

Therefore, Eq. (4.59) becomes

$$\bar{\epsilon} = \frac{1}{2} \hbar\omega_0 + \hbar\omega_0 e^{-\hbar\omega_0/k_B T} \quad (4.66)$$

It shows that, at low temperatures, the average vibrational energy decreases exponentially with decrease in temperature. The expression (4.62) for  $C_v$  becomes

$$C_v = 3Nk_B \left( \frac{\hbar\omega_0}{k_B T} \right)^2 e^{-\hbar\omega_0/k_B T} \quad (4.67)$$

or, in terms of  $\theta_E$ , it becomes

$$C_v = 3Nk_B \left( \frac{\theta_E}{T} \right)^2 e^{-\theta_E/T} \quad (4.68)$$

Thus, for  $T \ll \theta_E$ , the heat capacity is proportional to  $e^{-\theta_E/T}$  which is the dominating factor. However, experimentally it is found to vary as  $T^3$  for most of the solids.

A theoretical plot of  $C_v$  versus  $T/\theta_E$  using Eq. (4.64) for diamond using  $\theta_E = 1320$  K is shown in Fig. 4.15. Some experimental points are also shown for comparison. It is seen that the Einstein curve fits the experimental points well over a wide range of temperature except for very low (liquid helium) temperatures where it falls more rapidly than the observed decrease in  $C_v$  which follows  $T^3$  law.

The Einstein temperature defined by Eq. (4.63), which distinguishes between the low and high temperature behaviours, can be determined if  $\omega_0$  is known. As described in Secs. 4.2 and 4.3, the natural vibrational frequency can be determined from the atomic mass and the observed elastic constants of the crystal and, for monoatomic crystals, it is equal to  $\sqrt{4\beta/m}$ . For typical metallic elements, the value of  $\theta_E$  varies from 100 to 200K.

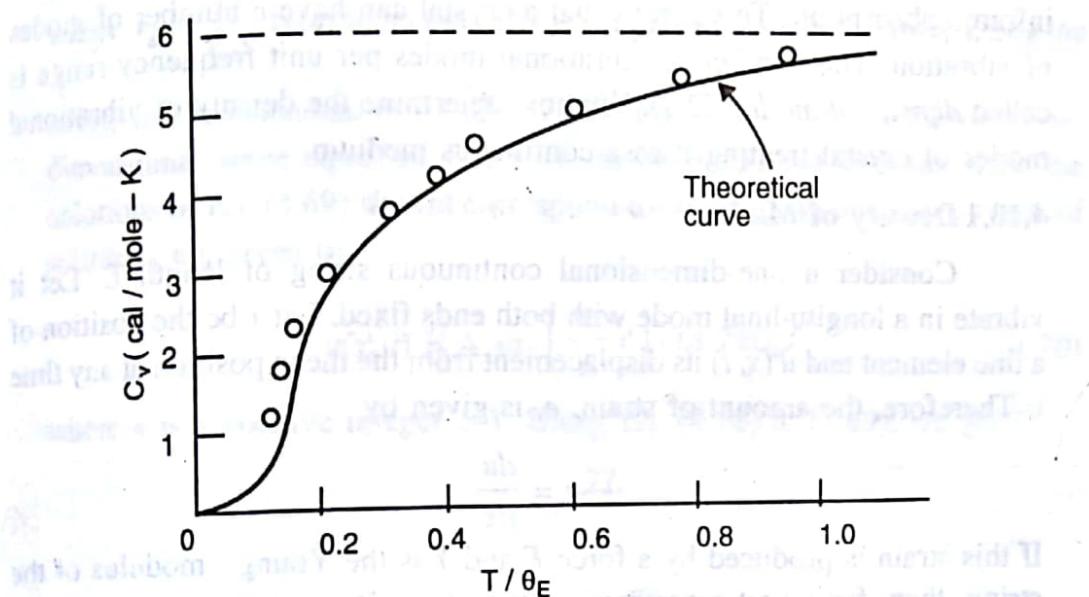


Fig. 4.15. Comparison of theoretical heat capacity of diamond calculated from Einstein's model with the experimentally observed values.

Although the Einstein's model provides a much better explanation for the variation of heat capacity with temperature than the classical theory, it fails to account for the values of specific heat at very low temperatures. The discrepancy arises due to the over-simplified assumption of the Einstein's model in which the atomic oscillators are considered to vibrate independently at the same frequency. These oscillators, in fact, are coupled together and there may be a number of possible vibrational frequencies rather than a single frequency  $\omega_0$ . This fact is accounted for in the Debye's model which is described below.

#### 4.10 DEBYE'S MODEL OF LATTICE HEAT CAPACITY

The Einstein's theory assumed that the atoms of a crystal vibrate totally independent of one another. The vibrational motion of the crystal as a whole was considered to be the same as the vibrational motion of a single atom and, therefore, all the atomic vibrations of the crystal were assigned a common frequency  $\omega_0$  which is the natural frequency of vibration of a single atom. This assumption is over-simplified since the atoms are bound together in a crystal and form a system of coupled harmonic oscillators which cannot

vibrate independently. This fact was taken into consideration by Debye who, in 1912, put forward his model of lattice heat capacity. In this model, the vibrational motion of the crystal as a whole was considered to be equivalent to the vibrational motion of a system of coupled harmonic oscillators which can propagate a range of frequencies rather than a single frequency. Debye proposed that crystals can propagate elastic waves of wavelengths ranging from low frequencies (sound waves) to high frequencies corresponding to infrared absorption. This means that a crystal can have a number of modes of vibration. The number of vibrational modes per unit frequency range is called *density of modes*,  $Z(v)$ . We now determine the density of vibrational modes of crystal treating it as a continuous medium.

#### 4.10.1 Density of Modes

Consider a one-dimensional continuous string of length  $L$ . Let it vibrate in a longitudinal mode with both ends fixed. Let  $x$  be the position of a line element and  $u(x, t)$  its displacement from the mean position at any time  $t$ . Therefore, the amount of strain,  $e$ , is given by

$$e = \frac{du}{dx}$$

If this strain is produced by a force  $F$  and  $Y$  is the Young's modulus of the string, then, for a unit cross-section, we can write

$$\frac{F}{e} = Y$$

Now consider an element of length  $\Delta x$ . If the strain at one of its ends is  $e(x)$ , then its value at the other end is

$$e(x) + \frac{\partial e}{\partial x} \Delta x = e(x) + \frac{\partial^2 u}{\partial x^2} \Delta x$$

The force at the two ends of the string is

$$e(x)Y \quad \text{and} \quad [e(x) + \frac{\partial^2 u}{\partial x^2} \Delta x]Y$$

Therefore, the net force on the element is

$$\left( \frac{\partial^2 u}{\partial x^2} \right) \Delta x Y$$

The force on the line element  $\Delta x$  can also be written as

$$\rho \Delta x \left( \frac{\partial^2 u}{\partial t^2} \right)$$

where  $\rho$  is the density of the string. Therefore, we have

$$\left( \frac{\partial^2 u}{\partial x^2} \right) \Delta x Y = \rho \Delta x \left( \frac{\partial^2 u}{\partial t^2} \right) \text{ or } \frac{\partial^2 u}{\partial x^2} = \frac{\rho}{Y} \frac{\partial^2 u}{\partial t^2}$$

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v_s^2} \frac{\partial^2 u}{\partial t^2} \quad (4.69)$$

where  $v_s = \sqrt{\frac{Y}{\rho}}$  represents the velocity of propagation of the wave along the string. It is independent of frequency. The Eq. (4.69) is the well known one-dimensional wave equation. Since the string is fixed at both the ends, the solutions of Eq. (4.69) should correspond to standing waves. These types of solutions are given by

$$u(x, t) = A \sin \left( \frac{n\pi}{L} x \right) \cos 2\pi v_s t \quad (4.70)$$

where  $n$  is a positive integer  $\geq 1$ . Using Eq. (4.70) in (4.69), we get

$$\lambda_n = \frac{2L}{n}$$

and  $v_n = \frac{v_s}{\lambda_n} = \frac{n\pi v_s}{2L} \quad (4.71)$

i.e.,  $v_1 = \frac{v_s}{2L}, v_2 = \frac{v_s}{L}, v_3 = \frac{3v_s}{2L}, \text{ etc.} \quad (4.72)$

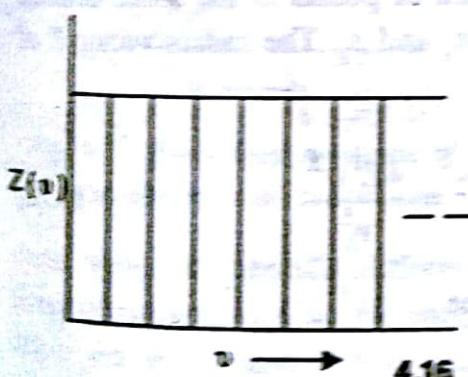


Fig. 4.16. Frequency spectrum of a continuous string.

This shows that the frequency of the string can have discrete values only and is

an integral multiple of  $\frac{v_s}{2L}$ . It implies that the frequency spectrum of a continuous string is discrete and contains an infinite number of parallel lines equidistant from each other as shown in Fig. 4.16.

From Eqs. (4.71), we have

$$n = \frac{2L}{v_s} v_n$$

$$dn = \frac{2L}{v_s} dv \quad (4.73)$$

This gives the number of possible modes of vibration in the frequency interval  $dv$ .

Considering now the three-dimensional case; the wave equation (4.69) can be written as

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{v_s^2} \frac{\partial^2 u}{\partial t^2} \quad (4.74)$$

The three-dimensional continuous medium can be taken as a cube of side  $L$  whose faces are fixed. In analogy with Eq. (4.70), the standing wave solutions of the wave equation (4.74) are

$$u(x, y, z, t) = A \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right) \cos 2\pi v t \quad (4.75)$$

where  $n_x, n_y, n_z$  are positive integers  $\geq 1$ . Substituting this solution into (4.74) and simplifying, we obtain

$$\frac{\pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2) = \frac{4\pi^2 v^2}{v_s^2} \quad (4.76)$$

or  $n_x^2 + n_y^2 + n_z^2 = \frac{4L^2 v^2}{v_s^2}$  (4.77)

This equation gives the possible modes of vibration. The integers  $n_x, n_y$  and  $n_z$  determine the possible frequencies or wavelengths. In order to determine the number of possible modes of vibration,  $Z(v)dv$ , present in the frequency range  $v$  and  $v + dv$ , we consider a network of points in the space defined by three positive integral coordinates  $n_x, n_y$  and  $n_z$ . The radius vector  $R$  of any point from the origin is given by

$$R^2 = n_x^2 + n_y^2 + n_z^2 = \frac{4L^2 v^2}{v_s^2} \quad (4.78)$$

This is the equation of a sphere of volume

$$V' = \frac{4}{3} \pi R^3$$

Differentiating it, we get

$$dV' = 4\pi R^2 dR$$

The number of modes present in the frequency range  $v$  and  $v + dv$  should be the same as number of points lying in the volume interval  $V$  and  $V + dV$  or in the range  $R$  and  $R + dR$  of the radius vector. Since each point occupies, on an average, a unit volume in the space of integers, the number of points

present in the volume  $dV$  of the spherical shell is numerically equal to the volume of the shell, i.e.,

$$dn = 4\pi R^2 dR$$

But since a mode of vibration is always determined by the positive values of  $n_x$ ,  $n_y$  and  $n_z$  only, we must consider the number of points lying in the octant defined by these positive integers only. Thus the number of possible modes of vibration is

$$\begin{aligned} Z(v)dv &= \frac{1}{8} (4\pi R^2 dR) \\ &= \frac{1}{8} 4\pi \frac{4L^2 v^2}{v_s^2} \frac{2L}{v_s} dv = \frac{4\pi L^3 v^2}{v_s^3} dv \\ &= \left( \frac{4\pi V}{v_s^3} \right) v^2 dv \end{aligned} \quad (4.79)$$

where  $V = L^3$  is the volume of the solid cube. For a perfect continuum, the possible frequencies vary between zero and infinity and the number of

possible vibrational modes increases with square of the frequency as shown in Fig. 4.17. This type of situation arises in case of electromagnetic waves travelling in a box. Thus Eq. (4.76) is fundamental to the theory of black body radiations.

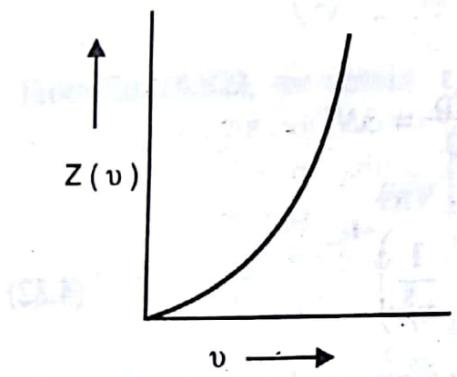


Fig. 4.17. Frequency spectrum of a three-dimensional continuum.

In general, the elastic waves propagating in a solid are of two types — transverse waves and longitudinal waves. The velocity of propagation,  $v_p$ , of trans-

verse waves is generally different from the velocity of propagation,  $v_l$ , of longitudinal waves. Also, for each frequency or direction of propagation, the transverse waves have two vibrational modes perpendicular to the direction of propagation whereas the longitudinal waves have only one mode which lies along the direction of propagation. For such a case, the total number of vibrational modes is expressed as

$$Z(v)dv = 4\pi V \left( \frac{2}{v_l^3} + \frac{1}{v_l^3} \right) v^2 dv \quad (4.80)$$

### 4.10.2 The Debye Approximation

If the interatomic distance is small as compared to the wavelength of elastic waves, the crystal can be regarded as a continuum from the point of view of the wave. Based on this idea, Debye assumed that the continuum model is applicable to all possible vibrational modes of the crystal. Further, the fact that the crystal consists of a finite number ( $N$ ) of atoms is taken into account by limiting the total number of vibrational modes to  $3N$ . This puts an upper limit to the frequency of the elastic waves which can propagate through the crystal. This highest frequency propagating through a crystal is called the *Debye frequency*,  $v_D$ . It is common to transverse and longitudinal modes of vibrations. Hence the frequency spectrum of a continuous medium is cut off at the Debye frequency as shown in Fig. 4.18. For the total number of vibrational modes with frequencies ranging from zero to  $v_D$ , we can write

$$\int_0^{v_D} Z(v) dv = 3N \quad (4.81)$$

Using Eq. (4.80), we obtain

$$\int_0^{v_D} 4\pi V \left( \frac{2}{v_t^3} + \frac{1}{v_l^3} \right) v^2 dv = 3N$$

or

$$4\pi V \left( \frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \frac{v_D^3}{3} = 3N$$

or

$$v_D^3 = \frac{9N}{4\pi V} \left( \frac{2}{v_t^3} + \frac{1}{v_l^3} \right)^{-1} \quad (4.82)$$

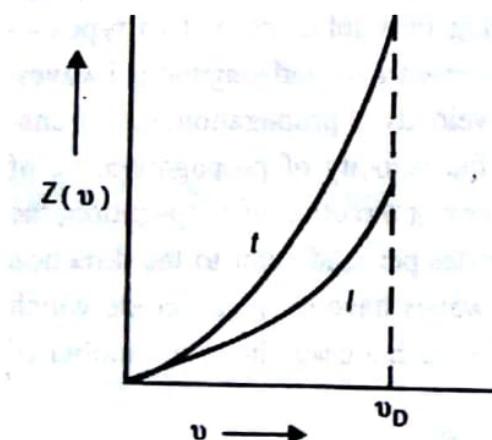


Fig. 4.18. Frequency spectrum of transverse (t) and longitudinal (l) modes in a continuum showing cut-off at the Debye frequency.

This equation can be used to determine  $v_D$ . Taking velocity of sound of the order of  $10^3 \text{ ms}^{-1}$  and  $N/V \approx 10^{28} \text{ m}^{-3}$ , we get  $v_D \approx 10^{13} \text{ s}^{-1}$ . This corresponds to the wavelength of about  $1 \text{ \AA}$  which is of the same order as interatomic distance. This violates the basic assumption of Debye and hence puts a question mark on the validity of the continuum theory, particularly in the high frequency region. Furthermore, the velocities  $v_t$  and  $v_l$  have been assumed to be independent of wavelength which may not be always true.

The vibrational energy of a crystal is determined by using the Planck's theory. The average energy of an oscillator having frequency  $\nu$  at a temperature  $T$  is given by

$$\bar{\epsilon} = \frac{h\nu}{e^{h\nu/k_B T} - 1} \quad (4.83)$$

We can associate a harmonic oscillator of the same frequency with each vibrational mode. Thus the vibrational energy of the crystal is given by

$$E = \int_0^{\nu_D} \bar{\epsilon} Z(\nu) d\nu$$

Using Eqs. (4.80) and (4.83) we get

$$\begin{aligned} E &= \int_0^{\nu_D} 4\pi V \left( \frac{2}{\nu_I^3} + \frac{1}{\nu_I^3} \right) \frac{h\nu^3}{e^{h\nu/k_B T} - 1} d\nu \\ &= 4\pi h V \left( \frac{2}{\nu_I^3} + \frac{1}{\nu_I^3} \right) \int_0^{\nu_D} \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1} \end{aligned}$$

From Eq. (4.82), we obtain

$$\begin{aligned} 4\pi V \left( \frac{2}{\nu_I^3} + \frac{1}{\nu_I^3} \right) &= \frac{9N}{\nu_D^3} \\ E &= \frac{9Nh}{\nu_D^3} \int_0^{\nu_D} \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1} \end{aligned} \quad (4.84)$$

Putting  $\frac{h\nu}{k_B T} = x$  and  $\frac{h\nu_D}{k_B T} = x_m$ , we get

$$\nu = \frac{x k_B T}{h}$$

or  $d\nu = \frac{k_B T}{h} dx$

Therefore, Eq. (4.84) becomes

$$\begin{aligned}
 E &= \frac{9Nh}{v_D^3} \left( \frac{k_B T}{h} \right)^4 \int_0^{x_m} \frac{x^3 dx}{e^x - 1} \\
 &= 9N \left( \frac{k_B T}{h v_D} \right)^3 k_B T \int_0^{x_m} \frac{x^3 dx}{e^x - 1}
 \end{aligned} \tag{4.85}$$

As in the Einstein's theory, we introduce here a characteristic temperature,  $\theta_D$ , called the *Debye temperature* defined as

$$\theta_D = \frac{h v_D}{k_B} \tag{4.86}$$

$$x_m = \frac{\theta_D}{T}$$

Equation (4.85) then becomes

$$E = 9Nk_B T \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1} \tag{4.87}$$

The specific heat is given by

$$\begin{aligned}
 C_v &= \left( \frac{\partial E}{\partial T} \right)_v = 9Nk_B \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx \\
 &= 3R \left( \frac{\theta_D}{T} \right) F_D \quad (\text{for } N = N_a)
 \end{aligned} \tag{4.88}$$

The function  $F_D$  is called the Debye function and is expressed as

$$F_D = 3 \left( \frac{T}{\theta_D} \right)^4 \int_0^{\theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx \tag{4.89}$$

We now consider the high and low temperature cases.

(i) *High temperature case*

For  $T \gg \theta_D$ ,  $x$  is small compared with unity for the complete range of integration. Therefore, we can write

$$e^x - 1 \approx x$$

Equation (4.87) then becomes

$$\begin{aligned}
 E &= 9Nk_B T \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} x^2 dx \\
 &= 3Nk_B T \\
 \therefore C_v &= \frac{\partial E}{\partial T} = 3Nk_B \\
 &= 3R \quad (\text{for } N = N_a)
 \end{aligned} \tag{4.90}$$

Thus at high temperatures, the Debye's theory also obeys the Dulong and Petit's law as obeyed by the classical theory and the Einstein's theory. This, in fact, means that the quantum considerations carry almost no significance at high temperatures.

(ii) *Low temperature case*

$$\text{For } T \ll \theta_D, x_m = \frac{\theta_D}{T} \rightarrow \infty$$

Therefore, Eq. (4.87) becomes

$$E = 9Nk_B T \left( \frac{T}{\theta_D} \right)^3 \int_0^{\infty} \frac{x^3 dx}{e^x - 1}$$

Now

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

$$\therefore E = 9Nk_B T \left( \frac{T}{\theta_D} \right)^3 \frac{\pi^4}{15}$$

$$= \frac{3}{5} \pi^4 N k_B \frac{T^4}{\theta_D^3} \tag{4.91}$$

This shows that the vibrational energy is proportional to  $T^4$  which is analogous to the Stefan's law of black body radiation.

Thus it follows that both phonons and photons obey the same statistics except with the difference that photons obey  $T^4$  law at all temperatures whereas phonons do so only at low temperatures.

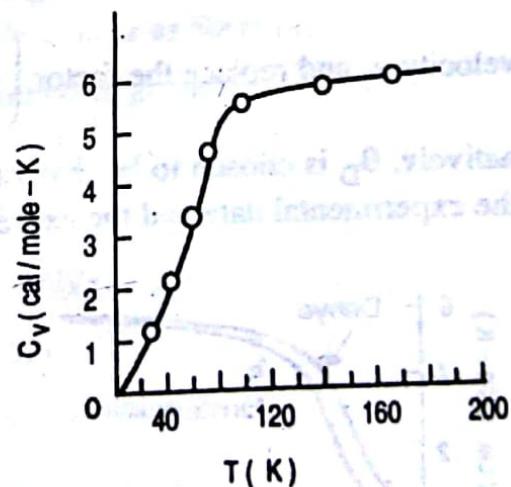


Fig. 4.19. Comparison of Debye heat capacity obtained from Eq. (4.87) using  $\theta_D = 225K$  with the experimentally observed values (circles) for silver.

The expression for specific heat is obtained as

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v = \frac{12}{5} \pi^4 N k_B \left( \frac{T}{\theta_D} \right)^3$$

(4.87)

$$= \frac{12}{5} \pi^4 R \left( \frac{T}{\theta_D} \right)^3 \quad (\text{for } N = N_a) \quad (4.92)$$

Thus, at very low temperatures, the specific heat is proportional to  $T^3$ . This is called the *Debye  $T^3$  law* and holds for  $T \leq \frac{\theta_D}{10}$ .

There is an excellent matching of the experimentally determined values of the specific heats at various temperatures with those calculated theoretically using the Debye's model as shown in Fig. 4.19 for silver with  $\theta_D = 225\text{K}$ . This also proves the validity of the Debye's approximation at sufficiently low temperatures.

A comparison of results of the specific heat obtained from the Einstein and Debye models is made in Fig. 4.20. The Debye model yields somewhat higher values of specific heat as compared to the Einstein model. This is because of the fact that the Debye model takes into account the low frequency modes which, at low temperatures, have higher vibrational energy and hence larger specific heat. The Debye temperature  $\theta_D$  can be obtained from Eqs. (4.82) and (4.86) provided the velocities of sound in transverse and longitudinal modes are known. For isotropic medium, one can use the average

velocity  $v_s$  and replace the factor  $\left( \frac{2}{v_t^3} + \frac{1}{v_l^3} \right)$  by  $3/v_s^3$  in Eq. (4.80). Alternatively,  $\theta_D$  is chosen to be that value which produces the best fit between the experimental data and the expression (4.88). There is, in general, a good agreement between the theoretical and experimental results.

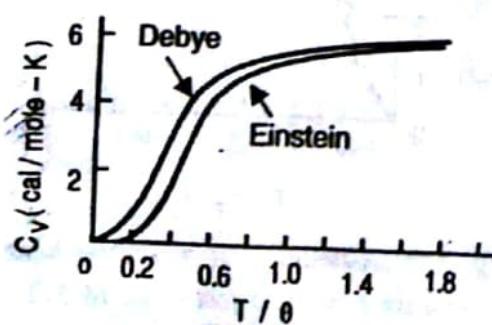


Fig. 4.20 Comparison of specific heats obtained from the Einstein and Debye models [Eqs. (4.63) and (4.87)].

Accurate measurements have indicated that the temperatures at which the  $T^3$  law holds are quite low. According to this model, the law should hold for temperatures below  $0.1 \theta_D$ , whereas it may be strictly valid for  $T \leq \theta_D/50$ . The specific heat is, however, relatively insensitive to the variations in the density of modes.

### 4.10.3 Limitations of the Debye Model

- (i) The Debye's continuum model is valid for long wavelengths only, i.e., only low frequencies are active in the solid.
- (ii) The total number of vibrational modes are assumed to be  $3N$ . This is difficult to justify as the solid is considered to be an elastic continuum which should possess infinite frequencies.
- (iii) The cut off frequency is assumed to be the same for both longitudinal and transverse waves. This is again difficult to justify because different velocities of transverse and longitudinal waves should imply different values of cut off frequency for these waves.
- (iv) According to the Debye's theory,  $\theta_D$  is independent of temperature, whereas actually it is found to vary up to an extent of 10% or even more.
- (v) The theory does not take into account the actual crystalline nature of the solid. The theory cannot be applied to crystals comprising more than one type of atoms.
- (vi) The theory completely ignores the interaction among the atoms and the contribution of electrons to the specific heat.

## SOLVED EXAMPLES

**Example 4.1.** The visible light of wavelength 5000 Å undergoes scattering from a crystal of refractive index 1.5. Calculate the maximum frequency of the phonon generated and the fractional change in frequency of the incident radiation, given the velocity of sound in the crystal as 5000 ms<sup>-1</sup>.

**Solution.** The frequency of the phonon emitted is given by

$$\omega = \frac{2v_s \omega_{ph} n}{c} \sin \frac{\phi}{2}$$

Velocity of sound in the crystal,  $v_s = 5000 \text{ ms}^{-1}$

Refractive index of the crystal,  $n = 1.5$

The frequency of incident radiation,  $\omega_{ph}$ , is calculated as :

$$\begin{aligned} \omega_{ph} &= 2\pi v = 2\pi \frac{c}{\lambda} \\ &= \frac{2\pi \times 3 \times 10^8}{5000 \times 10^{-10}} \end{aligned}$$