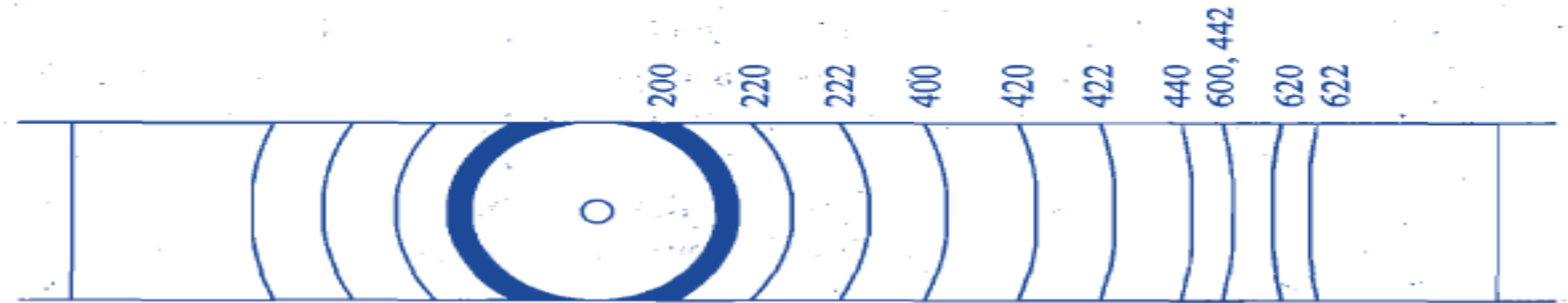


# SOLID STATE

## LECTURE-7

# CRYSTAL STRUCTURE OF POTASSIUM CHLORIDE

The powder pattern of KCl is shown in Fig, 3.17.1. At first glance the pattern looks like that of a primitive cubic lattice since there are six lines followed by a gap. However, KCl has a face-centred cubic lattice like that of NaCl. The



**Fig. 3.17.1** Diffraction pattern (only schematic) of potassium chloride

resemblance to a primitive lattice is a consequence of the fact that  $K^+$  ions and  $Cl^-$  ions have the same number of electrons and thus have the same scattering power for X-rays. The unit cell of the apparently primitive lattice formed by considering  $K^+$  and  $Cl^-$  ions as identical has half the edge length of the actual face-centred unit cell.

Another example exhibiting this type of behaviour is provided by RbBr in the series LiBr, NaBr and RbBr. All these molecules have face-centred lattices. However, X-ray diffraction indicates that RbBr has a simple cubic lattice. This results from the fact that  $Rb^+$  and  $Br^-$  have the same number of electrons.

Molybdenum forms body-centred cubic crystals whose density is  $10.3 \text{ g cm}^{-3}$ . Calculate: (a) edge length of the unit cube, (b) distance between the (110) planes and between the (111) planes. Molar mass of Mo =  $95.94 \text{ g mol}^{-1}$ .

(a) Since density of the crystal,

$$\rho = \frac{NM}{a^3 N_A}, \quad \text{therefore,} \quad a = \left( \frac{NM}{\rho N_A} \right)^{1/3}$$

Now, the number  $N$  of atoms per unit body-centred cubic cell = 2.

$$\begin{aligned} \text{Thus,} \quad a &= \left\{ \frac{2(95.94 \text{ g mol}^{-1})}{(10.3 \text{ g cm}^{-3})(6.022 \times 10^{23} \text{ mol}^{-1})} \right\}^{1/3} \\ &= 3.139 \times 10^{-8} \text{ cm} \equiv 313.9 \text{ pm} \end{aligned}$$

(b) Since  $d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$ , we get

$$d_{110} = \frac{a}{\sqrt{2}} = \frac{313.9 \text{ pm}}{1.414} = 222.0 \text{ pm}$$

and  $d_{111} = \frac{a}{\sqrt{3}} = \frac{313.9 \text{ pm}}{1.732} = 181.2 \text{ pm}$

The density of potassium chloride is  $1.9893 \text{ g cm}^{-3}$  and the length of a side of the unit cell is  $629.082 \text{ pm}$  as determined by X-ray diffraction. Calculate the value of Avogadro constant.

Since density,  $\rho = \frac{NM}{a^3 N_A}$ , therefore,  $N_A = \frac{NM}{a^3 \rho}$

Substituting the values, we have

$$N_A = \frac{4(74.55 \text{ g mol}^{-1})}{(629.082 \times 10^{-10} \text{ cm})^3 (1.9863 \text{ g cm}^{-3})} = 6.03 \times 10^{23} \text{ mol}^{-1}$$

Use the data given below to find the type of cubic lattice to which the crystal belongs:

	Fe	V	Pd
$a/\text{pm}$	286	301	388
$\rho/\text{g cm}^{-3}$	7.86	5.96	12.16

Now,  $\rho = \frac{NM}{a^3 N_A}$ , Therefore,  $N = \frac{\rho a^3 N_A}{M}$

Thus, we have

For Fe  $N = \frac{(7.86 \text{ g cm}^{-3}) (2.86 \times 10^{-8} \text{ cm})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}{(55.85 \text{ g mol}^{-1})} = 1.983 = 2$

Hence, the cubic lattice of Fe is *body-centred*.

For V  $N = \frac{(5.96 \text{ g cm}^{-3}) (3.01 \times 10^{-8} \text{ cm})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}{(50.94 \text{ g mol}^{-1})} = 1.921 = 2$

Hence, the cubic lattice for V is *body-centred*.

For Pd  $N = \frac{(12.16 \text{ g cm}^{-3}) (3.88 \times 10^{-8} \text{ cm})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}{(106.4 \text{ g mol}^{-1})} = 4.12 = 4$

Hence, the cubic lattice for Pd is *face-centred*.

X-ray analysis shows that the unit cell length in NaCl is 562.8 pm. Calculate the density you would expect on this basis. Avogadro constant is  $6.022 \times 10^{23} \text{ mol}^{-1}$ .

Since density  $\rho = \frac{NM}{a^3 N_A}$ , therefore, we get

$$\rho = \frac{4(58.5 \text{ g mol}^{-1})}{(5.628 \times 10^{-8} \text{ cm})^3 (6.022 \times 10^{23} \text{ mol}^{-1})} = 2.179 \text{ g cm}^{-3}$$

The X-ray powder pattern for molybdenum has reflections at  $\theta = 20.25^\circ, 29.30^\circ, 36.82^\circ, 43.81^\circ, 50.69^\circ, 58.80^\circ, 66.30^\circ$  and other larger angles when  $K_\alpha$  X-rays from Cu are used ( $\lambda = 154 \text{ pm}$ ).

- (a) What is the type of cubic crystal formed by Mo?
- (b) What is the length of a side of the unit cell?
- (c) What is the density of molybdenum?

(a) *Type of cubic crystal* The diffraction pattern is

$\theta$	$\sin \theta$	$\sin^2 \theta$	or	$1 \times 0.1198$	or	$2 \times 0.0599 = 2K$
$20.25^\circ$	0.346 0	0.119 8	or	$1 \times 0.1198$	or	$2 \times 0.0599 = 2K$
$29.30^\circ$	0.489 4	0.239 5	or	$2 \times 0.1198$	or	$4 \times 0.0599 = 4K$
$36.82^\circ$	0.599 0	0.358 8	or	$3 \times 0.1198$	or	$6 \times 0.0599 = 6K$
$43.81^\circ$	0.692 3	0.479 3	or	$4 \times 0.1198$	or	$8 \times 0.0599 = 8K$
$50.69^\circ$	0.773 6	0.598 4	or	$5 \times 0.1198$	or	$10 \times 0.0599 = 10K$
$58.80^\circ$	0.855 4	0.731 8	or	$6 \times 0.1198$	or	$12 \times 0.0599 = 12K$
$66.30^\circ$	0.915 7	0.838 3	or	$7 \times 0.1198$	or	$14 \times 0.0599 = 14K$

The above reflection pattern corresponds to body-centred cubic crystal. The primitive one is eliminated from the fact that the reflection corresponding to  $7K$  (which in the present case is  $14K$ ) is present.

(b) *Edge length of unit cell* We have

$$K = \frac{\lambda^2}{4a^2} \quad \text{Therefore,} \quad a = \frac{\lambda}{2\sqrt{K}}$$

Substituting the values, we have

$$a = \frac{154 \text{ pm}}{2 \times \sqrt{0.0599}} = \frac{154 \text{ pm}}{2 \times 0.2447} = 314.7 \text{ pm}$$

(c) *Density of molybdenum* We have

$$\text{Density } \rho = \frac{NM}{a^3 N_A}$$

Substituting the values, we have

$$\rho = \frac{(2)(95.94 \text{ g mol}^{-1})}{(3.147 \times 10^{-8} \text{ cm})^3 (6.022 \times 10^{23} \text{ mol}^{-1})} = 10.22 \text{ g/cm}^3$$

The unit cell of aluminium is a cube with edge length 405 pm. The density of aluminium is  $2.70 \text{ g cm}^{-3}$ . What is the structure of aluminium crystals?

Since density

$$\rho = \frac{NM}{a^3 N_A}, \quad \text{therefore} \quad N = \frac{\rho \cdot a^3 N_A}{M}$$

Substituting the given values, we get

$$N = \frac{(2.70 \text{ g cm}^{-3}) (4.05 \times 10^{-8} \text{ cm})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}{(26.98 \text{ g mol}^{-1})} = 4$$

Thus, the unit cell of aluminium is face-centred cubic.

A substance forms face-centred cubic crystals. Its density is  $1.984 \text{ g cm}^{-3}$  and the length of the edge of the unit is 630 pm. Calculate the molar mass.

Since  $\rho = \frac{NM}{a^3 N_A}$ , we get  $M = \frac{\rho a^3 N_A}{N}$

Substituting the values, we have

$$M = \frac{(1.984 \text{ g cm}^{-3}) (6.30 \times 10^{-8} \text{ cm})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}{4} \\ = 74.69 \text{ g mol}^{-1}$$

From the fact that the length of the side of the unit cell for lithium is 351 pm, calculate its atomic radius. Lithium forms body-centred cubic crystals.

In body-centred cubic crystals, atoms touch one another along the cross-diagonal of the cube.

Thus  $4r = \sqrt{3}a$  or  $r = \frac{\sqrt{3}a}{4}$

Substituting the value of  $a$ , we have

$$r = \frac{\sqrt{3} (351 \text{ pm})}{4} = 151.9 \text{ pm}$$

Magnesium oxide ( $M = 40.0 \text{ g mol}^{-1}$ ) is cubic and has a density of  $3.620 \text{ g/cm}^3$ . An X-ray diffraction diagram of MgO powder has lines at values of  $\sin \theta = 0.399, 0.461, 0.652, 0.764, 0.798$  and  $0.922$ . (a) Index the pattern and determine the type of cubic structure, (b) Calculate the wavelength of X-rays used. Assume that the number of MgO units per unit cell is the smallest consistent with the structure type.

(a) Type of cubic structure

$\sin \theta$	0.399	0.461	0.652	0.764	0.798	0.922
$\sin^2 \theta$	0.159 2	0.212 5	0.425 0	0.583 7	0.638 8	0.850 0

Obviously the cubic structure is neither primitive nor body-centred since for them the difference between any two successive values of  $\sin^2 \theta$  is constant. The diffraction pattern for the face-centred cubic lattice has  $\sin^2 \theta$  values at  $3K, 4K, 8K, 11K, 12K, 16K, \dots$ , corresponding to the planes (111), (200), (220), (311), (222), (400), ... respectively. This pattern is satisfied by the above values of  $\sin^2 \theta$  with  $K = 0.0529$ . Thus, magnesium oxide has a face-centred cubic lattice.

(b) Wavelength of X-rays used

Given that  $\rho = 3.620 \text{ g cm}^{-3}$

For a face-centred cubic lattice,  $n = 4$ . Therefore,

$$a = \left( \frac{NM}{\rho N_A} \right)^{1/3} = \left( \frac{4(40 \text{ g mol}^{-1})}{(3.62 \text{ g cm}^{-3})(6.022 \times 10^{23} \text{ mol}^{-1})} \right)^{1/3}$$

$$= 4.187 \times 10^{-8} \text{ cm}$$

According to Bragg's equation

$$n\lambda = 2d \sin \theta$$

or 
$$\lambda = 2 \left( \frac{d}{n} \right) \sin \theta = 2d_{hkl} \sin \theta = 2 \left( \frac{a}{\sqrt{h^2 + k^2 + l^2}} \right) \sin \theta$$

Taking  $\sin \theta = 0.399$  corresponding to the (111) planes, we have

$$\lambda = \left( \frac{2(4.187 \times 10^{-8} \text{ cm})}{\sqrt{3}} \right) (0.399) = 1.929 \times 10^{-8} \text{ cm} = 192.9 \text{ pm}$$

## Heat Capacities of Monoatomic Crystals

In 1819 the French physicists Dulong and Petit found that, at constant pressure, the molar heat capacity at constant volume of most of the solid elements at room temperature was given by

$$C_V \approx 6 \text{ cal} \cdot \text{K}^{-1} \text{ mol}^{-1} \quad \dots(295)$$

In order to account for this value, two theories of heat capacities were developed—the first by Albert Einstein in 1907 and the second (which is a modification of the Einstein theory) by Peter Debye in 1912.

**1. The Einstein Theory of Heat Capacities.** Einstein made the following assumptions in constructing his theory of heat capacities of monoatomic crystals.

1. The atoms in a crystal lattice undergo small oscillations (vibrations) about their equilibrium configurations. In fact, an ideal crystal can be considered as a system of  $N$  non-interacting particles (*i.e.*, atoms).

2. Each atom vibrates independently of the others and has three independent vibrational degrees of freedom. Thus, the crystal may be treated as a system of  $3N$  independent and distinguishable harmonic oscillators.

3. There are no electronic, translational or rotational modes of motion in a monoatomic crystal.

Using assumptions 2 and 3, the molar vibrational partition function of the crystal can be written as

$$Q_{\text{vib}} = (q_{\text{vib}})^{3N} \quad (\text{From Eq. 254}) \quad \dots(296)$$

$$\text{or} \quad \ln Q_{\text{vib}} = 3N \ln q_{\text{vib}} = -\frac{3}{2} \frac{N \Theta_E}{T} - 3N \ln(1 - e^{-\Theta_E/T}) \quad \dots(297)$$

where  $\Theta_E$  is the characteristic Einstein temperature for vibration.  $\Theta_E = h\nu/k$  where  $\nu$  is the vibrational frequency of the oscillator. Thus, the internal energy of an ideal Einstein crystal is given by

$$U = kT^2 \left( \frac{\partial \ln Q_{\text{vib}}}{\partial T} \right)_{V,N} = \frac{3}{2} N h \nu + \frac{3Nk\Theta_E}{e^{\Theta_E/T} - 1} \quad \dots(298)$$

$$\text{or} \quad U - U_0 = 3RT \frac{\Theta_E/T}{e^{\Theta_E/T} - 1} \quad \dots(299)$$

where  $U_0$  is the zero-point energy ( $= \frac{1}{2} N h \nu = \frac{3}{2} R \Theta_E$ ). Hence, the molar heat capacity

$$C_V = 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} \quad \dots(300)$$

Experimentally it is found that at temperatures approaching zero,  $C_V$  approaches zero and in the limit of high temperatures,  $C_V$  approaches the Dulong-Petit value of  $3R$  (*i.e.*,  $\approx 6 \text{ cal K}^{-1} \text{ mol}^{-1}$ ). Einstein's theory predicts these limiting values of  $C_V$  quite successfully. Thus, as

$$T \rightarrow 0, \quad e^{\Theta_E/T} - 1 \approx e^{\Theta_E/T} \quad \text{so that} \quad \dots(301)$$

$$\text{Limit}_{T \rightarrow 0} C_V \approx 3R (\Theta_E/T)^2 e^{\Theta_E/T} \approx 0 \quad \dots(302)$$

Again, as  $T \rightarrow \infty$ ,  $e^{\Theta_E/T} \approx 1 + (\Theta_E/T)$  so that

$$\text{Limit}_{T \rightarrow \infty} C_V \approx 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(1 + \Theta_E/T - 1)^2} \approx 3R \quad \dots(303)$$



The above results are illustrated in Fig. 17 for a number of metallic and non-metallic crystals.

Einstein's theory, however, is not successful in predicting the  $C_V$  values in the lower and intermediate temperature ranges; the values predicted by it are lower than those actually observed.

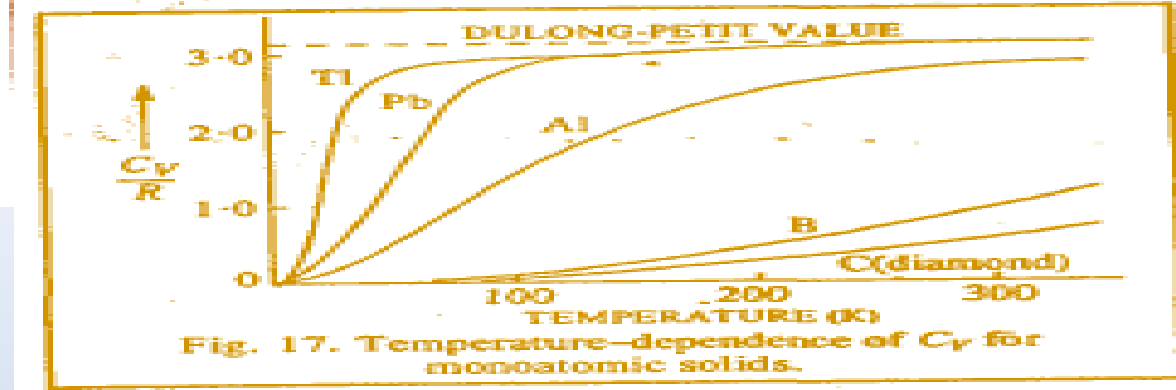


Fig. 17. Temperature-dependence of  $C_V$  for monoatomic solids.

## 2. Debye Theory of Heat Capacities.

Debye avoided the most serious assumption of the Einstein theory, namely, that the vibrations in a crystal lattice are independent. He recognized that the interatomic forces in a crystal are very strong and hence the atoms may not be treated as being

and hence the atoms may

independent. Debye assumed that the crystal behaves like a huge molecule wherein the motion of any one atom affects the motion of the neighbouring atoms. The oscillations or normal modes of vibration which characterize the motion of the crystal as a whole, have long wave lengths compared with the lattice spacings. The various vibrational modes are distinguished by their unique frequency. Debye further assumed that the properties of the crystal could be determined from a superposition of contributions due to each possible vibrational mode, rather than by summing the contributions made by individual atoms. Thus, the determination of the crystal properties depends upon determining the possible frequencies for the vibrational modes.

In order to determine the normal vibrational frequencies, Debye assumed them to be equivalent to the fundamental vibrational frequencies which are induced in an elastic solid of fixed boundaries. The oscillations represent acoustic standing waves in the elastic medium. We can also remark that each normal mode of vibration is equivalent to the motion of a hypothetical phonon (the phonon is to acoustics what the photon is to electromagnetic radiation).

The next task is to determine the frequency distribution of the normal modes. In a crystal containing  $N$  atoms, the number of degrees of freedom is  $3N$ . Subtracting the 3 translational degrees of freedom and the 3 rotational degrees of freedom, the number of vibrational degrees of freedom of the crystal is  $3N - 6$ . Since, however,  $N$  is very large, to an approximation, there are  $3N$  vibrational degrees of freedom. Therefore, Debye assumed the atomic crystal to have  $3N$  normal vibrations, each having a unique frequency.

distribution function is defined by

Assuming a continuous distribution of frequencies, the frequency distribution function is defined by

$$dN = f(\nu) d\nu \quad \dots(304)$$

where  $dN$  is the number of normal modes of vibration in the frequency range from  $\nu$  to  $\nu + d\nu$ . It is, thus, required that

$$\int_0^{\nu_D} f(\nu) d\nu = 3N \quad \dots(305)$$

where  $\nu_D$  (or  $\nu_{max}$ ) is the maximum possible oscillation frequency. Fig. 18 shows the plots of frequency distribution of normal modes in a crystal for both the Einstein and the Debye theories. The area under either curve between any two values of  $\nu$  is the number of vibrational quantum states in the crystal with frequency between the two values.

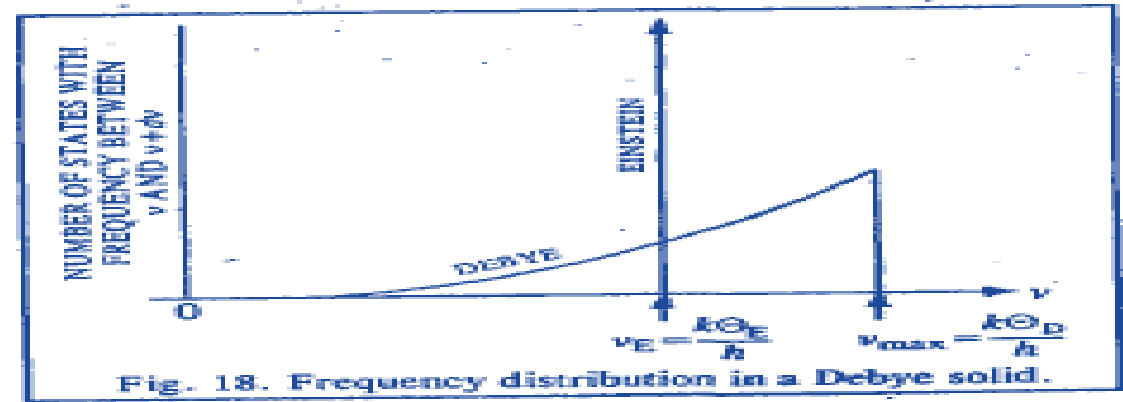


Fig. 18. Frequency distribution in a Debye solid.

The partition function for the system of the Debye oscillators is given by

$$Q = q(\nu_1)^{f(\nu_1)} q(\nu_2)^{f(\nu_2)} \dots q(\nu_D)^{f(\nu_D)} \quad \dots(306)$$

or 
$$\ln Q = \sum_{i=1}^{\nu_D} f(\nu_i) \ln q(\nu_i) \quad \dots(307)$$

As a result of the continuity, the summation may be replaced by integration so that

$$\ln Q = \int_0^{\nu_D} f(\nu) \ln q(\nu) d\nu \quad \dots(308)$$

where  $q(\nu)$  is the partition function of the oscillator defined by

$$q(\nu) = q_{vib} = \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} \quad \dots(309)$$

Debye used the Rayleigh-Jeans relation for the distribution function, viz.,

$$f(\nu) d\nu = c\nu^2 d\nu \quad \dots(310)$$

where the constant  $c$  is determined from the restriction that

$$\int_0^{\nu_D} f(\nu) d\nu = c \int_0^{\nu_D} \nu^2 d\nu = \frac{2}{3} c \nu_D^3 = 3N \quad \dots(311)$$

Thus, 
$$c = 9N/\nu_D^3 \quad \dots(312)$$

Hence, Eq. 310 is written as

$$f(\nu) d\nu = (9N/\nu_D^3) \nu^2 d\nu \quad \dots(313)$$

Thus, the partition function of the Debye crystal becomes

$$\ln Q = -\frac{9N}{\nu_D^3} \int_0^{\nu_D} \left[ \frac{h\nu}{2kT} + \ln(1 - e^{-h\nu/kT}) \right] \nu^2 d\nu \quad \dots(314)$$

which helps us to obtain

$$U = \frac{9NkT}{v_D^3} \int_0^{v_D} \left[ \frac{hv/kT}{e^{hv/kT} - 1} + \frac{hv}{2kT} \right] v^2 dv \quad \dots(315)$$

$$= \frac{9Nhv_D}{8} + \frac{9NkT}{v_D^3} \int_0^{v_D} \left[ \frac{hv/kT}{\exp(hv/kT) - 1} \right] v^2 dv$$

Putting  $\Theta = hv/k$  and  $\Theta_D = hv_D/k$ , where  $\Theta_D$  is called the characteristic Debye temperature of the crystal, we obtain

$$U = \frac{9R\Theta_D}{8} + 9RT \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \left[ \frac{(\Theta/T)^3}{e^{\Theta/T} - 1} \right] d\left(\frac{\Theta}{T}\right) \quad \dots(316)$$

The integral in Eq. 316 can be evaluated numerically. It is convenient to define the Debye function as

$$D(x) = \frac{3}{x^3} \int_0^x \frac{z^3 dz}{e^z - 1} \quad \dots(317)$$

where  $x = \Theta_D/T$  and  $z = \Theta/T$

(The Debye function is tabulated in standard books on Statistical Thermodynamics.) The energy of the crystal becomes

$$U = 9R\Theta_D/8 + 3RTD(\Theta_D/T) \quad \dots(318)$$

Differentiating  $D(\Theta_D/T)$  and then carrying out the integration by parts, we obtain

$$C_V = 3RD\left(\frac{\Theta_D}{T}\right) + 3RT \frac{\partial}{\partial T} \left[ D\left(\frac{\Theta_D}{T}\right) \right] = 3R \left[ 4D\left(\frac{\Theta_D}{T}\right) - \frac{3(\Theta_D/T)}{e^{\Theta_D/T} - 1} \right] \quad \dots(319)$$

At high temperatures,

$$e^{\Theta_D/T} - 1 \approx 1 + \Theta_D/T - 1 \approx \Theta_D/T \quad \dots(320)$$

and

$$\text{Limit}_{T \rightarrow \infty} D(\Theta_D/T) \approx 1 \quad \dots(321)$$

Hence,

$$\text{Limit}_{T \rightarrow \infty} C_V \approx 3R \quad \dots(322)$$

At low temperatures,

$$\text{Limit}_{T \rightarrow 0} D(\Theta_D/T) \approx \frac{\pi^4}{5} (T/\Theta_D)^3 \quad \dots(323)$$

so that

$$\text{Limit}_{T \rightarrow 0} C_V \approx 12/5 \pi^4 R (T/\Theta_D)^3 = 234R (T/\Theta_D)^3 \quad \dots(324)$$

The above results are illustrated in Fig. 19 in which  $C_V/R$  values are plotted against  $T/\Theta$ .

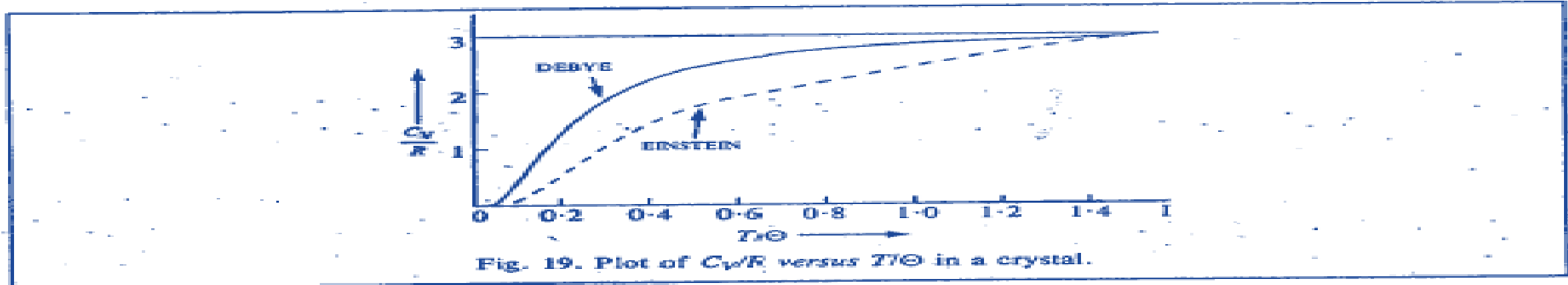


Fig. 19. Plot of  $C_V/R$  versus  $T/\Theta$  in a crystal.

The characteristic Debye temperatures for some solids are given in Table 8.

TABLE 8  
Debye Temperatures,  $\Theta_D$ , for Some Common Substances

Substance	$\Theta_D$ (K)	Substance	$\Theta_D$ (K)
Lead	88	Zinc	235
Mercury	97	Sodium chloride	281
Cadmium	168	Copper	315
Sodium	172	Aluminium	398
Potassium bromide	177	Iron	453
Silver	215	Diamond	1,860
Calcium	226		

Since all the quantities on the right side of Eq. 324 except the temperature are constant for a particular crystal, we can write this equation as

$$C_V = aT^3 \quad \dots(325)$$

where  $a = 12\pi^4 R / 5\Theta_D^3$ .

This is the famous Debye  $T$ -cubed law for the heat capacity of a crystal. It is in excellent agreement with experimental data at temperatures lower than  $\Theta_D$ , even for crystals which are more complex than those of the elements but the agreement is significantly poor at higher temperatures. The deficiencies of the Debye theory of heat capacity of crystals arise from the fact that it replaces the actual distribution of vibrational frequencies by an oversimplified distribution function which is obtained by ignoring the structure of the crystals.