CHAPTER II

THERMAL EXPANSION AND DEGREE TEMPERATURE OF SOLIDS

(1) Thermal expansion

Introduction

It is common knowledge that when a solid is heated, the atoms in the solid execute vibrations about their equilibrium positions, whose amplitude increases with temperature. If the vibrations are purely harmonic, the mean position of the atom would not alter with temperature and hence the solid would not expand. It is the anharmonicity of these atomic vibrations which causes a displacement of the mean position of the atoms and thus bring about an expansion of the crystal. When the mean position of rest of an atom gets displaced, the forces acting on the atom tending to restore it to its equilibrium position as it vibrates, also alter and cause a slight change in the frequency of the vibration. Some of these vibrations can be observed in the Raman effect and a change in their
frequencies can be studied by observing the temperature variation of the Raman spectrum.

The linear thermal expansion coefficient of a solid is defined as \( \alpha = \frac{1}{l_0} \frac{dl}{dT} \), where \( T \) denotes the temperature of the solid and \( l_0 \) its length at that temperature. Sometimes a mean coefficient of expansion \( \overline{\alpha} = \frac{1}{l_0} \frac{\Delta l}{\Delta T} \) over a temperature range \( T \) is also measured. Here \( l_0 \) is the length of the solid at some temperature \( T_0 \) (usually that of the room). The smaller the range of temperature \( T \), the more nearly does the mean coefficient \( \overline{\alpha} \) approach the true coefficient \( \alpha \). A similar definition holds for the volume expansion coefficient \( \beta \) of the solid.

To a first degree of approximation the volume expansion coefficient of a solid is equal to the sum of the linear expansion coefficients in three mutually orthogonal directions in the solid.

Thermal expansion coefficient \( \alpha \) is a second order symmetric tensor and hence has six components for a triclinic crystal. This number is reduced in the case of crystals of higher symmetry. In this thesis the discussion will be restricted, as far as possible, to crystals of cubic symmetry and hcp.

The general expression for the thermal expansion of a crystal is given by
\[ \beta = \left( \frac{X_0}{V_0} \right) \sum_j \frac{\gamma_j \left( \frac{\partial E_j}{\partial T} \right)_p}{\left[ 1 - K \frac{X_0}{V_0} \gamma_j E_j \right]^2} \] ... (2.1)

where \( X_0 \) = compressibility at absolute zero of temperature,
\( V_0 \) = molar volume, \( E_j \) = thermal energy of the solid per gram mole pertaining to the \( j \)th eigen frequency, \( \gamma_j = -\frac{\partial \log V_j}{\partial \log V} \),
the Grüneisen constant for the \( j \)th eigen frequency, and
\( K \) = a constant nearly equal to 2.

General observations:

A large number of measurements of the thermal expansion of various crystals has been made. The following are some of the results of general importance.

(a) The expansion coefficient of a solid is a function of temperature. It decreases with decreasing temperature and should approach zero value at the absolute zero of temperature.

(b) The expansion coefficient is large for crystals of low hardness (e.g. organic crystals) and small for crystals of high hardness (e.g. diamond).

(c) The anisotropy in the expansion of various crystals is itself a function of temperature. The anisotropy in the expansion is large for some crystals like sodium nitrate and small for others like haematite.
(d) From a study of the expansion of a number of halides using his pyknometer technique Klemm (1928) observed that:

(i) In ionic crystals, the expansion is smaller the greater the valency of the cation: e.g.

\[ \text{CsCl: } \beta = 136 \times 10^{-6}/\degree C; \]
\[ \text{ThCl}_4: \beta = 29 \times 10^{-6}/\degree C. \]

(ii) The expansion coefficient of the alkali halides is larger the greater the mass of the anion and the smaller the mass of the cation: e.g.

\[ \text{NaCl: } \beta = 120 \times 10^{-6}/\degree C; \]
\[ \text{KCl: } \beta = 108 \times 10^{-6}/\degree C; \]
\[ \text{KBr: } \beta = 114 \times 10^{-6}/\degree C. \]

(iii) The expansion coefficient increases with an increase in the coordination number: e.g.

\[ \text{CsCl: } \beta = 136 \times 10^{-6}/\degree C \quad (\text{C.N. } = 6); \]
\[ \text{RbCl: } \beta = 108 \times 10^{-6}/\degree C \quad (\text{C.N. } = 6). \]

(iv) The expansion coefficient of a monohalogenide of an element of a subgroup in the periodic table is smaller than that of an element of the same valency in the principal group containing the subgroup: e.g.

\[ \text{NaCl: } \beta = 120 \times 10^{-6}/\degree C; \]
\[ \text{AgCl: } \beta = 99 \times 10^{-6}/\degree C. \]
The converse is the case for dihalogenides:

CaF$_2$ : $\beta = 56 \times 10^{-6}/^\circ\text{C}$;

CdF$_2$ : $\beta = 80 \times 10^{-6}/^\circ\text{C}$.

For anisotropic crystals, the anisotropy of expansion shows a general correlation with the type of crystal structure (Wooster, 1949). In isothenic lattices, where the atoms or ions are linked to their neighbours with bonds of the same strength, the anisotropy of thermal expansion is small.

In layer structures like graphite the atoms in the layer are more tightly bound than atoms in the perpendicular direction. In such cases the expansion coefficient perpendicular to the layer is larger than that in the layer. In graphite parallel to the layer is $0.95 \times 10^{-6}$, while perpendicular to the layer it is $26.1 \times 10^{-6}$.

(e) The expansion coefficient of a crystal undergoes a detectable change when transformations in crystal structure take place. There are two types of transformations in crystal structure:
(i) heteromorphous transformation and 
(ii) homomorphous transformation.

A transformation of the first type is 
characterized by a sharp and reproducible 
temperature of transition, a latent heat of 
transformation and a sudden discontinuous 
change in the volume of the crystal at 
transformation. The crystal structure 
undergoes a radical change. Examples are 
the transformations of barium titanate at 
122°C and of CaCl from body-centred cubic 
lattice to the face-centred cubic lattice 
at about 470°C.

The second type of transformation takes 
place with a continuous change in volume 
over a small temperature range and exhibits 
the phenomenon of hysteresis. The specific 
heat exhibits an anomalous peak at the 
transition point and the expansion coefficient 
also behaves in a similar manner. A typical 
example of this type of transformation is 
ammonium chloride.

When a crystal undergoes a sudden change 
in its magnetic or electric behaviour as
the temperature is varied through the Curie point, a corresponding alteration in the expansion coefficient is observed. Typical examples are magnetite, Rochelle salt, potassium dihydrogen phosphate and potassium dihydrogen arsenate.

A number of investigators have attempted to find a relation between thermal expansion and melting point of crystals. Klein (1928) observed that for a number of ionic crystals $\alpha \cdot T_m$ is a constant having a value between 11 and $13 \times 10^{-2}$. This relation was inferred from Pictet's rule. Similar relations have been attempted by other workers (e.g. Straumanis, 1950; Van der Reyden, 1951).

The determination of the total expansion of a solid from the absolute zero to its melting point is of great interest as it would give a clue to the process underlying the phenomenon of melting. For a number of substances it is found that this expansion amounts to 6 to 8% of the original volume.

Theoretical investigations

Gruneisen (1926) was the first to provide a systematic theoretical investigation of the phenomenon of
thermal expansion of solids. He started with the equation of state

\[ PV + G(V) = \gamma E \]  \hspace{1cm} \ldots \ldots \ (2.2)

where

- \( P \) = pressure on the solid
- \( V \) = volume of the solid
- \( G(V) = \frac{d\Phi(V)}{dV} \); \( \Phi(V) \) = the potential energy per gram-atom of the solid when the atoms are at rest in their mean positions,
- \( E \) = the thermal energy of the solid,

and

\[ \gamma = \frac{\partial \log \Theta}{\partial \log V} = \frac{\partial \log \nu_m}{\partial \log V} \]

where \( \Theta \) = Debye temperature, and \( \nu_m \) = Debye maximum frequency. He derived two important results:

(i) the ratio

\[ \frac{\beta V}{\kappa C_v} = \gamma \]  \hspace{1cm} \ldots \ldots \ (2.3)

for any monatomic crystal is a constant of the order of magnitude 2 and it is independent of temperature for moderate temperatures. (Here \( \kappa \) = isothermal compressibility of the crystal and \( C_v \) its molar specific heat at constant volume),

and (ii) the volume coefficient of a solid is given by

\[ \beta = \frac{(dE/d\tau)_P}{\nu_0 \left( 1 - KE/Q_0 \right)^2} \]  \hspace{1cm} \ldots \ldots \ (2.4)
where \( Q_0 = (C_v/\beta) = \gamma/\gamma \chi_0 \) and \( K \) are constants; \( K \)
is theoretically expected to have a value between 2 and
3 and \( \chi_0 \) = adiabatic compressibility of the solid at 0\(^0\)K.

In the experimental verification of the Grüneisen's
equation for \( \beta \), the three constants \( \Theta_0 \), the Debye temperature
( to represent the specific heat ), \( Q_0 \) and \( K \) are chosen
arbitrarily to give the best fit with experimental values of
thermal expansion. If the theory is correct the value of \( \Theta_0 \)
so obtained should agree with the value used to explain the
specific heat of the solid. The value of \( Q_0 \) should agree
with the ratio of the specific heat to the volume expansion
coefficient and the value of \( K \) should be between 2 and 3.

The theory has been tested in the case of a number
of metals by Grüneisen (1926), Erfling (1939, 1942) and
Mix and McNair (1941a, 1941b, 1942). Glaring discrepancies
between theory and experiment have been observed in tungsten,
lithium, sodium, palladium and tantalum.

Grüneisen extended his equation to polyatomic
crystals ( e.g. fluor spar and iron pyrites ) and found that
their expansion could be well represented by his simple
equation. In these crystals the frequency spectrum should
consist, besides the Debye waves, of other branches which
are nearly monochromatic, the more so the greater the
difference between the masses of the atoms. An extension
of Grüneisen's theory to these cases presupposes an identical Grüneisen constant for all the different frequencies.

The prediction of Grüneisen that \( \gamma \) is a constant independent of temperature has been tested in a number of cases. Usually \( \gamma \) is evaluated from the equation \( \gamma = \frac{\beta V}{\chi c_v} \). But a proportionality between the volume expansion coefficient and specific heat holds on Grüneisen theory, only when the temperature is small compared to the Debye temperature. At high temperatures \( \beta \) increases faster than the specific heat because of the correction factor \( (1 - KE/q_o)^2 \) in the denominator and so the value of \( \gamma \) calculated from the simple equation given above should increase with temperature. Such an increase has been observed in a number of cases and it does not constitute a violation of Grüneisen law that \( \gamma \) should be constant as is believed by some workers. But there are certain cases like diamond, lithium fluoride etc. which have high Debye temperatures. In these crystals a definite drop in as the temperature is lowered has been observed which cannot be attributed to the effect of the correction factor mentioned above. Bijl and Pullan (1954, 1955) have observed such a temperature variation in the Grüneisen constant in the monatomic metals like copper and aluminium. This leads unmistakably to the conclusion that the Grüneisen's theory of thermal expansion is unable to predict the true behaviour of the solid precisely because of the simplicity of the assumptions on which it rests.
The temperature variation of the Grüneisen constant is obviously bound up with the presence of optical branches in the frequency spectrum of a polyatomic solid and Grüneisen's simple assumption of a constant value of \( \gamma \) for all these frequencies is not tenable. This is clearly shown by the temperature variation of the Raman effect in crystals. Many of the normal modes of vibration of the crystal lattice appear in its Raman spectrum. When the crystal is heated, the frequencies of these modes change because of the increase in volume of the crystal. If we define \( \chi_\nu = -\frac{1}{\gamma} \frac{d\nu}{dT} \), the coefficient of the change of frequency with temperature, then the Grüneisen's constant for that particular frequency is given by \( \gamma_\nu = \chi_\nu / \beta \).

There are certain crystals which exhibit negative volume expansion coefficient (e.g. \( \alpha \)-silver iodide and zinc sulphide below \(-195^\circ C\)). Such crystals possess a negative value of the Grüneisen constant in sharp contradiction to the theoretical requirement of Grüneisen that \( \gamma \) should be positive. Yet these are isolated cases and many more complex factors yet not understood might cause this type of anomaly.

Fletcher (1957) has examined the Grüneisen theory more critically. He has shown that the two well-known formulas of Grüneisen (eqs. 2.3 and 2.4) depend essentially on three assumptions: (a) that \( \phi \) (potential energy of
volume \( V \) of a solid is a function of \( V \) only, independent of \( T \), so that \( G \) is also, (b) that \( (\frac{\partial V}{\partial T})_V = 0 \) and (c) that the atoms are at rest in their equilibrium positions at \( T = 0 \). Using these same assumptions he has derived a direct relation between volume and temperature based as closely as possible on the theories of Debye and Grüneisen. Application to KCl shows that although the experimental observations on the thermal expansion of KCl may be explicable without postulating the occurrence of lattice defects at high temperatures, the Debye-Grüneisen theory does not give a good general agreement with experiment.

Since the thermal expansion \( \beta \) is intimately connected with \( \gamma \), several workers have concentrated on investigating the variation of \( \gamma \) with temperature. Born (1923) was the first to show that the Grüneisen constant \( \gamma \) did in fact depend on the temperature of the crystal. The value \( \gamma_0 \) (at \( 0^\circ K \)) was about 30% smaller than \( \gamma_\infty \).

One of the most systematic investigations on the variation of \( \gamma \) with temperature is carried out by Blackmann (1957). It is well-known that the standard method of calculating the volume expansion coefficient depends on the thermodynamical relation

\[
\frac{\beta}{\chi} = - \frac{\partial^2 F}{\partial V \partial T} \quad \cdots \quad \cdots \ (2.5)
\]
where $\chi$ is the isothermal compressibility, $F$ the free energy, $V$ the volume and $T$ the absolute temperature.

Assuming that the temperature dependent part of free energy of the crystal is entirely vibrational in character, the free energy can be written as

$$F = U_0 + \frac{1}{\nu} kT \log \left\{ 1 - \exp\left( -\frac{\hbar \nu}{kT} \right) \right\}$$

(2.6)

Here $U_0$ is the sum of the internal energy and the zero point energy of the crystal. The summation is taken over all the normal vibrations of the crystal. From eq. (2.5) it follows that

$$\frac{V_B}{\chi} = \sum_{\nu} \gamma_{\nu} E \left( \frac{\hbar \nu}{kT} \right)$$

(2.7)

where $B$ is the Einstein function for the heat capacity of a linear oscillator and

$$\gamma_{\nu} = -\frac{\nu}{\nu} \left( \frac{\partial \nu}{\partial \nu} \right)_T$$

(2.8)

This formula can be linked with the usual theoretical definition of Grüneisen constant $\gamma$ by the relation

$$\gamma = \frac{V_B}{\chi} = \sum_{\nu} \gamma_{\nu} E \left( \frac{\hbar \nu}{kT} \right)$$

(2.9)
The quantity $\gamma$ so defined is a parameter which in principle will vary with the temperature.

The Grüneisen relation in its strict sense, namely that $\gamma$ is independent of temperature, will follow if all $\gamma_\nu$'s are independent of frequency. This would not be expected in a lattice. In fact Blackman has shown that $\gamma_\nu$ varies over a very large range (from -ve to +ve values) even if special vibrations are considered.

Since in many cases experiments do not show any marked variation of $\gamma$ with temperature, a much less stringent condition should exist. Such a condition can be seen if one writes eq. (2.9) in the form

$$
\gamma = \frac{\int Y_\nu f(\nu) e^{(\hbar\nu/kT)} d\nu}{\int f(\nu) e^{(\hbar\nu/kT)} d\nu} \quad \cdots \cdots (2.10)
$$

Here $f(\nu)$ is the distribution function for the frequencies. A new quantity $Y_{\nu}$ has been introduced. This is defined by considering two contours (in reciprocal space), the frequencies associated with these being $\nu$ and $\nu + \Delta \nu$ respectively. An arithmetic average value of $Y_{\nu}$ is found for all vibrations lying between $\nu$ and $\nu + \Delta \nu$. This value is termed $\overline{Y}_{\nu}$. It then follows from eq. (2.10) that if

$$
\overline{Y}_{\nu} = \text{constant} \quad \cdots \cdots (2.11)
$$

then $\gamma = \overline{Y}_{\nu}$ and this is then independent of temperature in
the theory used. This condition should be the theoretical requirement for the Grüneisen rule.

Using this concept of $\bar{\gamma}_v$, Blackman has derived the values of $\gamma_0$ and $\gamma_\infty$ for low and high temperatures. The values are

- $\gamma_0 = 1.15$ (n=7) - nearest neighbour interaction
- $\gamma_0 = 1.46$ (n=8) - when all neighbours are taken into account
- $\gamma_\infty = 1.50$ (n=7)
- $\gamma_\infty = 1.76$ (n=8)

In a later paper Blackmann (1959) has investigated expansion coefficient of two dimensional ionic lattices. A survey has been made of the Grüneisen constants $\gamma_v$ of a representative set of vibrations in reciprocal space. It is shown that the ionic lattices are characterised by a large spread in $\gamma_v$ values, this being in the main due to the lower of the frequency branches.

The factors responsible for the negative volume expansion coefficients have also been analysed by Blackmann (1958). It is shown that the Grüneisen constant derived from elastic properties of a solid can be negative in certain cases. In the zinc blende structure a negative value is obtained over the whole range of parameters examined.
In the rocksalt structure, negative values are obtained when the shear modulus of the lattice is sufficiently small. In all these cases, the volume expansion coefficient of the cubic lattice would be negative at sufficiently low temperatures. It is also conceivable that a negative volume expansion can result if the free energy contains (in addition to the vibrational terms) configurational terms, and an electronic component has been suggested as responsible for negative values in uranium and plutonium.

It is shown theoretically that cubic lattices can have a negative volume expansion coefficient at low temperature when a normal type of potential interaction is used. This should arise from the fact that in certain types of transverse waves the quantity $\gamma_L = -d\log V / d\log V$ can be negative. This has been noted by Dayal (1944) and Barron (1955).

The starting point of the investigation was that for alkali halides of the rocksalt type, the quantity $d\mu/d\nu$ is positive (Blackmann, 1957) where $\mu$ is the shear modulus in Voigt's notation. Since at sufficiently low temperatures, the heat capacity and the energy are controlled by the $\mu$ value, if this is sufficiently small compared with the volume modulus (Blackmann, 1935), it seemed likely that for a suitable model, a negative volume expansion would be found. It is shown in the paper that this is indeed the case. On the other hand, such examples are rather special in that they do
not fall in the experimentally observed region of the alkali halides.

Arenstein (1964) has examined the problem of instability in crystals and its relation to thermal expansion coefficients and has concluded that those crystals which approach an instability in some of their normal mode frequencies will either undergo negative thermal expansion or anomalous positive expansion.

The suggestion that the instability or approach to instability may be the cause for negative expansion or anomalous positive expansion in real crystals is interesting since the explanations for the melting of solids (Born, 1939; Thompson, 1952) and the ferroelectric transition (Cochran, 1960) have been sought in the approach to instability of the acoustic modes in the former situation and the transverse optical modes in the latter.

A simplified version of the bond charge model to calculate the adiabatic potential for lattice vibration of Si is given by Ishida (1975). The Grüneisen constant for the transverse-acoustic mode is shown to be positive at small wave numbers and negative at large wave numbers. This anomalous behaviour comes from the volume dependence of the bond charge and is shown to be the origin of the negative thermal expansion.
Barron et al. (1957) have analysed the heat capacities of a number of alkali halides in terms of the vibrational frequency distribution, assuming quasi-harmonic approximation. In this approximation, the lattice vibrations are taken to be harmonic, but with frequencies varying with volume. As a model this is inconsistent since in a perfectly harmonic lattice the frequencies are independent of volume. But as an approximation it should give a good account of some equilibrium properties (Leibfried and Ludwig, 1961) including the thermal expansion up to temperatures not too near the melting point. The thermal expansion thus gives information about how the frequencies of the normal modes change with volume. Such information is used to reduce experimental heat capacities to a constant volume $V_0$.

In a later paper Barron and Leadbetter (1964) have analysed in detail the thermal expansion data of alkali halides by a somewhat similar procedure adopted in the above paper. The heat capacity gives us moments of the frequency distribution, $\bar{V}_n$, and also coefficients in the low frequency expansion. The thermal expansion should tell how these quantities vary with volume. A dimensionless parameter $\gamma(n)$ is introduced and is defined as

$$\gamma(n) = -\frac{1}{n} \frac{d \log \bar{V}_n}{d \log V}$$

\begin{equation} \quad \cdots \cdots \quad (2.12) \end{equation}
and the volume dependence of the moments is investigated in this paper. The function $\gamma(n)$ is important because it enables us to determine the volume dependence of certain properties of the crystal which depend in a simple and direct manner on individual moments of the frequency distribution. In particular, it is well known that the heat capacity at moderately high temperatures depends principally on $\frac{1}{T^2}$ and also that the limiting Debye-Waller factors for X-rays at low and high temperatures are simply related to $\frac{1}{T^3}$ and $\frac{1}{T^2}$ respectively (Barron, Leadbetter, Morrison and Salter, 1963). If, therefore, an appropriate $\gamma(n)$ can be obtained, it is then a simple matter to determine the change in heat capacity or in the Debye-Waller factors due specifically to the thermal expansion of the crystal at high temperatures.

The only attempt to work out in detail the variation of thermal expansion of the hop metals Mg, Zn and Be has been made by Srinivasan and Rao (1972). They have calculated the generalized Gruneisen parameters $\gamma'' = - \frac{\partial \log \omega}{\partial T''}$ and $\gamma' = - \frac{\partial \log \omega}{\partial T'}$ for various normal mode frequencies using the model described in their earlier paper (1971). The temperature dependence of the effective Gruneisen functions $\overline{\gamma}(T)$ and $\overline{\gamma}(T)$ have been calculated. While the shapes of the theoretically calculated lattice Gruneisen functions $\overline{\gamma}(T)$ and $\overline{\gamma}(T)$ curves are similar to the experimentally observed variation of the total Gruneisen functions, the theoretical values are much higher than the experimental values.
There are several methods of determining the temperature dependence of phonon frequencies, the most important of which is based on the coherent inelastic scattering of slow neutrons (e.g. Larson et al, 1960; Brockhouse et al, 1960; Brockhouse, 1961; Brockhouse and Dasannachary, 1963) which gives the temperature dependence of individual frequencies. Similar information can be derived from Raman spectroscopy of solids, but there are only a few frequencies, the Raman-active ones, accessible to this method. A method based on the temperature dependence of the intensity of X-ray diffraction spots (Paskin, 1957; Chipman, 1960) employing the Debye-Waller theory for evaluation provides an average over all frequencies. To date, the neutron spectroscopy method seems to be the most powerful tool for investigating the temperature behaviour of lattice vibrations although it is as yet applied to only a few substances.

Useful information on the temperature dependence of phonon frequencies can also be drawn from the measurement of thermal expansion coefficient $\beta$ of a material (Schaur, 1964). $\beta$ can be obtained from the relation

$$\beta = -\chi \frac{\partial^2 F}{\partial V \partial T} \quad \cdots \quad (2.13)$$
If the free energy $F$ is given by eq. (2.6), we can obtain

\[
\frac{\beta}{\chi_T} = \frac{1}{V} \sum_i \gamma_i \xi_i = \frac{1}{V} \sum_i \frac{\xi_i \gamma_i \xi_i}{\xi_i} \leq \gamma_i \leq c_i \quad \cdots \quad (2.14)
\]

where $C_i$ is the specific heat of a linear harmonic oscillator of frequency $\nu_i$ (Einstein function). Comparing this with the usual Grüneisen relation

\[
\beta = \gamma_i \frac{\chi_T}{V} \quad \cdots \quad (2.15)
\]

it is possible to define $\gamma$ as

\[
\gamma = \frac{\sum_i \gamma_i \xi_i}{\sum_i \xi_i} \quad \cdots \quad (2.16)
\]

Now

\[
\gamma_i = - \frac{d \log \nu_i}{d \log V}
\]

\[
= - \frac{V}{\nu_i} \frac{d \nu_i}{d V}
\]

\[
\frac{1}{\nu_i} \frac{d \nu_i}{d \tau} = \gamma_i \frac{1}{V} \frac{d V}{d \tau}
\]

\[
= - \gamma_i \beta \quad \cdots \quad (2.17)
\]

Multiplying eq. (2.17) by $C_i$ and summing gives

\[
\sum_i \xi_i \frac{1}{\nu_i} \frac{d \nu_i}{d \tau} = - \beta \sum_i \gamma_i \xi_i C_i
\]
\[ \sum c_i \frac{1}{\nu_i} \frac{d\nu_i}{dT} \leq \sum c_i = -\gamma \beta \quad \ldots \quad (2.18) \]

Since no model is employed to derive this equation, it is applicable to any frequency spectrum of lattice vibrations.

Thus the negative product of the Grüneisen parameter and the volume thermal expansion coefficient gives the mean temperature coefficient of the lattice vibration frequencies.

From a simple view one expects that with rising temperature, the interatomic bonding forces are weakening and the frequencies should therefore become smaller. From eq. (2.18) it follows that \( \gamma \) and \( \beta \) always have the same sign, the mean temperature coefficient of the frequencies is always negative so that on the average the frequencies always decrease with rising temperature. This is apparently accomplished by the overwhelming influence of the longitudinal modes in the case of positive thermal expansion and the determining role of the transverse modes in the case of negative thermal expansion.

\( \beta \) and \( \gamma \) are average properties of a solid resulting from summing over all the individual modes of the lattice vibrations. It is, therefore, not possible to get from \( \beta \) and \( \gamma \) quantitative information on single modes, but it is possible to get information on average or means as in
The type of information which is available differs in different temperature regions. For example if \( T \sim \Theta \) (\( \Theta = \) Debye temperature) the solid behaves classically and we have \( C_i = K \). From eq. (2.16) it follows for the high temperature limit of \( \gamma \) that

\[
\gamma_{\infty} = \frac{1}{3N} \sum_{i=1}^{3N} \gamma_i \quad \cdots \quad (2.19)
\]

In other words \( \gamma_{\infty} \) is simply the arithmetic mean of the individual \( \gamma_i \)'s. From eq. (2.17) and (2.19) we get

\[
\frac{1}{3N} \sum_{i=1}^{3N} \frac{d\nu_i}{dT} = -\gamma_{\infty} \beta \quad \cdots \quad (2.20)
\]

that is \( -\gamma_{\infty} \beta \) gives the arithmetic mean of all frequency temperature coefficients. Integration of (2.20) yields

\[
\frac{1}{3N} \sum_{i=1}^{3N} \int_{\nu_{i0}}^{\nu_i} \frac{d\nu_i}{\nu_i} = -\gamma_{\infty} \int_{T_0}^{T} \beta \, dT \quad \cdots \quad (2.21)
\]

or

\[
\frac{1}{3N} \sum_{i=1}^{3N} \log \frac{\nu_i}{\nu_{i0}} = \gamma_{\infty} \int_{T_0}^{T} \beta \, dT \quad \cdots \quad (2.22)
\]
where \( \nu_i \) is the frequency of the \( i \)-th mode at temperature \( T \) and \( \nu_{i0} \) is this frequency at a certain reference temperature \( T_0 \). This can be written

\[
\log \left( \prod_i \frac{\nu_i}{\nu_{i0}} \right)^{V_3N} = -\gamma_\infty \int_{T_0}^T \beta \, dT 
\]

or

\[
\left( \prod_i \frac{\nu_i}{\nu_{i0}} \right)^{V_3N} = e^{\gamma_\infty \int_{T_0}^T \beta \, dT} \quad \ldots \quad (2.23)
\]

As the exponential is small,

\[
\left( \prod_i \frac{\nu_i}{\nu_{i0}} \right)^{V_3N} = 1 - \gamma_\infty \int_{T_0}^T \beta \, dT \quad \ldots \quad (2.25)
\]

Thus the integrated form yields the geometric mean of the frequency ratios \( \nu_i / \nu_{i0} \).

The explicit anharmonic contributions to the entropy and specific heat are directly related to terms in the crystal potential energy of higher than second order in atomic displacements and the general treatment of crystal anharmonicity (Leibfried and Ludwig, 1961; Leibfried, 1965) has shown that at high temperature \( (T>\Theta) \) for a crystal containing
\[ \frac{\Delta S^{\text{anh}}}{3 N K} (T, V) = A + B T^2 + \cdots \]

\[ \frac{\Delta C^{\text{anh}}}{3 N K} (T, V) = A T + 2 B T^2 + \cdots \]

For metals the contribution to the thermodynamic properties from the conduction electrons must be considered, in addition to that from the lattice vibrations. The additional contributions to \( S \) and \( C \) are of the form

\[ S^d = C^d = \sigma^d (T, V) T \]

\( \sigma \) is expected to be a function of temperature due to electron phonon interaction (Buckingham and Schafroth 1954, Ashcroft and Wilkins 1965). As \( T \) approaches 0°K, \( \sigma \) should reach a constant value \( \sigma_0 \), which is easily determined from heat capacity measurements and its value should again become constant, at the free electron value \( \sigma_\infty \), at high temperatures.

Leadbetter (1968) has determined the constant \( A \) for Lead and Aluminium using the experimental value of \( \sigma_0 \) at all temperatures and the free electron value for \( \sigma_\infty \).
For \( \text{Pb} \)

(i) Using \( \sigma_\infty (v) \) to compute \( C^e_1 \)

\[
A(v_0) = (-1.0 \pm 0.3) \times 10^{-4} \text{ deg K}^{-1}
\]

\[
B(v_0) \sim 6 \times 10^{-8} \text{ deg K}^{-2}
\]

(ii) Using \( \sigma_\infty (v) \) to compute \( C^e_1 \)

\[
A(v_0) = (-1.6 \pm 0.4) \times 10^{-4} \text{ deg K}^{-1}
\]

\[
B(v_0) \sim 8 \times 10^{-8} \text{ deg K}^{-2}
\]

For \( \text{Al} \)

Using \( \sigma_\infty \)

\[
A(v_0) = (-1.9 \pm 0.9) \times 10^{-5} \text{ deg K}^{-1}
\]

and using \( \sigma_0 \)

\[
A(v_0) = (-3.5 \pm 1.5) \times 10^{-5} \text{ deg K}^{-1}
\]

Although no theoretical calculations of anharmonic effects have been performed on realistic models of \( \text{Pb} \) or \( \text{Al} \), several calculations have been done for simple models of close-packed crystals (Leibfried and Ludwig 1961, Maradudin et al 1961, Wallace 1965). In all cases \( A \) was found to be negative in agreement with experiment, showing that in close-packed crystals the symmetric quartic contribution is more important than asymmetric cubic form in determining the explicit anharmonic contributions. Maradudin et al found the value of \( A = -6 \times 10^{-5} \text{ deg K}^{-1} \)
for Pb. Wallace found the value \( A = -4 \times 10^{-5} \) and \( -2.5 \times 10^{-5} \) for Pb and Al respectively. The agreement with experiment is good in view of the crudity of the models and the approximate nature of the calculations.

A theory of melting based on lattice instability is proposed by Iida (1969). It rests on the supposition that the energy of thermal vibration cannot exceed a critical value, because of anharmonicity, and the lattice may be unstable above the temperature corresponding to this critical energy. The effect of anharmonicity arises from the effective increase in interatomic distances due to the lattice vibrations. This increase is termed "vibrational elongation". The critical temperature of instability is expressed in terms of atomic volume, elastic constants and the Grüneisen parameter under the assumption of a linear dispersion relation and is shown to be in fairly good agreement with the observed melting point. The theory predicts thermal expansion and elastic properties at high temperature and claims to explain the rapid increase of thermal expansion at high temperature without postulating the contribution of lattice defects. A relation between \( C_g \), thermal expansion and the vibrational elongation \( Q \) is derived. Here \( C_g \) is the elastic constant corresponding to the sound velocity \( c_s \) for mode \( S \frac{C_g}{p} \) . Graphs are drawn between \( C_{44} \) versus \( T/T_m (T_m = \text{melting point}) \) and between \( \frac{1}{2} (C_{11} - C_{12}) \) versus \( T/T_m \) and compared with the experimental curve. The agreement is rather poor.
The most widely used approximate frequency spectrum is the parabolic distribution first introduced by Debye (1912) and since known by his name. The frequency spectrum is usually described in terms of the characteristic or Debye temperature which is related to the maximum vibrational frequency of the lattice $\nu_m$ by $\Theta = h \nu_m / k$.

In the Debye approximation it is assumed that the crystal lattice can be treated as an isotropic elastic continuum. It follows that the frequency distribution function is

$$N(\nu)d\nu = 4\pi \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) V \nu^2 d\nu, \quad \nu \leq \nu_m$$

$$= 0, \quad \nu > \nu_m$$

(2.26)

where $N(\nu)$ is the number of frequencies between $\nu$ and $\nu + d\nu$, $c_l$ and $c_t$ are the velocities of the longitudinal and transverse elastic waves respectively and $V$ is the volume of the crystal. It was assumed that $c_l$ and $c_t$ are invariant with respect to direction in the crystal and wavelength of the elastic waves, i.e. there is no dispersion. The atomic structure of the crystal was then taken into account in the theory of specific heats by setting the same lower limit to the wavelength of the longitudinal and transverse waves. Consequently there will be different upper
limits to the frequency distributions of the transverse and longitudinal waves and an average maximum frequency $\nu_m$ must be chosen. This must be such that the number of normal vibrations is $3N$, where $N$ is the number of atoms in the crystal. Thus

$$\int_0^{\nu_m} a \nu^2 d\nu = 3N \quad \text{or} \quad \nu_m = \left(\frac{9N}{a}\right)^{\frac{1}{3}}$$

(2.27)

where $a = 4\pi \nu_c (c_1^{-3} + 2c_1^{-3})$

In order to test the Debye model, the specific heat of a given solid is measured at different temperatures by calorimetric methods. These values are substituted in the proper equation (eq. 2.30, page 44) and $\Theta$'s computed therefrom. If Debye's theory is correct, the $\Theta$ values for different temperatures must be the same. In practice $\Theta$ is found to vary with temperature and hence Debye model must be modified.

It may be pointed out that a plot of $C_V$ versus $T$ does not provide a suitable test for a given model. A more sensitive analysis is based on a plot of $\Theta$ versus $T$, in which $\Theta$ is computed separately for each experimental point.

Innumerable attempts have been made to work out the lattice dynamics of crystals employing various models and using various mathematical techniques. In this short thesis only a few of them which are important will be reviewed.
The theoretical techniques used to derive the dynamical properties of hop metals are practically the same as those used for cubic lattices. Hence some basic techniques used for cubic lattices will be described here just for continuity of discussion.

The first commendable attempt to explain the thermal properties of cubic metals was made by de Launay (1953, 1954, 1956, 1957). In this model the point ion lattice is superimposed on free electron gas which is supposed to behave like an ordinary gas responding in phase to the longitudinal part of the lattice waves and leaving the transverse part unaffected. Every crystal wave has thus been split up into longitudinal and transverse parts and the electronic effects is operated on the longitudinal part only. While this model is able to give a fair description of some thermal properties of cubic metals, such as lattice heat capacities and $\Theta$-$T$ curves, it fails to reproduce the experimental dispersion curves along the principal symmetry directions. This failure is probably due to the fact that the interionic interactions are terminated at the second neighbours only.

Bhatia (1955) utilized the Thomas-Fermi theory to calculate the screening of ionic charge due to the presence of electron gas and has been able to modify the longitudinal lattice waves. It is assumed in this model that the forces on an ion may be regarded as arising from (a) a central
interaction between the ions which is significant between the nearest neighbours only and (b) from certain energies which depend on the atomic volume only and which are due to the presence of the free electrons and their interactions with ions. The frequency spectrum, specific heat and Debye $\Theta$ of sodium are calculated. The agreement with experiment cannot be said to be good.

Sharma and Joshi (1963, 1963a, 1964, 1964a, 1965) take dispersion of lattice waves into account in a simple way. They assume that the dispersion is of the same form as given by the Born-von Karman theory for a linear chain of equally spaced mass points, each point carrying the same mass and with interactions confined between nearest neighbours. The authors attribute an isothermal compressibility to electron gas and average its response to ionic motion by partitioning the entire lattice into Wigner and Seitz's sphere. In this way they could also modify the longitudinal lattice waves. The model has been applied to copper, lithium and sodium. Frequency spectra and Debye temperatures have been calculated and compared with experimental results. The agreement is fair.

Krebs (1965) has given a 3-constant model for metals. The treatment takes complete account of the symmetry requirements of the lattice. The influence of the conduction electrons is considered through the screening of the long
range coulomb interactions between ions. The model includes an unklapp process and therefore modifies both the transverse as well as longitudinal waves. It is applied to the alkali metals Li, Na and K. The agreement with experiment is good for sodium but poor for the other two metals.

**hop metals**

Neutron spectroscopic determination of dispersion relations of a large number of hop metals in recent years has stimulated theoretical studies on this system resulting in a number of models using varying number of parameters. The lower symmetry of the hop system makes exact analysis rather difficult and theoretical calculations have therefore been generally based on various force constant models.

The various models used to analyse and interpret the experimental data are the tensor force models (Segbie and Born, 1946; Segbie, 1947; Pope, 1949), the central force models with and without electron gas (Slutsky and Garland, 1957; Gupta and Dayal, 1965) and the non-central force models (Metzbower, 1967, 1968, 1969). Many authors have used pseudopotential formalism also to investigate this problem.

The central force model was first used by Slutsky and Garland (1957). They considered central Hooka's law forces between an atom and three of its neighbours. This is actually a restricted form of the axially-symmetric (AS)
model in which the tangent force constants are set equal to zero without giving any reason. This and other restrictions introduced by them are so severe that one cannot obtain a fit to the dispersion curves of Be, Mg or Zn. The weakness in the use of the central forces is that they lead to the Cauchy relation which is not satisfied by the experimental data on the elastic constants of hexagonal metals. According to the relevant Cauchy relation in the case of hexagonal metals $C_{13}$ and $Q_{44}$ are equal. To avoid this inconsistency between the deduction from theory and experimental data, Slutsky and Garland adopted the same procedure as was used by Leighton (1948) in the case of cubic metals.

Collins (1962) obtained dispersion relations of Mg from the inelastic scattering of neutrons. He used the Slutsky and Garland (SG) and Regbie and Born (BB) models to fit the experimental data, using the BB model and general forces for first and second nearest neighbour interactions and SG model and central forces for treating interactions with more distant neighbours.

Borgonovi et al (1963) analysed their neutron inelastic scattering data on Zn by fitting these data to formulations of the Born-von Karman dynamical theory involving generalized forces between pairs of atoms. Forces have been extended to fourth nearest neighbours. The agreement can only be said to be fair. This is probably because they did
not impose the elastic equations as constraints in the determinations of the atomic force constants. They used the dynamical matrix derived by Collins (1962) for Mg and Be without taking note that the fourth-neighbour coordinates in these elements are the sixth-neighbour coordinates for Zn. This was corrected by Gupta and Dayal (1966) in their six-neighbour tensor force model for Zn.

Young and Koppel (1964) obtained lattice vibrational spectra of Be, Mg and Zn using the root sampling method. The force constants used in the calculations were those determined from measurements of the dispersion relations by slow neutron scattering techniques. They calculated the frequency distribution curves for both the models used by Collins (1962) and found that the models gave only a qualitative description of the experimental results especially in the long-wavelength region.

The weakness of the SG model was corrected by Gupta and Dayal (1965) who incorporated the effect of free electrons on the lattice vibrations. The contribution of the free electrons was calculated on the lines followed by Sharma and Joshi (1963) in the case of cubic metals. The major shortcoming of the electron gas models is that they do not satisfy the symmetry requirements in the sense that the frequencies given by them are not periodic in the reciprocal space.
Singh and Singh (1972) modified the electron gas model developed by Gupta and Dayal (1965) for hop metals by replacing the electronic contribution term by that given in the model of Bhatia (1955) without changing the ionic contributions. Dispersion relations for Mg have been calculated and good agreement with experimental results is claimed.

The phonon dispersion relations and lattice specific heats for Be and Mg have been calculated by Rajput and Kushwaha (1973) using Krebs' (1965) model, originally developed for bcc structure and extended to hop structure. The authors claim that their calculations explicitly obey the frequency periodicity condition and that they involve a much smaller number of force constants than used by other workers. The agreement with experimental results is claimed to be reasonably good.

Upadhyaya and Sinha (1975) have considered ion-ion interactions as a five-neighbour central pair potential and electron-ion interaction in a modified form of Bhatia's (1955) model. Complete account of the equilibrium of the hop lattice including the effect of electron pressure has been considered. Phonon dispersion curves for four hop metals, Be, Mg, Y and Ho have been computed for two symmetry directions. The agreement with neutron data can be said to be fair.
Sinha and Upadhyaya (1977) studied the phonon dispersion relations for Zn and Cd on the basis of a model which considers short range pairwise forces effective up to sixth nearest neighbours and long range forces on the lines of Krebs' work. The authors consider complete equilibrium of the ionic lattice in a medium of uniform electron gas.

Mishra and Kushwaha (1978) have used the modified Cheveau model (1968) to study the dynamical properties of Cd. Cheveau's model not only satisfies the requirements of translational invariance but is also in equilibrium without recourse to the external force. The authors have introduced three body forces phenomenologically by considering terms containing the first derivative of the potential energy in Taylor's expansion. The same considerations have been used by Kushwaha and Kushwaha (1978) and Mishra and Kushwaha (1978) to study Be and Mg.

Kumar and Upadhyaya (1979) have used the Heine-Abarenskov (HA) (1961) model potential in the local approximation to obtain dispersion relations for Zn. The non-locality of the HA potential is considered and no adjustable parameter is used. Agreement with experiment is poor but the work emphasises the importance of non-local effects in governing the dynamical behaviour of Zn.

In recent years pseudopotential methods have become very popular as a means for calculating phonon spectra,
elastic constants, band structures and other atomic and electronic properties of simple metals. A typical attempt in this direction is made by Floyd and Kleinman (1970) who computed the phonon spectrum of Mg with a local model pseudopotential containing two adjustable parameters. These authors use the Kleinman-Langreth dielectric function and have been able to obtain a close fit with the experimental data by selecting the parameters in their model pseudopotential.

King and Cutler (1971) have used Harrison's (1962) a priori theory to construct a first principles nonlocal pseudopotential for Mg. A response function for the exchange interaction among conduction electrons, which uses the Kohn-Sham approximation for the long wavelength limit is employed in the calculation of the energy-wave-number characteristic. The phonon spectra have been obtained for the (0001), (0110) and (1120) directions. Agreement with experiment is fair.

Phonon dispersion relations for Zn have been obtained by Panitz, Cutler and King (1972) for the first time with the fully nonlocal form of Harrison's generalised pseudopotential for d-band metals using a Lindgren-type approximation for the conduction-band/core electron exchange. Comparison with experiment shows fair agreement.

In many of the theories of metals, attempts are made to fit the measured dispersion curves with empirical parameters.
which in most cases lack clear physical meaning. In order to understand the lattice dynamics of metals one must know the entire interaction present in metals. While the ion-ion interaction is quite simple and can be represented by a two-body potential, the electron-ion interaction is quite complicated and, eventually, is a many-body problem. This therefore puts considerable difficulties in the development of fundamental theories of metals. Still however commendable efforts have been made to study the behaviour of phonons in metals from first principles. Brief reviews of the earlier attempts to develop these fundamental theories are given by Cochran (1963, 1965) and Sjolander (1965). The principal workers in this direction are Toya (1958), Vosko, Taylor and Keech (1965), Harrison (1966), Sinha (1969), Hanke (1971, 1973a, 1973b, 1973c), Price, Sinha and Gupta (1974) etc. Detailed discussion of these fundamental theories is beyond the scope of this short thesis.

In spite of concentrated efforts to understand a metal, no satisfactory theoretical model has yet been evolved which can explain all experimental observations on metals from very low temperatures up to the melting point. Under these circumstances, precise experimental determinations (of quantities like thermal expansion, Debye etc.) and possible correlations between various physical quantities assume special importance.
Experimental methods for determining Debye temperatures

The important methods by which Debye temperatures can be determined are

1) Specific heat measurements.
2) Entropy measurements.
3) Measurements of elastic constants.
4) Diffraction measurements.
5) Measurements using the Mossbauer effect.
6) Resistivity measurements.

i) The usual method of determining the Debye temperature is from measurement of specific heat. Debye's equation for the heat capacity of 1 gm. atom of a solid is

\[ C_V = \frac{3}{2} N k \left[ \frac{T}{\Theta_D} \right]^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \]  \hspace{1cm} (2.30)

where \( N \) is Avogadro's number, \( k \) Boltzmann's constant

\[ \chi = \frac{\Theta_D}{T} \quad \text{and} \quad \Theta_D = \frac{k T_D}{\chi} \]

It is necessary to subtract the electronic specific heat from the measured values and to convert the measured \( C_p \) to \( C_V \) using the thermodynamical equation \( C_p - C_V = \beta^2 V T / \chi \) where \( \beta \) is the coefficient of volume expansion and \( \chi \) the isothermal compressibility.

ii) \( \Theta_D \) values can be derived from calorimetric entropy measurements using the equation
where $X = \Theta_D / T$. The measured entropy values must, of course, be corrected for electronic and other non-vibrational contributions.

111) From Debye's theory, expressions for $\Theta_M$ and $\Theta_D$, the Debye temperatures appropriate to diffraction and specific-heat measurements respectively, can be obtained if appropriate methods of averaging over the longitudinal and transverse vibrations are used (see page 54). The expressions are

$$\Theta_M = \frac{\hbar \sqrt{3}}{k} \left( \frac{3N}{4\pi} \right)^{\frac{1}{3}} \frac{E^{\frac{1}{2}}}{m^{\frac{1}{3}}} \frac{\rho^{\frac{1}{2}}}{\sigma^{\frac{1}{6}}} f_1(\sigma) \quad \ldots \quad (2.32)$$

where, $E$ is Young's modulus, $\sigma$ Poisson's ratio, $m$ atomic weight, $\rho$ density, $N$ Avogadro's number and

$$f_1(\sigma) = \left[ \frac{3 - 5\sigma}{(1 - 2\sigma)(1 + \sigma)} \right] \quad \ldots \quad (2.33)$$

and

$$\Theta_D = \frac{\hbar}{k} \left( \frac{9N}{4\pi} \right)^{\frac{1}{3}} \frac{E^{\frac{1}{2}}}{m^{\frac{1}{3}}} \frac{\rho^{\frac{1}{2}}}{\sigma^{\frac{1}{6}}} f_2(\sigma) \quad \ldots \quad (2.34)$$
where

\[ f_1(\sigma) = \left( \frac{3 - 5\sigma}{1 + \sigma} \right)^{1/2} \left\{ 2^{5/2} (3 - 5\sigma) + 3^{3/2} (1 - 2\sigma)^2 \right\} \tag{2.35} \]

\[ f_2(\sigma) = \text{insensitive functions of } \sigma \]

in the range \(0.2 < \sigma < 0.5\) and hence simpler approximate forms of eqs. (2.32) and (2.34) can be found. For example \(M = 12(B/\lambda)^{1/2}\) for face-centred cubic materials, where \(B\) is in \(\text{kg/m}^2\), \(\lambda\) is in atomic units and \(a\) is the lattice parameter in angstroms.

iv) The intensity of a general Bragg reflection scattered from a mosaic, hexagonal crystal containing two similar atoms per primitive cell can be expressed, at a given temperature \(T\), in the following form:

\[ I_{\text{meas}}(S/\lambda, T) = C |F|^2 I_o(S/\lambda) \]

\[ x \exp \left[ -2M_\beta(\lambda)e^2 \right] - 2M_\gamma(\lambda)e^2 \]

\[ + I_{\text{TDS}}(S/\lambda, T) \text{…… (2.36)} \]

where \(C\) is a constant, \(F\) is the structure factor, \(I_o(S/\lambda)\) is the Laue interference function, \(S\) is the diffraction vector, \(\lambda\) is the wavelength of the x-radiation and \(\gamma\) is the angle between the hexagonal axis and \(S\). The exponential function in eq. (2.36) is commonly referred to as the Debye-Waller temperature factor; the terms in the Debye-Waller
temperature factor are related, within the quasi-harmonic approximation, to the components of the mean square atomic displacement in the following fashion:

\[ 2 W_{sp}(T) = (4 \pi \sin \theta / \lambda)^2 \langle u_{p}^2 \rangle_T; \quad p = c \text{ or } a \quad \ldots \ (2.37) \]

where \( \theta \) represents the Bragg diffraction angle, \( \langle u_{c}^2 \rangle_T \) denotes the component of the mean square displacement parallel to the hexagonal axis, and \( \langle u_{a}^2 \rangle_T \) refers to the projection of the mean square displacement into the basal plane.

The series of terms on the right-hand side of eq. (2.36) represents the thermal diffuse scattering (TDS). \( I_{TDS,j}(S/\lambda,T) \) denotes the \( j \)th order TDS, i.e., it represents the interaction between the incident x-ray photon and \( j \) phonons. If \( \psi \) is restricted to values of 0° or 90°, eq. (2.36) can be rewritten in terms of only one principal component of the atomic displacement as follows:

\[ I_{\text{meas}}(S/\lambda,T) = G \left| F \right|^2 I_0(S/\lambda) e^{-2W_s(T)} \quad \ldots \ (2.38) \]

where it is understood that \( S \) now refers to a principal direction.

Since it is rather difficult to evaluate the absolute value of the multiplicative constants in eq. (2.38), it is common practice to consider intensity ratios, usually referred
to some arbitrary reference temperature $T_0$. Evaluation of the intensity ratio, with the aid of eq. (2.37) yields the following expression:

$$\langle u_p^2 \rangle_T - \langle u_p^2 \rangle_{T_0} = \left( \frac{\lambda}{4\pi \sin \theta} \right)^2$$

$$\chi \ln \left[ \frac{R_p(T)}{R_p(T_0)} \right] \quad \ldots \quad (2.39)$$

$$= R_p(T) ; \quad p = a \text{ or } c ; \quad \ldots \quad (2.40)$$

where $Q(T)$ represents the measured intensity corrected for background contributions and TDS.

For the aforementioned hexagonal system, the atomic mean square displacements can be related to the frequency-distribution function $g(\nu)d\nu$ in the following fashion:

$$\exists \langle u^2 \rangle_T = \langle u_e^2 \rangle_T + 2 \langle u_a^2 \rangle_T$$

$$\exists \frac{3}{4\pi^2 m} \int_{\nu=0}^{\nu_{max}} \left[ \frac{1}{2} \nu^2 + \frac{\hbar \nu}{e^{\hbar \nu/kT_1}} \right] q(\nu)d\nu$$

$$\exists \int_{\nu=0}^{\nu_{max}} q(\nu)d\nu$$

$$\ldots \quad (2.41)$$

$$\ldots \quad (2.42)$$

where $m$ is the atomic mass, $\nu$ is the lattice frequency and
h and k have their usual meaning. If the Debye spectrum is employed in eq. (2.42), the following familiar relation is obtained:

\[ 3 \left< u^2 \right>_T = \left< u^2_\alpha \right> + 2 \left< u^2 \right>_T \quad \ldots \tag{2.43} \]

\[ \frac{9k^2 T}{4\pi^2 n_k \left[ \theta_d (\tau) \right]^2} \psi (\chi_T) \quad \ldots \tag{2.44} \]

where \( \psi (\chi_T) = \frac{1}{\chi_T} \int_0^{\chi_T} \frac{\xi}{\xi^2 - 1} d\xi \); \( \chi_T = \theta_d (\tau) / T \) \quad \ldots \tag{2.45}

A source of difficulty in the evaluation of the mean square displacement and hence of the x-ray Debye temperature, lies in the determination of the reference values \( \left< u^2_{\alpha, c} \right>_T \). Several techniques for solving the similar problem for cubic systems have been proposed in the literature (Chipman (1960); Flinn, McManus and Rayne (1961), Nicklow and Yound (1966). In the present work, Chipman's method has been extended to the hexagonal system. Once \( \left< u^2_{\alpha, c} \right>_T \) is obtained \( \left< u^2_{\alpha, c} \right>_T \) can be obtained from eq. (2.39). From \( \left< u^2_{\alpha, c} \right>_T \), the Debye temperature \( \Theta^M_p \) can be obtained from
For a nucleus bound in a crystal lattice, the probability of emission or absorption of a γ-ray without energy transfer to or from the lattice is governed by the Debye-Waller factor familiar from diffraction experiments. Thus measurement of the fraction of γ-rays emitted or absorbed without recoil will give the Debye temperature of the lattice. If the emitter and absorber are identical but at different temperatures $T_e$ and $T_a$ and moving with a uniform relative velocity $v$, then the self-absorption cross section for a crystal with a cubic Bravais lattice is given by

$$\sigma(S) = \frac{\pi \sigma_0 \tau}{\lambda} \exp \left[ - \left( 2W \xi + 2W \omega \right) \right] \times \left\{ \frac{\tau}{\pi} \frac{1}{s^2 + \tau^2} + \sum_{n=1}^{\infty} \frac{\left( 2W \xi + 2W \omega \right)^n}{n!} g_n(S) \right\} \quad \cdots \ (2.47)$$

In this expression $S = (v/c)E_o$ where $E_o$ is the energy of the γ-ray emitted, $\sigma_0$ is the resonance absorption cross
section, $\gamma$ is the natural width of the excited state of the nucleus, and $\bar{g}(s)$ are functions given in detail by Singwi and Sjolander (1960).

In the Debye approximation

$$2 \omega_e = \frac{E_0}{2mc^2} \cdot \frac{6T}{K \beta^2 \gamma} \psi(x) \quad \ldots \quad (2.48)$$

with a similar expression for $2\omega_a \psi(x)$ has been defined in eq. (2.45). The analogy between eq. (2.48) and the Debye-Waller formula for $2\omega$ (eq. 2.44a), remembering that $2\omega = 2B (\sin^2 \theta / \lambda^2)$, is clear if one writes the single equation

$$2M = E_R \cdot \frac{6T \psi(x)}{K \beta^2 \gamma} \quad \ldots \quad (2.49)$$

For X-ray diffraction $E_R$ is the recoil energy given to the free atom by a photon of energy $E (=hc/\lambda)$ scattered through a total angle $2\theta$. In this case

$$E_R = \frac{E^2}{mc^2} (1 - \cos 2\theta) = \frac{2h^2 \sin^2 \theta}{m \lambda^2}$$

For emission of $\gamma$-rays the photon of energy $E$ gives a recoil momentum $E/c$ to a free atom of mass $m$ and thus the kinetic energy of recoil is $E^2/2mc^2$. 
vi) Using Bloch (1928), 1929) theory of the temperature dependence of the electrical resistivity of metals, Gruneisen (1933) related the resistivity to a characteristic temperature $\Theta_R$. In general no close agreement is to be expected between the values of $\Theta_D$ and $\Theta_R$ as, according to Bloch theory, $\Theta_R$ depends on the longitudinal lattice vibrations only. Still, however, in practice $\Theta_R \approx \Theta_D$

vii) Some other methods of deriving $\Theta$ values have been discussed by Blackman (1955). For example, for ionic crystals infra-red data (Reststrahlen) and compressibilities can be used.

**Theoretical differences between Debye Temperatures determined by different experimental methods:**

In terms of general frequency distributions the formulae for the Debye-Waller factor (Blackman, 1937) and the specific heat can be written:

$$\Theta_B = \frac{4 k^2}{3 N m k T} \sum \int N_j (\nu) \left[ \frac{1}{\nu^3} \left( \frac{1}{e^\nu - 1} + \frac{1}{2} \right) \right] d\nu \quad (2.50)$$

$$\Theta_V = K \sum \int N_j (\nu) \left[ \frac{b^2}{(e^b - 1)^2} \right] d\nu \quad \ldots (2.51)$$
where \( p = kT / \hbar \) and \( N_j(\nu) \) is the frequency distribution function for elastic waves of polarization \( j \). If the quantities in the parenthesis in eqs. (2.50) and (2.51) are called \( W_1 \) and \( W_2 \), it can be easily shown by plotting \( W_1 \) and \( W_2 \) versus frequency \( \nu \) that the low frequency region is relatively much more important for the X-ray temperature factor than for the specific heat. Thus the effects of deviations from a parabolic (Debye) spectrum on B factor will be different from the effects on specific heats. As the actual frequency spectrum deviates least from a parabolic spectrum at low frequencies, the Debye approximation will fit the X-ray temperature factors better than the specific heats. This should be most marked at low temperatures. As only the very lowest lattice frequencies are excited in measurements of elastic constants, the Debye approximation will apply accurately to the \( \Theta_D \) values derived in this way, and deviations from the Debye approximation will not influence the shape of the \( \Theta_D \) (elastic) versus \( T \) curve.

Parabolic forms \( N_j(\nu) \) must be inserted in eqs. (2.50) and (2.51) when the Debye approximation is made, i.e., \( N_j(\nu) = (9\nu^3) \) where \( \nu_m \) will be different for the transverse and longitudinal modes of vibration. This substitution gives

\[
2B = \frac{4 \hbar^2 T}{mk} \left[ \frac{\psi(x_t)}{\Theta_t^2} + 2 \frac{\psi(x_t)}{\Theta_t^2} \right] \quad \ldots \quad (2.52)
\]
\[ C_\nu = 3 N K T^3 \left[ \frac{D(x_L)}{\Theta_L^3} + \frac{2 D(x_t)}{\Theta_t^3} \right] \]  \hspace{1cm} \text{(2.53)}

where \( \Theta_L \) and \( \Theta_t \) are Debye temperature appropriate to longitudinal and transverse vibrations respectively:

\[ \Theta_L = \frac{h \nu_m L}{k}, \quad \Theta_t = \frac{h \nu_m t}{k} \]

\( \psi(x) \) has been defined in eq. (2.55) and

\[ D(x) = \int_0^x \frac{p^4 e^p}{(e^p - 1)^2} \, dp \]

is the familiar Debye integral from specific heat theory. Except at low temperatures the difference between \( \psi(x_L) \) and \( \psi(x_t) \) will be small. If an average value of \( \Theta_M \) be chosen such that

\[ 3 \Theta_M^{-2} = \Theta_L^{-2} + 2 \Theta_t^{-2} \]  \hspace{1cm} \text{... \... (2.54)}

then eq. (2.52) will be identical with the Debye-Waller formula

\[ 2 B = \frac{12 h^2 T \psi(x)}{m k \Theta_M^2} \]  \hspace{1cm} \text{... \... (2.54a)}

Similar considerations apply to eq. (2.53); if an average value of \( \Theta_D \) be chosen such that

\[ 3 \Theta_D^{-3} = \Theta_L^{-3} + 2 \Theta_t^{-3} \]  \hspace{1cm} \text{... \... (2.55)}

then eq. (2.53) will become identical with eq. (2.30).
Zener and Bilinsky (1936) were the first to point out that the average Debye temperatures in eqs. (2.54) and (2.55) were defined differently and that their ratio could be expressed as a function of Poisson's ratio, using the expressions for $\Theta_M$ and $\Theta_D$ derived from elastic constants (eqs. 2.32 and 2.34). The differences between $\Theta_M$ and $\Theta_D$ are generally found to be about 3-4%.

One further consequence of the deviation of the true vibration spectrum from the parabolic form must be mentioned here. The limiting form of the true spectrum at low frequencies is generally found to be parabolic. Hence the value of $\Theta_D$ derived from measurements of elastic constants will be that appropriate to this part of the spectrum. However the X-ray value of $\Theta_D$ (i.e. after the correction for the difference between $\Theta_M$ and $\Theta_D$ has been applied) will be less than the elastic constant value if the real frequency spectrum rises above the initial parabolic shape. This is because the parabola that fits the true spectrum best over an appreciable part of the total frequency range will be steeper, and thus have a smaller value of $\nu_\infty$, than the parabola chosen from the limiting shape of $N(\nu)$ at the very lowest values of $\nu$. The rule $\Theta_D (X\text{-ray}) < \Theta_D (elastic)$ is a very general one as most real frequency spectra have "humps" in the lower frequency range. It is difficult to make a similar prediction for $\Theta_B$ (specific heat) as the higher frequencies play a much more
important role in determining \( C_v \) than \( B \).

A commendable effort has been made by Barron and Leadbetter (1966) to connect thermodynamic quantities with \( \Theta_H \). They have shown that Debye-Waller temperature factors and thermodynamic properties of crystals can be related easily and practically by use of the quasi-harmonic description of lattice vibrations. The explicit introduction of particular forms of frequency distribution or force constant models is not required.

They show that for cubic crystals containing one type of atom, temperature factors can usually be obtained more accurately from thermodynamic data than from scattering measurements. For more complicated structure containing different kinds of atoms, the thermodynamic data are related to a linear combination of temperature factors. It is shown by them that for crystals of cubic symmetry

\[
\sum_{k=1}^{n} \frac{m_k H_k}{Q^2} = X(T) \quad \ldots \quad \ldots \quad (2.56)
\]

where \( k \) is the number of atoms in the primitive cell, \( m \) is the mass of the atom, \( H \) temperature factor, \( Q = (4\pi/\lambda) \sin \theta \) and \( X(T) \) for high temperature is given by

...
where $\bar{\omega}^n$ are the moments of the frequency distribution and $B_{2n}$ are the Bernoulli numbers. For monatomic crystals like Cu, Al etc., $n = 1$ and eq. (2.56) reduces to

$$\frac{2\pi n M}{q^2} = X(T) \quad \ldots \ldots \quad (2.57)$$

The moments $\bar{\omega}^n$ can be found e.g. from specific heat measurements and hence $X(T)$ can be obtained. The value of $M$ can then be found from eq. (2.56).

In most of the theoretical treatments it is $\Theta_D$ which is generally evaluated instead of $\Theta_M$. But $\Theta_M$ can be calculated if the frequency spectrum is known either from theory or experiment. For example, in quasiharmonic approximation, the exponent of the Debye-Waller factor is related to the mean square displacement of the atoms and is given by

$$2\Theta = \left< |\vec{K}\vec{U}(n)|^2 \right> \quad \ldots \ldots \quad (2.58)$$

where $\vec{U}(n)$ is the displacement of the $n^{th}$ atom and $K$ is the difference of the initial and final wave vectors of the wave. Using the standard theory, eq. (2.58) can be
written in terms of eigenvalues and eigenvectors of the vibrational spectrum in the form

\[ 2M = \frac{h}{mN} \sum_{\mathbf{k},\mathbf{p},\mathbf{q}} \left( \frac{k \cdot \mathbf{p} \cdot \mathbf{q}}{\omega \cdot \mathbf{q}} \right)^2 \left( \frac{1}{2} + \frac{1}{e^{\frac{h \omega}{kT}} - 1} \right) \]  

(2.59)

where \( m \) is the mass of an atom in the lattice, \( N \) is the total number of unit cells in the crystal, \( \omega_{\mathbf{q}} \cdot \mathbf{p} \cdot \mathbf{q} \) is the angular frequency of a phonon of wave vector \( \mathbf{q} \) and polarization \( \mathbf{p} \). \( \mathbf{p}_{\mathbf{q}} \) is the polarization vector of \( \mathbf{q} \) lattice mode and the summation extends over all the normal vibrations of the crystal. In the case of cubic crystals, using symmetry considerations, the polarization factor \( (k \cdot \mathbf{p} \cdot \mathbf{q})^2 \) can be replaced by its average value outside the summations. If \( G(\omega) \) is the frequency distribution function for the phonon giving the number of vibrational modes in the frequency interval \( \omega \) and \( \omega + d\omega \), eq. (2.59) becomes

\[ 2M = \frac{8\pi^2 h}{3mN} \left( \frac{\sin \theta}{\lambda} \right)^2 \int_0^{\omega_m} \frac{G(\omega)}{\omega} \coth \frac{h\omega}{2kT} d\omega \]  

(2.60)

where \( \omega_m \) is the maximum frequency of the vibration spectrum, \( \theta \) the Bragg angle and \( \lambda \) is the wavelength of the incident radiation.

If \( G(\omega) \) is known, eq. (2.60) can be used to calculate \( 2M \) and hence \( \langle u^2 \rangle \) and \( M \).
EXPERIMENTAL METHODS

(1) Thermal expansion

The thermal expansion of polycrystalline solids e.g., metals available in the form of bars, etc., can be determined easily by employing an optical lever or even a simple spherometer. Various modifications employing such simple instruments are available in literature. But the measurement of expansion of crystals requires a delicate arrangement because the crystals are usually small in size. Moreover, such small crystals are to be cut along a particular axis to measure the expansion along it. The measurement of thermal expansion of crystals is usually carried out by two methods: (i) dilatometric methods and (ii) X-ray methods.

(1) DILATOMETRIC METHODS

Variety of methods can be described under this head. Measurement of the displacement of a liquid in a pyknometer as a result of the expansion of a crystal is a way by which thermal expansion is measured (Baxter and Wallace 1916). Unless extreme precautions are taken such methods do not give very accurate results. Most dilatometric methods are generally based on the phenomenon of interference of light. Earliest measurements on thermal expansion using this phenomenon were undertaken by Fizeau (1856, 1864a, 1864b,
1866). His original apparatus is shown in Figure 1. B is the crystal in the form of a slab whose expansion is to be measured. Its upper and lower faces are flat and it is placed on a metal plate A having levelling screws SS. A lens L whose surface has a large radius of curvature rests on the screws as shown in the figure. Newton’s rings are formed between the lower surface of L and the upper face B, and are observed by a telescope T. When the thickness of the air film between the specimen and the lens changes due to the expansion of the specimen the rings appear to pass across the cross wire in the telescope. When two successive bright rings pass the cross wire it is clear that the thickness of the film must have changed by $\lambda/2$. Hence if the assembly producing the air film is enclosed in a heating chamber, and the rings which pass the cross wire are counted, the expansion of the specimen relative to that of the screws can be calculated. If the expansion of the screws is known that of the specimen can be estimated.

This simple method of Fizeau (1856, 1864a,b, 1866) was improved by Abbe (1889), Pulfrich (1893), Priest (1920), Mix and MacNair (1941), etc. A modern instrument widely used for the measurement of expansion of single crystals is shown (in principle and not in details) in Figure 2.

The interferometer consisting of two silica or
glass plates A and B are placed in the middle part of the cylindrical furnace. Three similar pieces, cut from the same crystal, of very nearly equal lengths and having their ends made conical are placed between the plates A and B. When the interferometer is illuminated by a monochromatic beam of light and the reflected beam of light received inside a telescope, a system of interference fringes is observed. When the interferometer is heated by passing an electric current in the furnace, the fringes move across the cross wire of the telescope. From the knowledge of the temperature and the number of fringes passing the cross wire, the thermal expansion of the crystal can be calculated. The rate of heating is usually kept low, about 12°C/hr., so that precise observations are possible.

In the heterodyne beat method the capacity of a condenser in an oscillatory circuit is altered by the expansion of the specimen. The changes in the frequency of the oscillator can be detected by the heterodyne beat method and can be compensated for by altering the capacity of a standard condenser. The change in capacity needed for compensation is a direct measure of the expansion of the specimen. The accuracy of the method is high and it compares favourably with the interference method described above.
(ii) X-RAY METHODS

(a) High Temperature Cameras Employing Films

With the advent of the discovery of X-ray diffraction, a vast field was opened for the study of the structure of solids. Physicists, chemists, and metallurgists were not satisfied with the work at room temperature. Before the discovery of X-rays, the properties of matter at high temperature such as dilatation, specific heat, conductivity etc. were studied, but they gave the properties of the sample in bulk.

Westgren (1921) among the early workers was the first to employ the high temperature X-ray technique and showed that \( \alpha/\gamma \) transformation in iron was associated with the change from body-centered to the face-centered cube and that \( \beta \)-iron does not exist. He heated iron wire (specimen) by passing an electric current through it and no specimen movement was provided.

Since then a number of high temperature cameras, too numerous to be included in this thesis, have been published. Many of them have been designed for some special work e.g., for precise determination of cell constants, for rapid exposures, for vacuum work, etc. Some of the early
designs are those of Becker (1927), Cohn (1928), Ruff and Ebert (1929), and Braseken and Barng (1930). The noteworthy feature of Becker's (1927) camera was that temperatures up to 2200°C were attained, while Cohn's (1928) camera is unique because the specimen is heated by convection.

Subsequent development was rapid and designs incorporating some of the features of the most modern camera appeared in literature. Some of the important ones are those of Jay (1933), Schossberger (1938), Hume-Rothery and Reynolds (1938), Wilson (1941), Owen (1943), Gordon (1949), Owen (1949), Edwards, Speiser and Johnston (1949), Williams (1950), Johnson (1954), Matuyama (1955), Goon, Mason and Gibb (1957), commercial camera of Unicam, etc.

The camera of Edwards, Speiser and Johnston (1949) is unique because the temperature of the specimen is raised by high frequency induction heating. The camera of Straumanis and Ievins (1938) is noteworthy because of its rigid temperature control. Although the maximum temperature is 700°C, it is used for high precision measurements of cell constants of crystals.

A typical high temperature camera (Hume-Rothery and Reynolds (1938) is shown in Figure 3. The specimen is heated by two bell-shaped furnaces. It is sealed into a fine silica capillary which is joined to a silica rod.
Botatlon of the rod is possible and the maximum temperature of 1400°C can be attained. Film is placed inside a chamber and held to water-cooled flanges by rubber bands. It is protected by black paper and above 600°C by an aluminium screen.

(b) **Geiger Counter Diffractometer**

Another method, which is a recent development, of measuring the cell constants of a crystal (and hence its thermal expansion) is to use a diffractometer and a Geiger counter (to locate the positions of X-ray lines). A typical arrangement of such a diffractometer is shown in Figure 4. The specimen is put at the centre of a graduated circular disc. A beam from an X-ray tube is incident on the specimen and the diffracted beam received by a Geiger counter. The incident beam is allowed to pass through a slit or a number of slits and the diffracted beam is focused on a slit placed in front of the Geiger counter. In order to make the arrangement sensitive, a focusing arrangement, called Seemann-Bohlin parafocusing arrangement, is used. It is shown in Figure 5. The X-ray beam passing through a slit *F* is incident on a curved specimen *S*, and the beam diffracted by different crystal places of the specimen is brought to focus at points like *G*₁, *G*₂, *G*₃, etc., on the photographic film. Here the radius of the focusing circle is constant but the distances *SG*₁, *SG*₂, *SG*₃, etc., for the various
FIG 3

COVER UNIT
FURNACE
SLIT SYSTEM
INCIDENT BEAM
FILM
WATER COOLING QUARTZ TUBE FOR FURNACE MOUNTING (ADJUSTABLE)
BLACK PAPER AL FOIL
THERMOCOUPLE SPECIMEN

FIG 4
reductions are different. Now in the diffractometer the Geiger counter rotates about the specimen $S$ and hence the distance $SG$ remains constant (Fig. 6). In order to obtain a sharp focus on the counter throughout its rotation the sample is made flat and is allowed to rotate at half the speed at which the counter rotates, so that the specimen surface remains tangential to the focusing circle at all times. It can be seen from Figure 6 that as the angle $2\theta$ becomes larger, the radius of the focusing circle decreases. For $2\theta = 0$, $R = \infty$ while for $2\theta = 180^\circ$, $R$ reaches its minimum values of $SF/2 = SG/2$.

In Figure 7 is shown the complete geometry of the diffractometer. The focusing circle and the circle in which the counter moves are shown with respect to the sample. The distance $SF = SG = 1$. It is seen that $R$ is connected with $\theta$ by the relation:

$$ R = \frac{\lambda}{2} \sin \theta $$

The chief advantage of the Geiger counter diffractometer lies in the facility with which rapid scanning of the diffracted pattern is possible and is, therefore, especially suitable for high temperature work. In the photographic method the exposures are usually long and unless special precautions are taken, the temperature during the interval may not remain constant. Moreover, phase changes in the sample may occur during exposure and the resulting photograph would be
misleading. Moreover, lattice spacing changes may occur with time due to precipitation or diffusion process and would give line broadening. In the case of the diffractometer the temperature and the position of the line are noted simultaneously and this is a great advantage over the photographic method.

The resolving power of the counter arrangement is much higher than that available in the photographic method. This can be seen from the fact that the \( \alpha_1, \alpha_2 \) doublet from a CuK\(\alpha\) radiation can be resolved even at an angle \( 2\theta = 30^0 \) approximately, while in the Debye-Scherrer cameras such a resolution is not possible at an angle much below \( 2\theta = 90^0 \).

In order to measure the thermal expansion of a specimen situated at the centre of the diffractometer plate, it must be heated and hence a small furnace must be devised. Although high temperature cameras were developed as early as 1921, high temperature diffractometer furnaces are of recent origin. Hence although a large number of cameras has appeared in literature, the number of diffractometer furnaces are few. The important ones are due to Wangsgard (1942), Birks and Friedman (1947), Heal (1949), Heal and Nykura (1950), Sosman and Andrew (1951), Chiotti (1954), Butters and Parr (1955), Williamson and Moore (1956), Kennedy and Calvert (1958), Perri, Banks and Post (1957), Pathak and Pandya (1959), Holden (1964), Moss and Smith (1965) etc.
Out of these the Beal (1949) and Beal and Akyura (1950) diffractometers were specially designed to have a stationary counter to follow isothermal transformations in steels by measuring time changes of total intensity of a given line. The furnaces of Wanggard (1942) and of Birks and Friedman (1947) were designed for the study of transformations in metals, the former employing rod specimens and the latter flat sheet ones.

Variety of heating devices are used in such diffractometer furnaces. Most of the furnaces to be used in oxidising atmosphere employ platinum, platinum - 10% rhodium or platinum - 20% rhodium windings as heaters. The highest temperature reported with such windings is about 1500°C. Somam and Andrews (1951) employ a Pt - 20% Rh strip as a heater and the sample powder is placed in a small draw made in the strip. Birks and Friedman (1947) and also Pathak and Pendya (1959) use hotplate heaters. Cylindrical tantalum metal foil through which a heavy current is passed is used by Chittit (1954) and Spreadborough and Christian (1959). Silicon carbide heaters are also tried especially by Perri, Banks and Post (1957). Holden (1964) uses rhenium trough as a sample holder as well as heater. High current is passed through the trough and temperatures of 2100°C are reported. Attempts have also been made to heat the sample by induction heated furnaces. Moss and Smith (1965) employ a focussed
heat source (150 W DFA internally focussed projection lamp).

MEASUREMENT OF THERMAL EXPANSION

In the case of an x-ray diffraction pattern for a hexagonal close packed substance, we can write

\[ \sin \theta = \frac{\lambda}{2a} \sqrt{\left( \frac{k}{3} \left( h^2 + 3k^2 + k^2 \right) + \left( \frac{a_0}{c} \right)^2 \right)} \]

where \( a \) and \( c \) are the lattice parameters along \( x \) and \( z \) directions, \( h, k, l \), Miller indices and \( \theta \) the angle of diffraction.

Values of \( a \) and \( c \) can be obtained by taking two \( hkl \) reflections or taking \( 00l \) and \( h00 \) reflections.

By heating the specimen the lattice parameters \( a \) and \( c \) will change and hence \( \theta \) will change. By measuring the shift of lines on the photographic film or by determining the shift in the position of the peak of the diffraction profiles on a chart recorder, we can determine the change in the lattice parameters \( a \) and \( c \). The values \( a_t \) and \( c_t \) of the lattice parameters at different temperatures \( t^\circ C \) are obtained and graphs drawn between \( a_t \) versus \( t \) and \( c_t \) versus \( t \). The equations are obtained for the curves. In the case of the hop metals mentioned in this thesis, equations of the form
\[ s_t = s_0 + bt + ct^2 + dt^3 \]

and \[ c_t = c_0 + ct + ft^2 + gt^3 \] are obtained.

The linear coefficients of expansion are calculated from the formulae

\[ \alpha = \frac{1}{a_t} \frac{da_t}{dt} ; \quad \gamma = \frac{1}{c_t} \frac{dc_t}{dt} \]

or \[ \alpha = \frac{1}{a_t} ( b + 2ct + 3dt^2 ) \]

\[ \gamma = \frac{1}{c_t} ( s + 2ct + 3gt^2 ) \]

\[ \alpha_{av} = \text{average } \alpha = \frac{1}{3} ( 2\alpha + \gamma ) \]

(ii) **Debye temperature**

In order to obtain the value of \( \Theta_H \) both the photographic as well as diffractometer methods described above are used. In the photographic method the X-ray reflections are obtained on a photographic film and a microdensitometer plot is obtained. The integrated intensity of a particular line is then given by the area between the peak and the background of the plot. In the case of a diffractometer, the pulses from the Geiger counter (or preferably, proportional or scintillation counter) are fed to a chart recorder and the line profile is obtained. The
integrated intensity is again the area between the peak and the background. Once the integrated intensities are measured, \( \Theta \) can be obtained by making use of eq. (2.39).