3.1 Investigations on the thermal expansion of alkali halides:

The thermal expansion of alkali halides has been investigated by various workers. Some of the principal workers and their investigations may be briefly mentioned as under:

- Eucken & Dannohl (LiF, KCl, KBr, NaCl, KI, 193+);
- Basu & Maitra (NaCl, 1938);
- Gott (LiF, KI, KBr, 1942);
- Sharma (LiF, 1950);
- Connell & Martin (KI, KBr, 1951);
- Glover (KCl, 1954);
- Johnson et al (CsBr, CsI, 1955);
- Srinivasan (NaCl, KCl, 1955);
- Fischmeister (NaCl, 1956);
- Krishnan & Srinivasan (CsBr, 1956);
- Pathak & Pandya (CsI, 1960a; KBr, KI, CsBr, 1960b);
- Deshpande (NaF, NaBr, 1961);
- Deshpande & Sirdeshmukh (RbBr, RbCl, 1961);
- Enck et al (KCl, 1962);
- Merrium et al (NaCl, 1962);
- Vishwanitra & Ramaseshan (KI, 1962);
- Pathak et al (LiF, NaF, 1963);
- Christian & Lynch (CsCl, 1964);
- Sirdeshmukh & Deshpande (RbI, 1964);
- Enck & Dommel (NaCl, 1965);
- Laredo (NaCl, 1969);
- Leadbetter &
Some of the above investigations have been carried out with the help of X-ray diffraction while the others have used macroscopic methods. From the discussion in Chapter II, it can be seen that the determination of thermal expansion of a solid can give us insight into various natural phenomena occurring in the solid. In this chapter, discussion will be restricted to the attempts made by different workers to investigate the role of lattice defects in the thermal expansion of solids and to the "law of corresponding states" which is shown to hold in the case of cubic metals.

3.2 attempts to investigate the role of lattice defects in thermal expansion of alkali halides:

The fact that ionic crystals conduct an electrolytic current which obeys Ohm's law at sufficiently high temperatures shows that these crystals possess imperfections at elevated temperatures. This observation is attributed to Frenkel (1926) who pointed out that the crystals could not be ionic conductors unless a fraction of the ions was wandering about in the crystal lattice in a more or less random fashion. The applied field supplies only a directional component to the otherwise random motion.
Schottky (1935), Wagner (1936) and Jost (1933, 1934a, 1934b, 1937) carried out careful investigations on the nature of the imperfections that occur in various types of crystals and which are responsible for the ionic conductivity. Two principal types of imperfections—interstitial atoms and vacancies—are of general interest. Vacancies may be formed by the migration of atoms or ions to the surface, where they form additional layers to the lattice or by the migration of atoms or ions from normal lattice sites to interstitial positions. In the later case, both vacancies and interstitial ions are formed together. These imperfections are produced in a thermodynamically reversible manner at sufficiently high temperature because of the entropy gained by the lattice as a result of the increase in disorder.

It has been found that the ionic conductivity of ionic crystals increases as the temperature increases showing that concentration of defects also increases with temperature.

When a lattice vacancy is created by removing an ion from its site and placing it in an interstitial position within the lattice, the defect is called a Frenkel defect. When a lattice vacancy is created by removing an ion from its site and placing it on the surface of a crystal, the defect is called a Schottky defect.
Schottky (1935) and Jost (1933, 1934a, 1934b, 1937) have shown that it is exceedingly unlikely that interstitial ions occur in any appreciable quantity in the alkali halides. This is because the energy required to force an alkali metal ion or a halogen ion into an interstitial position is prohibitively high. Mott and Littleton (1938) have carefully refined the type of calculations carried out by Schottky (1935) and Jost (1933, 1934a, 1934b, 1937). They have shown in the case of sodium chloride, for example, that the energy required to take Na$^+$ ion from a normal lattice position to an interstitial position is 2.9 ev., whereas the energy required to form a pair of vacancies is 1.86 ev. Thus the number of interstitial ions is less than one per cent of the number of vacancies indicating that in alkali halides the Frenkel defects are practically absent while the Schottky defects predominate.

Since the calculations of Mott and Littleton (1938), many other workers have done valuable work in connection with the calculation of the energy of formation of Schottky defects in alkali halides with more refined methods. Notable among them are Reitz and Gammel (1951), Bassani and Fumi (1954), Kurosawa (1958, 1962), Tosi and Fumi (1958, 1964), Fumi and Tosi (1964), Tosi and Doyama (1966), Boswarva and Lidiard (1967), Boswarva (1967), Rao
Since the interior of the crystal must remain electrostatically neutral, it follows that vacancies of both types (positive and negative) must occur in equal numbers in a normal crystal.

When ion pairs are removed from an interior of the lattice and placed on the surface, additional unit cells are added to the crystal so that its volume is increased. Since the number of defects increases as the temperature increases the total dilatation of the crystal is the sum of two separate dilatations (i) due to heat and (ii) due to the presence of defects. Since the X-rays do not penetrate much below the surface, and since the lattice parameters of the unit cells formed on the surface are not likely to be affected by the creation of vacancies, the dilatation and the thermal expansion determined by the macroscopic (where the crystal as a whole expands) and X-ray methods are likely to differ, the difference being greater at high temperatures.

The coefficient of thermal expansion $\alpha$ in almost all alkali halides increases with temperature. Lawson (1950) assumed that $\alpha$ should be constant for a perfect crystal lattice and deduced that defects do play a part and contribute to the thermal expansion. He
succeeded in proving his point in the case of silver bromide but not for silver chloride. Uno (1951) has introduced the same assumption in the case of sodium chloride.

Miller and Russell (1952) suggested that there is a difference between the geometrical volume change of a crystal containing defects and the volume change deduced from X-ray measurements. They calculated that for a uniform distribution of Frenkel defects the latter should be about twice the former. In a later paper (1953) they corrected their calculations and showed that both should be practically equal. Eshelby (1954) from an elastic approach, has also pointed out that a random distribution of uniform point singularities deform the crystal in such a way that both expansions are equal.

In order to explain his viewpoint in the case of silver bromide, Lawson (1950) had to assume the defects to be of the Schottky type. Wagner and Beyer (1936), however, have shown that pyknometric and X-ray densities of silver bromide near the melting point are equal. This result has been verified by Berry (1951). This equality of the two densities speaks strongly in favour of Frenkel defects and rules out the existence of Schottky defects. Since, as shown above, the Frenkel defects are not likely to occur in the alkali halides, the explanation of the
Increase of $\alpha$ with temperature must be searched elsewhere.

Fischmeister (1956) has shown that the increase in $\alpha$ with temperature can be explained by the usual Debye-Grüneisen theory of solids and that the effects of defects need not be considered at all. This theory gives:

$$\frac{a_T - a_o}{a_o} = \frac{V_T - V_o}{V_o} = \frac{E/Q}{1 - \beta E/Q} \quad \ldots \quad (29)$$

where $a_T$ and $a_o$ are the lattice constant at $T^0_K$ and $0^0_K$ respectively, $E$ internal energy and $p$ and $q$ are constants called Grüneisen's parameters. In the case of alkali halides, $E$, the vibrational energy is given by

$$E = 6\hbar \kappa D(\theta/T) \quad \text{where } D(\theta/T) \text{ is given by} \quad \ldots \quad \ldots \quad (30)$$

$$D(\theta/T) = \left\{1 - \frac{3}{9} \left(\frac{\theta}{T}\right) + 0.050 \left(\frac{\theta}{T}\right)^2 - 0.0005905 \left(\frac{\theta}{T}\right)^4\right\}$$

From the above two equations we get:

$$\frac{a_o}{a_T - a_o} = \frac{Q}{2R T D(\theta/T)} = 3\beta \quad \ldots \quad \ldots \quad (31)$$

Hence the graph of $\frac{a_o}{a_T - a_o}$ against $\frac{1}{T D(\theta/T)}$ in the case
of a crystal must be a straight line. Fischmeister (1956) does obtain such straight lines in the case of a number of alkali halides. The data for sodium chloride are obtained by himself while those for other crystals are taken from the macroscopic observations of Lucken and Dannöhl (1934) and X-ray measurements of Johnson, Agron and Breding (1955).

Fletcher (1957) has criticised the work of Fischmeister (1956) on the ground that Fischmeister's method of drawing graphs is too insensitive to reveal the contribution of defects especially at high temperature. Fletcher has obtained a direct relation between volume and temperature for a solid on the same assumptions made in the Debye-Grüneisen theory. He has drawn a graph of \( \kappa \) against \( T \) for potassium chloride and shown that although \( \kappa \) increases with temperature as observed experimentally the agreement between theory and experiment is not good. The theoretical values of Fletcher (1957) are rather low, probably because the value of \( K_0 \), the compressibility at \( 0^\circ K \), assumed by him is too low. A larger value for \( K_0 \) could increase both \( \kappa \) and \( d\kappa/dT \) and the agreement between theory and experiment would be much better.

Following the work of Fischmeister (1956), Eastabrook (1957) has examined the validity of Grüneisen's equation and has shown clearly that if the
temperature variation of $\gamma$, the Grüneisen's constant, is taken into account the Debye-Grüneisen theory completely accounts for the observed thermal expansion without postulating the existence of lattice defects.

Merrium et al (1962) have suggested that the thermal expansion of NaCl could be separated in two parts, viz. "normal" contribution and an "anomalous" part. According to them the thermal expansion should be given by

$$\alpha(T) = \alpha(T_0) + \left( \frac{d\alpha}{dT} \right)_{T=T_0} (T - T_0) + \Delta\alpha \ldots (3.2)$$

where $\alpha(T)$ is the thermal expansion at some temperature $T$ between $T_0$ and the melting point and $\Delta\alpha$ is the anomalous part which is the contribution of thermally generated defects at high temperatures. Since $n/N$, the defect concentration, is small (of the order of $10^{-4}$) a linear relationship $\Delta\alpha = b \cdot n$ can be expected, where $b$ is a constant. With the help of the data of Eucken and Dannöhl (1934) on NaCl, they have shown that the plot of $\log \Delta\alpha$ versus $1/T$ is a straight line whose slope is consistent with the activation energy of about 2.0 ev.

Recently Laredo (1969) has measured the expansion.
of NaCl by X-ray method and supported the observations of Merrium et al (1962) and Buck et al (1965). He has also discussed the order of magnitude of the different terms that contribute to the "anomalous" part of the thermal expansion. He defines a mean coefficient of linear expansion $\alpha'$ as

$$\bar{\alpha} = \frac{1}{T - 273} \int_{273}^{T} \alpha \, dT$$

where $\alpha = \frac{\alpha'}{V}$, $\alpha'$ being the absolute expansion ($\partial V / \partial T$). Thus

$$\bar{\alpha} = \frac{1}{T - 273} \frac{\Delta a}{a_0}$$

where $a_0$ is the lattice constant at 273°C K and $\Delta a$ the increase in the lattice constant at $T^0$ K above $a_0$. The plot of $\bar{\alpha}$ versus $T$ shows a sudden rise above 550°C which is the temperature corresponding to the 'knee' of the electrical conductivity versus $1/T$ plot. $\Delta \bar{\alpha}$ is the anomalous part of the coefficient of expansion and the plot of $\log \Delta \bar{\alpha} / \Delta T$ versus $1/T$ gives a slope consistent with the energy of formation of Schottky defects of about 2.0 ev.
3.3 **Law of corresponding states**:

Considering the temperature variation of thermal diffuse X-ray scattering, Catz (1955) has shown that the amplitude of thermal vibrations of the atoms in cubic crystals can be expressed in terms of the distance between neighbouring atomic positions and the melting point. He has also shown that a "law of corresponding states" exists in the case of physical properties like thermal expansion which depend on atomic vibrations.

Lindemann (1910) assumed that at the time of melting the amplitude of oscillations of the atoms becomes so large that direct collisions occur between neighbouring atoms. Then

\[ \frac{1}{2} y^2 = \text{constant} \cdot \frac{T_m}{y^{2/3}} a \]  \hspace{1cm} (34)

where \( y \) is the frequency of the vibrating atoms, \( V \) the atomic volume, \( T_m \) the melting point and \( A \) the atomic weight. Equating \( y \) to the maximum frequency of Debye's theory of specific heat, and if \( a \) is the lattice parameter, we have

\[ A a^2 e^2 = \frac{T_m}{L} \]  \hspace{1cm} (35)
where \( L \) is a constant (Lennard-Jones and Devonshire, 1933; Blom, 1913; Furth, 1944 and Born, 1939).

The mean square amplitude of atomic vibrations \( \overline{u^2} \) can be expressed in terms of the Debye characteristic temperature (James 1948, p. 220, Lonsdale, 1948). For \( T > \theta \)

\[
\overline{u^2} = \frac{9}{4} \frac{h^2 T}{4 \pi^2 \hbar^2} = 4.364 \times 10^{-14} \frac{T}{\Lambda \theta^2} \quad \ldots \quad (3.2)
\]

Combining eqs. (3.5) and (3.4) we get:

\[
\left( \frac{\overline{u^2}}{a} \right)^{\frac{1}{2}} = (4.364 \times 10^{-14} \frac{L_T}{T_m})^{\frac{1}{2}} \quad \ldots \quad \ldots \quad (3.7)
\]

For face-centred and body-centred cubic structures, \( L = (r/a)^2 L_r \), where \( L_r = 11.4 \times 10^{10} \) and \( r \) is half the distance between neighbouring atomic positions so that eq. (3.7) becomes:

\[
\left( \frac{\overline{u^2}}{a} \right)^{\frac{1}{2}} = 0.22 \ r \left( \frac{T}{T_m} \right)^{\frac{1}{2}},
\]

or

\[
\left( \frac{\overline{u^2}}{a} \right)^{\frac{1}{2}} = 0.22 \ r \quad \ldots \quad \ldots \quad (3.8)
\]
where \( \frac{(u^2)_m}{(u^2)} \) is the mean square amplitude of vibration at the melting point. Thus

\[
\frac{\frac{u^2}{(u^2)_m}}{T} = \frac{T}{T_m}
\]

Thus the physical quantities such as electrical resistance, specific heat, thermal expansion, elastic constants, thermal conductivity etc. which depend on atomic vibrations, should show similar variation with reduced temperature.

If a thermal property is denoted by a parameter \( \xi \), then:

\[
\frac{\xi}{\xi_{m/2}} = f \left( \frac{T}{T_m} \right)
\]

(The value of \( \xi_{m/2} \), i.e., at \( T = \frac{1}{2} T_m \), has been used as the value at the melting point may be influenced by other factors.)

Catz (1955) has shown that the plot of the reduced thermal expansion \( \xi / \xi_{m/2} \) and the reduced temperature \( T/T_m \) for cubic metals is a straight line in
the range \(0.2 < T/T_m < 0.7\) and is given by:

\[
\frac{\lambda}{\lambda_{n/2}} = 0.74 + 0.52 \left(\frac{T}{T_m}\right) \quad \ldots \quad (4.1)
\]

Now

\[
T_m = \text{constant} \times T_C \quad \ldots \quad (4.2)
\]

where \(T_C\) is the critical temperature of the solid. Thus a "law of corresponding states" holds for these cubic solids, where eq. (4.0) is the "reduced equation of state".