CHAPTER VI

DISCUSSION OF THE RESULTS

Equations giving the variation of the lattice constants with temperature of the various alkali halides are presented in this chapter. The equations were obtained with the help of an IBM 1620 computer. It was found that a single equation could not cover the entire $a_t$ versus $t$ curve. In all cases it was necessary to form two equations—one applicable from room temperature to approximately the temperature corresponding to the 'knee' of the electrical conductivity versus $1/T$ plot, and the other for higher temperatures.

The values of the thermal expansion of the various alkali halides obtained in this investigation are compared with those of other workers. The role of lattice defects in the thermal expansion is discussed. The "law of corresponding states" is examined and conclusions are derived. A relation between the energy of formation of Schottky defects and the melting temperature is derived probably for the first time and agrees with the empirical relation given by Barr and Lidiard (1969).
The equations representing the temperature variation of the cell constant $a_t$ were found as follows:

(1) From 0 to $550^\circ$C

$$a_t = 5.6233 + 2.2393 \times 10^{-4} t + 7.692 \times 10^{-8} t^2$$
$$+ 2.281 \times 10^{-11} t^3 \quad \ldots \quad \ldots \quad (43)$$

(11) From 500 to $765^\circ$C

$$a_t = 5.7576 + 3.3147 \times 10^{-4} (t-500) - 2.870 \times 10^{-8}$$
$$\quad (t-500)^2 + 5.140 \times 10^{-10} (t-500)^3 \quad \ldots \quad (44)$$

NaCl has been investigated by many authors. Some of the results are given in table II. Author's room temperature value agrees excellently with those of other workers. At high temperatures, author's values are in good agreement with those of Enck and Dommel (1965) but vary considerably from those of Bucken and Dannöhl (1934) and Pathak and Pandya (1959). The former values are much higher while the later are lower. The lower values of Pathak and Pandya at high temperatures are probably due to the fact that they tried to fit a single equation to the entire $a_t$ versus $t$ curve. The $\alpha$ values are very sensitive to the constants of the $a_t$ vs. $t$ equation.
The equations representing the temperature variation of $a_t$ are as follows:

(i) From 0 to 750°C

$$a_t = 6.295 + 1.5432 	imes 10^{-4} t + 5.727 	imes 10^{-8} t^2$$
$$+ 6.35 	imes 10^{-12} t^3$$

(ii) From 700 to 930°C

$$a_t = 4.7677 + 2.4460 	imes 10^{-4} (t-700) + 7.363 	imes 10^{-8}$$
$$+ (t-700)^2 + 2.236 	imes 10^{-10} (t-700)^3$$

The only systematic investigations of this salt are those due to Deshpande (1961) and Pathak, Pandya and Ghadiali (1963). Deshpande has obtained values of $a_t$ only up to 250°C while Pathak et al have extended the observations up to 600°C. The values of $a_t$ between 600 & 930°C are probably determined for the first time. The comparative values are shown in table IV. The room temperature values agree well but author's values at high temperatures tend to be higher. The reason for the low values of $a_t$ presented by Pathak et al (1963) is probably the same as that given in the case of NaCl.
The equations showing variation of $a_t$ with temperature were found as follows:

(i) From 0 to 550°C

$$a_t = 6.2861 + 2.2753 \times 10^{-4} t + 1.9693 \times 10^{-7} t^2$$

(ii) From 500 to 750°C

$$a_t = 6.4265 + 3.4695 \times 10^{-4} (t-500) - 3.470 \times 10^{-8} (t-500)^2 + 6.678 \times 10^{-10} (t-500)^3$$

This salt appears to be very popular with the workers in this field and several investigations are reported in literature. Author's values are compared with those of other workers in table VI. Author's room temperature value agrees well with that of Inck et al but is considerably higher than that given by Lucken and Dannöhl (1934). Author's values show excellent agreement with those determined by Leadbetter and Newsham (1969) with their precision immersion method. At high temperatures the values of Inck et al are found to be lower.
CsCl

This salt is investigated by the author up to the temperature of transition which is found to be 470°C in the present investigation. The temperature variation of $a_t$ was found to obey the following equation:

From 0 to 453°C

$$a_t = 4.1172 + 1.942 \times 10^{-4} t + 7.695 \times 10^{-8} t^2$$

$$+ 1.76 \times 10^{-11} t^3 \quad \ldots \quad \ldots \quad (4.1)$$

The systematic investigations of this salt are few. The comparative results are shown in table VIII. Author's results are found to agree excellently with those of Menary et al (1951) especially beyond 150°C. The values of Pathak and Pandya are consistently lower (Private communication).

CsBr

The temperature variation of $a_t$ was found to obey the following equations:

(1) From 0 to 450°C

$$a_t = 4.2931 + 1.958 \times 10^{-4} t + 9.435 \times 10^{-8} t^2 \quad \ldots \quad (5.0)$$

(ii) From 425 to 600°C
\[ a_t = 4.3933 + 2.7461 \times 10^{-4}(t-425) + 1.120 \times 10^{-7} \]
\[ (t-425)^2 + 4.315 \times 10^{-10}(t-425)^3 \] 

The comparative values of \( \alpha \) determined by other workers are shown in Table X. Krishnan and Srinivasan have investigated this salt up to 300°C with their interference method and their values are in reasonable agreement with those of present study. The room temperature value of Johnson, Agron and Bredig (1955) appears to be too low and appears definitely in error. Their values are also found to increase rapidly between room temperature and 300°C. The values of Pathak and Pandya (1960) are in good agreement with the present values up to about 400°C but differ considerably at higher temperatures.

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The variation of \( a_t \) with temperature is found to follow the equations:

(i) From 0 to 500°C
\[ a_t = 6.5637 + 2.3564 \times 10^{-4}t + 7.210 \times 10^{-8}t^2 \]
\[ + 4.19 \times 10^{-11}t^3 \] 

\[ (5.4) \]

(ii) From 450 to 700°C
There is hardly any work done on this salt. The only investigation is due to Deshpande and Sirdeshmukh (1961) up to 193°C. They find that the lattice expands linearly with temperature and their value of the mean coefficient $\alpha$ between 20-190°C is $38.13 \times 10^{-6} (^\circ \text{C}^{-1})$ which is in reasonable agreement with value obtained in this study. The old value of Baxter and Wallace (1916) between 25-50°C viz $27.33 \times 10^{-6} (^\circ \text{C}^{-1})$ is too low.

**LIF**

The variation of $a_t$ with temperature was found to obey the following equations:

1. From 0 to 625°C
   
   $a_t = 6.6381 + 3.3434 \times 10^{-4}(t-450) + 1.40 \times 10^{-9}$
   \[ (t-450)^2 + 6.945 \times 10^{-10}(t-450)^3 \]  
   (53)

2. From 575 to 850°C
   
   $a_t = 4.1096 + 2.1595 \times 10^{-4}(t-575) + 3.400 \times 10^{-9}$
   \[ (t-575)^2 + 3.204 \times 10^{-10}(t-575)^3 \]  
   (55)

This salt has been investigated by different workers but the agreement among their values is rather poor as can be seen from table XIV. The values of Eucken
and Dannöhl (1934) increase very rapidly with temperature compared with author's values while those of Sharma (1950) increase even more rapidly. No values are available for comparison beyond 700°C. X-ray data on this salt are presented probably for the first time.

The thermal expansion of all the salts investigated in the present investigation was found to consist of two parts - a normal part and an anomalous part (Ref. Chapter III). It is assumed that the defects do not play any significant role below the temperature corresponding to the 'knee' of the electrical conductivity versus 1/T plot. Thus it is assumed that eqs. (43), (45), (47), (50), (52) and (54) etc. represent expansion of crystals without defects and hold up to the melting point and that any deviation $\Delta \alpha$ from them are due to defects (fig. 15). The plots of $\log \Delta \alpha$ versus 1/T for all the salts are given in figures 28 to 33. The energies of formation, $W_g$, of the Schottky defects, determined from the slopes, are given in table XVI and compared with experimental and theoretical values.

In the present investigation, CsCl was included to see if vacancies in appreciable number to influence thermal expansion were created near the temperature of transition ($\sim 470°C$) from bcc to fcc form. Since the $\alpha - t$
Fig. 28: Logarithm of excess expansion of NaCl versus reciprocal of temperature.

Fig. 29: Logarithm of excess expansion of NaF versus reciprocal of temperature.
Fig. 30: Logarithm of excess expansion of KCl versus reciprocal of temperature.

Fig. 31: Logarithm of excess expansion of CsBr versus reciprocal of temperature.
Fig. 32: Logarithm of excess expansion of RbCl versus reciprocal of temperature.

Fig. 33: Logarithm of excess expansion of LiF versus reciprocal of temperature.
TABLE XVI  

<table>
<thead>
<tr>
<th>Substance</th>
<th>$h_s$ (ev)</th>
<th>$W_s$ (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIF</td>
<td>2.42</td>
<td>2.34–2.68$^{a,b,c}$ (Exp.)</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.19</td>
<td>2.17$^d$   (Exp.)</td>
</tr>
<tr>
<td>NaF</td>
<td>2.42</td>
<td>2.52$^e$   (Theo.)</td>
</tr>
<tr>
<td>KCl</td>
<td>2.24</td>
<td>2.26$^f$   (Exp.)</td>
</tr>
<tr>
<td>RbCl</td>
<td>2.06</td>
<td>1.98$^g$   (Theo.)</td>
</tr>
<tr>
<td>CsBr</td>
<td>1.74</td>
<td>2.0$^g$    (Exp.)</td>
</tr>
</tbody>
</table>

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- $^a$ Haven (1950);
- $^b$ Barsis et al. (1967);
- $^c$ Stoebe and Praat (1967);
- $^d$ Allnatt and Pantelis (1968);
- $^e$ Boswarva and Lidiard (1967);
- $^f$ Beaumont and Jacobs (1966);
- $^g$ Boswarva (1967).
curve is practically linear, this is not found to be the case. This substantiates the conclusion of Moodless and Morrison (1962) who measured the diffusion of Cl\textsuperscript{−} and the electrical conductivity of CsCl crystals over the temperature range 230°C to 500°C.

Cartz (1955) showed that the plot of the reduced expansion $\alpha / \alpha_{m/2}$ versus $T/T_m$ for cubic metals is a straight line in the range $0.2 < T/T_m < 0.7$ and is given by:

$$\frac{\alpha}{\alpha_{m/2}} = 0.74 + 0.52 \left(\frac{T}{T_m}\right)$$

($T_m$ is the melting point and $\alpha_{m/2}$ is the coefficient of thermal expansion at $T = \frac{1}{2} T_m$.)

In view of the present accurate determinations it was thought to be of interest to draw the curve between $\alpha / \alpha_{m/2}$ and $T/T_m$ in the case of the alkali halides investigated in this thesis. This curve is shown in fig. 24. (The full curve with the points for all alkali halides is shown in fig. 35.) It was found that the curve is linear only in the range $0.30 < T/T_m < 0.65$ and is given by

$$\frac{\alpha}{\alpha_{m/2}} = 0.65 + 0.70 \left(\frac{T}{T_m}\right)$$

Beyond about $0.63(T/T_m)$ the curve deviates.
Fig. 34: Plot of reduced expansion $\alpha/\alpha_{m/2}$ versus reduced temperature $T/T_m$. $T_m$ is the melting temperature (°K) and $\alpha_{m/2}$ is the value of $\alpha$ at $T = \frac{1}{2}T_m + \text{NaCl}$, ○ KCl, Leadbetter & Newsham (1969); ■ CsBr, Krishnan & Srinivasan (1956); □ NaCl, ▽ KCl, △ CsBr, author
considerably from linearity although the points corresponding to all the alkali halides fall approximately on a common curve shown in full line.

Assuming that the law of corresponding states as given by eq. (57) holds up to the melting point and that the deviation $\Delta (\propto/\propto m/2)$ from linearity is due to vacancies, it is possible to estimate the energy of formation $W_s$ of a Schottky pair. Since thermally generated defects are randomly distributed in a crystal and since $n/N$, the defect concentration, is only of the order of $10^{-1}$ even at the melting point, we can expect a linear relationship $\Delta \propto = \beta \propto$ where $\beta$ is a constant.

Fig. 36 shows the plot between the reduced quantities log$_e$ $\Delta (\propto/\propto m/2)$ and $T_m/T$. This graph should be common to all the alkali halides. The slope of the line was found to be 11.91 and the intercept on the y-axis 10.70 so that we have

$$\log_e \Delta \left(\frac{\propto}{m/2}\right) = 10.70 - 11.91 \left(\frac{T_m}{T}\right) \quad \ldots \quad (S^?)$$

or $$\log_e \Delta \propto = (10.70 + \log_e \propto m/2) - 11.91 \left(\frac{T_m}{T}\right) \quad \ldots \quad (S^?)$$

Thus the slope of the graph between log$_e$ $\Delta \propto$ and $1/T$ for any alkali halide should be 11.91 $T_m$. Since under
the present circumstances, \( \zeta \) should be proportional to

\[ e^{-W_g/2kT} \]

we should have

\[ 11.91 \ T_m = \frac{W_g}{2k} \]

or

\[ W_g = 23.32 \ kT_m \]

\( \text{eq. (61)} \)

If \( W_g \) is expressed in \( \text{eV} \), we have

\[ W_g(\text{eV}) = 2.05 \times 10^{-3} \ T_m \] \( \text{eq. (61)} \)

which is in excellent agreement with the empirical relation

\[ W_g = 2.14 \times 10^{-3} \ T_m \]

given by Barr and Lidiard (1969).

The values of \( W_g \) calculated from eq. (61) for various alkali halides are given in tables XVII and XVIII and compared with the experimental values where available. Column III, table XVIII, gives the nearest theoretical values of \( W_g \) calculated by Boswarva and Lidiard (1967), while column IV gives those calculated by Rao and Rao (1968) employing a modified Born model with a higher Van der Waals term.

**Conclusion:**

In all the alkali halides investigated here, it
## Table XVII

Comparison of $W_g$ Values from eq.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$W_g$ (eq)</th>
<th>$W_g$ (exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>2.35</td>
<td>2.34 - 2.68$^a,b,c$</td>
</tr>
<tr>
<td>LiCl</td>
<td>1.82</td>
<td>2.12$^d$</td>
</tr>
<tr>
<td>LiBr</td>
<td>1.68</td>
<td>1.80$^d$</td>
</tr>
<tr>
<td>LiI</td>
<td>1.47</td>
<td>1.34$^d$</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.20</td>
<td>2.17$^e$</td>
</tr>
<tr>
<td>NaBr</td>
<td>2.11</td>
<td>1.68$^d$</td>
</tr>
<tr>
<td>KCl</td>
<td>2.15</td>
<td>2.26$^f$</td>
</tr>
<tr>
<td>KBr</td>
<td>2.06</td>
<td>2.53$^d$</td>
</tr>
<tr>
<td>CsBr</td>
<td>1.85</td>
<td>2.0$^g$</td>
</tr>
<tr>
<td>CsI</td>
<td>1.83</td>
<td>1.9$^g$</td>
</tr>
</tbody>
</table>

$^a$ Haven (1950);  
$^b$ Barsis et al. (1967);  
$^c$ Stoebbe and Praat (1967);  
$^d$ Boswarva and Lidiard (1967);  
$^e$ Allnatt and Pantelis (1968);  
$^f$ Beaumont and Jacobs (1966);  
$^g$ Boswarva (1967).
### TABLE XVIII

**Comparison of \( W_s \) Values from eq. (61) with those of other workers**

<table>
<thead>
<tr>
<th>Substance</th>
<th>( W_s ) (ev)</th>
<th>( W_s ) (ev)</th>
<th>( W_s ) (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(equation 61)</td>
<td>(Theoretical)</td>
<td>(Theoretical)</td>
</tr>
<tr>
<td>NaF</td>
<td>2.59</td>
<td>2.517</td>
<td></td>
</tr>
<tr>
<td>NaI</td>
<td>1.90</td>
<td>1.603</td>
<td></td>
</tr>
<tr>
<td>KF</td>
<td>2.37</td>
<td>2.419</td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td>2.64</td>
<td>1.924</td>
<td>1.87</td>
</tr>
<tr>
<td>RbF</td>
<td>2.12</td>
<td>2.138</td>
<td></td>
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<tr>
<td>RbCl</td>
<td>2.03</td>
<td>1.998</td>
<td>2.17</td>
</tr>
<tr>
<td>RbBr</td>
<td>1.96</td>
<td>1.979</td>
<td>1.99</td>
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<tr>
<td>RbI</td>
<td>1.88</td>
<td>1.900</td>
<td>1.88</td>
</tr>
<tr>
<td>CsF</td>
<td>1.96</td>
<td>1.954</td>
<td></td>
</tr>
<tr>
<td>CsCl</td>
<td>1.89</td>
<td>1.734</td>
<td>1.06 (CsCl)</td>
</tr>
</tbody>
</table>

- \( a \) Boswarva and Lidiard (1967);  
- \( b \) Boswarva (1967);  
- \( c \) Rao and Rao (1968).
has been found that the deviation $\Delta \alpha$ at high temperatures increases exponentially according to the relation

$$\Delta \alpha = A e^{-U/kT}$$

where $A$ is a constant. The energy $U$ has been identified with the activation energy for a vacancy. The values of $U$ for the different halides, obtained in this investigation, agree closely with the experimental and theoretical values of different workers. It has also been found that the plot of the reduced expansion $\alpha / \alpha_m$ against the reduced temperature $T/T_m$ gives a common curve for all the alkali halides. The deviations $\Delta (\alpha / \alpha_m)$ for this curve are also found to increase exponentially. Using this fact, a common equation for the alkali halides connecting the energy of formation of a Schottky pair and the melting temperature is derived (probably for the first time) and is found to agree excellently with the empirical relation given by Barr and Lidiard (1969). The results of this investigation show that the thermal expansion of alkali halides is intimately associated with the creation of Schottky defects. A more detailed study of this phenomenon, especially at high temperatures, may lead to a better understanding of the thermal expansion of solids.