

THERMAL EXPANSION OF SOME ALKALI HALIDES BY X-RAY DIFFRACTION

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ABSTRACT In this paper the X-ray data on the thermal expansion of KBr, KI and CsBr upto their melting points is reported for the first time. The contribution of lattice defects to the thermal expansion is discussed. The applicability of the Debye-Grüneisen theory to explain the variation of thermal expansion with temperature is examined. An explanation of the difference in the observed values by the X-ray and the macroscopic methods is given, and an application of it to obtain a quantitative measure of the Schottky defects is indicated.

INTRODUCTION

In the field of solids, the study of the alkali halides has provided us with a number of most interesting properties. But when the literature about the variation of lattice constants with temperature by X-ray method is examined, we find that the crystals are not studied as a group. Scattered data are available on lattice constant variation (and hence on thermal expansion variation) with temperature, in some cases up to the melting point and in others within a limited range of temperature.

Reliable data on KBr and KI especially at high temperature are not available. Gott (1942) studied these salts between 20°C and 190°C but the X-ray expansion values obtained by him differ by about 5 per cent in the case of KBr and about 15 per cent in the case of KI from his values determined by the macroscopic methods, thus indicating a large concentration of defects (especially in KI). Connell and Martin (1951) repeated the observations under identical conditions and found their X-ray values agreeing closely with the macroscopic values of Gott.

The only X-ray data available so far up to the melting point of CsBr is that of Johnson, Agron and Breeding (1955). But their value of α at 25°C is about 20 per cent lower than that of Krishnan and Srinivasan (1950) obtained by precision interferometric method.

The present measurements were, therefore, undertaken (i) to provide accurate

X-ray data on the thermal expansion of KBr, KI and CsBr by employing a diffractometer, Geiger counter, ratemeter and an automatic chart recorder, (ii) to study the role of lattice defects on the thermal expansion and (iii) to examine the validity of the Debye-Grüneisen equations.

The diffractometer disc had a diameter of 500 mm. and was calibrated in degrees (2θ , each degree divided into four parts). The Geiger counter could be moved over the graduated scale either by means of a spherometer (whose disc had a diameter of about 70 mm.) or by a synchronous motor. The disc of the spherometer carried graduations so that readings of the counter positions could be read up to 1 minute of arc and by estimation up to $\frac{1}{2}$ minute.

OBSERVATIONS AND RESULTS

A special small furnace (Pathak and Pandya, 1959) which was fitted to the centre of the diffractometer was constructed in the laboratory. The temperatures were measured by a platinum-platinum plus 10% rhodium thermocouple. The furnace was calibrated by observing the meltings of (i) acetamide (115°C), (ii) NaNO_3 (310°C), (iii) $\text{K}_2\text{Cr}_2\text{O}_7$ (400°C), (iv) CsCl (616°C), (v) KCl (790°C) and NaCl (800°C). The results on NaCl (Pathak and Pandya, 1959) and CsI (Pathak and Pandya, 1960) obtained by using the furnace have already been reported. Since the earlier results agreed with those of the most reliable workers, it was decided to extend the observations to other alkali halides. The results now obtained are given in Table I.

TABLE I

KBr		KI		CsBr	
Temperature degree C	Cell constant a_f Å	Temperature degree C	Cell constant a_f Å	Temperature degree C	Cell constant a_f Å
30	6.579	28	7.052	31	4.292
72	6.589	78	7.066	81	4.303
110	6.601	118	7.081	120	4.312
170	6.618	159	7.092	182	4.327
226	6.631	204	7.105	263	4.346
281	6.652	261	7.125	295	4.353
350	6.670	320	7.143	340	4.364
415	6.686	376	7.160	368	4.371
497	6.714	432	7.182	389	4.376
553	6.732	495	7.204	442	4.391
611	6.753	542	7.224	495	4.407
		601	7.244	540	4.422
				601	4.445

TABLE II

KBr		KI		CaBr	
Temperature degree C	$\alpha \times 10^6$	Temperature degree C	$\alpha \times 10^6$	Temperature degree C	$\alpha \times 10^6$
30	38.6	28	40.4	31	47.8
72	39.4	78	41.6	81	50.0
110	40.0	118	42.5	120	51.6
170	41.1	159	43.4	182	54.1
226	42.2	204	44.5	263	57.3
281	43.1	261	45.7	295	58.6
350	44.3	320	47.1	340	60.4
415	45.5	376	48.4	368	61.4
497	46.9	432	49.6	389	62.3
553	48.0	495	50.0	442	64.4
611	48.9	542	51.9	495	66.4
		601	53.2	540	68.1
				601	70.3

TABLE III

Substance	Temperature range °C	$\alpha \times 10^6$			
		Connell band Martin (X-ray values)	Gott (X-ray values)	Gott (Macro- scopic values)	Authors' (X-ray values)
KBr	18-100	40.5	38.8	40.8	39.2
	18-190	41.7	40.5	41.4	40.0
KI	20-100	40.6	37.2	40.8	41.2
	20-190	42.1	36.1	42.7	42.4

TABLE IV
Caesium bromide

Temperature degree C	$\alpha \times 10^6$		
	Authors' (X-ray values)	Krishnan & Srinivasan (Macroscopic values)	Johnson <i>et al.</i> (X-ray values)
0	46.6	46.6	37.2
31	47.8	48.0	39.5
81	50.0	50.3	43.0
120	51.6	51.9	45.7
182	54.1	54.5	50.0
263	57.3	57.6	55.5
295	58.6	58.7	57.7
340	60.4		60.8
368	61.4		62.7
389	62.3		64.1
442	64.4		67.6
495	66.4		71.0
540	68.1		74.0
601	70.3		77.8

The equations satisfying the smooth curves drawn from the observed points are given below.

$$\text{KBr} \quad -\alpha_t = 6.5725 + 2.499 \times 10^{-4}t + 6.557 \times 10^{-8}t^2.$$

$$\text{KI} \quad -\alpha_t = 7.0436 + 2.801 \times 10^{-4}t + 8.780 \times 10^{-8}t^2$$

$$\text{CsBr} \quad -\alpha_t = 4.2870 + 1.998 \times 10^{-4}t + 9.378 \times 10^{-8}t^2$$

The coefficient of thermal expansion α was calculated from the equation $\alpha = \frac{1}{\alpha_t} \cdot \frac{d\alpha_t}{dt}$. The values of α thus obtained for the three salts are given in Table II.

II. Our results are compared with those of the earlier workers in Table III and IV.

The satisfactory agreement between our values and those of Connell and Martin as well as with the macroscopic values of Gott at comparatively low temperatures indicates not too large a concentration of the migrated defects at the surface at these temperatures. (vide section 4)

It can be seen from Table IV that our results with CsBr agree quite satisfactorily with those of Krishnan and Simivasan but disagree widely with those of Johnson *et al*

DEBYE GRUNEISEN EQUATIONS

Debye-Grüneisen theory gives (Roberts, 1951)

$$\frac{V_T - V_0}{K_0} \left\{ 1 - \frac{n+m+1}{2} \frac{V_T - V_0}{V_0} \right\} = \gamma E \quad \dots (1)$$

In this equation V_T and V_0 are the volumes of the crystal at $T^\circ K$ and $0^\circ K$ respectively, K_0 the compressibility at $0^\circ K$, E the vibrational energy of the crystal, γ the Grüneisen constant and m and n are constants obtained from the potential energy of the crystal,

$$W(V_0) = \frac{A}{V_0^n} + \frac{B}{V_0^m} \quad \dots (2)$$

The thermal expansion of a solid is always small so that $\frac{n+m+1}{2} \frac{V_T - V_0}{V_0}$ is small compared with unity. Neglecting it the Eq. (1) can be written as

$$V_T - V_0 = \gamma K_0 E \quad \dots (3)$$

Dividing both sides of the equation (1) by V_0 and transposing we obtain

$$\frac{V_T - V_0}{V_0} = \frac{\gamma E K_0 / V_0}{\left\{ 1 - \frac{n+m+1}{2} \frac{V_T - V_0}{V_0} \right\}} \quad \dots (4)$$

Writing $Q = V_0/\gamma K_0$ and $p = \frac{n+m+1}{2}$ in equation (4) we get

$$\frac{V_T - V_0}{V_0} = \frac{E/Q}{\left\{ 1 - p \cdot \frac{V_T - V_0}{V_0} \right\}} \quad \dots (5)$$

Substituting for $V_T - V_0$ in the small correction term from Eq. (3), Eq. (5) becomes

$$\frac{V_T - V_0}{V_0} = \frac{E/Q}{1 - p \cdot E/Q} \quad \dots (6)$$

Remembering that

$$\frac{V_T - V_0}{V_0} = 3 \cdot \frac{a_T - a_0}{a_0}$$

where a_T and a_0 are the lattice constants at $T^\circ K$ and $0^\circ K$ respectively. Eq. (6) can be written as

$$3 \cdot \frac{a_T - a_0}{a_0} = \frac{V_T - V_0}{V_0} = \frac{E/Q}{\rho \cdot D(\theta/T)} \quad \dots (7)$$

In the case of alkali halides, E the vibrational energy is given by $E = 6RT \cdot D(\theta/T)$. Putting this value of E in Eq. (7) and transposing we get

$$\frac{a_T - a_0}{a_0} = \frac{Q}{2R} \cdot \frac{1}{T \cdot D(\theta/T)} = 3\rho \quad \dots (8)$$

This equation shows that the graph of $\frac{a_T - a_0}{a_0}$ against $\frac{1}{T \cdot D(\theta/T)}$ should be a straight line. If for a given crystal the above graph is really a straight line, we can (i) show that the substance obeys Gruneisen's law and (ii) determine the Gruneisen's parameters $Q/2R$ and 3ρ from the graph.

The value of a_0 can be estimated from the low temperature approximation to Eq. (7)

$$\begin{aligned} 3 \cdot \frac{a_{273} - a_0}{a_0} &\approx \left(\frac{E}{Q} \right)_{273} \approx \left(\frac{3\alpha E}{C_v} \right)_{273} \\ &= \frac{3\alpha_{273} \cdot 273 \cdot D(\theta/273)}{C_v(\theta/273)} \end{aligned}$$

where $C_v(\theta/273)$ is the specific heat function and $\frac{C_v}{3\alpha} = Q = \text{constant}$ for low temperatures.

In the case of alkali halides investigated in the present experiments the graphs of $\frac{a_T - a_0}{a_0}$ against $\frac{1}{T \cdot D(\theta/T)}$ are straight lines, as predicted by the Gruneisen theory. The Gruneisen's parameters $Q/2R$ and 3ρ , therefore, assume great importance. The parameters determined from the above graphs for the different halides are compiled in Table V. The values of these parameters for CsBr calculated from the X-ray measurements of Johnson *et al.*, are given for comparison.

TABLE V
Grüneisen parameters

Substance	$(Q/2R) \times 10^3$	β_p	Reference
KBr	28.81	7.25	Present values
	28.60	—	Eq. 9
KI	27.12	6.50	Present values
	25.20	—	Eq. 9
CsBr	23.56	7.25	Present values
	27.10	10.80	Johnson <i>et al.</i> (1955)
	23.20	—	Eq. 9 \mathcal{L}

The value of Q can also be obtained from the relation

$$Q = \frac{V_0}{\gamma \cdot K_0} \quad \dots (9)$$

where K_0 and V_0 are the compressibility and molar volume at 0°K. The values of $Q/2R$ calculated from this equation are also given in Table V, the values of V_0 , γ and K_0 being taken from Born and Huang (1954).

ROLE OF LATTICE DEFECTS IN THE EXPANSION OF IONIC CRYSTALS

The fact that the ionic crystals conduct an electrolytic current which obeys Ohm's law at high temperatures shows that these crystals possess imperfections at elevated temperatures. It has been found that the ionic conductivity increases as the temperature increases showing that the concentration of the defects increases with temperature. Schottky (1935) and Jost (1933-37) have shown that it is exceedingly unlikely that interstitial ions occur in any appreciable quantity in alkali halides. Mott and Littleton (1938) have refined the calculations and have shown in the case of Sodium chloride, for example, that the energy required to take a 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 very much less than the number of vacancies indicating that in alkali halides the Frankel defects are practically absent while the Schottky defects predominate.

As the temperature increases more and more ion pairs which were forming the part of the Schottky defects migrate to the surface. At the surface these ions are not surrounded by the bulk of the lattice and they cease to be defects. Now they could be reasonably expected to behave as fresh ions which are

deposited on the surface of an ionic crystal, forming the same structure as the bulk of the crystal. This happens because the ions are of the same type as constitute the crystal. These fresh deposits will increase the total volume of the crystal but will not modify the cell size. The cell size will alone be measured in the X-ray pictures, while in the macroscopic measurement of volume we measure the total volume (due to thermal expansion of the cell and that due to the surface deposits).

We are thus led to believe that the difference in the measured values of α by the X-ray and the macroscopic methods may be due to the fresh deposits at the surface due to the migration of the ions forming the Schottky defects. If this is correct we could expect the divergence in the two values to increase with the temperature. It thus appears plausible that we could estimate the degree and the extent of the migration of the defects by carrying out accurate measurements of α by the X-ray and the macroscopic methods. This work has been started by us and appears hopeful.

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