Acta Cryst. (1970). A**26**, 655

Thermal Expansion of NaCl, KCl and CsBr by X-ray Diffraction and the Law of Corresponding States

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(*Received* 5 *January* 1970)

The coefficients of thermal expansion of NaCl, KCl and CsBr are determined accurately at different temperatures using a diffractometer, Geiger counter, chart recorder and a specially designed furnace. Equations are given for the variation of the lattice constants with temperature. The temperature dependence of the thermal expansion at high temperatures is shown to be related to the concentration of thermally generated Schottky defects. The energies of formation of Schottky pairs in the three halides are estimated and are found to be consistent with those deduced from ionic conductivity studies. The reduced parameters $\alpha/(\alpha)_{M/2}$ and T/T_M give a common curve for all the halides, T_M being the melting point and $(\alpha)_{M/2}$ the value of α at $T=\frac{1}{2}T_M$. The curve is a straight line in the limits $\sim 0{\cdot}30 < T/T_M < \sim 0{\cdot}65$ and is found to deviate considerably at higher temperatures. Assuming that the deviation is due to defects, the energies of formation of Schottky defects for the varies halides of Li, Na, K, Rb and Cs are estimated and found to agree excellently with the experimental and theoretical values.

Introduction

The thermal expansion of NaCl, KCl and CsBr has been investigated by many workers both by the X-ray and macroscopic methods, notably by Eucken & Dannöhl (1934), Basu & Maitra (1938), Enck, Engle & Marks (1962), Enck & Dommel (1965), Srinivasan (1955), Glover (1954), Krishnan & Srinivasan (1958), Johnson, Argon & Bradig (1955), Leadbetter & Newsham (1969) and Pathak & Pandya (1959, 1960).

On examination of the results of the various workers it is found that although the results agree at lower temperatures, there are wide discrepancies at higher temperatures. This can be seen from Tables 1, 2 and 3.

One of the aims of the present experiments was, therefore, to determine accurate values of the thermal expansion of these salts especially at high temperatures.

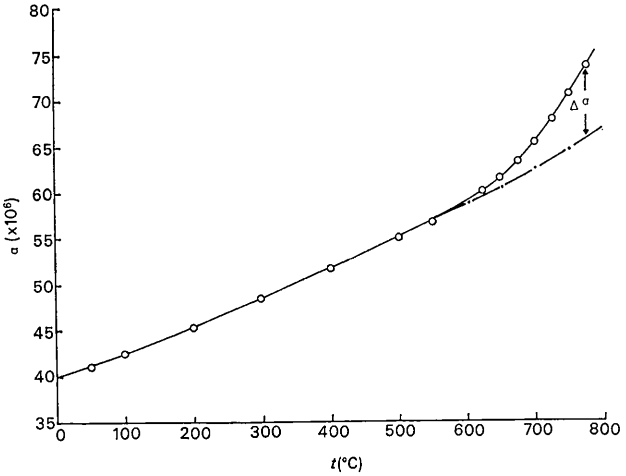

Fig. 1. Plot of coefficient of linear expansion of NaCl *versus* temperature.

Experimental

One of the principal causes of the wide discrepancies in the values of the thermal expansion at high temperatures, especially in X-ray determinations with a diffractometer, is the large temperature gradient which may exist in the powder sample, *e.g.* when it rests on a hot metallic surface. A special furnace (Pathak & Vasavada, 1969) was, therefore, constructed in which there was a reasonably large volume of uniform temperature. The furnace was placed at the centre of a horizontal diffractometer (Seifert) having a diameter of 500 mm. The X-ray lines were detected by Geiger counter and recorded on a chart recorder. The diffractometer had various speeds ranging from $\frac{1}{2}$ to 30 min.deg^{-1} (2θ). The salts were obtained either from Merck or B.D.H. The accuracy of the results is estimated to be about $\frac{1}{2}$%.

Results and discussion

The lattice constants of the different salts were found to vary with temperature according to the following equations. The equations were obtained with the help of an IBM 1620 computer.

NaCl:

From 0 to 550 °C,

$$a_t = 5{\cdot}6238 + 2{\cdot}2393 \times 10^{-4}t + 7{\cdot}692 \times 10^{-8}t^2 + 2{\cdot}281 \times 10^{-11}t^3; \quad (1)$$

from 500 to 765 °C,

$$a_t = 5{\cdot}7576 + 3{\cdot}3147 \times 10^{-4}(t-500) - 2{\cdot}870 \times 10^{-8}(t-500)^2 + 5{\cdot}140 \times 10^{-11}(t-500)^3. \quad (2)$$

KCl:

From 0 to 550 °C,

$$a_t = 6{\cdot}2861 + 2{\cdot}2753 \times 10^{-4}t + 1{\cdot}0693 \times 10^{-7}t^2; \quad (3)$$

from 500 to 750 °C,

$$a_t = 6{\cdot}4265 + 3{\cdot}4695 \times 10^{-4}(t-500) - 3{\cdot}470 \times 10^{-8}(t-500)^2 + 6{\cdot}678 \times 10^{-10}(t-500)^3 . \quad (4)$$

CsBr:

From 0 to 450 °C,

$$a_t = 4{\cdot}2931 + 1{\cdot}958 \times 10^{-4}t + 9{\cdot}435 \times 10^{-8}t^2 ; \quad (5)$$

from 425 to 600 °C,

$$a_t = 4{\cdot}3933 + 2{\cdot}7461 \times 10^{-4}(t-425) + 1{\cdot}120 \times 10^{-7}(t-425)^2 + 4{\cdot}315 \times 10^{-10}(t-425)^3 . \quad (6)$$

The coefficients of linear expansion, defined by $\alpha = (1/a_t)(\mathrm{d}a_t/\mathrm{d}t)$, are given in Tables 1, 2 and 3 along with those determined by other workers.

Table 1. *Coefficients of linear expansion α of* NaCl

Temperature (°C)	α (× 10⁶) *a*	*b*	*c*	*d*	Authors
0	40·3	38·4		40·2	39·8
50	40·6	39·9	40·3	41·2	41·1
100	41·3	41·4	42·0	43·6	42·5
200	43·5	44·8	45·5	47·1	45·4
300	47·0	48·3	49·0	53·4	48·5
400	51·8	52·1	52·4	53·7	51·8
500	57·8	56·2	55·6	57·1	55·2
550	62·3	58·3	57·4	58·6	57·0
600	65·2	60·5	59·1	60·3	59·2
650	69·3	63·7	61·2	61·9	61·6
700	73·8	66·3	63·9	63·5	65·5
750	78·5	72·6		65·0	70·7
765					72·5

a Eucken & Dannöhl (1934); *b* Enck & Dommel (1965); *c* Leadbetter & Newsham (1969); *d* Pathak & Pandya (1959).

Table 2. *Coefficients of linear expansion α of* KCl

Temperature (°C)	α (× 10⁶) *a*	*b*	*c*	*d*	Authors
0	31·9	36·5		34·6	36·2
50	33·6	37·4	38·0	36·3	37·9
100	35·4	38·4	39·4	38·0	39·4
200	39·3	41·2	42·3	41·3	42·7
300	43·6	44·6	45·4	44·6	45·8
400	48·3	48·0	48·7	47·8	49·0
500	53·2	51·3	52·3	51·0	52·2
550	55·4	53·0	54·2	52·6	53·9
600	58·8	54·7	56·5	54·2	55·7
650	62·0	56·6	59·7		58·9
675	63·0	57·5	61·7		61·0
700	64·6	58·4			63·6
725					66·4
750					69·7

a Eucken & Dannöhl (1934); *b* Enck *et al.* (1962); *c* Leadbetter & Newsham (1969); *d* Glover (1954).

Table 3. *Coefficients of linear expansion α of* CsBr

Temperature (°C)	α (× 10⁶) *a*	*b*	*c*	Authors
0	46·6	37·3	46·6	45·6
50	48·9	40·8	48·6	47·7
100	51·1	44·3	50·6	49·8
200	55·2	51·2	54·7	53·9
300	59·0	58·1	58·8	57·9
400		64·8	62·8	61·8
450		68·0	64·6	63·8
500		71·4	66·6	67·6
550		74·5	68·5	72·8
600		77·7	70·2	79·5
625		79·4		

a Krishnan & Srinivasan (1956); *b* Johnson *et al.* (1955); *c* Pathak & Pandya (1960).

According to Grüneisen's theory the thermal expansion of these salts should be a slowly varying function of temperature especially above the Debye temperature and can be represented by

$$\alpha(T) = \alpha(T_0) + \left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{T=T_0}(T-T_0) + \Delta\alpha . \quad (7)$$

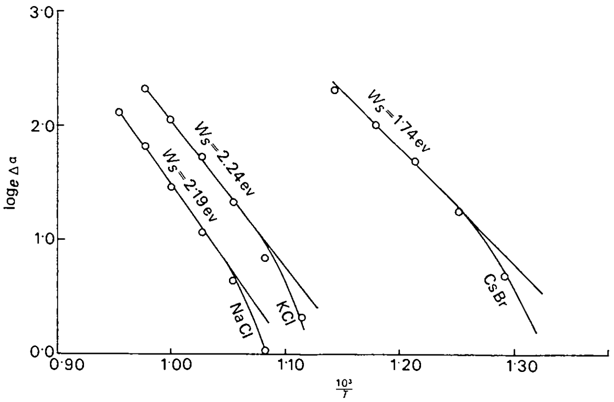

Fig. 2. Plots of logarithm of excess expansion *versus* reciprocal of temperature.

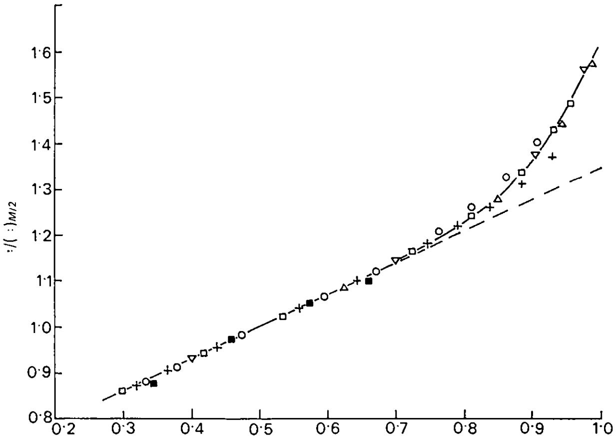

Fig. 3. Plot of reduced expansion $\alpha/\alpha_{M/2}$ *versus* reduced temperature T/T_M. T_M is the melting temperature (°K) and $\alpha_{M/2}$ is the value of α at $T = \frac{1}{2}T_M$. + NaCl, ○ KCl, Leadbetter & Newsham (1969); ■ CsBr, Krishnan & Srinivasan (1956); □ NaCl, ▽ KCl, △ CsBr, authors.

Here $\alpha(T)$ is the linear coefficient of thermal expansion at any temperature T between T_0 and the melting point and $\Delta\alpha$ is the 'anomalous' part of the expansion which may be due to the thermally generated defects at high temperatures. Merrium, Smoluchowski & Wiegand (1962) and Enck & Dommel (1965) have shown that the energy of vacancy formation can be deduced from the slope of the plot of log $\Delta\alpha$ *versus* $1/T$.

It is assumed in this paper that the defects do not play any significant role below the temperature corresponding to the 'knee' of the electrical conductivity *versus* $1/T$ plot. The 'knee' temperature for NaCl, KCl and CsBr are approximately 550, 575 and 450°C respectively. Thus it is assumed that equations (1), (3) and (5) hold up to the melting point and that any deviations $\Delta\alpha$ from them are due to defects (Fig. 1). The plots of log $\Delta\alpha$ *versus* $1/T$ for the three salts are shown in Fig. 2. The energies of formation, W_s, of the Schottky defects, determined from the slopes, are given in Table 4 and compared with the experimental values.

Table 4. W_s values

Salt	W_s (eV) (from Fig. 2)	W_s (eV) (experimental)
NaCl	2·19	2·12*
KCl	2·24	2·22*
CsBr	1·74	2·0†

* Boswarva & Lidiard (1967);
† Boswarva (1967).

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. The graph given by him between the reduced expansion $\alpha/(\alpha)_{M/2}$ and the reduced temperature T/T_M for cubic metals is a straight line in the range $\sim 0{\cdot}2 < T/T_M < \sim 0{\cdot}7$ and is given by

$$\frac{\alpha}{(\alpha)_{M/2}} = 0{\cdot}74 + 0{\cdot}52\left(\frac{T}{T_M}\right). \tag{8}$$

Here T_M is the melting point and $(\alpha)_{M/2}$ is the coefficient of thermal expansion at $T = \frac{1}{2}T_M$.

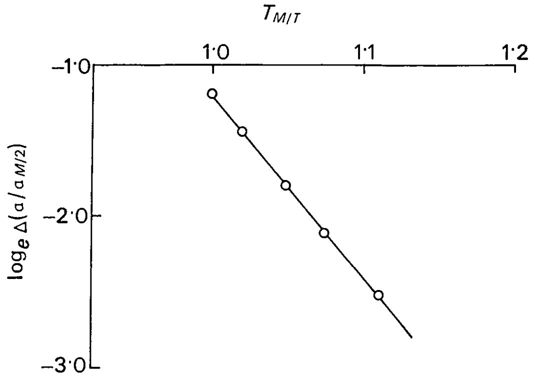

Fig. 4. Plot of logarithm of excess reduced expansion *versus* reciprocal of reduced temperature.

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 paper. This curve is shown in Fig. 3. It was found that the curve is linear only in the range $\sim 0{\cdot}30 < T/T_M < \sim 0{\cdot}65$ and is given by

$$\frac{\alpha}{(\alpha)_{M/2}} = 0{\cdot}65 + 0{\cdot}70\left(\frac{T}{T_M}\right). \tag{9}$$

Beyond about 0·65 (T/T_M) the curve deviates 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 equation (9) holds up to the melting point and that deviation $\Delta(\alpha/\alpha_{M/2})$ 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^{-4} even at the melting point, we can expect a linear relationship $\Delta\alpha = Cn$ where C is a constant.

Fig. 4 shows the plot between the reduced quantities $\log_e \Delta(\alpha/\alpha_{M/2})$ 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

$$\log_e \Delta \frac{\alpha}{\alpha_{M/2}} = 10{\cdot}70 - 11{\cdot}91 \frac{T_M}{T} \tag{10}$$

or

$$\log_e \Delta\alpha = (10{\cdot}70 + \log_e \alpha_{M/2}) - 11{\cdot}91\left(\frac{T_M}{T}\right). \tag{11}$$

Thus the slope of the graph between $\log_e \Delta\alpha$ and $1/T$ for any alkali halide should be 11·91 T_M. Since under the present circumstances, $\Delta\alpha$ should be proportional to $\exp\{-W_s/2kT\}$, we should have

$$11{\cdot}91\ T_M = \frac{W_s}{2k}$$

or

$$W_s = 23{\cdot}82\ kT_M. \tag{12}$$

If W_s is expressed in eV, we have

$$W_s\,(\text{ev}) = 20{\cdot}52 \times 10^{-4} T_M. \tag{13}$$

Table 5. *W_s values*

Salt	W_s (eV) (equation 13)	W_s (eV) (experimental)
LiF	2·35	2·68*
LiCl	1·82	2·12*

Table 5 (*cont.*)

Salt	W_s (eV) (equation 13)	W_s (eV) (experimental)
LiBr	1·68	1·80*
LiI	1·47	1·34*
NaCl	2·20	2·12*
NaBr	2·11	1·68*
KCl	2·15	2·22*
KBr	2·06	2·53*
CsBr	1·86	2·0†
CsI	1·83	1·9†

* Boswarva & Lidiard (1967);
† Boswarva (1967).

Table 6. *W_s values*

Salt	W_s (eV) (equation 13)	W_s (eV) (Theoretical)	W_s‡ (eV) (Theoretical)
NaF	2·59	2·517*	
NaI	1·90	1·603*	
KF	2·37	2·419*	
KI	2·04	1·924*	1·87
RbF	2·12	2·188*	—
RbCl	2·03	1·984*	2·17
RbBr	1·96	1·979*	1·99
RbI	1·88	1·900*	1·88
CsF	1·96	1·954†	—
CsCl	1·89	1·784†	1·06 (CaCl) 2·00 (NaCl)

* Boswarva & Lidiard (1967);
† Boswarva (1967);
‡ Rao & Rao (1968).

The values of W_s calculated from equation (13) for various alkali halides are given in Tables 5 and 6 and compared with the experimental values where available. Column 3 of Table 6, gives the nearest theoretical values of W_s calculated by Boswarva & Lidiard (1967), while column 4 gives those calculated by Rao & Rao (1968) employing a modified Born model with a higher Van der Waals term. In view of the simple model used and the uncertainties in the experimental observations, the agreement is excellent.

Financial assistance to one of us (NGV) by the Ministry of Education is gratefully acknowledged.

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Acta Cryst. (1970). A**26**, 658

General Method of Obtaining Best Helical Parameters from the Diffraction Pattern

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(*Received* 12 *September* 1969 *and in revised form* 20 *October* 1969)

A practical method of obtaining the best helical parameters p/P and p, where p is the rise per unit length along the screw axis and P is the pitch of the helix, is given, which consists of a graphical method followed by a least-squares analysis, and is particularly useful when the helix is non-integral and when the diffraction pattern is complicated by the existence of other crystalline or amorphous phases. The extension of the method to a coiled coil is also described.

1. Introduction

A theory of diffraction by helical structures was given by Cochran, Crick & Vand (1952) (hereafter referred to as CCV) and has been successfully applied to various substances. A helical structure in which scattering units are arranged around a screw axis at a regular interval is fully described by three parameters p, p/P and r, where p is the rise per unit along the screw axis, P and r are the pitch and radius of the helix, respectively. The parameter p/P represents the angle of rotation per unit in fractions of 2π and was called 'unit twist' by