A SIMPLE METHOD FOR CALCULATING THERMAL EXPANSION OF IONIC CRYSTALS

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Simple methods for computing the properties of solids are very useful from a practical standpoint. Smyth (1955) and Kumar (1959, 1960) developed such a simple method for calculating the coefficient of thermal expansion, α. According to them

$$\alpha = \frac{C_p}{2E} \frac{(n+4)}{n} \sqrt{\overline{Z}'}. \qquad \dots (1)$$

Here C_p and E are the specific heat at constant pressure and cohesive energy per mole respectively, n is the repulsive index, and $Z' = (Z_c N_c + Z_a N_a)(N_c + N_a)^{-1}$, where Z_c, N_c and Z_a, N_a are the charge and number of the cation and anion respectively. The potential energy function, $\phi(r)$, assumed was

$$\phi(r) = -\frac{\alpha Z^2 e^2}{r} + \frac{A}{r^n}, \qquad \dots (2)$$

where α is the Madelung constant, e the charge of an electron, Z is the valency, r the interionic distance and A and n are the familiar potential parameters. The other relevant details will not be reproduced here for brevity and further because these are not pertinent for our discussion in this note.

A more general form of Eq. (1) is

$$\alpha = -\frac{C_P}{2r_0} \frac{\phi'''(r_0)}{[\phi''(r_0)]^2} \sqrt{\overline{Z}'}, \qquad \dots (3)$$

in which r_0 is the interionic equilibrium separation distance, $\phi'''(r_0)$ and $\phi''(r_0)$ refer to the values of third and second derivatives of $\phi(r)$ at $r = r_0$ respectively. Equation (3) will be convenient to use when more complicated forms for $\phi(r)$ than given by Eq. (2) are considered. The purpose of this note is to point out that much more reliable values of α are obtained if one uses an appropriate form for $\phi(r)$.

Kachhava and Saxena (1964a) have recently shown that a very appropriate and accurate empirical form for $\phi(r)$ is

$$\phi(r) = -\frac{\alpha Z^2 e^2}{r} + B \exp(-r/\rho) - \frac{C}{r^6} - \frac{D}{r^8} \qquad \dots (4)$$

where B and ρ are the potential parameters, C and D are the van der Waals' constants. The potential parameters may be obtained by the familiar conditions of Born and Mayer (1964b). As α is very sensitive (1964b) to the overlap forces it is likely that the use of Eq. (4) instead of Eq.(2) may result in considerable improvement for the α values. We will examine this for the case of alkali halide crystals where experimental data are also available.

TABLE I

Thermal expansion of alkali halide crystals, α

Crystal	Cohesive energy KCal/mole	Cp(298°K) Cal/deg. mole	$\alpha \times 10^6$ per deg.				
			Exptl.	Eqs. (3) and (2)	%dev.	Eqs. (3) and (4)	%dev.
LiF	238.9a	10.04c	34.0c	34.85	+ 2.5	29.16	−14.2
LiCl	192.1a	12.20c	44.0e	49.53	+12.6	44.76	+ 1.7
LiBr	181.9a	12.40c	50.0e	52.01	+ 4.0	44.68	−10.6
LiI	169.5a	13.00c	59.0e	52.31	−11.3	50.08	−15.1
NaF	213.8a	11.00c	36.0e	40.27	+11.9	34.29	− 4.7
NaCl	179.2a	11.88c	40.0e	49.50	+23.7	42.90	+ 7.2
NaBr	170.5a	12.50c	43.0e	41.66	− 3.1	46.45	+ 8.0
NaI	159.6a	13.00c	48.3e	57 58	+19.2	51.66	+ 7.0
KF	189.2a	11.73c	36.7e	46.27	+26.1	38.62	+ 5.2
KCl	163.2a	12.31c	38.3e	54.23	+41.6	47.29	+23.5
KBr	156.6a	12.82c	40.0e	57.86	+44.7	51.05	+27.6
KI	147.8a	13.16c	45.0e	61.32	+36.3	55.00	+22.2
RbF	180.6a	12.20c	31.67f	49.33	+55.7	41.99	+34.1
RbCl	157.7a	12.30c	36.0e	55.40	+53.7	47.58	+32.2
RbBr	151.3a	12.68c	38.0e	58.56	+54.1	51.61	+35.8
RbI	153.0a	12.50c	43.0e	59.32	+38.0	52.98	+23.2
CsCl	155.1b	12.22d	56.0g	58.79	5.0	49.36	−11.8
			Mean		26.1		16.7

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Kumar (1959, 1960) used the expression given by Eq. (1) in conjunction with relation (2) and n values fixed by Pauling (1927). Kumar (1959, 1960) also used the experimental values of cohesive energy but the values of E obtained from Eq.(2) and Pauling's n values agree with the experimental E values very well so that his calculation-procedure becomes consistent with Eq. (3). We will therefore base all our discussion on Eq. (3) only. Values of α so obtained are given in the Table I along with the experimental values and the percentage deviations. The values of some of the necessary constants are also tabulated.

If we employ potential form given by Eq. (4) in Eq. (3) for evaluating α we get the values given in Table I, column 7. The constants required in these calculations are those already given by us (1963, 1964b) earlier. The calculated values are now in somewhat better agreement with the experimental values. The average absolute deviation is only 16.7% as compared to the previous value of 26.1%.

A few remarks regarding the experimental α values listed in the Table I are relevant. The values given in the Table 1 does not include the results of a few measurements reported in recent years. Pathak and Pandya (1959, 1960a, 1960b) and Pathak, *et al*, (1963) have reported α values on a few alkali halide crystals as a function of temperature using X-ray diffraction technique. For NaCl the results have been reported by Pathak and Pandya (1959) in a graphical form and therefore we could not include them here for comparison. These authors also represent their data (except for NaCl) by a quadratic equation in temperature and we have calculated the α values at 25°C in each case. This involves back extrapolation of 5°C which is reasonable. We report these values in Table II. These values on the average differ from the recorded values in Table

TABLE II

Experimental α ($\times 10^6$ per deg) values at 25°C

Crystal	α
LiF	33.8
NaF	32.0
KBr	38.5
KI	40.3

I by about 6%. It may further be remarked that in certain cases other authors have also reported the α values. Using the same technique, earlier α values for LiF, KBr and KI are in good agreement with the values listed in Table II. For NaF Deshpande's (1961) value at 30°C is greater by about 6% than given in Table II and is again obtained by X-ray data. From this analysis it is clear that α values are correct to within about 6%, if the relative consistency of the data of different workers is any guide. However, this uncertainty does not vitiate in any way the conclusion derived here.

One of the endeavours of this work was to demonstrate the necessity and importance of using the correct potential energy expression in calculating the properties of solids. The success achieved by theory even now is not very satisfactory but this is essentially because of the simple picture of the lattice vibrations we have assumed in developing theory following Einstein.

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