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THERMOELASTIC INSTABILITY OF ALKALI HALIDES AT HIGH TEMPERATURE

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ABSTRACT

The thermodynamic and thermoelastic behaviour of solids at high temperatures, thermal expansivity and isothermal bulk modulus are vital parameters (Anderson, 1995). In the present study I have obtained a relation between potential energy and its derivatives with bulk modulus for ionic solids to estimate temperature dependence of thermal expansivity and bulk modulus at high temperature. Calculated values of interionic separations(r), potential energy parameters (Point of inflection) and isothermal bulk modulus are calculated and are in good agreement with the reported experimental values.

Key Words: Isothermal bulk modulus; thermal expansivity; Point of inflection of alkali halides.

I. INTRODUCTION

The study of thermoelastic properties of minerals is essential for examine and understanding of the dynamic effect of earth's interior. Lindemann [1] gave a formula assuming that the amplitude of thermal vibration of atom about their equilibrium position in lattice must increase progressively with increase in temperature. Cartz and Gilverry [2] have reformulated the Lindemann criterion utilizing the Debye- Waller theory. Born [3] suggested that shear modulus of a crystal decreases rise in temperature. According to Thompson [4] a crystal become unstable only when a normal frequency become imaginary. In mechanical theory of the difference between solid and liquid is that solid has elastic moduli against shearing stress, while the liquid has not. Instability of the solid lattice is sometime defined as the onset of lack of long rang order of the sudden loss of rigidity (vanishing of the shear velocity). Ida [5] developed a theory of vibration elongation, which is define as the effective increase in interatomic distance due to the lattice vibration, the anharmonicity of the lattice play an important role in the concept of vibrational elongation by Ida. The theory of melting as proposed by Ida has been reformulated by Ishizaki et al [6]. That ultrasonic sound velocity tends to zero corresponding to high temperature at which melting occurs. Hence the two theories due to Born and Ida imply that the velocity tends to zero at high temperature approaches to melting temperature. Hunter and Siegel [7], have show the inadequacy of concept of melting through their observations shear modulus did not vanish even at melting temperature. Enck [8], Slagle and Mckinstry [9] and others [10-11] also failed to reveal a vanishing shear elastic constant.

In present study, I develop the formulation for thermodynamic and thermoelastic behaviour of solids at high temperatures, thermal expansivity and isothermal bulk modulus are vital parameters [12] (Anderson, 1995). In the present study I have obtained a relation between potential energy and its derivatives with bulk modulus for ionic solids to estimate temperature dependence of thermal expansivity and bulk modulus at high temperature. Calculated values of interionic separations(r) and isothermal bulk modulus are calculated and are in good agreement with the reported experimental values (Anderson, 1995). The point of inflection in potential energy is identified corresponding to $d^2\Phi/dr^2 = 0$. Value of interionic separation (r_m) at melting temperature (T_m) is calculated by using the Anderson formula for thermal expansivity. Isothermal bulk modulus (K_T) also calculated by using the Born-Mie potential form [13, 14]. The temperature dependence of isothermal bulk modulus (K_T) is also predicted on the basis of non-linear dependence of (K_T) with temperature starting from room temperature. A close agreement between theory and experiment reveals the validity of extrapolated data.

II. METHOD OF ANALYSIS

The value of potential energy (Φ) for ionic solid such as alkali halides can be written as

$$\Phi = -\frac{Me^2}{r} + \Phi_R \qquad \text{….(1)}$$

Where the first term on right represents the electrostatic Colombian energy and Φ_R is the overlap repulsive short range energy arising from the Pauli's exclusion principle. M is the Medelung's constant and which is equal to 1.7476 for NaCl- type solids. The overlap repulsive energy by Born-Mie potential form [15] in inverse power form is

$$\Phi_R = B\left(\frac{r}{r_0}\right)^{-n} \qquad \text{….(2)}$$

Potential energy Φ can given as by using these formulas

$$\Phi = -\frac{Me^2}{r} + B\left(\frac{r}{r_0}\right)^{-n} \qquad \text{…..(3)}$$

Melting of solids takes place when the interionic separation corresponds to the point of inflection in potential energy [16-17]. At the point of inflection the second order derivatives of potential energy (Φ) with respect to r vanishes and therefore the value of r_i are calculated from condition

$$\left(\frac{d^2\Phi}{dr^2}\right)_{r=r_i} = 0 \qquad \text{…(4)}$$

The potential energy is determined using the Hildebrand EOS [18]

$$P = \frac{d\Phi}{dV} + T\alpha K_T \qquad \text{…(5)}$$

The expression for isothermal bulk modulus K_T derived from equation (5) using the relationship $K_T = -V\,(dP/dV)_T$. The expression thus obtained is as follow:

$$K_T = V\frac{d^2\Phi}{dV^2} + \xi T K_T \qquad \text{….(6)}$$

Where $\xi = (d\ln K_T/dT)$. Since $V = r^3$ for solids with NaCl type structures we can express the volume derivatives of potential energy in term of derivative with respect to interionic separation (r) as:

$$\frac{d\Phi}{dV} = \frac{1}{6r^2}\frac{d\Phi}{dr} \qquad \text{…..(7)}$$

$$V\frac{d^2\Phi}{dV^2} = \frac{1}{18r}\left(\frac{d^2\Phi}{dr^2} - \frac{2d\Phi}{rdr}\right) \qquad \text{…..(8)}$$

Now equation (6) can be written as with the help of Eq.(7) & Eq.(8)

$$K_T = \frac{1}{18r}\left(\frac{d^2\Phi}{dr^2} - \frac{2}{r}\frac{d\Phi}{dr}\right) + \xi T K_T \qquad \text{….(9)}$$

$$K_T = \frac{\frac{1}{18r}\left(\frac{d^2\Phi}{dr^2} - \frac{2}{r}\frac{d\Phi}{dr}\right)}{(1-\xi T)} \qquad \text{....(10)}$$

For calculating K_T from Eq. (10), we used the Anderson formula for thermal expansivity α for determining the values r at different temperatures (T). According Anderson formula

$$\alpha = \alpha_0\left[1 - \alpha_0\delta_T\left(T - T_0\right)\right]^{-1}$$

….(11)

δ_T remains constant at higher temperature T ≥ θ_D, the Debye temperature according to Anderson. The product of αK_T remains constant at T ≥ θ_D, which gives relation

$$\alpha/\alpha_0 = (V/V_0)^{\delta_T} \quad \text{…..(12)}$$

Since $(V/V_0) = (r/r_0)^3$, following relationship is obtained by using Eq. (11) & Eq. (12)

$$r(T) = r_0[1-\alpha_0\delta_T(T-T_0)]^{-1/3\delta_T} \quad \text{…..(13)}$$

Where r(T) is interionic separation hold good results for alkali halides. In present study we calculated interionic separation at higher temperature close to melting temperature and temperature close to where isothermal bulk modulus vanishes of alkali halides. The input data for α_0 and δ_T from Kumar [19] .For calculating K_T from Eq. (10), we used Eq. (3) for determining $\frac{d\Phi}{dr}$ and $\frac{d^2\Phi}{dr^2}$ at different interionic separation r.

Thus for the inverse power form first and second derivative of potential energy are given as:

$$\frac{d\Phi}{dr} = \frac{Me^2}{r^2} - \frac{Bn}{r_0}\left(\frac{r}{r_0}\right)^{-(n+1)} \quad \text{……(14)}$$

$$\frac{d^2\Phi}{dr^2} = -\frac{2Me^2}{r^3} - \frac{Bn(n+1)}{r_0^2}\left(\frac{r}{r_0}\right)^{-(n+2)}$$

……(15)

II. RESULT AND DISCUSSIONS

In present paper, I calculated the values of melting temperature(T_m) for Alkali halides, Isothermal bulk modulus (K_T) using the Anderson formula. I have calculated values $\frac{d^2\Phi}{dr^2}$ and temperature where $\frac{d^2\Phi}{dr^2}$ becomes zero of alkali halides (LiF, LiCl, NaF, NaCl, KF, KCl, RbF, RbCl). The result are found be in close agreement with the experiment which in turn reveals the validity of present work.

Table 1: Calculated values of r_i, r', r_m and T_m for power inverse potential form in the present study experimental values of r′ , r_i, r_m and T_m are given within parentheses ( )

Crystal	r_i (Ǻ)	r ′ (Ǻ)	r_m (Ǻ)	T (K)
LiF	2.538 (2.539)	1.715 (1.716)	2.127 (2.218)	1331
LiCl	3.154 (3.157)	2.226 (2.227)	2.69 (2.692)	972
NaF	2.86 (2.862)	2.008 (2.009)	2.434 (2.435)	1330
NaCl	3.423 (3.427)	2.467 (2.465)	2.945 (2.946)	1062

KF	3.241 (3.246)	2.347 (2.348)	2.794 (2.796)	1183
KCl	3.769 (3.772)	2.782 (2.784)	3.276 (3.278)	1162
RbF	3.398 (3.398)	2.5 (2.50)	2.949 (2.949)	1207
RbCl	3.914 (3.918)	2.93 (2.929)	3.422 (3.424)	1085

Where r_i is the value of interionic separation at the point of inflection and r' is the values of interionic distance where potential energy of the solid equals to the potential energy of solid at point of inflection.

Table 2: Values of 2/r (dΦ/dr), $d^2\Phi/dr^2$, K_T calculated from inverse power potential form and value of r calculated from the Anderson formula for LiF

Temp (K)	**r (Å)**	**(2/r)(dϕ/dr)(10^4) erg/cm^2**	**$d^2\phi/dr^2$ (10^4) erg/cm^2**	**K_T (GPa)**
300	2.57	0.366	14.671	29.550
400	2.582	0.497	13.866	27.087
600	2.61	0.770	12.145	22.152
800	2.646	1.063	10.222	17.109
972	2.690	1.346	8.246	12.384
1000	2.699	1.396	7.886	11.566
1200	2.791	1.765	4.907	5.273
1300	2.885	1.956	2.858	1.445
1331	2.937	2.007	2.03	0.035
1385	3.154	1.989	0.012	-2.866

Table 3: Values of 2/r (dΦ/dr), $d^2\Phi/dr^2$, K_T calculated from inverse power potential form& value of r calculated from the Anderson formula for LiCl

Temp (K)	r (Å)	$(2/r)(d\phi/dr)(10^4)$ erg/cm^2	$d^2\phi/dr^2\,(10^4)$ erg/cm^2	K_T (GPa)
300	2.57	0.366	14.671	29.550
400	2.582	0.497	13.866	27.087
600	2.61	0.770	12.145	22.152
800	2.646	1.063	10.222	17.109
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1300	2.885	1.956	2.858	1.445
1331	2.937	2.007	2.03	0.035
1385	3.154	1.989	0.012	-2.866

Table 4: Values of 2/r (dΦ/dr), $d^2\Phi/dr^2$, K_T calculated from inverse power potential form and value of r calculated from the Anderson formula for NaF

Temp (K)	r (Å)	$(2/r)(d\phi/dr)(10^4)$ erg/cm^2	$d^2\phi/dr^2\,(10^4)$ erg/cm^2	K_T (GPa)
300	2.317	0.373	20.058	46.447
450	2.329	0.572	18.863	42.596
600	2.341	0.756	17.735	39.029
750	2.356	0.969	16.414	35.003
900	2.372	1.175	15.106	31.117
1050	2.39	1.383	13.749	27.202
1200	2.412	1.607	12.24	23.001

1330	2.434	1.801	10.881	19.336
1500	2.47	2.063	8.939	14.306
1650	2.512	2.295	7.05	9.655
1800	2.573	2.522	4.887	4.655
1925	2.66	2.682	2.688	0.011
2039	2.86	2.654	0.008	-4.630

Table 5: Values of 2/r (dΦ/dr), $d^2\Phi/dr^2$, K_T calculated from inverse power potential form and value of r calculated from the Anderson formula for NaCl

Temp (K)	**r (Å)**	**$(2/r)(d\phi/dr)(10^4)$ erg/cm^2**	**$d^2\phi/dr^2(10^4)$ erg/cm^2**	**K_T (GPa)**
300	2.82	0.287	12.518	23.622
450	2.838	0.438	11.523	21.065
600	2.858	0.589	10.504	18.529
750	2.881	0.743	9.435	15.960
900	2.909	0.905	8.269	13.263
1050	2.942	1.067	7.061	10.574
1062	2.945	1.080	6.960	10.355
1200	2.985	1.236	5.721	7.727
1350	3.043	1.401	4.258	4.783
1500	3.136	1.557	2.539	1.580
1569	3.206	1.613	1.619	0.009
1668	3.423	1.599	0.002	-2.331

Plots of K_T vs Temperature for inverse power potential form for Lithium halides and Sodium halides

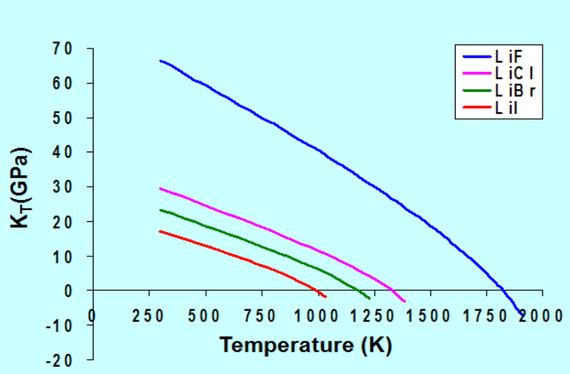

Fig 1: Plots of K_T vs Temperature for inverse power potential form for Lithium halides

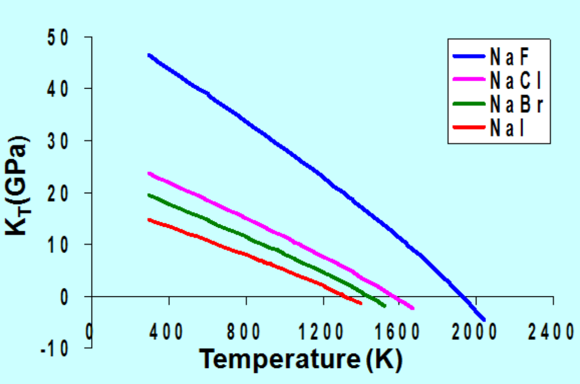

Fig 2: Plots of K_T vs Temperature for inverse power potential form for sodium halides

Table 6: Values of 2/r (dΦ/dr), $d^2\Phi/dr^2$, K_T calculated from inverse power potential form and value of r calculated from the Anderson formula for KF

Temp (K)	r (Å)	$(2/r)(d\phi/dr)(10^4)$ erg/cm^2	$d^2\phi/dr^2(10^4)$ erg/cm^2	K_T (GPa)
300	2.674	0.298	15.164	30.171
450	2.688	0.449	14.159	27.362
600	2.704	0.607	13.087	24.480
750	2.723	0.778	11.913	21.448
900	2.743	0.937	10.782	18.616
1050	2.768	1.112	9.506	15.557
1183	2.794	1.267	8.323	12.831
1300	2.821	1.404	7.234	10.412
1450	2.866	1.584	5.688	7.138
1600	2.931	1.760	3.937	3.663
1744	3.041	1.902	1.913	0.018
1846	3.241	1.887	0.021	-2.792

Table 7: Values of 2/r (dΦ/dr), $d^2\Phi/dr^2$, K_T calculated from inverse power potential form and value of r calculated from the Anderson formula for KCl

Temp (K)	r (Å)	$(2/r)(d\phi/dr)(10^4)$ erg/cm^2	$d^2\phi/dr^2(10^4)$ erg/cm^2	K_T (GPa)
300	3.146	0.218	10.304	17.338
450	3.164	0.329	9.504	15.476
600	3.185	0.446	8.644	13.559
750	3.21	0.570	7.716	11.577
900	3.238	0.691	6.784	9.663
1050	3.272	0.814	5.79	7.712
1062	3.275	0.824	5.709	7.557
1300	3.352	1.024	3.935	4.314
1450	3.429	1.147	2.641	2.138
1588	3.553	1.239	1.247	0.011
1685	3.769	1.229	0.005	-1.564

Table 8: Values of 2/r (dΦ/dr), $d^2\Phi/dr^2$, K_T calculated from inverse power potential form and value of r calculated from the Anderson formula for RbF

Temp (K)	r (Å)	$(2/r)(d\phi/dr)(10^4)$ erg/cm^2	$d^2\phi/dr^2(10^4)$ erg/cm^2	K_T (GPa)
300	2.826	0.255	14.241	26.654
450	2.84	0.390	13.29	24.096
600	2.856	0.532	12.277	21.493
750	2.873	0.668	11.279	19.021
900	2.894	0.818	10.151	16.369

1100	2.927	1.019	8.583	12.869
1207	2.949	1.133	7.662	10.916
1300	2.971	1.232	6.829	9.209
1450	3.016	1.395	5.363	6.344
1600	3.083	1.559	3.664	3.248
1740	3.199	1.691	1.696	0.008
1828	3.398	1.676	-0.007	-2.308

Table 9: Values of 2/r (dΦ/dr), d$^2\Phi$/dr^2, K$_T$ calculated from inverse power potential form and value of r calculated from the Anderson formula for RbCl

Temp (K)	r (Å)	(2/r)(dϕ/dr)(10^4) erg/cm^2	d$^2\phi$/dr^2 (10^4) erg/cm^2	K$_T$ (GPa)
300	3.291	0.190	9.738	15.580
450	3.309	0.291	8.979	13.869
600	3.329	0.392	8.202	12.192
750	3.353	0.500	7.351	10.449
900	3.38	0.607	6.492	8.766
1085	3.422	0.745	5.334	6.624
1200	3.454	0.829	4.578	5.299
1350	3.51	0.944	3.474	3.467
1500	3.595	1.054	2.216	1.531
1610	3.704	1.119	1.127	0.010
1699	3.914	1.112	0.011	-1.307

Plots of K$_T$ vs Temperature for inverse power potential form for Potassium halides and Rubidium halides

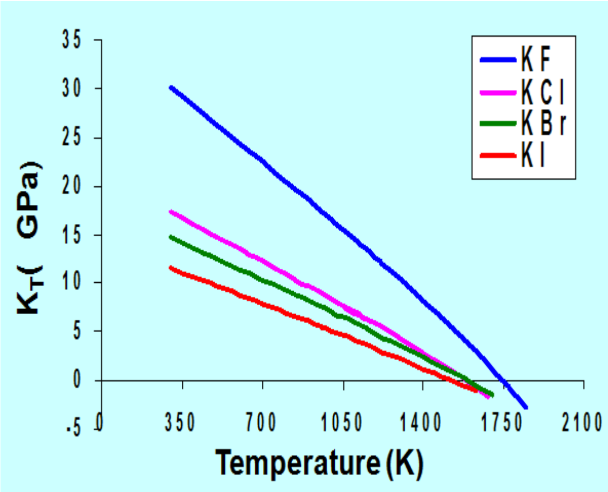

Fig 3: Plots of K_T vs Temperature for inverse power Potential form for Lithium halides

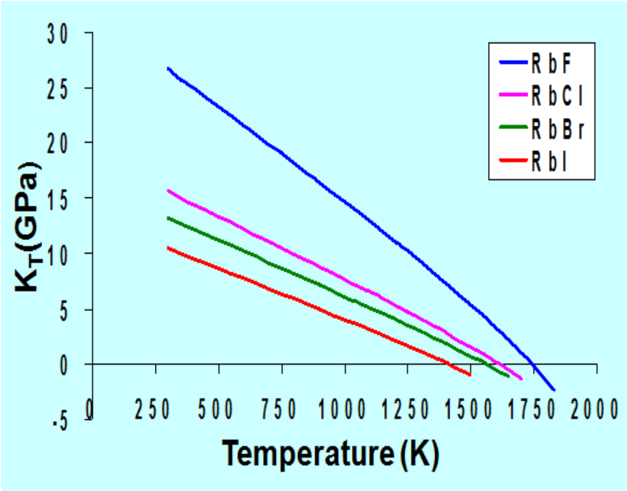

Fig 4: Plots of K_T vs Temperature for inverse power Potential form for sodium halides

Figure 1,2,3&4 shows the variation of Isothermal bulk modulus with increasing temperature. By above tables we can see that shear modulus vanish (K_T) when temperature more than melting temperature. In present paper I have calculated interionic separation (r) temperature and isothermal bulk modulus at point of inflection (where $d^2\Phi/dr^2$ vanishes). In present paper results shows very good agreement with the experimental data.

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