HIGH TEMPERATURE BEHAVIOUR OF ALKALI HALIDES AT MELTING

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We present a simple method for calculating thermal expansivity, bulk modulus, interatomic distances at melting for sixteen alkali halides using the Anderson formulation. The results obtained are found to agree closely with the corresponding values determined from the interatomic potential functions. It is found that in case of alkali halides the melting takes place when the thermal expansivity increases rapidly and becomes nearly twice the value at room temperature. The bulk modulus decreases in the same proportion at the melting point. The interatomic distances increase by about four percent at melting temperature as compared to values at room temperature. The magnitudes of diffusional force responsible for melting of alkali halides have been calculated and reported.

KEYWORDS : Melting, thermal expansivity, bulk modulus, interatomic potential, alkali halides.

INTRODUCTION

In order to understand the high temperature behaviour of materials, we need adequate knowledge of thermoelastic properties at melting temperature [1, 2]. The simplicity and usefulness of the Anderson formulation [3] has been demonstrated here in case of alkali halides by calculating thermoelastic properties at their melting temperatures. We have selected sixteen alkali halides with NaCl structure for which the reliable and accurate data at room temperature and atmospheric pressure are available [4, 5].

Thermal expansion and melting both are related to the anharmonicity is the potential energy curve [6]. The point of inflection in the potential energy curve is related to the melting point. The potential energy functions can be used to determine diffusional force responsible for melting [7, 8]. We present an analysis of these aspects of melting describing a phase transition from solid to liquid state at high temperatures.

METHOD OF ANALYSIS

We have the following thermodynamic identity

$$\left(\frac{d\alpha}{dT}\right)_P = \left(\frac{d\alpha}{dV}\right)_T \left(\frac{dV}{dT}\right)_P + \left(\frac{d\alpha}{dT}\right)_V \qquad \dots (1)$$

where α is the volume thermal expansion coefficient or simply known as thermal expansivity

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P \qquad \dots (2)$$

Table – 1. Values of input data for alkali halides [3 – 6].

Crystal	$r_0(10^{-10}m)$	$\alpha_0(10^{-4}\,\mathrm{K}^{-1})$	δ_T	K_{T_0} (GPa)	$T_m(K)$
LiF	2.013	0.999	6.15	66.5	1115
LiCl	2.570	1.320	6.88	29.7	887
LiBr	2.751	1.500	7.08	23.5	820
LiI	3.006	1.800	7.47	17.2	723
NaF	2.317	0.960	5.84	46.5	1261
NaCl	2.820	1.190	5.95	24.0	1074
NaBr	2.989	1.260	6.23	19.9	1028
NaI	3.236	1.370	6.46	15.1	924
KF	2.674	1.020	6.26	30.5	1119
KCl	3.146	1.110	6.29	17.5	1049
KBr	3.300	1.160	5.88	14.8	1003
KI	3.533	1.230	5.83	11.7	959
RbF	2.826	0.940	6.86	26.7	1048
RbCl	3.291	1.030	6.73	15.6	988
RbBr	3.445	1.080	6.64	13.2	955
RbI	3.671	1.230	6.53	10.5	915

The last term in Eq. (1) is a small contribution and it can be ignored to a good approximation, Eq. (1) then can be written as :

$$\left(\frac{d\alpha}{dT}\right)_P = \alpha^2 \delta_T \qquad \dots (3)$$

where δ_T is the Anderson-Grüneisen parameter

$$\delta_T = \frac{V}{\alpha}\left(\frac{d\alpha}{dV}\right)_T \qquad \dots (4)$$

It has been found [3] that δ_T can be assumed to remain constant with the change in temperature. Then we can use Eq. (3) to determine α as a function of temperature. On integrating Eq. (3) from $T = T_0 = 300$ K, the room temperature up to $T = T_m$, the melting temperature, we get the following expression for $\alpha_m = \alpha\,(T = T_m)$

$$\alpha_m = \alpha_0 \left[1 - \alpha\delta_T\left(T_m - T_0\right)\right]^{-1} \qquad \dots (5)$$

where α_0 is the thermal expansivity at $T = T_0$, the room temperature. It has been established by Tallon [9] that the product αK_T, where K_T is the isothermal bulk modulus, remains nearly constant for various materials at high temperatures ranging from the Debye

temperatures θ_D up to the melting temperatures T_m. The expression for bulk modulus is then written as

$$K_{T_m} = K_{T_0}\left[1 - \alpha_0 \delta_T \left(T_m - T_0\right)\right] \qquad \ldots (6)$$

Eqs. (5) and (6) give

$$\alpha_m K_{Tm} = \alpha_0 K_{T_0} \qquad \ldots (7)$$

Now, integrating Eq. (4), we get

$$\frac{\alpha_m}{\alpha_0} = \left(\frac{V_m}{V_0}\right)^{\delta_T} \qquad \ldots (8)$$

where V_m is the volume at $T = T_m$, and V_0 at $T = T_0$. If r_0 is the nearest neighbour interatomic distance at room temperature, and r_m is the same at $T = T_m$ then we have

$$\frac{V_m}{V_0} = \left(\frac{r_m}{r_0}\right)^3 \qquad \ldots (9)$$

Equations (5) and (8) give

$$V_m = V_0\left[1 - \alpha_0 \delta_T \left(T_m - T_0\right)\right]^{-1/\delta_T} \qquad \ldots (10)$$

Equations (9) and (10) the yield

$$r_m = r_0\left[1 - \alpha_0 \delta_T \left(T_m - T_0\right)\right]^{-1/3\delta_T} \qquad \ldots (11)$$

RESULTS AND DISCUSSIONS

Values of input parameters used in calculations are given in Table 1. The results obtained in the present study using Eqs. (5), (6) and (11) are reported in Table 2 for sixteen alkali halides. We note that the thermoelastic properties α and K_T change very significantly for the solids under study at their melting temperatures as compared to the corresponding values at room temperature. At melting points, the thermal expansivity increases and becomes nearly twice the values at room temperatures. On the other hand, the bulk modulus decreases in the same proportion at melting with a constant value of the product αK_T. Values of interatomic distances r_m at melting temperatures of alkali halides are found to be about four percent larger than the corresponding values at room temperature. This finding is consistent with the results based on computer simulation studies for melting [10-12]. Values of diffusional force responsible for melting of alkali halides [8] can be determined using the following relationship

$$\left(\frac{d\phi}{dr}\right)_{r=r_m} = 6r_m^2 \alpha_m K_{T_m} T_m \qquad \ldots(12)$$

where ϕ is the lattice potential energy. The results obtained from Eq. (12) are given in Table 2. It is found that the magnitude of diffusional force $(d\phi/dr)$ decreases from each alkali metal fluoride to the corresponding alkali metal iodide as the size of halide ion increases. The

ratio of ionic radii plays the significant role in melting of alkali halides. Thermoelastic properties at high temperatures analysed in the present study are of central importance for understanding the physical mechanisms responsible for melting of alkali halides [13, 14].

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Table – 2. Results for alkali halides at melting points.

Crystal	$r_m(10^{-10}$ m$)$	$\alpha_m(10^{-4}\mathrm{K}^{-1})$	K_{Tm}	$(d\phi/dr)_m 10^{-9}\mathrm{N}$
LiF	2.090	2.000	33.2	1.94
LiCl	2.665	2.826	13.9	1.48
LiBr	2.856	3.349	10.5	1.40
LiI	3.123	4.173	7.40	1.31
NaF	2.421	2.081	21.5	1.96
NaCl	2.948	2.632	10.8	1.57
NaBr	3.128	2.939	8.5	1.48
NaI	3.372	3.059	6.8	1.28
KF	2.781	2.137	14.5	1.60
KCl	3.272	2.326	8.3	1.29
KBr	3.424	2.228	7.7	1.19
KI	3.665	2.331	6.2	1.09
RbF	2.927	1.815	13.8	1.34
RbCl	3.398	1.969	8.2	1.09
RbBr	3.556	2.036	7.0	1.03
RbI	3.801	2.430	5.3	1.02

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