Analysis of Melting for Alkali Halides Based on Diffusional Force Theory

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The theory for melting based on the concept of diffusional force is used for studying the melting of alkali halides. Values of the thermal expansivity and the Anderson–Grüneisen parameter are used to predict the interionic distances for 19 alkali halides at melting with the help of Kumar's formula. A simple model for melting has been developed by estimating the diffusional force from knowledge of interionic potentials. The values of T_m thus obtained are found to show fairly good agreement with experimental values of melting temperatures and to be better than those obtained by Bosi.

1. INTRODUCTION

Melting of solids is a commonly observed phenomenon at high temperatures. However, its physical mechanism is not properly understood. Several attempts have been made to review various theories of melting of solids based on different criteria [1–5]. Bosi [1] has developed a model for predicting the melting temperature of ionic solids using the concept of diffusional force. By considering the balance between the diffusional force and the Coulomb force existing in ionic materials, Bosi found that much larger values of dielectric constants (ε) were needed to obtain agreement with the experimental values of melting temperatures of alkali halides. The values of ε for alkali halides at higher temperatures close to melting temperatures

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$(T \to T_m)$ thus required are about three to five times larger than the corresponding values of ε at room temperature. The larger values of ε at high temperatures $(T \to T_m)$ have been explained on the basis of the data for molar lattice energy and molar heat of fusion [1]. A direct experimental study of ε for NaCl at 1000 K also yields larger values for ε in agreement with the value predicted by Bosi [1].

In the present paper, we develop a model for melting using the concept of diffusional force. The Coulomb force considered by Bosi [1] has been replaced by the interionic force derived from the lattice potential energy. We use Harrison's potential form for the overlap repulsive energy and also include van der Waals (vdW) dipole–dipole and dipole–quadrupole interactions [6]. We use the interionic distances for alkali halides at melting estimated with the help of Kumar's formula for thermal expansivity [7].

2. METHOD OF ANALYSIS

In a liquid, two microscopic spherical particles have a tendency to wander away from each other by means of a three-dimensional "random walk." This is assumed to be due to the presence of a diffusional force that can be expressed as [1]

$$F_r = T \left(\frac{dS}{dr} \right)_T \tag{1}$$

where S is the entropy and r is the distance between particles. The radial force F_r is responsible for an increase in r resulting from the tendency towards maximum entropy. Using Maxwell's thermodynamic relations we can write

$$\left(\frac{dS}{dV} \right)_T = \left(\frac{dP}{dT} \right)_V = \alpha B_T \tag{2}$$

where α and B_T are the coefficient of volume thermal expansion and isothermal bulk modulus, respectively. Equations (1) and (2) yield

$$F_r = 3xr^2 T\alpha B_T \tag{3}$$

We have used the relationship $V = xr^3$ for crystals, where x is a constant which depends on the structure of a solid and x is equal to 2 for NaCl-type and 1.54 for CsCl-type structures, and r is the interatomic separation.

At the melting temperature, Bosi [1] has considered the equivalence between the diffusional force and the attractive Coulomb force between the ions in a medium of dielectric constant ε to obtain the formula for the

melting temperature. In the present study we consider that the melting of solids takes place when the diffusional force is balanced by the interionic force derived from the lattice potential energy ϕ. Thus, at the melting temperature, we can write

$$F_{\mathrm{r}} = \left(\frac{d\phi}{dr}\right)_{r=r_m} \tag{4}$$

Equations (3) and (4) then lead to the following relationship for the melting temperature:

$$T_{\mathrm{m}} = \frac{1}{3xr_m^2\alpha B_T}\left(\frac{d\phi}{dr}\right)_{r=r_m} \tag{5}$$

For determining the values of r_m, we use the thermal expansivity equation obtained by Kumar [7], which is expressed as follows:

$$\frac{\alpha}{\alpha_0} = \frac{V_0}{V}\exp\left[A\left(V/V_0 - 1\right)\right] \tag{6}$$

where, α_0 is the value of the thermal expansion coefficient at $V = V_0$ and the constant A is determined from the initial condition, viz. at $V = V_0$, $A = \delta_{T_0} + 1$. Here δ_{T_0} is the value of the Anderson–Grüneisen parameter δ_T at $V = V_0$.

Now using the definition $\alpha = (1/V)\ (dV/dT)_P$ in Eq. (6) and integrating, we obtain the following relations:

$$\frac{V}{V_0} = \left\{1 - A^{-1}\left[\ln\left(1 - A\alpha_0\left(T - T_0\right)\right)\right]\right\} \tag{7}$$

In Eq. (7), we put $V/V_0 = (r/r_0)^3$ and we get the expression for r_m,

$$r_m = r_0\left\{1 - A^{-1}\left[\ln\left(1 - A\alpha_0\left(T_{\mathrm{m}} - T_0\right)\right)\right]\right\}^{1/3} \tag{8}$$

For estimating the values of $(d\phi/dr)$ at $r = r_m$, we use Harrison's potential form for the overlap repulsive energy [8] and also consider van der Waals (vdW) dipole–dipole and dipole–quadrupole interactions [9]. Within the framework of this model, the total lattice potential energy ϕ is expressed as follows [6]:

$$\phi = -\frac{a_M Z^2 e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + \phi_{\mathrm{rep}} \tag{9}$$

where, the first term on the right-hand side of Eq. (9) is the electrostatic Coulomb energy with a_M as Madelung's constant which is equal to

1.7476 for NaCl-type structures and 1.7627 for CsCl-type structures, e is the charge of the electron, and Z is the valence. The second and third terms are van der Waals (vdW) dipole–dipole and dipole–quadrupole energies. The constants C and D are related to the dipole–dipole (c_{ij}) and dipole–quadrupole (d_{ij}) interaction coefficients as follows [9]:

$$C = S_{+-}c_{+-} + S_{++}c_{++} + S_{--}c_{--} \tag{10}$$

$$D = T_{+-}d_{+-} + T_{++}d_{++} + T_{--}d_{--} \tag{11}$$

where, S_{ij} and T_{ij} are lattice sums which were given by Tosi [10]. The subscripts $+-$, $++$, and $--$ represent the cation–anion, cation–cation, and anion–anion interactions, respectively. The values of c_{ij} and d_{ij} are obtained from the Kirkwood–Muller formula given below [9]:

$$c_{ij} = -\frac{6mc^2}{N} X_i X_j \left(\frac{X_i}{a_i} + x_j a_j \right)^{-1} \tag{12}$$

$$d_{ij} = -\frac{9mc^2}{Ne^2} c_{ij} \left(\frac{X_i}{n_i} + \frac{X_i}{n_j} \right)^{-1} \tag{13}$$

where, c is the velocity of light, and a and X are the polarizabilities and molar susceptibilities, respectively. N is Avogadro's number, and n_i and n_j are the number of outermost electrons. The values of C and D calculated from Eqs. (10)–(13) were used in the present work.

For the overlap repulsive energy, we use the analytical form proposed by Harrison [8]. The normalized charge density as used by Harrison from quantum mechanical consideration is

$$n(r) = \frac{6\mu^3}{\pi} \exp(-2\mu r) \tag{14}$$

where μ is related to the valence p and state energy (ε_p) as follows:

$$\varepsilon_p = -\frac{\hbar^2 \mu^2}{2m} \tag{15}$$

where, $\hbar$ is Planck's constant h divided by 2π. The total overlap interaction has been considered as arising from three contributions, viz., (i) the kinetic energy, (ii) the exchange energy, and (iii) the coulombian energy of electrons in the overlap region. These contributions to the overlap repulsive potential are given below:

$$\phi^{\text{ke}} = 70.8\varepsilon_p \mu r \exp\left(-\frac{5\mu r}{3}\right) \tag{16}$$

$$\phi^{\text{ex}} = -2.728e^2 \mu^2 r \exp\left(-\frac{4\mu r}{3}\right) \tag{17}$$

$$\phi^{\text{coul}} = -6e^2 \mu^3 r^2 \exp\left(-2\mu r\right) \tag{18}$$

Harrison [8] assumed that the total overlap interaction is of the form of the kinetic energy term and can be expressed by an equation similar to that given by Eq. (16). Following the previous work [6] on Harrison's potential for ionic crystals, we can write the overlap repulsive potential for alkali halides as follows:

$$\phi_{\text{rep}} = \frac{n_0 \hbar^2}{2m}\Big[M\bar{\mu}^3 r \exp(-k\bar{\mu}r) + \frac{1}{2}M'\mu_1^3 r' \exp(-k\mu_1 r')$$

$$+ \frac{1}{2}M'\mu_2^3 r' \exp(-k\mu_2 r')\Big] \tag{19}$$

where, m is the mass of an electron. For NaCl-type structures, $M=6$ and $M'=12$ are the numbers of first and second neighbor ions. Similarly, r and $r'=\sqrt{2}r$ are the first and second nearest-neighbor distances. For CsCl-type structures $M=8$, $M'=6$, and $r'=\left(2/\sqrt{3}\right)r$. The values of μ_1 and μ_2 are calculated using the valence p state energy (ε_p) given by Eq. (15), and $\bar{\mu}$ is the arithmetic average of μ_1 and μ_2 for the cation and anion.

In order to calculate the lattice potential energy ϕ from Eq. (9), there remain only two unknown parameters, viz., n_0 and k which are obtained from the equilibrium condition and the following relations:

$$\left(\frac{d\phi}{dr}\right)_{r=r_0} = 0 \tag{20}$$

$$\left(\frac{d^2\phi}{dr^2}\right)_{r=r_0} = 9xr_0 B_{T_0} \tag{21}$$

The potential parameters thus calculated from Eqs. (20) and (21) are assumed to be independent of pressure.

Now, with the help of Eqs. (8) and (9), Eq. (5) can be evaluated iteratively after a trial value of T_m is selected. Furthermore, trial values of T_m appear explicitly on the right-hand side of Eq. (5). Computed values of T_m were used in each ensuing cycle, until no changes were observed between the input and output T_m This process results in the self-consistent set of values listed in Table I along with the available experimental data [11] and

Table I. Input Data and Calculated Values of Melting Temperature for Alkali Halides using Eq. (5). (The experimental values of melting temperature are also shown for comparison)

Crystal	r_0 [13] (Å)	α_0 [13] (10^{-4} K^{-1})	B_{T_0} [13] (kbar)	δ_{T_0} [13]	μ_1[14] (10 nm^{-1})	μ_2[14] (10 nm^{-1})	C (10^{-79} J·m^6)	D (10^{-99} J·m^8)	n_0	k	T_m[1] Bosi(K)	T_m Cal (K)	T_m[11] Exp (K)
LiF	2.013	0.999	665	6.15	3.962	2.112	46	26	3	1.34	1149	1142	1115
LiCl	2.570	1.32	297	6.88	3.962	1.799	317	221	11.6	1.41	828	870	887
LiBr	2.751	1.50	235	7.08	3.962	1.716	594	286	9.5	1.34	734	843	820
LiI	3.006	1.80	172	7.47	3.962	1.619	1265	584	61.6	1.57	609	735	723
NaF	2.317	0.96	465	5.84	3.087	2.112	139	98	11.5	1.54	1361	1244	1261
NaCl	2.820	1.19	240	5.95	3.087	1.799	561	455	19.6	1.49	1106	1045	1074
NaBr	2.989	1.26	199	6.30	3.087	1.716	930	537	30.7	1.52	1030	1040	1028
NaI	3.236	1.37	151	6.46	3.087	1.619	1755	942	48.3	1.53	924	935	924
KF	2.674	1.02	305	6.16	2.487	2.112	227	75	40.2	1.70	1105	1132	1119
KCl	3.146	1.11	175	6.29	2.487	1.799	607	285	70.9	1.67	1020	1051	1049
KBr	3.289	1.16	14	5.88	2.487	1.716	1854	962	112	1.71	975	1013	1003
KI	3.525	1.23	17	5.83	2.487	1.619	2745	1430	64.5	1.57	911	938	959
RbF	2.826	0.94	67	6.80	2.297	2.112	359	110	78.2	1.79	997	1040	1048
RbCl	3.291	1.03	156	6.73	2.297	1.799	843	373	230	1.85	896	969	988
RbBr	3.445	1.08	132	6.64	2.297	1.716	2391	1212	259	1.83	884	947	955
RbI	3.668	1.23	105	6.53	2.297	1.619	3210	1579	372	1.83	833	920	915
CsCl	3.571[a]	1.37[a]	180[a]	5.89[a]	2.116	1.799	333	357	974	2.08	759	904	919
CsBr	3.720[a]	1.39[a]	159[a]	5.71[a]	2.116	1.716	461	386	752	2.01	885	895	909
CsI	3.959[a]	1.46[a]	128[a]	5.79[a]	2.116	1.619	679	555	728	1.95	880	902	894

[a] Data from Ref. 12.

the results given by Bosi [1]. The input data [12–14] for various properties/parameters used in the calculations are also given in Table I.

3. RESULTS AND DISCUSSION

Using the values of various parameters given in Table I, we have obtained the values of T_m with the help of Eq. (5). The values of T_m thus obtained are found to show fairly good agreement with the experimental values [11] of the melting temperatures and to be better than those obtained by Bosi [1].

For estimating the values of $d\phi/dr$ at $r = r_m$ we have used the potential energy expression given in the form of Eq. (9). Within the framework of this model [6], we have considered van der Waals (vdW) dipole–dipole and dipole–quadrupole interactions. The dipole–dipole energy term, which arises from the interaction between induced dipole moments of different atoms, is actually the first term in an infinite series of rapidly converging terms. The dipole–quadrupole term is interpreted as arising from the interaction of a dipole moment on one atom with a quadrupole on the other. Actually, there exists a third term, which varies inversely as the tenth power of interatomic distance, which is called the quadrupole–quadrupole term [9]. In the present article we discuss only the dipole–dipole and dipole–quadrupole interactions because the quadrupole–quadrupole term is negligible in ionic crystals.

It should be mentioned that the overlap potential forms as given by Eq. (19) are based on Harrison's quantum mechanical formulation and differ from the traditional Born–Mayer exponential forms ($D \exp[-r_0 (r/r_0 - 1)/\rho]$) [4] in some important aspects. First, the pre-exponential factors appearing in Eq. (19) also depend directly on the interionic separation whereas in the Born–Mayer exponential forms, only the exponential factors depend on r. Secondly, ionic radii have been introduced arbitrarily as adjustable parameters in the Born–Mayer exponential forms. On the other hand, in Eq. (19) the pre-exponential as well as exponential factors depend on fundamental factors like Planck's constant, electronic mass, and energy term values. Moreover, the exponential factors are different in different pair interactions, whereas in the Born–Mayer potential a common value of hardness parameters has been taken for the cation–anion, cation–cation, and anion–anion interactions. This is not justified for the reasons discussed by Shanker and Kumar [14]. If one takes unequal values of hardness parameters for the crystal, then the number of parameters becomes too large to be determined from the input data for the lattice parameter and bulk modulus. Thus, the Harrison potential form is superior to the Born–Mayer exponential forms.

4. SUMMARY

To summarize, from the new relationship, we can predict adequately the melting temperature for alkali halides in agreement with experimental data [11]. Thus, the results obtained in the present study clearly demonstrate that the formulations originally due to the diffusional force theory [1], Harrison's potential function [8], and the Kumar formulation [7] provide a useful method for studying the melting temperature for alkali halides. Finally, it should also be mentioned that the relationship proposed in the present study is of a general nature and, therefore, its application may be extended to different classes of solids. The results of the present investigation also lead to the understanding of the physical mechanism of melting based on the microscopic details of the theory of interionic potentials.

REFERENCES

1. L. Bosi, *Phys. Status solidi (a)* **101**:K111 (1987).
2. Z. H. Fang and L. R. Chen, *J. Phys: Condens. Matter* **6**:6937 (1994).
3. J. Shanker, M. P. Sharma, and S. S. Kushwah, *J. Phys. Chem. Solids* **60**:603 (1999).
4. R. S. Chauhan and C. P. Singh, *Physica B* **324**:151 (2002).
5. O. L. Anderson, D. G. Isaak, and V. E. Nelson, *J. Phys. Chem. Solids* **64**:2125 (2003).
6. Q. Liu and L. R. Chen, *Chinese J. High Press. Phys*. **19**: 1–7 (2005).
7. M. Kumar, *Physica (c)* **229**:421 (1997).
8. W. A. Harrison, *Phys. Rev. B* **23**:5230 (1981).
9. J. Shanker and G. G. Agrawal, *Phys. Status solidi (b)* **123**:11 (1984).
10. M. P. Tosi, "Cohesion of Ionic Solids in the Born Model," in *Solid State Physics,* Vol. **16**, F. Seitz, D. Thurnbull, and H. Ehrenreich, eds. (Academic Press, New York, San Francisco, 1964), p. 1.
11. A. R. West, ed., *Handbook of Chemistry and Physics*, 51st Ed. (CRC Press, Boca Raton, Florida, 1970/71).
12. O. L. Anderson, in *Earth's Core: Dynamics, Structure, Rotation,* Geodynamics Series, Vol. **31**, V. Dehant, K. C. Creager, S. I. Karato, and S. Zatman, eds. (American Geophysical Union, Washington DC, 2003).
13. Q. He and Z. T. Yan, *Phys. Status solidi (b)* **223**:767 (2001).
14. J. Shanker and M. Kumar, *Phys. Status solidi (b)* **142**:325 (1987).