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SIMPLE INTERPRETATION OF MELTING FOR ALKALI METAL HALIDES. II.

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Abstract: The melting mechanism for alkali metal halides is explained by discussing volume and enthalpy change at melting. Additional oscillatory jumps of cations and anions are assumed to be restricted to the sites of their own sublattices. The resulting volume change and enthalpy of melting are correlated with parameters such as ionic radius ratio and change of Madelung constant.

1. Introduction

In our study of volume change at melting for elements a simple model of ionic motion is introduced$^{1)}$. One may try to apply the same model to typical ionic substances like alkali metal halides. Ions in molten salts are dissociated$^{2)}$, and thus in the introduced model ions of opposite signs must be treated equally. Namely, in liquid too, each ion is surrounded, as a rule, by ions of opposite charge, as confirmed by X-ray experiments$^{3)}$ and MD "computer experiments"$^{4)}$. Therefore, the motion of ions can be allowed, roughly, only through the sites of their own sublattices. It is shown that the enthalpy of melting is influenced by the ionic radius ratio $\varrho = r_+/r_-$ through Pauling's correction function$^{5)}$ $F(\varrho)$, while the volume change is influenced by the increase of the Madelung constant α as a consequence of ionic motion.

2. Change of volume

For the calculation of the volume change at melting, one may apply the following relation, which leads to good results for elements$^{1)}$, i.e.

$$V_1/V_s = (1 + \Delta/n)^3 \qquad (1)$$

where V_1 and V_s are volumes of liquid and solid, respectively, n=12 is the coordination number of the sublattice and Δ is the relative hypothetical regular increase of lattice constant, which is necessary for the geometrically free motion of ions to their neighbouring sublattice sites. This regular increase is shown in Fig.1, from which follows $a'=4(r_+ + r_-)/\sqrt{2}$ with $a=2(r_+ + r_-)$ and $\Delta = (a'-a)/a=\sqrt{2}-1=0.414$. According to eq.(1), the change of volume for alkali halides is expected to be $V_1/V_s=1.107$ or $\Delta V/V_s=10.7\%$. However, the experimental data listed in the Table lie within the interval from 31.7% for LiF to 10.5% for CsCl. Therefore, the calculated constant 10.7% may be considered

as an extrapolation value for this series.

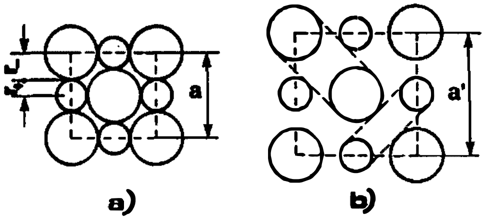

Fig.1 Arrangement of cations and anions in a face-cube layer for alkali halides; a) in a solid, and b) in a regularly enlarged crystal lattice.

The main reason for this behaviour may be sought in correlation with ionic radius ratios. For, it is well known, that the influence of ϱ on various physical parameters is more pronounced

TABLE

	$\Delta V/V_s$ exp.	$\Delta V/V_s$ calc.	$\frac{3\Delta H_m}{U_o}$	$\alpha_{liq.}$	$\alpha_{liq.}$ MC, MD	ΔH_{me} (kcalmole^{-1})	ΔH_{mc} (kcalmole^{-1})	$\frac{\Delta H_{mc}}{F^9(\varrho)}$
LiF	0.317	0.333	0.079	1.89	-	6.47	8.95	6.58
Cl	0.250	0.262	0.070	1.85	1.91	4.72	8.19	4.58
Br	0.221	0.241	0.067	1.84	1.85	4.22	7.95	4.16
I	0.202	0.209	0.060	1.83	-	3.50	7.63	3.58
NaF	0.282	0.263	0.110	1.85	-	8.03	8.77	8.51
Cl	0.230	0.214	0.107	1.82	1.82	6.69	7.61	6.39
Br	o.212	0.199	0.106	1.81	-	6.24	7.35	5.93
I	0.193	0.178	0.102	1.80	-	5.64	6.97	5.13
KF	0.198	0.184	0.104	1.80	1.84	6.75	7.35	7.50
Cl	0.168	0.160	0.110	1.78	1.8,1.78	6.25	6.62	6.55
Br	0.160	0.153	0.112	1.78	1.76	6.10	6.20	6.02
I	0.15o	0.142	0.113	1.77	1.77	5.74	5.43	5.09
RbF	-	0.150	0.092	-	-	5.82	5.94	6.00
Cl	0.134	0.136	0.103	1.77	1.76	5.67	5.78	5.90
Br	0.128	0.132	0.106	1.76	-	5.57	5.64	5.64
I	0.123	0.127	0.106	1.76	-	5.27	5.41	5.25
CsF	0.110	0.107	0.086	1.76	-	5.19	(5.78)	-
Cl	0.105	0.107	0.110	1.75	-	5.84	(5.13)	-

as it becomes smaller than one[5,6]. By investigating the experimental values of $\Delta V/V_s$ in dependence on r_+ and r_-, their mutual correlation is found. This approach is different from Furukawa's, who considered the influence of ϱ on $\Delta V/V_s$ including polarisatic effects[7]. Our correlation may be written in the form

$$\Delta V/V_s = 0.107 + (r_{-m}/r_{+m} - 1)(r_+/r_{+m} - 1)(r_-/r_{-m} - 1) \qquad (2)$$

Here, $r_{-m} = 2.85$ Å is the extrapolated maximum anion radius, and $r_{+m} = 1.67$ Å is the extrapolated maximum cation radius. Both may be considered as fitting parameters. Values calculated by means of eq.(2) are compared with the experimental values in the Table.

Another approach to show the existence of constant 10.7% would be done by analysing the interionic potential and the lattice energy. Taking a very simple form of this potential$^{8)}$

$$U_{ij} = \begin{cases} (-e^2/R) + \lambda \exp(-R/\rho_0) & \text{nearest neighbours} \\ \pm (1/p_{ij})/R & \text{otherwise} \end{cases} \qquad (3).$$

the lattice energy results as

$$U_o = (-N\alpha e^2/R_o)(1 - \rho_0/R_o) \qquad (4)$$

where e is the electric charge of an ion, λ and ρ_0 are empirical parameters, and R_o is the equilibrium interionic distance. If this distance for a given substance is increased by a very small amount, the associated small change of lattice energy ΔU_o can be identified as an enthalpy change at melting, i.e.,

$$\Delta H_m \simeq \Delta U_o = (-\Delta R_o/R_o)(U_o + N\alpha e^2 \rho_0/R_0^2) + U_o \Delta\alpha/\alpha$$

From the proportionality of V_s with R_o^3 it follows that $\Delta V/V_s \simeq 3\Delta R_o/R_0$, and using the expression for ΔH_m

$$\Delta V/V_s \simeq (3/(U_0 - N\alpha e^2 \rho_0/R_0^2))(\Delta H_m + U_o \Delta\alpha/\alpha) \qquad (5)$$

In this equation U_o is taken as an absolute value. Neglecting the term $N\alpha e^2 \rho_0/R_o^2$, which is about 1/10 of U_o we obtain

$$\Delta V/V_s \simeq 3\Delta H_m/U_o + 3\Delta\alpha/\alpha \qquad (6)$$

The calculated values of $3\Delta H_m/U_o$ are shown in the Table. These values are fairly constant (except for Li halides) and they may be identified as a calculated constant 0.107 for a rigid sphere model. In order to obtain agreement of $\Delta V/V_s$ in eq.(6) with experimental values, one should determine the only variable term $\Delta\alpha/\alpha$. The constant α is known for a solid fcc crystal structure and consequently from the experimental data of $\Delta V/V_s$, ΔH_{me} and $U_0$$^{9)}$, the Madelung constant of liquid can be estimated as $\alpha_\ell = \alpha + \Delta\alpha$. No other method is known for the estimation of α, excluding MC or MD computer simulations from which α_ℓ is deduced for certain compounds$^{10-12)}$ and used in the Table for comparison.

There appears a good general behaviour of the deduced values in relation to those calculated by the present method.

3. Enthalpy of melting

In order to calculate the enthalpy of melting one may apply the same harmonic approximation as that used for metals[1]. The following relation is expected to be valid

$$\Delta H_m \simeq 2\pi^2 (A_+ + A_-)(\nu_0/n)^2 (a\sqrt{2}/2)^2 = CM\nu_0^2 a^2 \qquad (7)$$

where A_+ and A_- are the atomic masses of a cation and anion, and $M=A_+ + A_-$ is the molecular mass. Frequency ν_0 is the Einstein frequency of ionic vibration in solid, approximated by the Debye characteristic temperature Θ_D as in the case for metals[1], and $C=2.456\cdot 10^{-12}$ for ΔH_m in kcal mole^{-1}. The values ΔH_{mc} calculated by eq. (7) are given in the Table. The agreement with experimental values ΔH_{me} appears satisfactory for K and Rb halides but not for Na and, especially, for Li halides. This means that harmonic approximation becomes invalid in the case of lighter alkali halides. It is also possible that the deviation is partially due to a certain tendency towards the ion-pair formation suggested by "computer experiments"[11,12].

4. Discussion

Pauling has suggested that the ionic radius ratio has an effect on certain physical properties of alkali halides[5] through the phenomenon of double repulsion when $a \neq 2(r_+ + r_-)$.

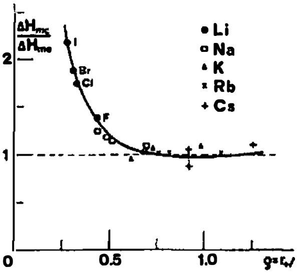

Fig.2 Dependence of the ratios of calculated and experimental enthalpy change at melting, upon the ionic radius ratio. The curve is the ninth power of Pauling's function F(ρ).

He found a correction function $F(\rho)$ which brings into mutual relation the real equilibrium distance R_o between ions in crystal and the radii of ions

$$R_0 = (r_+ + r_-)\, F(\rho) \qquad (8)$$

by using the interionic potential of the form

$$u_{ij} = -e^2/r_{ij} + \beta_{ij} B_o e^2 (r_+ + r_-)^{m-1} r_{ij}^{-m} \qquad (9)$$

where β_{ij} and B_o are constants, and m is assumed to have the value 9 for all alkali halides$^{5)}$. In our model of melting, ions move from site to site within their respective sublattices. Because of double repulsion, simple harmonic approximation has to be corrected in the case of lighter halides, i.e. if $\rho < 0.7$. Eqs.(8) and (9) suggest that the necessary correction could be achieved using the m-th power of the function $F(\rho)$. If the ratio $\Delta H_{mc}/\Delta H_{me}$ is plotted against ρ, then the deviation from one for Li and Na halides is very well described by $F^9(\rho)$, as can be seen in Fig.2. The Table shows the values $\Delta H_{mc}/F^9(\rho)$, and agreement with the experimental data appears very good.

Theoretical proof of the introduced correction is being investigated.

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