Theoretical Melting Curves of Alkali Halides

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An analysis of the melting curves of alkali halides is given. The study is based on the Improved Unsymmetrized Self-Consistent Field Method (IUSCFM) for strongly anharmonic crystals with complex lattice and the energy, entropy and Ross's criterions in calculating the melting curves of alkali halides. The anharmonicities up to sixth order have been taken into consideration. The energy criterion was proven to be the most correct one along the melting curves of the high pressure modification (CsCl structure) while the entropy and Ross's criterions lead to a little better agreement with experiment than the energy criterion when dealing with rocksalt structure. Calculations of the melting curves of KCl and CsCl are compared with the experimental results.

Key words: Alkali halides, Melting curves, Energy criterion, Entropy criterion, Ross's criterion.

1. Introduction

The development of a quantitative theory of the phase equilibrium and phase transition is among the most complicated problems of statistical mechanics.In the case of the crystalline phase the difficulty is that at high temperatures the lattice vibrations are strongly anharmonic and it is not allowed to adopt the quasiharmonic approximation even as a zeroth approximation [1–3]. This adds to the known difficulties of formulating a sufficiently suitable model of melting that could reflect reality faithfully even for simple compounds.

The situation is further complicated when polyatomic substances are investigated. In this connection, the study of the behaviour of the thermodynamic functions of the crystalline phase along the experimental melting curve is quite justifiable in the field of melting [4].

One of the oldest and most widely used attempts to predict the melting curves of solids is that due to Lindemann [5]. Assuming that melting occurs when the amplitude of lattice vibrations becomes larger than a certain fraction of the lattice spacing, Lindemann arrived at a relationship between the melting temperature T_m, the molecular volume of the crystal in equilibrium with the liquid phase V_s, and the force constants of the harmonic oscillator.

The Lindemann principle was reformulated by Ross [6] by stating that for a given substance at all points along its melting curve, the solid always occupies the same fraction of configurational phase space. This assumption is identical to assuming that

$$\begin{aligned}\varrho(T, V_s) &= \frac{F(T, V_s) - F_{id}(T, V_s) - U_0(V_s)}{RT} \\ &= \varrho_s = \text{const} \qquad (1)\end{aligned}$$

along the melting curve, where $(F - F_{id})$ is the excess or configurational Helmholtz free energy of the crystal and U_0 is the static lattice energy.

Lindemann's melting principle was also reformulated in terms of the reduced entropy [4, 6, 7] or the reduced energy [6, 8]. The entropy criterion postulates that along the melting binodale the configurational entropy is constant:

$$\sigma(T, V_s) = -\frac{1}{R}(\mathrm{d}(F - F_{id})/\mathrm{d}T)_{V=V_s} = \sigma_s = \text{const}\,, \quad (2)$$

and the energy criterion is

$$\tau(T, V_s) = \frac{U(T, V_s) - U_0(V_s)}{RT} = \tau_s = \text{const}\,, \quad (3)$$

where $U(T, V)$ is the potential energy of the crystal. Here it must be mentioned that (1)–(3) are not valid in the quantum region. On the other hand there is a mutual relationship between ϱ, σ and τ:

$$\tau = \varrho + \sigma\,, \quad (4)$$

which can be derived using the second thermodynamic law.

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The work presented here is intended to complete the previous analyses [9] of (1)–(3) for their applicability in the case of alkali halides using the Improved Unsymmetrized Self-Consistent Field Method (IUSCFM) for strongly anharmonic multi compound crystals with lattice [3, 10, 11]. The results of the mentioned analyses are demonstrated by calculating the melting curves of KCl, CsCl, NaCl, NaBr and NaI.

2. Helmholtz Free Energy

In IUSCFM which was originally presented by Terletsky and Zubov [12] for describing strong anharmonic monoatomic crystals, each ion (atom) of a crystal is described by its one-particle probability density which is distinct from those of other atoms. In thermodynamic equilibrium, the spatial parts of the one-particle functions obey a set of nonlinear integral equations [11].

For a perfect crystal with "S" atoms (ions) in an elementary cell, interacting by means of pair wise central forces, the system of equations takes the form

$$\begin{aligned}\ln\{\Lambda_\mu\, w_\mu(\boldsymbol{q}_\mu, \boldsymbol{Q}_\mu)\} + (1/\theta)\Big[\Phi^{\mu\mu}(\boldsymbol{q}_\mu, \boldsymbol{Q}_\mu)\\ + \sum_{\nu=1}^{S} \int \varphi^{\mu\nu}(\boldsymbol{q}_\mu, \boldsymbol{Q}_\mu, A\boldsymbol{n} + \boldsymbol{R}_\nu - \boldsymbol{R}_\mu + \boldsymbol{q}'_\nu, A\boldsymbol{n}\\ + \boldsymbol{R}_\nu - \boldsymbol{R}_\mu + \boldsymbol{Q}'_\mu)\, w(\boldsymbol{q}'_\nu, \boldsymbol{Q}'_\nu)\, \mathrm{d}\boldsymbol{q}'_\nu\, \mathrm{d}\boldsymbol{Q}'_\nu\Big] = 0\,, \qquad (5)\end{aligned}$$

where $\theta = kT$ and $\Phi^{\mu\mu}$, $\varphi^{\mu\nu}$ are the interaction potentials for atoms (ions) of the μ-th and ν-th components, A lattice matrix, $\boldsymbol{n}$ a vector with integer valued projections. $A\boldsymbol{n}$ defines the position of the elementary cell and $\boldsymbol{R}_\mu$ defines points in it. $\boldsymbol{q}_\mu$ and $\boldsymbol{Q}_\mu$ are displacements of the atom core and its shell, respectively.

As usual it is convenient to present the one-particle functions in the exponential form

$$w_\mu(\boldsymbol{q}_\mu, \boldsymbol{Q}_\mu) = \exp\{(1/\theta)\,[f_\mu - u_\mu(\boldsymbol{q}_\mu, \boldsymbol{Q}_\mu)]\}\,, \qquad (6)$$

in which

$$\begin{aligned}u_\mu(\boldsymbol{q}_\mu, \boldsymbol{Q}_\mu) &= \Phi^{\mu\mu}(\boldsymbol{q}_\mu, \boldsymbol{Q}_\mu)\\ &+ \sum_{\nu=1}^{S} \Big[\int \varphi^{\mu\nu}\, w_\nu(\boldsymbol{q}'_\nu, \boldsymbol{Q}'_\nu)\, \mathrm{d}\boldsymbol{q}'_\nu\, \mathrm{d}\boldsymbol{Q}'_\nu \qquad (7)\\ &- 0.5 \int \varphi^{\mu\nu}\, w_\nu(\boldsymbol{q}'_\nu, \boldsymbol{Q}'_\nu)\, w_\mu(\boldsymbol{q}_\mu, \boldsymbol{Q}_\mu)\, \mathrm{d}\boldsymbol{q}_\mu\, \mathrm{d}\boldsymbol{q}'_\nu\, \mathrm{d}\boldsymbol{Q}_\mu\, \mathrm{d}\boldsymbol{Q}'_\nu\Big]\,,\end{aligned}$$

$$f_\mu = -\theta\, \ln \int \exp(-u_\mu/\theta)\, \mathrm{d}\boldsymbol{q}_\mu\, \mathrm{d}\boldsymbol{Q}_\mu\,. \qquad (8)$$

Using the adiabatic approximation $\nabla_{\xi\mu} u_\mu = 0$ ($\xi_\mu = \boldsymbol{Q}_\mu - \boldsymbol{q}_\mu$) one can exprime ξ_μ [11] as a function of $\boldsymbol{q}_\mu$, temperature and external parameters a'.

In the considered zeroth approximation, which contains the contribution of the main anharmonic terms, the Helmholtz free and internal energies of a strongly anharmonic multi compound crystal are determined by [11]

$$\begin{aligned}F_0 = -\theta \ln \int \exp\{-(1/\theta)\,[(\boldsymbol{p}^i_\mu)^2/(2m_\mu) + U^0]\}\, \mathrm{d}\boldsymbol{r}^1_1 \ldots\\ \ldots \mathrm{d}\boldsymbol{p}^N_s/(2h)^{3SN}\,, \qquad (9)\end{aligned}$$

$$E_0 = 0.5\, NS + U^0\,, \qquad (10)$$

where h is Planck's constant and U^0 is the self consistent potential energy:

$$U^0 = \sum_{\mu=1}^{S} u^i_\mu = \sum_{\mu=1}^{S} u_\mu(\boldsymbol{q}^i_\mu, \xi^i_\mu(\boldsymbol{q}^i, \theta, a'))\,. \qquad (11)$$

The statistical perturbation theory can be used to calculate the correction F' to the Helmholtz free energy (9):

$$F' = \langle (U - U^0) \rangle - \langle (U - U^0 - \langle U - U^0 \rangle)^2 \rangle / (2\theta) + \ldots\,, \qquad (12)$$

where $\langle\ \rangle$ means the average over $\boldsymbol{q}$. On the other hand, one can take into consideration quantum corrections too [10]:

$$F_Q = h^2/(24\theta) \sum_{\mu=1}^{S} \sum_{\nu=1}^{S} (1/m_\mu)\, \langle \nabla^2_r U^0 \rangle\,. \qquad (13)$$

Then the corresponding corrections to the internal energy (10) can be obtained using the Gibbs-Helmholtz equation.

3. Numerical Results and Discussion

Alkali halides (KCl, KBr, KI, RbCl, RbBr, RbI and CsCl) have two crystalline modifications: low pressure structure (NaCl-structure) and high pressure one (CsCl-structure). Therefore, we have studied ϱ, σ and τ along the experimental melting curves of these modifications. Experimental data are taken from [13–15].

For each compound we have first calculated the equilibrium nearest neighbour distance a for the crystalline phase versus the experimental melting temperature $(T_\mathrm{m})_\mathrm{exp}$ at the experimental melting pressure $(P_\mathrm{m})_\mathrm{exp}$. To do this we have solved numerically the equation of state

$$\begin{aligned}P &= -(a/(3V))\,(\partial F/\partial a)_\mathrm{T}\\ &= -(a/(3V))\,[\partial(F_0 + F' + F_Q)/\partial a]_\mathrm{T} \qquad (14)\end{aligned}$$

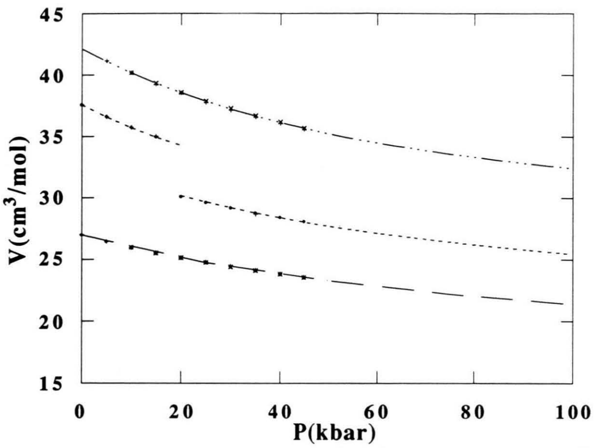

Fig. 1. Calculated dependence of volume on pressure of NaCl ——, KCl - - - and CsCl — - - -. Experimental results ●, + and × are taken from [21], [23], and [26], respectively.

along the experimental melting curve in relation to the volume V of the crystalline phase. Equation (14) has two real roots $a_1(T_m, P_m) < a_2(T_m, P_m)$. The lower root represents the stable thermodynamic solution $(\partial V_1/\partial P)_T < 0$, while the upper root represents the unstable one $(\partial V_2/\partial P)_T > 0$.

In these calculations the Born-Mayer-Huggins potential [16–18] describing the effective force between two ions and three body interactions [19] is used. The coefficients of the used potentials are given in [9]. The polarizabilities of the ions, used for determining the interionic potential $\Phi^{\mu\mu}$, are given in Table 1 [20].

The parameters of the above mentioned potentials were obtained by using low pressure experimental data (P = 1 bar). Some of alkali halides (like KCl) change their structure with pressure. Therefore, the equilibrium nearest neighbour distance a (or compressibility $V(P, T_0)/V(P_0, T_0)$) of the crystalline phase versus pressure at a fixed temperature T_0 was calculated for NaCl, KCl and CsCl in order to demonstrate the applicability of USCFM to study high pressure solid isotherms.

In order to realize the calculation of the compressibility of NaCl, KCl and CsCl up to 100 kbar, the transition pressure (P_{tr}) was firstly searched in the mentioned pressure interval for the three studied salts. In this case the system of equations

$$\mu_I(T, P) = \mu_{II}(T, P)\,, \tag{15}$$

$$P = -(a_I/(3V_I))(\partial F_I/\partial a_I)_T\,, \tag{16}$$

$$P = -(a_{II}/(3V_{II}))(\partial F_{II}/\partial a_{II})_T \tag{17}$$

was solved numerically for $T = 298$ K with taking into consideration the conditions of the thermodynamic stability of the structure

$$(\partial^2 F_I/\partial a_I^2)_T > 0\,, \tag{18}$$

$$(\partial^2 F_{II}/\partial a_{II}^2)_T > 0\,. \tag{19}$$

μ is the chemical potential and I, II denote the low and high pressure structure, respectively. It was found that NaCl does not change its structure when pressure increases up to 100 kbar. Our results ascertain the experimental results of Vaidya and Kennedy [21] while they are in a disagreement with the results of Pistorius [22]. The same was found for CsCl, while KCl does with the following parameters:

Reference	P_{tr} (kbar)	$-\Delta V = V_{II} - V_I$ (cm^3/mol)	$\Delta S = S_{II} - S_I$ (J/mol K)
This work	20.13	4.07	0.05
[23]	19.7	4.20	
[24]	20.0		
[22]	19.27 ± 0.08		0.03
[25]	19.55 ± 0.13	4.11	0.02

This means that our finding is in a good agreement with the experimental data. Here it must be mentioned that the pressure induced phase transition in the alkali halides and the influence of temperature on it is beyond the frame of this work and will hopefully be the subject of a forthcoming communication.

After the determination of the pressure for KCl, V_I and V_{II}, the volume of NaCl and KCl versus pressure was calculated using (16) up to 100 kbar and P_{tr}, respectively. Equation (17) was used to calculate V_{II} (P, $T = 298$ K) for KCl and CsCl up to 100 kbar. The calculated results were compared with experimental data [22, 24, 26], where a remarkable agreement, specially in the case of KCl and CsCl, was found. The results of the calculation and corresponding experimental data are given in Figure 1. So, the compressibility V (P, $T = 298$ K)/V ($P = 1$ bar, $T = 298$ K) is then calculated.

3.1. On the Applicability of Ross's, the Entropy and Energy Criterions

After obtaining $a_1(T_m, P_m)$ along the experimental melting curves, we have calculated ϱ, σ, τ using (1)–(3) and (9)–(13). The results are presented in Figs. 2–4. The phase transition between two crystalline phases

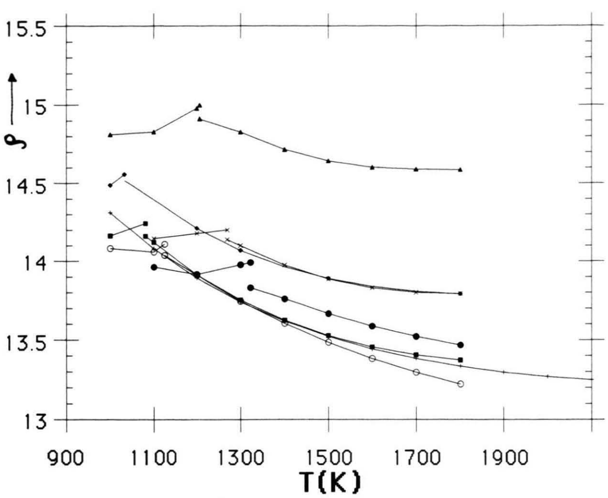

Fig. 2. Temperature dependence of $\varrho(T, V)$ along the melting curves of seven alkali halides: CsCl (+), RbI (◆), RbBr (■), RbCl (○), KI (▲), KBr (×) and KCl (●).

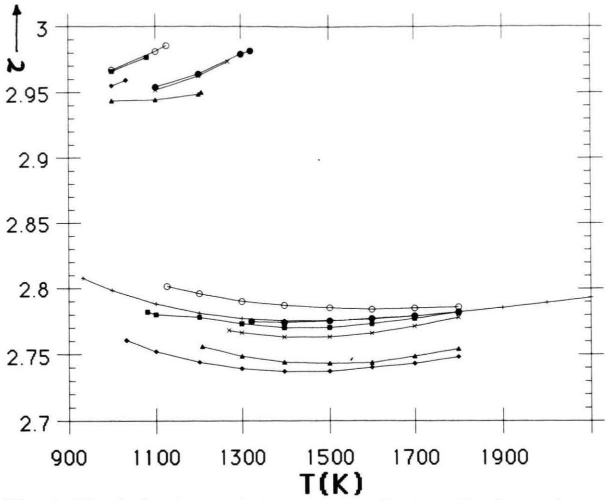

Fig. 4. The behaviour of the energy criterion (3) along the melting curves of CsCl (+), RbI (◆), RbBr (■), RbCl (○), KI (▲), KBr (×), and KCl (●).

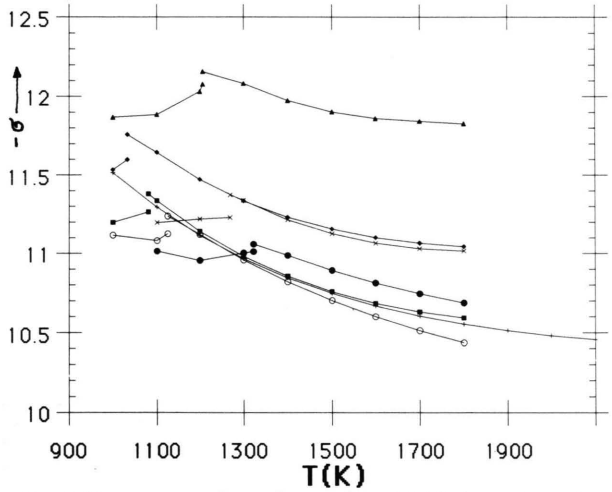

Fig. 3. Temperature dependence of $-\sigma(T, V)$ along the melting curves of CsCl (+), RbI (◆), RbBr (■), RbCl (○), KI (▲), KBr (×), and KCl (●).

(rocksalt structure – CsCl structure) is well demonstrated for all studied crystals at their triple points (low pressure modification – high pressure modification – liquid phase) by breaks in the mentioned curves at these points.

Figure 2 gives the studied crystals as a function of melting temperature. It is clear from Fig. 2 that ϱ does not change much for the low pressure modification of KCl, KBr, and RbCl, while for KI, RbBr and RbI it increases remarkably. On the other hand, ϱ decreases continuously along the melting curves of the high pressure modification of all studied crystals.

Figure 3 presents the absolute value of the configurational entropy $|\sigma|$ as a function of melting temperature. The behaviour of $|\sigma|$ is similar to that of ϱ along the melting curves of all studied compounds. Here it must be mentioned that ϱ is always positive while σ is always negative.

Figure 4 illustrates the dependence of τ on the melting temperature. It is apparent that τ increases on increasing the melting temperature when the compounds have the rocksalt structure. At the high pressure modification (CsCl structure) τ initially decreases to its minimum value and then begins to increase. However the changes along the melting curves of the high pressure modification are smaller than those along the melting curves of low pressure modification.

Figures 2–4 show that the relative changes of τ are remarkably smaller than those of σ and ϱ along the melting curves of the high pressure crystalline phase of the studied salts. These changes are of the same order when the studied crystals have rocksalt structure. This is well demonstrated by the example of KBr (see Figure 5). This means that the energy criterion (3) is more effective than the entropy criterion (2) and that of Ross (1) in describing the melting curves of the high pressure modifications. As the relative changes of τ are a little bigger than those of σ and ϱ for the NaCl structure it is expected from (1) and (2) to give a little better agreement with experiment than (3) when dealing with

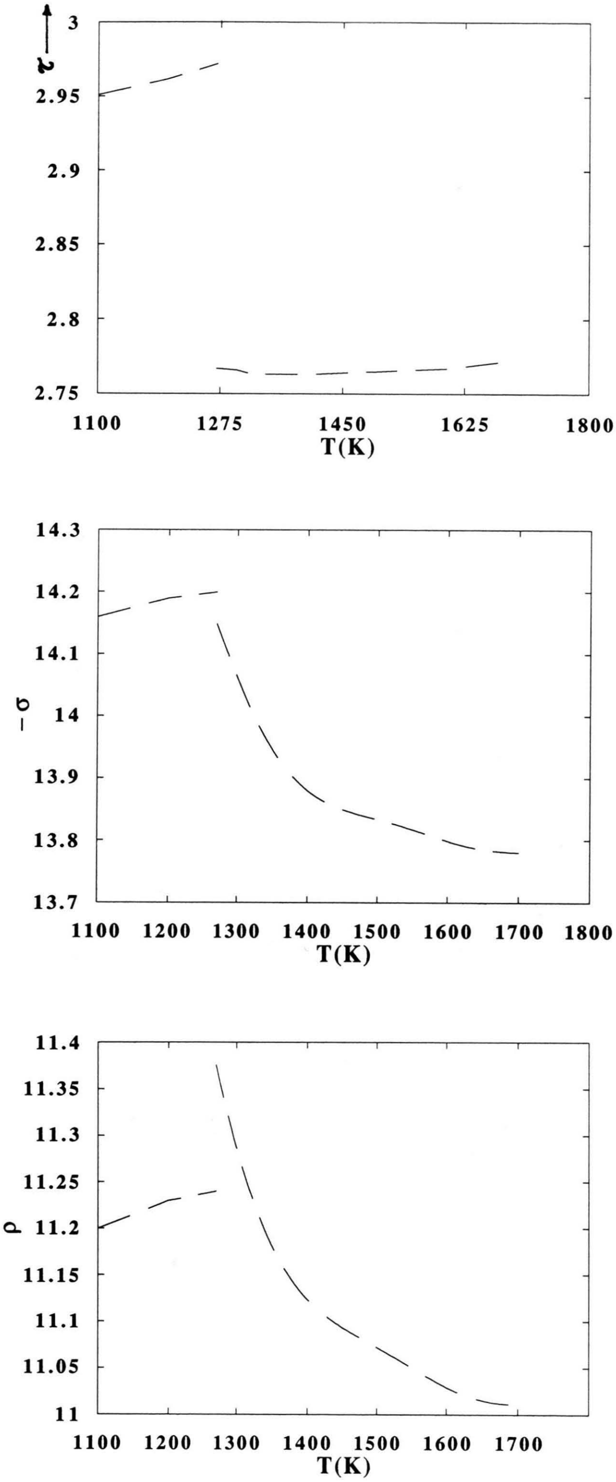

Fig. 5. The behaviour of three melting criterions along the melting curve of KBr: energy criterion (a), entropy criterion (b) and Ross's criterion (c).

crystals having rocksalt structure. Therefore (1)–(3) were used to calculate the melting curves of KCl and CsCl in order to verify the above conclusion. Results are given in Figs. 6 and 7.

Figure 6, which gives the melting pressure of CsCl as a function of the melting temperature, calculated from the equation of state (14) and from (1), (2) or (3) after calculating ϱ_s, σ_s, and τ_s at the melting temperature $T_m = 1270$ K, shows that the agreement between the experimental and theoretical results using (3) is remarkable. This result agrees well with that of Soulayman and Harfoush [9], which was obtained on the assumption of rigid ions. The comparison between (1) and (2) (see Fig. 6) shows that both relations give nearly the same results. This finding is in good agreement with that of Zubov [8]. Therefore we give the results of the entropy criterion (2) only to compare them with those of the energy criterion (3) and the experimental ones in the case of KCl (Figure 7). In this Figure σ_s and τ_s are determined at the triple point (NaCl structure – CsCl structure – liquid phase). For the low pressure modification the entropy and energy criterions give good results, but (2) is little better than (3) while the energy criterion remains the best for the high pressure modification.

Here it must be mentioned that KCl was chosen because it has the rocksalt structure up to relatively high temperatures and the experimental melting data of its crystalline modifications are extended and allow for a comparison between the studied melting criteria. On the other hand, CsCl was chosen because it has a different crystal structure from NaCl and is a material that remains in a single phase (CsCl structure) to a very high pressure. In addition, experimental melting data for CsCl are extended up to 2100 K [15].

3.2. Sodium Halide Melting Curves

For the calculation of the melting curves of sodium halides, the equation of state (14) was solved for an experimental triple point (crystalline – liquid – gaseous) in relation to the volume V. After that, depending on (2) and (3), σ_s and τ_s were determined at this point. Then, depending on (14) and (2) or (3), we calculated the melting curves

$$P_m = P_m(T); \quad V = V_s(T), \tag{20}$$

where P_m is the pressure along the melting curve. It was found that the discrepancy between the calculated results, using (2) and (3), does not exceed 2.1% at

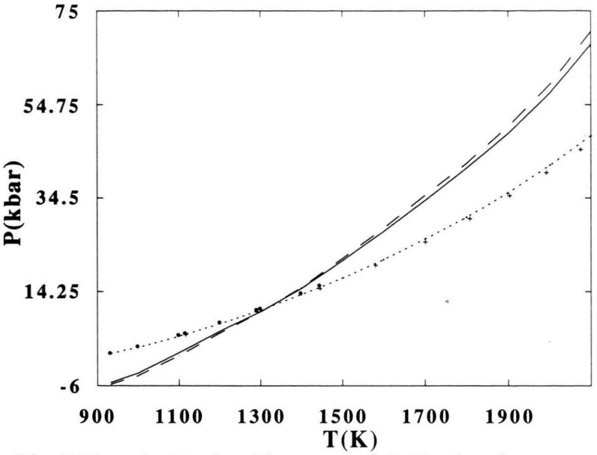

Fig. 6. The calculated melting curve of CsCl using the energy criterion (– – –), entropy criterion (——) and Ross's criterion (— —). Experimental data + and ● are taken from [15] and [13], respectively.

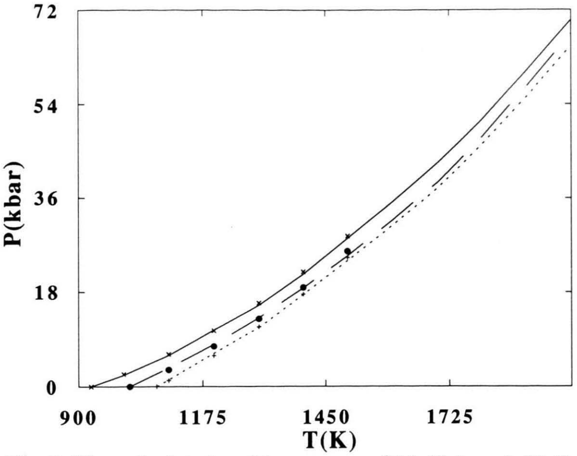

Fig. 8. The calculated melting curves of NaCl (– – –), NaBr (— —) and NaI (——). Experimental data taken from [13]: (+) for NaCl, (o) for NaBr, and (×) for NaI.

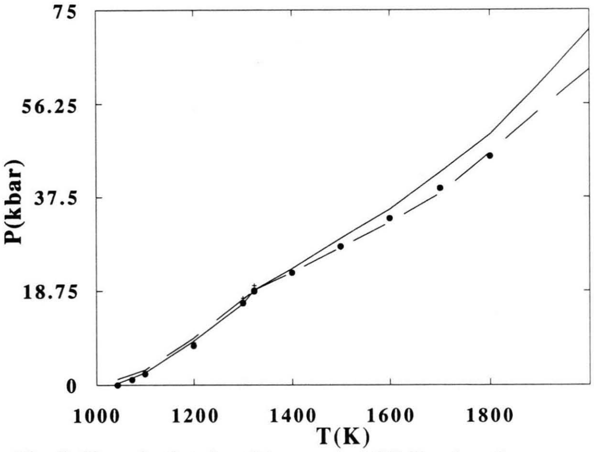

Fig. 7. The calculated melting curve of KCl using the energy criterion (— —) and entropy criterion (——). Experimental data: (+) [13] and (●) [14].

$T_m = 2000$ K, while this discrepancy becomes within the experimental error at $T_m < 1500$ K, where experimental data are available [13]. Therefore we present in Fig. 8 the calculated results using the entropy criterion only.

It is clear from Fig. 8 that, for each fixed melting pressure, the melting temperature of the halides of sodium decreases in the sequence Cl^-, Br^-, I^-. At the same time, the initial slope (dP/dT) of the melting curves decreases in the same sequence. This behaviour remains unchanged when dealing with the halides of K, Rb, and Cs [9]. Here it was found that the melting curves of all studied K and Rb halides exhibit cusps at pressures <20 kbar. These cusps reflect the transformation of the solid phase from the NaCl structure to CsCl structure (see, for example, Figure 7).

On the other hand, for all studied compounds it was found that $P_m(T)$ exhibits a marked curvature towards the pressure axis. This behaviour is more remarkable in the case of the iodides than of the chlorides.

In the calculation of the melting curves of sodium halides (NaCl, NaBr, and NaI) the modified Born-Mayer-Huggins potential [27] was used:

$$\varphi^{\mu\nu}(r) = e_\mu e_\nu / r + \beta_{\mu\nu} b_{\mu\nu} \cdot \exp[\alpha_{\mu\nu}(R_\mu + R_\nu - r)] - C_{\mu\nu}/r^6 - D_{\mu\nu}/r^8 , \quad (21)$$

where e_μ is the electric charge of μ-th ion and the factor $\beta_{\mu\nu}$ originates from certain quantum-mechanical considerations and depends only on the charges of the interacting ions:

$$\beta_{\mu\nu} = 1 + Z_\mu/N_\mu + Z_\nu/N_\nu , \quad (22)$$

Z being $+Z$ for cations and $-Z$ for anions and N_μ is the number of electrons in the outer shell of the μ-th ion. The parameters $b_{\mu\nu}$ and $\alpha_{\mu\nu}$ are related to the ions involved:

$$b_{\mu\nu} = b + B_\mu B_\nu , \quad (23)$$

$$\alpha_{\mu\nu} = t/(R_\mu + R_\nu) + S_\mu S_\nu . \quad (24)$$

Z, b, and t are global parameters with the following values: 0.97, 0.29373×10^{-12} erg and 9.75986, respectively. R_μ and R_ν are the ionic radii. The parameters of the overlap repulsive interactions are given in Table 1.

Table 1. The parameters of overlap repulsive term in modified Born-Mayer-Huggins potential.

Ion	α_μ (Å^{-3})	B_μ (10^{-6} erg$^{1/2}$)	R_μ (Å)	S_i (Å$^{-1/2}$)
Na^+	0.2495	0.6545	0.8513	2.8421
K^+	1.0571	0.3963	1.2804	2.3243
Rb^+	1.5600	0.3245	1.4627	2.3668
Cs^+	2.5880	0.3370	1.6552	2.9857
Cl^-	3.2350	0.3414	1.7393	0.0064
Br^-	4.5330	0.2031	1.9451	0.0111
I^-	6.7629	0.1200	2.1842	0.0268

On the other hand, as the three body interactions, which have proved [9, 19, 28, 29] very useful to explain the structural stability of alkali halides, (this was proven in this work also, see Figs. 2–7), are not included in calculating the melting curves of sodium halides we have taken into consideration the conclusion of Wallat and Holder [30] concerning Van der Waals potentials. They concluded [30] that the experimental data on phase transitions demand larger values of these potentials than the traditional sets given by Mayer [16]. This adds to the conclusion of Shanker and Agrawal [31] about the significant role of Van der Waals potentials in studying the structural phase transitions of ionic crystals. Therefore, Van der Waals dipole-dipole and dipole-quadrupole interactions were evaluated using the London-Margenau formulation [32, 33]:

$$C_{\mu\nu} = 1.5\,\alpha_\mu\,\alpha_\nu\,E_\mu\,E_\nu/(E_\mu + E_\nu)\,, \tag{25}$$

$$D_{\mu\nu} = 2.25\,(C_{\mu\nu}/e^2)\,(E_\mu\,\alpha_\mu/n_\mu + E_\nu\,\alpha_\nu/n_\nu)\,, \tag{26}$$

where E_μ is an energy parameter which is obtained from the polarizability α_μ by the relation [34]

$$E_\mu = e\,h(n_\mu/m_e\,\alpha_\mu)^{1/2}\,. \tag{27}$$

n_μ is the total number of electrons in the ion μ, m_e and e are the mass and charge of the electron, respectively.

4. Conclusion

Our approach has the advantage of being entirely consistent with the framework of the Improved Unsymmetrized Self-Consistent Field Method for strongly anharmonic crystals with complex lattice, in contrast to most other melting studies which often use empirical assumptions.

We conclude that Ross's and the entropy criterions, which are sometimes called the generalized Lindemann melting laws [4, 6, 7], can not be derived from the Lindemann criterion in the case of strongly anharmonic alkali halide crystals. This is due to the anharmonic effects. In the classical quasi-harmonic approximation, where Ross's and the entropy criterion follow from the Lindemann criterion, the energy criterion is actually an identity ($\tau_s = 3$ for alkali halides). But the calculations presented in this work demonstrate that the τ_s values are different from 3 by about 10% (see Figure 4).

Our finding concerning the curvature of $P_m(T)$ toward the pressure axis in all studied compounds agrees well with the measurements. This result can be developed as follows: like other first-order phase transitions, melting is governed by the Clausius-Clapeyron equation

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S}\,.$$

The entropy of the liquid phase is always greater than the entropy of the crystalline one. So, the change in entropy upon melting is always positive: $S_{\text{liquid}} - S_{\text{crystal}} > 0$. The change in volume upon melting ($V_{\text{liquid}} - V_{\text{crystal}}$) has the same feature as dT/dP. As dT/dP exhibits a large negative curvature, ($V_{\text{liquid}} - V_{\text{crystal}}$) decreases along the melting curve. The rate of decrease of the volume change upon melting of the low pressure modification is remarkable. One can explain this phenomenon by suggesting that the liquid phase of this modification reorders itself with pressure to a more densely packed arrangement because of the short-range repulsive potential. Our findings are consistent with those of Adams [35], who found that under increasing pressure the structure of liquid KCl gradually alters from an open, charge-ordered arrangement to one more nearly resembling that of a simple nonionic mixture, and confirm the conclusion of Tallon [36] that the liquid undergoes a continuous transition from a simple-cubic-like sixfold-coordinated structure to a body-centered-like eightfold-coordinated structure and the speculation of Ross [37–40], who argued that the structural changes taking place in compressed alkali halide melts lead to an increase in the local coordination number with increasing pressure. On the other hand, our results are consistent with the prediction of Ross [37, 38] about the limitations of the Lindemann law.

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