

## Stability and melting of simple ionic systems

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A melting criterion for binary ionic compounds is formulated in terms of an instability due to the overlap between the larger ions (generally anions). This model provides a simple explanation of the linear behavior of the ratio of the ionic radii versus the square root of the melting temperature observed for alkali halides and pointed out here for the first time. It is then shown that the variation of the melting temperature with pressure is mainly due to the change of the force constants between the ions and that covalent or polarization effects are essential for the stability of binary superionic conductors like AgI.

Of the most familiar phase transitions, condensation and melting, the former is much better understood than the latter.<sup>1</sup> This is due to a variety of reasons, for example, the identification of the order parameter. In the case of condensation, the density is the proper order parameter, while for melting a more sophisticated concept is required.

A theory of melting should start from the evaluation of the free energies for the solid and liquid phases. There is no need to comment about the difficulty of calculating the difference of the cohesive energies of the two states.<sup>2</sup> The entropy change shows a simple behavior for monoatomic systems,<sup>3</sup> but already for binary compounds the situation is much more complicated.<sup>4,5</sup>

The alternative, although empirical, approach is to define melting as arising from an instability of the solid or the liquid, the prototype of these theories going back to Lindemann.<sup>6</sup> These methods are not directly connected to free-energy considerations and are justified only if a specific mechanism dominates the process that therefore shows regularities with respect to an appropriate variable. Within such a spirit the phase diagram of simple semiconductors has been studied a few years ago,<sup>7,8</sup> while for ionic crystals regularities have been pointed out with respect to their dielectric properties.<sup>9,10</sup>

In this paper I formulate a microscopic criterion of melting for binary ionic compounds based on a lattice instability due to the overlap between ions of the same kind (anions). This criterion allows for a simple interpretation of the linear behavior (reported here for the first time) of the ratio of the ionic radii versus the square root of the melting temperature observed for alkali halides. I then discuss the pressure dependence of the melting temperature and derive general conditions for the stability of binary ionic systems.

I start from a picture of an ionic solid based on hard spheres with Coulomb potentials.  $R_2$  is the

radius of the larger ion (generally the anion) and  $R_1$  the radius of the smaller. In order to be stable a given packing of hard spheres has to satisfy simple geometrical conditions.<sup>11</sup> For example, a rocksalt structure is stable only if

$$R_2/R_1 < 1 + \sqrt{2}. \quad (1)$$

In fact for  $R_2/R_1 > 1 + \sqrt{2}$  the anions come into mutual contact and the symmetric position for the cation is not any more stable (see the upper corner of Fig. 1).

Suppose a system for which condition (1) is satisfied. At zero temperature the distance  $\Delta$  (Fig. 1) between nearest anions is

$$\Delta = \sqrt{2} R_1 - (2 - \sqrt{2}) R_2. \quad (2)$$

Equation (2) holds if the lattice constant is equal to the sum of the radii. For real systems there are, in general, small differences<sup>12</sup> that I do not consider here. Increasing the temperature the effective distance between anions decreases because of the thermal motion and at a given temperature the anions come into effective contact.

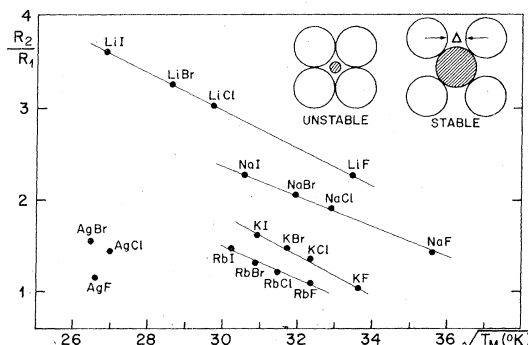


FIG. 1. Ratio of Pauling's ionic radii vs the square root of the melting temperature for compounds with rocksalt structure. The values of  $T_M$  are from Ref. 5 (for the compound RbF  $R_2$  refers to the cation and  $R_1$  to the anion).

In analogy with the static case I conjecture that this *effective contact* between anions also determines an instability that manifests now with the melting. The melting criterion is, therefore,

$$\langle |\delta R_2 - \delta R_2'|^2 \rangle_{T_M}^{1/2} = \Delta, \quad (3)$$

where  $\delta R_2$  and  $\delta R_2'$  are the displacements from equilibrium of two neighboring anions and  $T_M$  is the melting temperature. Defining  $\eta$  as an effective force constant for the relative motion of the anions, taking the high-temperature limit (for alkali halides  $T_M \gg \Theta_D$ ) and using the equipartition principle

$$\langle |\delta R_2 - \delta R_2'|^2 \rangle_{T_M}^{1/2} = (KT_M/\eta)^{1/2}, \quad (4)$$

where  $K$  is the Boltzmann constant.

From Eqs. (2)-(4) the melting criterion can be rewritten

$$R_2/R_1 = \sqrt{2}/(2 - \sqrt{2}) - [1/R_1(2 - \sqrt{2})](KT_M/\eta)^{1/2}. \quad (5)$$

For a fixed  $R_1$  and assuming  $\eta$  to be a weak function of  $R_2$ , Eq. (7) predicts a linearly decreasing behavior of  $R_2/R_1$  vs  $T_M$ . The idea is that the effect of  $R_2$  is predominant and this is what the model explicitly contains.

This qualitative behavior is remarkably well verified for the class of alkali halides (see Fig. 1 in which Pauling's radii<sup>12</sup> have been used). This set of radii is used here just as an example. It is important to remark that the linear behavior is also present if a different set of radii is used (for example, the Fumi and Tosi radii<sup>13</sup>).

In order to also obtain quantitative agreement I consider a more realistic model. The standard ionic radii are in fact defined to reproduce the distance between unlike ions. For like ions the hard-core part of the potential also plays a major role in determining the distance of closest approach<sup>14</sup> and justifies a hard-sphere approach. But, of course, this distance cannot be directly given by the standard ionic radii. This explains why no anomaly is observed in Fig. 1 for those compounds (lithium halides) that have the anions in contact with respect to the standard radii.<sup>12</sup> To take into

account this difference we have to allow a certain overlap  $\delta$  between the anions before the instability occurs. It is convenient to write  $\delta$  in terms of a fractional overlap  $\delta_0$  as  $\delta = \delta_0 R_2$ .  $\Delta$  is then replaced by

$$\Delta^* = \sqrt{2} R_1 - (2 - \sqrt{2} - \delta_0) R_2. \quad (6)$$

By using Eqs. (3) and (4) the new relation is

$$\frac{R_2}{R_1} = \frac{\sqrt{2}}{2 - \sqrt{2} - \delta_0} - \frac{1}{R_1(2 - \sqrt{2} - \delta_0)} \left( \frac{KT_M}{\eta} \right)^{1/2} \quad (7)$$

From the experimental data of Fig. 1 (in particular the value  $R_2/R_1$  extrapolated for each line at  $T_M = 0$  one can deduce  $\delta_0$  for the various classes of compounds. These values, all about 0.4, are reported in Table I. The reason for these large values can be found in the very simple model used. The inclusion of thermal expansion in the model reduces in fact the value of  $\delta_0$ . To see this, one has to add to the expression (6) for  $\Delta^*$  the extra distance between two anions (at the melting temperature) due to the thermal expansion. This extra distance is  $\Delta l_0 = l_0 \lambda T_M$ , where  $\lambda$  is the linear expansion coefficient and  $l_0$  is the equilibrium distance between anions at zero temperature. Using the value of  $\lambda$  of NaCl at room temperature  $\lambda = (1/l)(\partial l/\partial T) = 40.5 \times 10^{-6} \text{ K}^{-1}$  (this corresponds to a lower limit for  $\Delta l_0$ ) one obtains a more realistic upper limit for the fractional overlap:  $\delta_0 \leq 0.29$ . A further reduction of  $\delta_0$  of about 10% is obtained by taking into account anharmonic contributions also in the expression (4) (see Appendix).

It is interesting to look at the pressure dependence of  $T_M$  as given by Eq. (7). To this purpose it is convenient to rewrite Eq. (7)

$$T_M = \omega^2 (\sqrt{2} R_1 - \beta R_2)^2, \quad (8)$$

having defined

$$\beta = 2 - \sqrt{2} - \delta_0, \quad \omega = \sqrt{\eta}. \quad (9)$$

Note that the quantity  $\omega$  defined in (9) is proportional to the effective frequency for the relative motion of two nearest anions. By deriving Eq. (8) with respect to the pressure  $P$  one obtains

TABLE I: Values of the fractional overlap  $\delta_0$  between larger ions at the melting temperature for the various classes of compounds. The values are obtained analyzing the data of Fig. 1 through Eq. (7). These values are appreciably reduced by including the effects of thermal expansion and anharmonicity (see text).

	Li compounds	Na compounds	K compounds	Rb compounds
$\delta_0$	0.43	0.39	0.42	0.37

$$\frac{dT_M}{dP} = 2\omega \frac{d\omega}{dP} (\sqrt{2} R_1 - \beta R_2)^2 + 2\omega^2 (\sqrt{2} R_1 - \beta R_2) \times \left( \sqrt{2} \frac{dR_1}{dP} - \beta \frac{dR_2}{dP} - R_2 \frac{d\beta}{dP} \right). \quad (10)$$

Analytical expressions are now needed for the terms  $dR_i/dP$  ( $i = 1, 2$ ),  $d\delta_0/dP$ , and  $d\omega/dP$  appearing in Eq. (10). To this purpose note that the compressibility  $C$  for alkali halides<sup>15</sup> can be fitted rather well by the analytical expression

$$C \simeq \alpha(R_1^3 + R_2^3) = C_1 + C_2, \quad (11)$$

where  $\alpha = 6.2 \times 10^{-7} \text{ atm}^{-1}$  (this value is obtained from the data of NaCl) is a constant for all the compounds and  $C_i$  ( $i = 1, 2$ ) represents the partial compressibility of each ionic species. One can then write

$$\frac{dR_i}{dP} = -\frac{1}{3} R_i C_i = -\frac{1}{3} \alpha R_i^4 \quad (i = 1, 2). \quad (12)$$

From Eq. (12) and remembering the definition of  $\delta_0$  (fractional overlap between anions) there results

$$\frac{d\delta_0}{dP} = -\frac{1}{3} \alpha R_2^3 [(1 - \delta_0) - (1 - \delta_0)^4]. \quad (13)$$

For the last term one has

$$\frac{d\omega}{dP} = \omega \left( \frac{V}{\omega} \frac{d\omega}{dV} \right) \left( \frac{1}{V} \frac{dV}{dP} \right) = \omega \gamma' C, \quad (14)$$

where  $\gamma'$  is the Grüneisen parameter corresponding to the effective frequency  $\omega$ . Since this frequency mainly refers to the border zone modes  $\gamma'$  it is expected to be larger than the average Grüneisen parameter  $\gamma$ .<sup>15</sup> By making use of Eqs. (12)–(14) and deducing the value of  $\omega$  from the slope of the lines in Fig. 1 [using Eq. (7)] one can finally evaluate the various terms of Eq. (10). For NaCl and taking  $\gamma' \approx \gamma = 1.6$ ,<sup>15</sup> there results  $dT_M/dP \approx 0.013 \text{ }^\circ\text{K/atm}$ . The experimental value is  $0.0238$ .<sup>5</sup> The difference can be easily due to the Grüneisen parameter used. I then fix the effective Grüneisen parameter  $\gamma'$  to fit the pressure dependence of one compound (NaCl) and compute the pressure dependence of the others. This gives  $\gamma' = 2.9$ . The corresponding results, reported in Table II, are in good agreement with the experimental values. The same analysis, performed for Lindemann criterion, would instead yield too large a difference (a factor of 2) between the value for NaI and that for NaCl.

In Eq. (10) the term with  $d\omega/dP$  gives the largest contribution. This means that pressure stabilizes an ionic solid mainly by increasing the force constant  $\eta$  (and frequency  $\omega$ ). The changes of the ionic radii produce only a small effect. This would also be the case for Lindemann criterion.

TABLE II: Values of  $dT_M/dP$  as given by Eq. (10) compared to the experimental results. The value of NaCl is taken as reference to fix the effective Grüneisen parameter  $\gamma' = 2.9$ .

	$dT_M/dP$	
	expt	calc
NaCl	0.0238	0.0238
NaBr	0.0287	0.0274
NaI	0.0327	0.0336

Important implications can be obtained about the stability of the so-called superionic conductors.<sup>16</sup> It can be recalled that a superionic conductor, for example, AgI, is a material in which one ionic species (Ag) has a liquidlike motion in the host lattice provided by the other ionic species (I). Now, according to this melting criterion based on hard spheres with Coulomb potentials, this situation is unstable (see the upper corner of Fig. 1). This implies that these materials cannot be simply described in terms of hard spheres but *covalent or polarization effects are essential for their stability*. Other silver compounds<sup>17</sup> that present a rocksalt liquid transition, in fact, do not behave like alkali halides (see Fig. 1). Of special relevance, in this respect, are the molecular dynamics calculations recently reported by Schommers.<sup>18</sup> In his calculations, in fact, it was not possible to obtain a stable binary superionic conductor with interionic interactions simply described by Born-Mayer potentials.<sup>19</sup> Let me point out that the other hypothesis on which the model was based can also be tested by molecular dynamics calculations.

With respect to other melting theories like Lindemann<sup>6</sup> and the law of corresponding states<sup>20</sup> I can say that, while they are more concerned about the absolute value of the melting temperature, my arguments mainly refer to the relative melting temperatures of various compounds.

In summary, I conclude that (a) in simple ionic solids (alkali halides) the melting instability is dominated by the dynamics of the larger ion; (b) the variation of  $T_M$  with pressure is mainly due to the change of the force constants between ions and not to the change of their radii; and (c) covalent or polarization effects are essential for the stability of binary superionic conductors like AgI.

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## APPENDIX: ANHARMONIC CONTRIBUTIONS

The inclusion of anharmonic effects modifies expression (4) to

$$\langle |\delta R_2 - \delta R_2'|^2 \rangle_{T_M}^{1/2} = [KT_M/\eta + (KT_M)^2/\eta' + \dots]^{1/2}, \quad (\text{A1})$$

where  $\eta'$  is a parameter responsible for the anharmonic terms. The melting relation (7) is correspondingly modified and the slope at a given  $T_M$  is now given by

$$\left. \frac{\partial(R_2/R_1)}{\partial\sqrt{T}} \right|_{T=T_M} = -\frac{1}{R_1\beta} \frac{[K\sqrt{T_M}/\eta + 2K^2(T_M^3)^{1/2}/\eta']}{[KT_M/\eta + (KT_M)^2/\eta']^{1/2}}. \quad (\text{A2})$$

From Ref. 21 one can estimate the anharmonic contributions to the mean-square displacement to be of the order of 20% for NaCl at melting temperature. This fixes the ratio  $\eta'/\eta$ . Then, by fitting the slope (A2) and the position of the theoretical expression to the observed line (Fig. 1) one obtains the new  $\eta$  and  $\delta_0$ . The inclusion of these anharmonic contributions has the effect to reduce the value of  $\delta_0$  of about 10%.

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<sup>17</sup>Note that these materials have a smaller ionicity than alkali halides. See, J. C. Phillips, *Rev. Mod. Phys.*, **42**, 317 (1970).

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<sup>19</sup>Of course our instability argument only applies to binary systems and not to  $\text{CaF}_2$  for which stability can be obtained. See, A. Rahman, *J. Chem. Phys.* **65**, 4845 (1976).

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