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1989 J. Phys.: Condens. Matter 1 6881

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LETTER TO THE EDITOR

The Lindemann criterion of melting for pure and mixed ionic crystals

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Received 14 July 1989

Abstract. A generalisation of the Lindemann criterion of melting for ionic crystals and their solid solutions is suggested. The calculated phase diagrams for such mixtures appear to be in good agreement with the available experimental data. A criterion of solubility in the solid phase for these substances and their possible classification are discussed.

The Lindemann criterion of melting, while not fundamentally justified, is nevertheless valid to some degree not only for pure monatomic substances [1] but also for mixed disordered crystals [2, 3]. We shall show below that it is also applicable for ionic crystals and the mixed salts formed from them. We shall use the same arguments as in [2] with appropriate modifications.

The main feature of the ionic crystal is the perfect order of ions within the pair. This means that both the cations and the anions form homogeneous sublattices. In contrast, in the liquid phase the nearest neighbour of an ion is random. Thus, our considerations should account for the fact that the melting process destroys not only the long-range order of the crystal but, first of all, the stability of the pair. All the salts we shall deal with in this Letter belong to the same order of one-mode ionic crystals [4]. For this case the lattice dynamics suggests [5] use of a reduced mass $M_r^{-1} = M_1^{-1} + M_2^{-1}$ rather than a simple sum $M_s = M_1 + M_2$ to characterise the lattice.

By analogy with the usual form of the Lindemann criterion [2], the equation for the melting temperature of the crystal reads

$$T_m = (M_r k_B \theta^2 a^2 / 9 \hbar^2) x_m^2 \quad (1)$$

where M_r for the ionic crystal is the reduced mass of a pair: $M_r^{-1} = M_1^{-1} + M_2^{-1}$ where M_1 and M_2 are the anion and cation masses; θ is the Debye temperature of the ionic crystal; a is its lattice parameter; and x_m^2 is the empirical constant.

There are specific features of (1) to be emphasised here. The standard version of the Lindemann criterion, in contrast to (1), contains M as a mass per atom and a as a distance between the nearest neighbours. These distinctions are not critical while there is no proof of the general validity of the Lindemann criterion itself. Thus we accept (1) as an *ad hoc* equation for ionic crystals.

Table 1. Lindemann constants for FCC ionic crystals. First column: chemical formula of the ionic crystal; second column: reduced mass of pair (au); third column: melting temperature (K); fourth column: lattice parameter (Å) for the temperature (K) in parentheses; fifth column: empirical Lindemann constant calculated by making use of the second column of table 2; sixth column: relevant references.

Salt	M_r	T_m (K)	a (Å)	$x_m^2 \times 10^{-2}$	References
NaCl	13.95	1078	5.78 (870 K)	1.27	[15–18]
KCl	18.59	1043	6.49 (760 K)	1.12	[18, 12–15, 19]
RbCl	25.06	975	6.76 (900 K)	1.29	[18, 19]
NaBr	17.85	1028	5.97 (300 K)	1.40	[18, 20]
KBr	26.25	1007	6.80 (715 K)	1.22	[18, 12–15, 19]
RbBr	41.30	966	7.04 (900 K)	1.10	[18, 19]
NaI	19.46	934	6.47 (300 K)	1.85	[18, 20]
KI	29.89	954	7.23 (700 K)	1.54	[18, 19]
RbI	51.07	920	7.54 (857 K)	1.30	[18, 19]
NaF	10.40	1285	4.62 (300 K)	1.04	[21, 20]
KF	12.78	1131	5.35 (300 K)	1.19	[18, 20]
AgCl	26.68	728	5.55 (300 K)	1.15	[18, 12–15, 20]
AgBr	45.90	708	5.77 (300 K)	1.17	[18, 12–15, 20]
CsCl [†]	27.99	906	7.02 (723 K)		[18, 22]
AgI [†]	58.31	828	6.10 (800 K)		[18, 23]

[†] Data for FCC symmetry.

Table 1 illustrates the validity of (1) for a few alkali halides. The experimental data used for the calculation are not perfect. The lattice parameters do not always correspond to the proper temperature interval and the characteristic Debye temperatures originate from different procedures and correspondingly have different accuracies. Nevertheless the values of x_m^2 are scattered reasonably closely around $x_m^2 = 0.013$. This value agrees well with $x_m^2 = 0.0128$ computed by Curtin and Runge [6] for FCC hard-sphere crystals.

Since the Debye temperature is the least well defined value in (1), one may actually prefer θ as a fitting parameter within an interval of about 10%. Table 2 shows these Debye temperatures recalculated from the fixed value of $x_m^2 = 0.0128$ chosen in accordance with [6]. Only for two cases does the deviation of the experimental data from the estimated figures exceed 10%.

Now let us apply the same approach once successfully implemented for the mixture of elements [2] to the mixture of salts. We have assumed Vegard's law to be valid: $a = p_1 a_1 + p_2 a_2$, and the value of θ of a mixture to be given by $\theta^{-2} = p_1 \theta_1^{-2} + p_2 \theta_2^{-2}$, where p_1 and p_2 are concentrations of components, and a , a_1 , a_2 and θ , θ_1 , θ_2 are the lattice parameters and Debye temperatures of a mixed and two pure crystals correspondingly. Both relations for mixed salts are experimentally based [7].

For random mixing we have to write down a generalised Lindemann criterion for mixed salt analogous to [2]:

$$T_m = (M_r k_B \theta^2 a^2 / 9 \hbar^2) [x_m^2 - 4 \langle (\Delta r)^2 \rangle / a^2] \quad (2)$$

where M_r is the reduced mass of the averaged pair, θ and a are the averaged characteristics of the lattice, and $\langle (\Delta r)^2 \rangle$ is the size dispersion of the mixture under consideration.

Figures 1–4 illustrate the validity of criterion (2), which works rather well while the mixture is really random. It appears from comparison of figures 1 and 2 that there is

Table 2. Comparison of the measured and estimated Debye temperatures. First column: chemical formula of the ionic crystal; second column: experimental Debye temperature (K)—most of the data are extracted from specific heat measurements extrapolated to zero temperature and the rest are from elastic constant measurements; third column: estimated Debye temperature (K) calculated by assuming the value $\chi_m^2 = 0.0128$ to be universal for all the FCC lattices; fourth column: relative error; fifth column: relevant references.

Salt	Exp. θ_D (K)	Est. θ_D (K)	$\Delta\theta_D/\theta_D$ (%)	References
NaCl	281 (0 K)	280	-0.4	[24]
KCl	227 (0 K)	212	-7.1	[24]
RbCl	169 (0 K)	170	0.6	[25]
NaBr	224 (4.2 K)	234	4.3	[26]
KBr	172 (0 K)	168	-2.4	[27]
RbBr	137 (0 K)	127	-7.9	[25]
NaI	164 (0 K)	197	16.8	[26]
KI	131 (0 K)	144	9.0	[26]
RbI	103 (0 K)	104	1.0	[26]
NaF	492 (4.2 K)	443	-11.1	[26]
KF	336 (4.2 K)	327	-2.8	[26]
AgCl	183 (0 K)	174	-7.5	[24]
AgBr	131 (300 K)	125	-4.8	[28]
CsCl†		149		
AgI†		114		

† Data for FCC symmetry are not available.

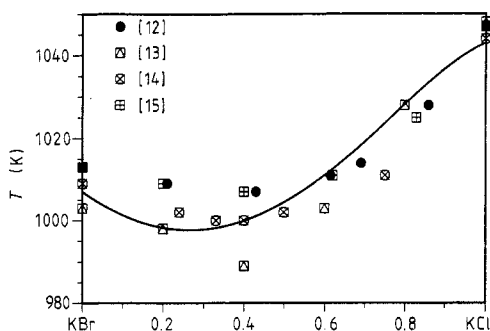


Figure 1. The phase diagram of KBr–KCl. The full curve represents our calculation. $r_{Br} = 1.68 \text{ \AA}$, $r_{Cl} = 1.52 \text{ \AA}$ [29]. The points are experimentally measured T_m .

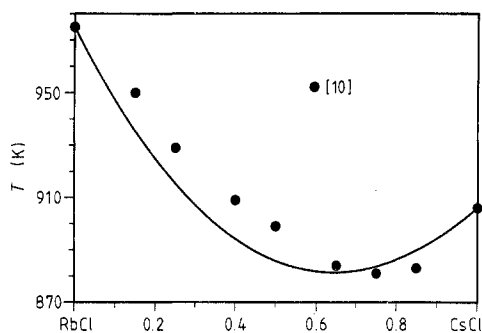


Figure 2. The phase diagram of RbCl–CsCl. The full curve represents our calculation. $r_{Rb} = 1.28 \text{ \AA}$, $r_{Cs} = 1.47 \text{ \AA}$ [29]. The points are experimentally measured T_m .

no substantial difference between the roles of cations and anions in these mixtures. Randomisation of any of the constituents produces roughly the same effect. Figure 1 demonstrates the scattering of experimental data obtained from different references.

An analogous approach can be applied to the system with three or more components. The calculation of the phase diagram of $\text{AgCl}_x\text{Br}_{1-x-y}\text{I}_y$ shows that the iodine ligand of about $y = 0.15$ should push down the minimum 45 K more. This might have practical importance for fibre preparation. We did not make an experimental check of this diagram, but we know from qualitative observations that it corresponds to what is actually found [8].

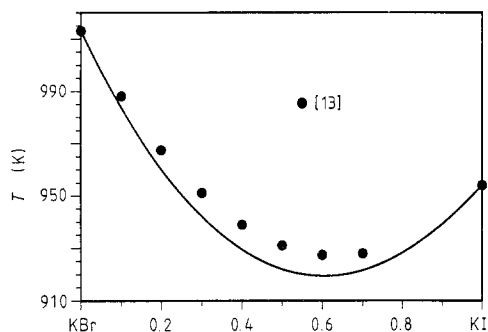


Figure 3. The phase diagram of KBr–KI. The full curve represents our calculation $r_{\text{Br}} = 1.68 \text{ \AA}$, $r_{\text{I}} = 1.88 \text{ \AA}$ [29]. The points are experimentally measured T_{m} .

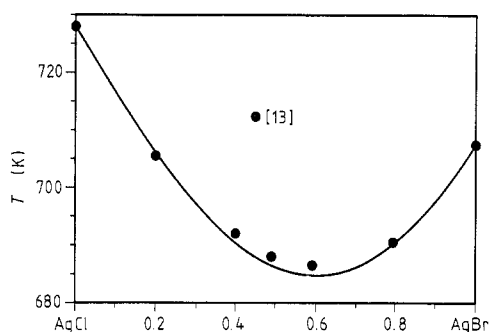


Figure 4. The phase diagram of AgCl–AgBr. The full curve represents our calculation. $r_{\text{Cl}} = 1.52 \text{ \AA}$, $r_{\text{Br}} = 1.68 \text{ \AA}$ [29]. The points are experimentally measured T_{m} .

Recently we have suggested a certain criterion for the onset of the miscibility gap in mixtures [2], based on the size dispersion of their constituents. It indicated that T_{m} cannot lie below a certain limit $T_{\text{g}} \approx \frac{2}{3}T_{\text{m}}$, which is defined by the equation of state in a liquid phase [9]. This remains true for the molten salts. The distinction between salts and simple mixtures is that instead of the ratio of the radii of constituent atoms r_1/r_2 used for salts we have to consider the ratio of the minimal inter-atomic distances $(r_0 + r_1)/(r_0 + r_2)$, which contains r_0 , the radius of the corresponding intermediate ion. Thus for our value of $x_{\text{m}}^2 = 0.0128$, in analogy with [2] we have the criterion for solubility within the crystalline state:

$$(r_0 + r_1)/(r_0 + r_2) \geq 0.878 \quad (3)$$

where r_1 and r_2 are radii of the randomly distributed ions and r_0 is the radius of the oppositely charged intermediate ion.

This criterion predicts full solubilities for NaCl–KCl [10], NaI–KI [11], KBr–KCl [12–15] (and figure 1) and KBr–KI [16] (and figure 3) and a separation (and consequently eutectic type of diagram) for AgCl–AgI and KCl–KI [17] in full agreement with experiment.

Since the choice of size for alkali halides is much wider than that for alkali metals [3] we expect to find among these mixtures some that are really ‘glassifying’ close to their freezing points [9].

It is interesting that while the mixture of metals Na and K separates with crystallisation (since $r_1/r_2 \approx 0.8$ does not fit criterion [2]), the mixtures of salts NaCl–KCl and NaI–KI are completely soluble close to their crystallisation points (920 K and 840 K respectively) since the ratio $(r_0 + r_1)/(r_0 + r_2) \geq 0.89$ obeys criterion (3) in agreement with [10] and our own observations. At lower ($T < 800 \text{ K}$) temperature it still separates, creating two crystalline phases.

In this particular case one can see that the critical separation point may be in rather close proximity to crystallisation, which makes the latter particularly interesting. Indeed, the melting point of such a mixture is comparatively low and should be close to its glass point [9]. This makes us expect, in the vicinity of the freezing point of this mixture, strong precrystallisation effects with huge equilibrium times. In our preliminary observation of the system we have indeed found this.

We are grateful to D Quitmann and W Kohn for fruitful discussions.

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