Classification of phase diagrams for alkali halide mixtures and the generalized Lindemann criterion

Classification of phase diagrams for alkali halide mixtures and the generalized Lindemann criterion

D Berrebi, L Grigoryan, S Rabinovich, E Shasha and A Voronel

Raymond and Beverly Sackler Faculty of Exact Sciences, School of Physics and Astronomy, Tel Aviv University, 69978 Ramat Aviv, Israel

Abstract. Thorough analysis of experimental data (our own as well as those from the literature) on alkali halides and their mixtures with a view to application of a generalized Lindemann criterion for melting is presented. The result of a fitting procedure is ionic radii to be used in phase diagram calculations. It is shown that a successful choice of the radii allows one to predict new phase diagrams reliably. Our criterion of miscibility was used to finalize the choice.

Three years ago we published a letter [1] suggesting a generalization of the Lindemann criterion for melting of pure and mixed ionic crystals. That letter contained a brief description of the generalization proposed and four phase diagrams from the literature to demonstrate the effectiveness of our approach.

This paper is chiefly to present much thorough analysis of the existing experimental data and our own measurements as well as our fitting parameters and more elaborate computational considerations. As many as 25 binary phase diagrams of alkali halides were fitted with 9 parameters (ionic radii).

The basic feature of ionic crystals is the perfect order of ions, i.e. anions and cations form two homogeneous sublattices and the nearest neighbours of any particular ion have the opposite charges. In the liquid phase the order ceases to be an ideal one although the strong preference for oppositely charged neighbours is still preserved [2]. Thus, our consideration should take into account the fact that the melting process destroys not only the long-range order within the crystal but also the stability of a cation–anion pair. All the salts we are dealing with here are one-mode ionic crystals [3] of the same symmetry close to melting. For this case the lattice dynamics suggests [4] the use of the reduced mass of anion–cation pair in primitive cell, $M_r^{-1} = M_a^{-1} + M_c^{-1}$, rather than a simple sum, $M_s = M_a + M_c$, to characterize the lattice. One also observes that an inter-ionic force between anion and cation does not depend on their mutual orientation [5]; thus a hard-sphere concept is very suitable here, particularly for alkali halides.

Modelling the melting of a pure ionic crystal in this way, one can apply the Lindemann criterion in its usual form

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

where M_r is the reduced mass of a cation–anion pair (M_c and M_a are anion and cation masses); θ is the Debye temperature of the ionic crystal; a is its lattice parameter; x_m^2 is an empirical constant; and k_B is the Boltzmann constant.

The standard version of the Lindemann criterion, unlike equation (1), includes M as a mass per atom and a as a distance between the nearest neighbours. These differences are not essential as a rigorous substantiation of the Lindemann criterion is still lacking. So for the time being one can accept equation (1) as an *ad hoc* equation. The empirical constant x_m^2 is chosen to provide a reasonable fit to experimental data and other information at hand.

To make the choice we have analysed the experimental data collected in table 1. Unfortunately the data available are far from being perfect. The lattice parameters do not always correspond to the proper temperature interval (i.e. the melting vicinity). The characteristic Debye temperatures have been obtained in a variety of ways and correspondingly have different accuracies. Nevertheless the quantity x_m^2 is 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 an FCC hard-sphere crystal.

Table 1. Empirical data on ionic crystals.

Salt	T_m (K)	a (Å)	M_r	$x_m^2 \times 10^{-2}$	References
Fluorides					
NaF	1285	4.62(300 K)	10.40	1.31	[10, 11]
KF	1130	5.35(300 K)	12.78	1.20	[10, 11]
RbF	1066	5.64(300 K)	15.54		[10, 11]
CsF	976	6.01(300 K)	16.62		[9, 10]
Chlorides					
LiCl	883	5.13(300 K)	5.81	1.18	[9, 10]
NaCl	1078	5.78(870 K)	13.95	1.28	[11, 15, 18, 19]
KCl	1047	6.49(760 K)	18.59	1.14	[11, 12, 13, 14, 15, 17]
RbCl	993	6.76(900 K)	25.06		[9, 17]
CsCl	917	7.02(723 K)	27.99	1.19	[11, 16]
Bromides					
LiBr	823	5.50(300 K)	6.39	1.24	[9, 10]
NaBr	1028	5.97(300 K)	17.85	1.41	[10, 11]
KBr	1007	6.80(715 K)	26.25	1.22	[11, 12, 13, 14, 15, 17]
RbBr	966	7.04(900 K)	41.30	1.10	[11, 17]
CsBr	913	7.23(300 K)	49.86		[20]
Iodides					
LiI	742	6.00(300 K)	6.58	1.25	[10, 11]
NaI	934	6.47(300 K)	19.46	1.28	[10, 11]
KI	954	7.23(700 K)	29.89	1.55	[11, 17]
RbI	920	7.54(857 K)	51.07		[11, 17]
CsI	914	7.66(300 K)	64.92		[20]

Another reason to adopt the FCC value of x_m^2 for these ionic crystals is that the calculation for a single (average) atom would supply a value with the factor 0.5 in mass and with the factor $\sqrt{2}$ in lattice parameter i.e. making the FCC Lindemann constant hold true.

Since the Debye temperature is the least well defined value in equation (1), one may actually prefer θ as a fitting parameter within an interval of about 10%. Table 2 presents these Debye temperatures recalculated from the fixed value of $x_m^2 = 0.0128$ chosen according to [6].

A generalization of the Lindemann criterion on an ionic-crystal mixture can be achieved in the same way as we did for a mixture of pure elements [1, 7]. We have

Table 2. Debye temperatures, experimental and estimated.

Salt	Exp θ_D (K)	Est θ_D (K)	$\Delta\theta_D/\theta_D(\%)$	Reference
Fluorides				
NaF	439	443	1.0	[5]
KF	336(4.2 K)	325	−3.4	[21]
RbF		271		
CsF		236		
Chlorides				
LiCl	463 calc.	444	−4.3	[21]
NaCl	281(0 K)	280	−0.4	[22]
KCl	227(760 K)	213	−6.6	[22]
RbCl	169	170	0.6	[23]
CsCl		150		
Bromides				
LiBr	387 calc.	381	−1.6	[21]
NaBr	224(4.2 K)	234	4.3	[5]
KBr	172(0 K)	168	−2.4	[25]
RbBr	137(4.2 K)	127	−7.9	[23]
CsBr		109		
Iodides				
LiI	331 calc.	327	−1.2	[21]
NaI	198	197	−0.5	[26]
KI	131(0 K)	144	9.0	[5]
RbI		104		
CsI		91		

assumed Vegard's law, $a = p_1 a_1 + p_2 a_2$, to be valid for the lattice parameter of the mixed crystal and the value of θ of the mixture to be given by $\theta^{-2} = p_1\theta_1^{-2} + p_2\theta_2^{-2}$, where p_1 and p_2 are the 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, respectively. Both relations for mixed salts are well founded experimentally [8].

Thus, by analogy with [7], the generalized Lindemann criterion for a random mixture of ionic salts can be written as

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

where the reduced mass, M_r, and the static disorder term, x_s^2, will now be defined; now θ and a are the averaged lattice characteristics defined above. The definition of x_s^2 refers to the size disorder and therefore to a sublattice with randomly substituted atoms. For example, in the mixture $(C1A)_{p_1}(C2A)_{p_2}$ the size disorder term equals [1]

$$x_s^2 = 4p_1 p_2(r_{C1} - r_{C2})^2/a^2 \qquad (3)$$

and the reduced mass should be defined as

$$1/M_r = 1/M_A + 1/(p_1 M_{C1} + p_2 M_{C2}) \qquad (4)$$

where p_1 and p_2 are corresponding molar concentrations of the constituents.

These equations were used to calculate all the 25 experimentally investigated solid state binary diagrams of fully soluble alkali halide mixtures [9]. The atomic radii, $r_{a,c}$, were fitting parameters to visually minimize the differences between the experimental

data and the diagrams calculated. The resulting radii are collected in table 3. As one can observe, most of them closely resemble those proposed by Krasnov [28]. However, a satisfactory explanation for the kind of radii to be chosen [29] is still lacking.

To illustrate our fitting we present a number of diagrams along with experimental data available. One has to realize that while the experimental data are related to solidus and liquidus lines of diagrams, the calculated curve is expected to be situated somewhere between them, being close to a margin line of stability of the crystalline phase. The experimental points on the diagrams KCl–NaCl (figure 1) and CsCl–KCl (figure 2) seem to be quite reliable and, therefore, they were given more weight during a fitting procedure. The next three systems, in contrast, looked less convincing and for this reason we have made a new set of measurements of their liquidus points (see appendix A for more details). For two systems, NaBr–KBr (figure 3) and KBr–RbBr (figure 4), more weight has been given again to our experimental points than to the previous findings. For the third (KI–NaI, figure 5) the new measurement shows no appreciable difference. For one of them (figure 4) we have displayed two sets of liquidus points due to different authors. The common-cation systems, LiCl–LiBr, NaBr–NaCl, RbBr–RbI (figures 6–8), demonstrate better agreement with our calculations. However, for all the systems studied the deviation does not exceed 2–3% at most. Moreover, the quantitative agreement with thermo-chemical calculations of Sangster and Pelton [9] is generally much better.
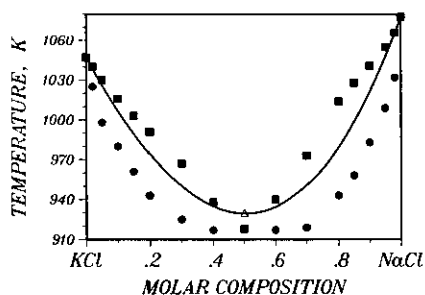

Figure 1. KCl–NaCl [9, 30]. Filled squares: liquidus, filled circles: solidus. Open triangle: our measurement. Solid line: our calculation.
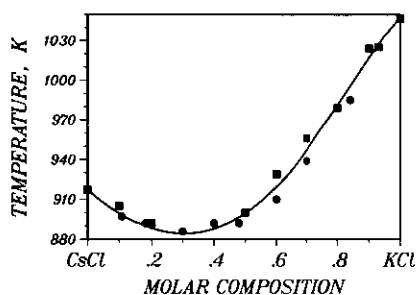
Figure 2. CsCl–KCl [9, 31]. Filled squares: liquidus, filled circles: solidus. Solid line: our calculation.

The radii from table 3 enable a criterion for intermiscibility in a crystalline state to be checked [1, 7]. It allows a prediction to be made for the binary diagram to be of a eutectic type. Obeying the inequality

$$\delta \equiv (r_0 + r_1)/(r_0 + r_2) \geqslant 0.88 \tag{5}$$

for FCC crystals is supposed to indicate a full miscibility diagram and *vice versa*. Here $r_{1,2}$ are the radii of the randomly distributed ions while r_0 is the radius of the oppositely charged intermediate ion. The value of the parameter, δ, controls the width of a miscibility range. The experimental information on all the systems known is summarized in table 4. It can be seen that the agreement is even better than one might have expected for such a simple model. Marginal cases with $\delta \approx 0.88$ (which
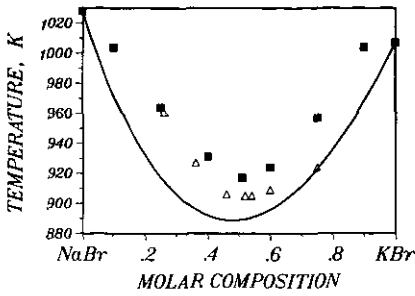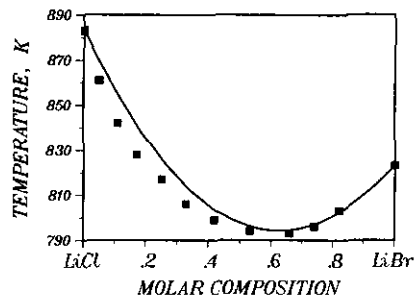
Figure 3. NaBr–KBr [9, 32]. Filled squares: liquidus, open triangles: our measurements. Solid line: our calculation.
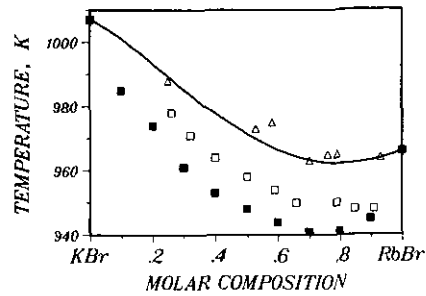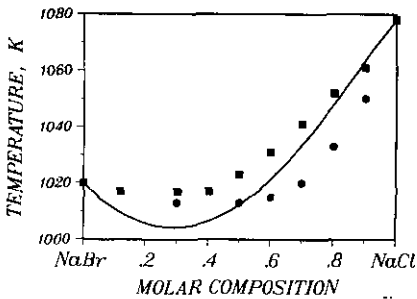

Figure 4. KBr–RbBr [9]. Filled squares: liquidus [33], open squares: liquidus [34], open triangles: our measurements. Solid line: our calculation.
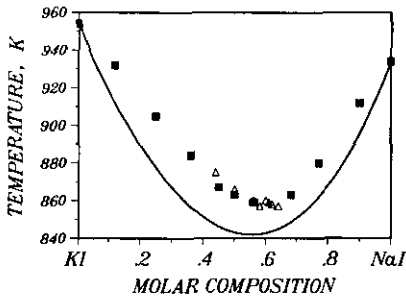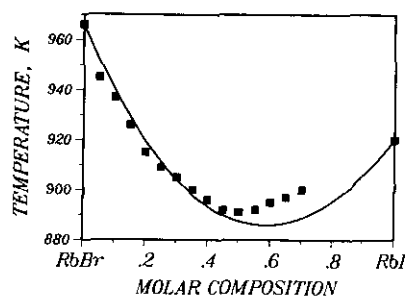

Figure 5. KI–NaI [9, 35]. Filled squares: liquidus, open triangles: our measurements. Solid line: our calculation.

Figure 6. LiCl–LiBr [9, 36]. Filled squares: liquidus. Solid line: our calculation.

Figure 7. NaBr–NaCl [9, 32, 37]. Filled squares: liquidus, filled circles: solidus. Solid line: our calculation.

Figure 8. RbBr–RbI [9, 38]. Filled squares: liquidus. Solid lines: our calculation.

are underlined in table 4) require more thorough analysis as they are most sensitive to the parameter values chosen.

It should be pointed out that the diagram fitting depends on radius differences only, while the solubility criterion depends on radius ratios. Jointly, they lead to an unambiguous choice of radius.

Table 3. Ionic radii used in this work.

Ion	r (Å)	Reference
Cations		
Li^+	0.59	[27]
Na^+	0.88	Our choice
K^+	1.12	[28]
Rb^+	1.27	[28]
Cs^+	1.38	Our choice
Anions		
F^-	0.75	Our choice
Cl^-	1.52	[28]
Br^-	1.68	[28]
I^-	1.88	[28]

Table 4. Solubility parameter, δ, for mixed ionic crystals.

Azeotropies	$\delta \geqslant 0.88$	Eutectics	$\delta \leqslant 0.88$
RbF–CsF	0.95	LiF–KF	0.72
KF–RbF	0.93	NaF–CsF	0.77
		LiF–NaF	0.82
		NaF–KF	0.87
		KF–CsF	0.88
RbCl–CsCl	0.96	LiCl–KCl	0.80
KCl–RbCl	0.95	NaCl–CsCl	0.83
NaCl–KCl	0.91	NaCl–RbCl	0.86
KCl–CsCl	0.91		
LiCl–NaCl	0.88		
KBr–RbBr	0.95	LiBr–KBr	0.81
NaBr–KBr	0.91		
LiBr–NaBr	0.89		
KI–RbI	0.95	LiI–CsI	0.76
NaI–KI	0.92	LiI–KI	0.82
LiI–NaI	0.89	NaI–CsI	0.85
		NaI–RbI	0.88
LiCl–LiBr	0.93	LiF–LiI	0.54
LiBr–LiI	0.92	LiF–LiBr	0.59
		LiF–LiCl	0.64
		LiCl–LiI	0.85
NaCl–NaBr	0.94	NaF–NaI	0.59
NaBr–NaI	0.93	NaF–NaBr	0.64
		NaF–NaCl	0.68
		NaCl–NaI	0.87
KCl–KBr	0.94	KF–KI	0.62
KBr–KI	0.93	KF–KBr	0.67
		KF–KCl	0.71
		KCl–KI	0.88
RbCl–RbBr	0.95	RbF–RbI	0.64
RbBr–RbI	0.94	RbF–RbBr	0.68
RbCl–RbI	0.89	RbF–RbCl	0.72
CsBr–CsI	0.94	CsF–CsI	0.65
		CsF–CsBr	0.70
		CsF–CsCl	0.73

Having made the choice one would expect the analysis of more complicated systems also to be successful. Indeed, we have found two published diagrams, KBr–NaCl and NaBr–KCl (figure 9 and 10), to be in remarkable agreement with our calculations. It makes us confident that we are able to correctly predict the behaviour of a general system: $Na_xCl_yK_{1-x}Br_{1-y}$. Two previous diagrams (figures 9 and 10) are just diagonal cross sections of this surface (figure 11). Our calculation shows a slight reduction of a minimal temperature $T_m = 873$ K at $x = 0.53$ and $y = 0.32$ in comparison with the diagrams mentioned above. The practical preparation of such a mixture can be achieved by mixing all the four (or at least three) pure salts in the required proportion. Appendix B lists all the formulae needed for these calculations. Other candidates to produce azeotropic diagrams with lower minima are NaI–KBr, KBr–RbCl, KCl–RbCl, RbBr–KCl, KBr–RbI, RbBr–KI, NaBr–LiCl, LiBr–NaCl, LiBr–NaI and NaBr–LiI. These have been chosen as each pair of ions (like KBr–KCl, KBr–NaBr and so on) forms a system with full miscibility.
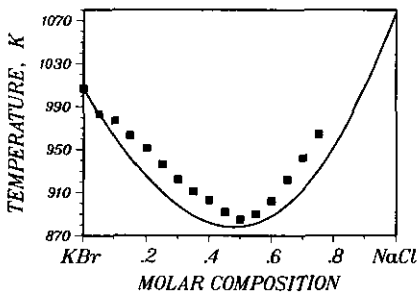

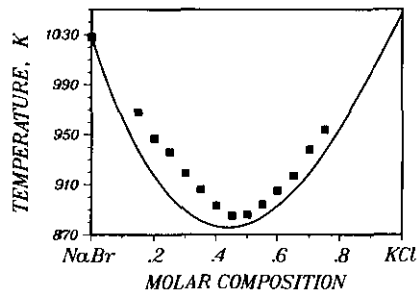**Figure 9.** KBr–NaCl [39]. Filled squares : liquidus. Solid line: our calculation.

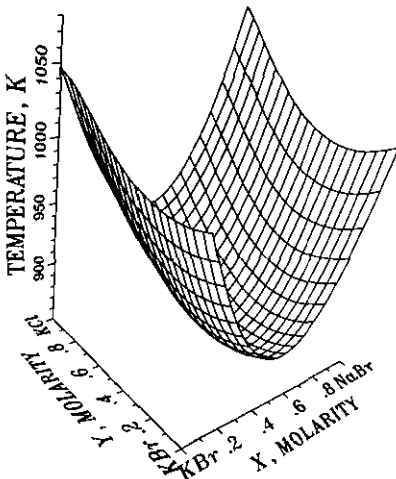**Figure 10.** NaBr–KCl [39]. Filled squares: liquidus. Solid line: our calculation.

Figure 11. Calculated melting temperature for $Na_xCl_yK_{1-x}Br_{1-y}$ system.

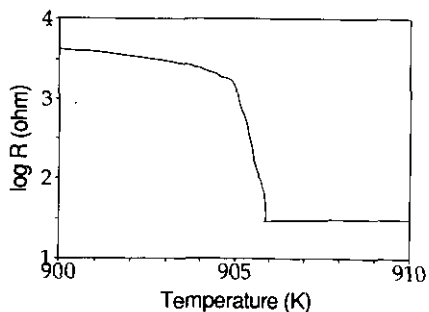**Figure 12.** Logarithm of resistance versus temperature for $Na_{0.54}K_{0.46}Br$ mixture. The cooling rate was $10°$ h^{-1}.

To summarize, a generalization of the Lindemann criterion for melting to deal with pure and mixed disordered ionic crystals is suggested.

(i) The generalization was used to fit calculated diagrams to all the experimental data known. The fitting parameters, ionic radii in the melting vicinity, were obtained.

(ii) These ionic radii were used to calculate the miscibility parameter, δ. Meeting both requirements, (the best-fitting and the miscibility criteria), the choice of radius becomes unambiguous.

(iii) Two four-component mixture diagrams were calculated for comparison with experimental data, and finally to verify the radii.

(iv) Some new experimental data on mixed-ionic-crystal phase diagrams are communicated to correct the old data.

Acknowledgments

Appendix A

Here we wish to describe briefly our experimental set up.

In order to prevent possible corrosion, the cell was made from 99.7% pure alumina tube with platinum electrodes.

The system was designed to measure the resistance of a sample as a function of temperature at constant cooling or heating rates. To eliminate the possible influence of experimental configuration on the results, cells and electrodes of different geometries were tested.

The measurement system was fully monitored by a PC through the GP–IB bus and RS–232 serial port.

The temperature was measured by a Pt versus Pt–10%Rh (type S) thermocouple connected through a reference junction to a voltmeter controlled by the PC. The thermocouple was used at the same time as one of the electrodes to provide a good contact with the sample. The temperature stability within the sample was monitored over 70 hours and the standard error did not exceed 0.035 K.

The temperature gradient along the sample was measured by a differential thermocouple and was found to be at most 2 K for all the configurations.

The resistance measurement was performed using an AC bridge (Hewlett–Packard 4276 LCZ Meter) in a four-probe arrangement at 400 Hz. This frequency is sufficiently low to avoid the influence of stray wire capacitance. While measuring the resistance, frequency dependence was checked in the range from 100 Hz to 20 KHz. The standard error of resistance was 0.15%.

Figure 12 shows typical resistance behaviour in the vicinity of melting of an alkali halide mixture close to its minimal point (azeotropic concentration). It can be seen that the solidification interval does not exceed 1 K as expected for the first-order phase transition.

Table A1 illustrates the reliability of our measurements in comparison with other investigators [9] for pure salts.

Table A1. Comparison of melting temperatures, T_m (K).

Salt	This work	Ref. [9]
KBr	1010	1007
NaBr	1017	1020
KCl	1046	1046
KI	955	954
NaI	933	933
NaCl	1077	1074

Appendix B

In order to calculate a phase diagram of a mixed salt $C1_x A1_y C2_{1-x} A2_{1-y}$ we should consider all the possible salts as pure components. The following notation is transparent.

$$p_{A1C1} = xy \qquad\qquad 1/M_{A1C1} = 1/M_{A1} + 1/M_{C1}$$
$$p_{A2C2} = (1-x)(1-y) \qquad 1/M_{A2C2} = 1/M_{A2} + 1/M_{C2}$$
$$p_{A1C2} = x(1-y) \qquad\qquad 1/M_{A1C2} = 1/M_{A1} + 1/M_{C2}$$
$$p_{A2C1} = (1-x)y \qquad\qquad 1/M_{A2C1} = 1/M_{A2} + 1/M_{C1}.$$

Now it is possible to calculate the corresponding Debye temperatures as

$$\theta_\alpha^2 \, 9\hbar^2 T_\alpha / k_B M_\alpha a_\alpha^2 x_m^2$$

where α = A1C1, A2C2, A1C2, A2C1; M_α have been defined above and T_α and a_α are corresponding melting temperatures and lattice parameters for pure salt components. As usual, for the mixed crystal we accept

$$1/\theta^2 = \sum_\alpha p_\alpha / \theta_\alpha^2 .$$

The size dispersion is calculated in the same manner. First of all we introduce the radii corresponding to individual salts

$$r_{A1C1} = r_{A1} + r_{C1} \qquad r_{A2C2} = r_{A2} + r_{C2}$$
$$r_{A1C2} = r_{A1} + r_{C2} \qquad r_{A2C1} = r_{A2} + r_{C1}$$

and then evaluate

$$x_s^2 = (4/a^2) \sum_{\alpha < \beta} p_\alpha p_\beta (r_\alpha - r_\beta)^2 \qquad a = \sum_\alpha p_\alpha a_\alpha .$$

Introducing the masses of the average anion and cation

$$M_C = x M_{C1} + (1-x) M_{C2} \qquad M_A = y M_{A1} + (1-y) M_{A2}$$

calculate a reduced mass

$$1/M_r = 1/M_A + 1/M_C .$$

Then the generalized Lindemann criterion, equation (2), holds true.

Taking $x = y$ one gets the formulae to calculate the solid lines shown on figures 9 and 10.

References

[1] Rabinovich S, Berrebi D and Voronel A 1989 *J. Phys.: Condens. Matter* **1** 6881
[2] Ross M and Wolf G 1986 *Phys. Rev. Lett.* **57** 214
[3] Chang I F and Mitra S S 1968 *Phys. Rev.* **172** 924
[4] Hardy J R and Karo A M 1979 *The Lattice Dynamics and Statistics of Alkali Halide Crystals* (New York: Plenum)
[5] Ashcroft N W and Mermin N D 1976 *Solid State Physics* (New York: Holt, Rinehard and Winston)
[6] Curtin W A and Runge K 1987 *Phys. Rev.* A **35** 4755
[7] Rabinovich S, Voronel A and Peretzman L 1988 *J. Phys. C: Solid State Phys.* **21** 5943
[8] Sirdeshmukh D B and Srinivas K 1986 *J. Mater. Sci.* **21** 4117
[9] Sangster J and Pelton A D 1987 *J. Phys. Chem. R F Data* **16** 509
[10] Wyckoff R W G 1960 *Crystal Structures* vol 1 (New York: Wiley)
[11] *Handbook of Chemistry and Physics* 64th edn (Boca Raton FL: Chemical Rubber Company)
[12] Venudhar Y C, Iyengar L and Krishna Rao K V 1986 *J. Mater. Sci.* **21** 110
[13] Mozer F 1982 *European Patent Specification* 0056262
[14] Smakula A, Maynard N and Repucci A 1962 *J. Appl. Phys. Suppl.* **33** 453
[15] Slage O D and McKinstry H A 1967 *J. Appl. Phys.* **38** 446
[16] Shanh N B and Pellissac B L 1968 *Bull. Soc. Fr. Minéral. Crystallogr.* **91** 13
[17] Srivastava K K and Merchant H D 1973 *J. Phys. Chem. Solids* **34** 2069
[18] Shahi K and Wagner J B 1983 *J. Phys. Chem. Solids* **44** 89
[19] Rostrovsky A P 1929 *Zh. Russk. Fiz.-Khim. Obshch.* **41** 595
[20] Kitaigorodski A I 1984 *Mixed Crystals* (Heidelberg: Springer)
[21] Lonsdale K 1948 *Acta Crystallogr.* **1** 142
[22] Seitz F 1940 *The Modern Theory of Solids* (New York: McGraw-Hill)
[23] Ho J C and Dandekar D P 1984 *Phys. Rev.* B **30** 2117
[24] Srinivas K and Sirdeshmukh D B 1985 *Curr. Sci.* **54** 740
[25] Srinivas K and Sirdeshmukh D B 1986 *Indian J. Pure Appl. Phys.* **24** 95
[26] Leibfreid G 1955 *Flügge's Handbuch der Physik* (Berlin: Springer) **7** 104
[27] Shanonn R D 1976 *Acta Crystallogr.* A **32** 751
[28] Krasnov K S 1960 *J. Struct. Chem.* **1** 191
[29] Corkill J L and Cohen M L 1992 *J. Phys. Chem. Solids* submitted
[30] Colemann D S and Lacy P D A 1967 *Mater. Res. Bull.* **2** 935
[31] Dombrovskaya O S 1933 *Zh. Obshch. Khim.* **3** 1047
        Thoma R E 1975 *Adv. Molten Salt Chem.* **3** 275
[32] Bellanca A 1939 *Period. Mineral.* **10** 9
[33] Gromasov S P and Gromasova L M 1953 *Zh. Fiz. Khim.* **27** 1545
[34] Diogenov G G and Ermachkov V I 1976 *Zh. Neorg. Khim.* **12** 573
[35] Bergman A G and Platonov F P 1937 *Izv. Sekt. Fiz.-Khim. Anal. Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR* **11** 253
[36] Bochvar A A 1933 *Z. Anorg. Allg. Chem.* **210** 163
[37] Ruff O and Plato W 1903 *Berichte* **36** 2357
        Amadori M 1912 *Atti R. Accad. Naz. Lincei Mem. Cl. Sci. Fis. Mat. Nat.* II **21** 467
        Gromakov S P and Gromakova L M 1955 *Zh. Fiz. Khim.* **29** 746
[38] Il'yasov I I and Volchanskaya V V 1974 *Soviet Prog. Chem.* **40** 56
[39] Radichev U 1935 *Zh. Obshch. Khim.* **5** 455