ON THE EXCESS ENTROPY OF ALKALI HALIDE SOLID SOLUTIONS

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It may be concluded from experimental solubility curves[1-5], specific heat[6], free energy[7] and X-ray intensity[8] measurements that the binary alkali halide solid solutions exhibit an entropy which exceeds the entropy of random mixing. It has been verified for the K(Cl, Br) and Na(Cl, Br) mixed crystals[9, 1i)] that the direct density measurements overestimate the vacancy content. Therefore it is assumed in this paper that the deviation from ideal mixing is predominantly due to the vibrational contribution of the entropy and that a single frequency is representing the average lattice vibrational frequencies of a crystal. In calculating the single frequency in a solid solution the isotopic approximation of Iosilevskii[11] was used

$$\nu^{-2} = \sum_{1}^{2} x_i \nu_i^{-2} , \qquad (1)$$

where x_i and ν_i are the mole fraction and single frequency of the component i, respectively. For the K(Cl, Br) solid solution this equation holds quite well at not very high temperatures[6, 12]. The frequencies used for the pure components are calculated from the centro frequencies by Plendi[13] and are given in Table 1.

Table 1.

The single centro-frequencies of some alkali halides.

	ν_c 10^{12} s^{-1}		ν_c 10^{12} s^{-1}		ν_c 10^{12} s^{-1}
NaCl	5.655	KCl	4.475	RbCl	3.700
NaBr	4.755	KBr	3.610	RbBr	2.855
NaI	4.105	KI	3.155	RbI	2.42

The change of entropy due to thermal vibration in mixing is given by

$$\Delta S^{th} = S^{th} - (x_1 S_1^{th} + x_2 S_2^{th}).\tag{2}$$

The entropy connected with the assumed single frequency vibrations was calculated with the aid of Einstein entropy relation

$$S_i^{th} = -6 R \{\ln [1 - f(\nu_i)^{-1}] - h \nu_i [k T (f(\nu_i) - 1)]^{-1}\},\tag{3}$$

with $f(\nu_i) = \exp [h \nu_i (k T)^{-1}]$; R, h and k are the ideal gas, Planck and Boltzmann constants.

Combining Eqs. (2) and (3) a simple formula for the excess entropy is obtained

$$S^{th} = -6 R \{- h (k T)^{-1} (\nu - \sum_1^2 x_i \nu_i) + \ln f(\nu) - \sum_1^2 x_i \ln f(\nu_i) +$$

$$\tag{4}$$

$$- h (k T)^{-1} [\nu/f(\nu) - \sum_1^2 x_i \nu_i/f(\nu_i)]\}.$$

The results calculated with the aid of Eqs. (1) and (4) for some binary alkali halide solid solutions may be given at 300 K

$$S^{th} \propto - \sigma R \sum_1^2 x_i \ln x_i, \quad \text{where } \sigma = \Delta S^{th} (x_1 = 0.5) R^{-1}/\ln 2.\tag{5}$$

The vibrational entropy parameters σ are given in Table 2 together with the theoretical values using data of Fancher and Barsch[14] and some experimental (except for RbBr — RbI solid solution the theoretical) value for heat of formation at 300 K and maximum critical temperature of the solubility gap data referred to by Ahtee and Koski[5] The entropy values calculated from solid solubility curves are inaccurate due to the lack of experimental information on the temperature dependence of the heat of formation and of

Table 2.

The vibrational entropy parameters for some binary alkali halide
solid solutions

Solid solution		σ	Fancher and Barsch[14]	Experimental
(Na, K)	Cl	0.11	0.25	0.20[1], 0.38[5]
	Br	0.15	0.18	0.35[5]
	I	0.14		0.22[5]
Na		0.04		0.12[5]
K	(Br, I)	0.04	0.15	~0[5]
Rb		0.06		0.12[5]
Na		0.06	0.23	0.08[6, 7], 0.09[8]
K	(Cl, Br)	0.09	0.15	0.07[15]
Rb		0.14		
(K, Rb)	Cl	0.07		
	Br	0.11		
	I	0.15		

accurate specific heat and vacancy concentration measurements which may
be significant to the excess entropy at high temperatures. The parameters σ
are in good agreement with the experimental excess entropy values.

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