Vibrational Excess Entropy of Equimolar KCl–KBr Solid Solution

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The Debye-Waller factors of the ions in equimolar KCl—KBr solid solution at 300 K have been determined from X-ray diffraction data. It was observed that the amplitudes of thermal vibration are slightly higher in the solid solution than in the pure components. The corresponding vibrational excess entropy was found to be about 10% of the entropy of ideal mixing.

In solid solutions, the differences in the sizes of the component atoms give rise to small random displacements from the sites of the average lattice. One effect which arises from these static displacements is that the intensities of the X-ray reflexions are reduced by an exponential factor, which is similar to the Debye-Waller (D-W) factor produced by the thermal displacements. In addition to the existence of the size effects, the vibrational states of the constituent atoms may change in the solid solution formation as a result of new interatomic interactions. If these changes occur, the entropy of the solid solution will deviate from that of ideal mixing. Since it is well known for metallic alloys that the vibrational contribution is crucial in accounting for deviations from the entropy of ideal mixing [1, 2], the question arises of whether this contribution is also of importance in alkali halide solid solutions. In the present work, the vibrational excess entropy of equimolar KCl – KBr solid solution was determined from X-ray diffraction data. The data of diffuse X-ray scattering indicate [3] that no departures from random distribution appear in this system.

The component salts utilized in preparation of the solid solution were of quality "supra pure", supplied by E. Merck A. G. (Darmstadt, Germany). The mixture, consisting of 50 mole per cent of both components, was melted in an evacuated quartz ampulla at 800 °C. The solid solution was annealed at 600 °C for 2 h for homogenization, and subsequently ground in a ball-mill at room temperature until the average particle size was about 4 μm.

The integrated intensities of the Bragg reflexions from three samples, which were prepared in a mould under uniaxial pressure, were measured on the same relative scale using monochromatized CuKα radiation. The experimental procedure was essentially similar to that described by INKINEN et al. [4]. After the measured intensities had been corrected for preferred orientation [5] and for thermal diffuse scattering [6], they were converted to the experimental structure factors, F_{exp}. The theoretical structure factors, F_{theor}, were calculated from relativistic Hartree-Fock free-ion form factors [7]. The scale factor of the values F_{exp} and the D-W parameters, B_{K}^{ss} and $B_{\text{Cl,Br}}^{\text{ss}}$, of the ions in solid solution were determined on the assumption that the values F_{exp} and F_{theor} coincided at high values of $\sin\theta/\lambda$, by employing the difference-Fourier method. The dispersion-corrected [8] values of F_{exp} are listed in Table 1, together with the values F_{theor} and the differences $\Delta F = F_{\text{exp}} - F_{\text{theor}}$. The limits of error of the values F_{exp} do not include the estimated uncertainty of 1.5% in the scale factor.

hkl	F_{exp}	F_{theor}	ΔF
111	27.93 ± 0.30	27.07	0.86
200	135.95 ± 1.25	139.11	−3.16
220	114.70 ± 0.60	114.93	−0.23
311	20.84 ± 0.25	21.14	−0.30
222	96.32 ± 0.65	98.30	−1.98
400	87.29 ± 0.65	85.93	1.36
331	19.69 ± 0.45	18.97	0.72
420	77.47 ± 0.75	76.24	1.23
422	67.82 ± 0.70	68.36	−0.54
333, 511	16.22 ± 0.45	16.87	−0.65
440	55.54 ± 0.75	56.11	−0.57
531	14.97 ± 0.30	14.73	0.24
442, 600	51.90 ± 0.60	51.18	−0.72
620	47.34 ± 0.50	46.81	0.53
622	42.34 ± 0.50	42.90	−0.56
444	37.94 ± 0.75	39.38	−1.44
551, 711	10.85 ± 0.30	10.95	−0.10
640	36.40 ± 0.50	36.20	0.20
642	33.17 ± 0.45	33.32	−0.15
800	28.83 ± 0.55	28.31	0.52

Table 1. Experimental dispersion-corrected structure factors F_{exp} of equimolar KCl – KBr solid solution at 300 K, theoretical structure factors F_{theor} calculated from relativistic Hartree-Fock free-ion scattering factors with Debye-Waller parameters evaluated in the present work, and differences $\Delta F = F_{\text{exp}} - F_{\text{theor}}$.

The D-W parameters arrived at in the present work are indicated in Table 2, together with the previous experimental and theoretical results for the ions in KCl and KBr. Since the spread in the B values of the component salts is comparable to the average uncertainty interval (± 0.10 Å^2) of the experimental data, justification exists for regarding their mean values as the D-W parameters of the pure components.

Comparison of the D-W parameters of the ions in solid solution with the values obtained by averaging the results for KCl and KBr discloses that the values of the positive and negative ions are increased in the

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Crystal	Debye-Waller parameter	
KCl−KBr	$B_{\mathrm{K}}^{\mathrm{ss}} = 2.71 \pm 0.10$ [a]	$B_{\mathrm{Cl,Br}}^{\mathrm{ss}} = 2.26 \pm 0.10$ [a]
KCl	$B_{\mathrm{K}} = 2.08 \pm 0.05$ [b]	$B_{\mathrm{Cl}} = 2.06 \pm 0.05$ [b]
	1.93 [c]	1.99 [c]
KBr	$B_{\mathrm{K}} = 2.45 \pm 0.15$ [d]	$B_{\mathrm{Br}} = 2.23 \pm 0.15$ [d]
	2.20 ± 0.10 [e]	2.28 ± 0.10 [e]
	2.21 [c]	2.24 [c]

[a] Present work.
[b] Ref. [9]: Observed; polycrystal, X-rays.
[c] Ref. [10]: Calculated from the normal mode data.
[d] Ref. [11]: Observed; polycrystal, X-rays.
[e] Ref. [12]: Observed; single crystal, neutrons.

Table 2. Debye-Waller parameters B (in Å^2) of the ions in the equimolar KCl−KBr solid solution and in its pure components at 300 K.

solid solution formation by $\Delta B_{\mathrm{K}} = 0.54$ Å^2 and $\Delta B_{\mathrm{Cl,\,Br}} = 0.10$ Å^2, respectively. The large change in the value of the K ion, as compared with the small increase in $B_{\mathrm{Cl,\,Br}}$, gives an indication of a local static distortion arising from different sizes of the Cl and Br ions. The size-effect displacement of the K ion is [13] $s = 0.0766$ Å, so that $\Delta B_{\mathrm{K}}(\text{static}) = 8\,\pi^2\,s^2 = 0.46$ Å^2. Subtraction of this value from the results obtained for $B_{\mathrm{K}}^{\mathrm{ss}}$ and ΔB_{K} gives
$B_{\mathrm{K}}^{\mathrm{ss}}(\text{thermal}) = 2.25$ Å^2 and $\Delta B_{\mathrm{K}}(\text{thermal}) = 0.08$ Å^2. The latter value is comparable to the difference $\Delta B_{\mathrm{Cl,\,Br}}$ mentioned above. The results obtained have thus indicated that the amplitudes of thermal vibration are slightly higher in the actual solid solution than in the ideal one, which implies slightly looser binding and higher vibrational entropy in the former.

The entropy ΔS of the solid solution is composed of the entropy of ideal mixing and of additional contributions, the number of which will depend upon the physical properties of the system under consideration. For metals, additional entropy terms attributable to differences in electronegativity and valence contribute [1] to ΔS, but may be ignored for alkali halide solid solutions. Since the electrical conductivity measurements of AMBROSE and WALLACE [14] gave no indication of an abnormal population of vacancies in KCl−KBr solid solution, the entropy contribution attributable to the existence of vacancies is insignificant in this system.

The above considerations lead to the assumption that ΔS is composed of the entropy of ideal mixing and of the vibrational contribution: $\Delta S = \Delta S^{\mathrm{id}} + \Delta S^{\mathrm{vib}}$. For the equimolar solid solution, $\Delta S^{\mathrm{id}} = 5.76$ J/deg. mole. The molar vibrational entropy was calculated from equation [2]

$$\Delta S^{\mathrm{vib}} = \tfrac{3}{2}\,R\,\ln\left(\overline{B^{\mathrm{ss}}}/\overline{B}\right)\,, \tag{1}$$

where R is the gas constant, $\overline{B^{\mathrm{ss}}}$ the average D-W temperature parameter of the solid solution, and $\overline{B}$ the corresponding quantity calculated from the B values of the pure components. By application of the averaging scheme [2], which weights the B values of the individual components in proportion to both their concentration and the number of electrons associated with each component, there is obtained from Eq. (1)

$$\Delta S^{\mathrm{vib}} = 0.5 \pm 0.2 \text{ J/deg. mole}\,.$$

This result is somewhat less than the value $\Delta S^{\mathrm{vib}} = 0.84$ J/deg. mole calculated [15] on the basis of the Debye temperatures derived from experimental elastic-constant data. With the value of ΔS^{vib} obtained in this work, the total entropy will be $\Delta S = 6.3$ J/deg. mole. This result coincides with that deduced [16] from data of the experimental heat of formation and activity. It thus appears safe to conclude that the formation of an equimolar KCl−KBr solid solution is characterized by a positive vibrational excess entropy, which is about 10% of ΔS^{id}. This result is at variance with one of the basic ideas of WASASTJERNA's theory [17], that the vibrational contribution to ΔS is zero.

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