

## Debye–Waller factors and Debye temperatures of alkali halide mixed crystals

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**Abstract.** The Debye–Waller factors of  $K_xRb_{(1-x)}I$  and  $NaCl_xBr_{(1-x)}$  mixed crystals have been determined from X-ray diffraction intensities. The mean Debye–Waller factor is found to vary non-linearly with the composition with positive deviations from linearity. The Debye temperatures (calculated from the Debye–Waller factors) are found to vary slightly non-linearly with composition with negative deviations from linearity. The Debye temperatures of seven alkali halide mixed crystal systems are critically compared with values predicted from six laws for composition variation. Using the estimated standard deviation as the criterion for the goodness of the fit, it is shown that the inverse cube (Kopp–Neumann) law provides the best description for the composition dependence of Debye temperatures of mixed crystals.

**Keywords.** Alkali halides; mixed crystals; Debye–Waller factors; Debye temperature.

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### 1. Introduction

A comprehensive programme on the physical properties of alkali halide mixed crystals is on hand in this laboratory. As a part of the programme, the Debye–Waller factors and Debye temperatures have been determined from X-ray diffraction intensities for several mixed crystal systems. The systems so far studied are KCl–KBr [1], KBr–RbBr [2], RbCl–RbBr [3], KCl–RbCl [4] and RbBr–RbI [5]. In all these cases, the Debye–Waller factor showed a non-linear composition dependence with positive deviations from linearity.

This article has two objectives. The first is to report results of an experimental determination of the Debye–Waller factors of two more mixed crystals systems viz. KI–RbI and NaCl–NaBr. Such measurements have not been made on NaCl–NaBr earlier. For the KI–RbI system, neutron-diffraction results have been reported (Beg *et al* [6]). But this work was sketchy as only three compositions were studied and the observed composition variation was not smooth. The second objective is to attempt a critical examination of the observed composition dependence of the Debye temperatures in alkali halide mixed crystal systems.

## 2. Experimental

The detailed procedure for determination of the Debye–Waller factor and the Debye temperature has been discussed in our earlier papers [7], [2]; hereinafter referred to as, I and II respectively. The method of growing mixed crystals and the determination of their composition is discussed in II. The instrumental conditions for recording intensities and the care taken in preparation of the powder sample to minimise spurious effects on the intensities are discussed in I. A difference between our earlier work and the present work is the use of a JEOL JDX-8P diffractometer fitted with a NaI(Tl) scintillation counter which obviates the necessity of a dead-time correction. The methods of applying background correction and TDS correction are again given in I. The integrated intensity of a given Bragg reflection after these corrections is denoted by  $I_0$ . The intensity of the same reflection for a static lattice is denoted by  $I_c$ . The expression for  $I_c$  is given in I. The structure factors for the two systems used in evaluating  $I_c$ , are

$$F_{hkl} = 4\{xf_K + (1-x)f_{Rb}\} \pm f_I, \quad (1)$$

$$F_{hkl} = 4[f_{Na} \pm \{xf_{Cl} + (1-x)f_{Br}\}] \quad (2)$$

for the two systems. Here  $f_i$  denotes the atomic scattering factor for ion  $i$ .

The mean Debye–Waller factor  $B$  is obtained from half the slope of the linear plot between  $\log(I_0/I_c)$  and  $(\sin\theta/\lambda)^2$ . This is termed the observed value ( $B_{obs}$ ). In mixed crystals, the presence of the two ‘mixing’ ions creates a static contribution ( $B_{static}$ ) which is included in  $B_{obs}$ . The method of calculating  $B_{static}$  and obtaining the corrected experimental value  $B_{exp}(= B_{obs} - B_{static})$  is discussed in II. The Debye temperature  $\theta_M$  (exp) is obtained from  $B_{exp}$  from the Debye–Waller theory expression:

$$B_{exp} = \frac{6h^2}{mk_B\theta_M} \left[ \frac{\phi(x)}{x} + \frac{1}{4} \right], \quad (3)$$

where the symbols have the usual meaning [8].

## 3. Results

The values of the Debye–Waller factors for the  $K_xRb_{(1-x)}I$  and  $NaCl_xBr_{(1-x)}$  mixed crystals for different values of  $x$  are given in table 1; these are already corrected for the static component. The values of the Debye temperatures are also included in the same table.

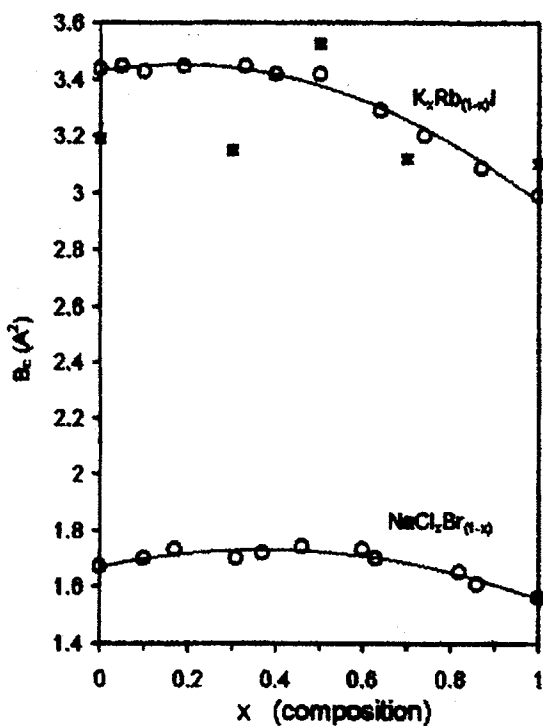
The Debye–Waller factors for the pure alkali halides NaCl, KI and RbI agree with literature values given in a recent compilation [14]; the Debye–Waller factors for NaBr were recently reported [15].

To get an idea of the trends in composition variation, the two parameters are plotted as a function of  $x$  in figures 1 and 2. It can be seen that in both systems, the Debye–Waller factor is a non-linear function of  $x$  with positive deviations from linearity. The extent of deviation is different in the two systems. It may be noted that whereas the present data points for  $K_xRb_{(1-x)}I$  lie on a smooth curve, the same is not true of the data points from the work of Beg *et al* [16]. The composition variation of the Debye–Waller factor observed here for the two systems is similar to that observed in the systems studied earlier, quoted

in §1. As far as the Debye temperature is concerned, it is a slightly non-linear function of  $x$  with negative deviations from linearity. Again, the extent of deviation is different for the two systems, being more for the NaCl–NaBr system than for the KI–RbI system.

**Table 1.** Debye–Waller factors  $B(A^2)$  and Debye temperatures  $\theta_M(K)$  of  $K_xRb_{(1-x)}I$  and  $NaCl_xBr_{(1-x)}$  systems. The maximum uncertainties in the experimental values are also given.

$K_xRb_{(1-x)}I$			$NaCl_xBr_{(1-x)}$		
$x$	$B$ (exp)	$\theta_M$ (exp)	$x$	$B$ (exp)	$\theta_M$ (exp)
0.00	$3.44 \pm 0.11$	$98 \pm 1$	0.00	$1.67 \pm 0.10$	$202 \pm 6$
0.05	$3.45 \pm 0.13$	$98 \pm 2$	0.10	$1.70 \pm 0.09$	$204 \pm 5$
0.10	$3.43 \pm 0.11$	$98 \pm 1$	0.17	$1.73 \pm 0.09$	$206 \pm 5$
0.19	$3.45 \pm 0.13$	$99 \pm 2$	0.31	$1.70 \pm 0.10$	$215 \pm 6$
0.33	$3.45 \pm 0.15$	$101 \pm 2$	0.37	$1.72 \pm 0.10$	$217 \pm 6$
0.40	$3.42 \pm 0.16$	$102 \pm 2$	0.46	$1.74 \pm 0.10$	$221 \pm 6$
0.50	$3.42 \pm 0.17$	$104 \pm 2$	0.60	$1.73 \pm 0.11$	$231 \pm 7$
0.64	$3.29 \pm 0.13$	$107 \pm 2$	0.63	$1.70 \pm 0.10$	$235 \pm 6$
0.74	$3.20 \pm 0.16$	$110 \pm 3$	0.82	$1.65 \pm 0.11$	$253 \pm 8$
0.87	$3.09 \pm 0.14$	$114 \pm 3$	0.86	$1.61 \pm 0.12$	$260 \pm 9$
1.00	$2.99 \pm 0.13$	$118 \pm 3$	1.00	$1.56 \pm 0.11$	$278 \pm 8$



**Figure 1.** Plot of Debye–Waller factor  $B$  (exp) versus composition ( $x$ ) for  $K_xRb_{(1-x)}I$  and  $NaCl_xBr_{(1-x)}$  systems. (o) present work; (\*) Beg *et al.*, continuous curve guide to the eye.

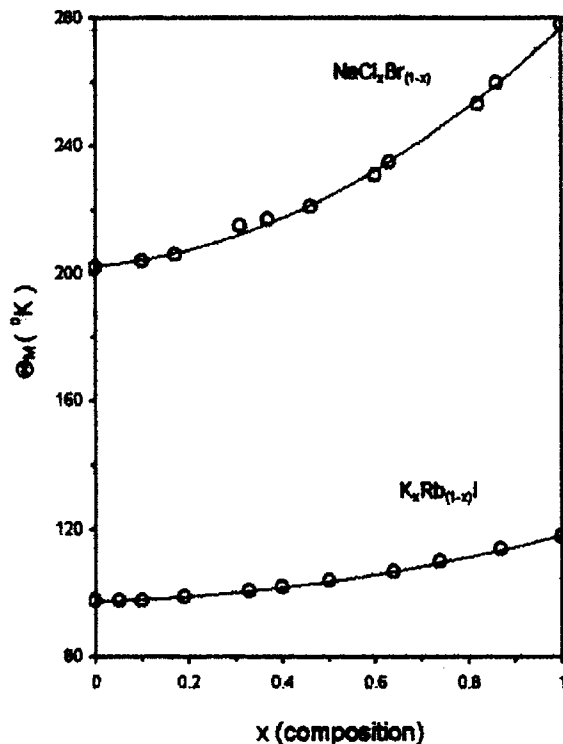


Figure 2. Plot of Debye temperature ( $\theta_M$ ) versus composition ( $x$ ) for  $K_xRb_{(1-x)}I$  and  $NaCl_xBr_{(1-x)}$  systems. (o) present work; continuous curve guide to the eye.

#### 4. Discussion

Several laws have been proposed for the composition dependence of Debye temperatures of mixed crystals. Assuming the additivity of specific heats and assuming the Debye theory expression for specific heat at low temperatures, Kopp and Neumann (see Ghatak and Kothari [9]) proposed the following law:

$$\theta_C^{-3} = x\theta_A^{-3} + (1-x)\theta_B^{-3}. \quad (4)$$

Karlsson [10] empirically proposed the law:

$$\theta_C^{-2} = x\theta_A^{-2} + (1-x)\theta_B^{-2}. \quad (5)$$

Nagaiah and Sirdeshmukh [11] empirically proposed the following relations:

$$\theta_C^{-1} = x\theta_A^{-1} + (1-x)\theta_B^{-1}, \quad (6)$$

$$\theta_C^2 = x\theta_A^2 + (1-x)\theta_B^2. \quad (7)$$

If  $\nu$  is the Debye frequency, the parameter  $m\nu^2$  (and hence  $m\theta^2$ ) has the significance of the associated force constant,  $m$  being the mass. Assumption of the additivity of force constants leads to the equation [12].

$$m_C\theta_C^2 = xm_A\theta_A^2 + (1-x)m_B\theta_B^2. \quad (8)$$

In a review of the physical properties of alkali halide mixed crystals, Sirdeshmukh and Srinivas [13] pointed out that properties which depend on interatomic forces have a linear composition dependence. Since the vibration spectrum is very much dependent on interatomic forces, the Debye temperature may be expected to follow the additivity rule:

$$\theta_C = x\theta_A + (1-x)\theta_B. \quad (9)$$

In the above equations,  $\theta_C$  is the Debye temperature of the mixed crystal,  $\theta_A$  and  $\theta_B$  those of the two end members,  $m_A$ ,  $m_B$  and  $m_C$  the molecular masses of the end members and  $x$  and  $(1-x)$  are the molar concentrations.

Nagaiah and Sirdeshmukh [11] applied (4), (6) and (7) to three mixed crystal systems including only one alkali halide mixed crystal system and concluded that (6) gives the best fit; the Debye temperature data was obtained from elastic constants. Giri and Mitra [12] applied (8) to three alkali halide mixed crystal systems and compared their results with values from elastic constants but did not make any comparison with other equations. Sirdeshmukh and Srinivas [13] summarized the results on eight alkali halide mixed crystal systems. They merely quoted the conclusions of the respective authors and observed that the Kopp-Neumann law (4) was favoured in only four out of the eight systems. Here again, the data was a mix of results from elastic constants and X-ray diffraction; it may be mentioned that Debye temperature values from elastic constants and X-ray diffraction do not always agree.

We have carried out a more systematic analysis. We make a comparative assessment of the above mentioned equations using results on seven alkali halide mixed crystal systems. The Debye temperatures for all these systems have been determined in our laboratory by the X-ray diffraction method; the maximum fractional error in  $(\Delta\theta/\theta)$  in these values is  $\pm 0.03$ . The values of the Debye temperatures calculated from each law ( $\theta_C$ ) are compared with the  $\theta_M$  (exp) values. As the  $\theta_C$  values from the several laws differ only slightly from one another, a graphical comparison is avoided as it leads to cluttering and overlapping in the diagram. Instead, for each law and each system, we calculate the estimated standard deviation  $\delta$  defined by:

$$\delta = \left[ \frac{\sum_n \{(\theta_C - \theta_M)/\theta_M\}^2}{n} \right]^{1/2}, \quad (10)$$

where  $n$  is the number of compositions studied in each system. These  $\delta$  values are taken as the criterion for deciding the goodness of fit.

The  $\delta$  values for the various systems and the several laws are collected in table 2. It can be seen that for each and every system the least  $\delta$  value is obtained for (4). The  $\delta$  values for (5), (6) and (8) are slightly larger. The  $\delta$  values for (7) and (9) are clearly the largest. Further, the  $\delta$  values for (4) are within the fractional error in the experimental values whereas those for (7) and (9) are very much greater than the fractional error. In the case of the RbBr-RbI system also, the  $\delta$  value is the least for (4). However, in this case the

**Table 2.** Values of estimated standard deviation ( $\delta$ ) for the difference between experimental ( $\theta_M$ ) and calculated ( $\theta_C$ ).

System	Source of $\theta_M$ (exp.)	$\delta$					
		Eq. (4)	Eq. (5)	Eq. (6)	Eq. (7)	Eq. (8)	Eq. (9)
KCl-KBr	[1]	0.016	0.023	0.032	0.058	0.030	0.049
KBr-RbBr	[2]	0.015	0.018	0.020	0.027	0.017	0.024
RbCl-RbBr	[3]	0.020	0.023	0.026	0.035	0.024	0.032
KCl-RbCl	[4]	0.008	0.014	0.020	0.044	0.017	0.036
RbBr-RbI	[5]	0.079	0.084	0.089	0.104	0.092	0.099
KI-RbI	Present work	0.013	0.016	0.020	0.030	0.021	0.027
NaCl-NaBr	Present work	0.014	0.023	0.033	0.064	0.028	0.053

$\delta$  values for all the equations exceed the fractional error in the experimental values. The cause of the discrepancy is not clear and is being examined.

On the basis of the analysis, it may now be taken as clearly established that among the several laws, the inverse cube (Kopp-Neumann) rule represented by (4) based on the assumption of the additivity of specific heats provides the best description for the composition dependence of the Debye temperatures of alkali halide mixed crystals.

## 5. Summary

The Debye-Waller factors and Debye temperatures of KI-RbI and NaCl-NaBr mixed crystals have been determined from X-ray diffraction intensities. It is pointed out that in these and several other alkali halide mixed crystal systems, the Debye-Waller factor varies non-linearly with composition with positive deviations from linearity. On the other hand, the Debye temperatures show a slightly non-linear composition dependence with negative deviations from linearity. The Debye temperatures of seven alkali halide mixed crystal systems are compared with values predicted from six equations for the composition variation of Debye temperatures. From a critical analysis, it is established that the inverse cube (Kopp-Neumann) law provides the best fit with experimental values.

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