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X-ray determination of mean Debye-Waller factors and Debye temperatures of the $K_xRb_{(1-x)}Br$ mixed crystal system

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Abstract. The integrated intensities of Bragg reflections have been measured for mixed crystals in the $K_xRb_{(1-x)}Br$ system with an x-ray powder diffractometer. From the intensities, the mean Debye-Waller factors are determined. The Debye-Waller factors are corrected for static contribution and Debye temperature values are determined for the entire composition range. The x-ray Debye temperatures follow the Kopp-Neumann equation closely.

Keywords. Debye-Waller factors; Debye temperatures; alkali halide mixed crystals.

PACS No. 61·10; 61·14; 63·20; 65·90

1. Introduction

In earlier papers (Subhadra and Sirdeshmukh 1977, 1978; Srinivas and Sirdeshmukh 1984), the results of x-ray determination of Debye-Waller factors and Debye temperatures for several crystals with NaCl structure were reported. The results of similar studies on the $K_xRb_{(1-x)}$. Br mixed crystal system are reported in this paper.

Among the mixed crystal series of alkali halides, experimental values for the Debye-Waller factors are available for a single composition in the series $KCl_xBr_{(1-x)}$ (Ahtee *et al* 1970) and $K_xRb_{(1-x)}Cl$ (Wasastjerna 1946) from x-ray intensities and $K_xRb_{(1-x)}F$ (Beg *et al* 1981) from neutron diffraction.

2. Experimental

Pure KBr and RbBr powders were supplied by BDH. Mixed crystals of $K_xRb_{(1-x)}Br$ with different compositions were prepared by the melt growth technique. Mixtures of weighed amounts of each component were ground to a fine powder and placed in a crucible. These mixtures were allowed to remain in the molten state for about an hour in a furnace, followed by slow cooling. The exact composition of the mixed crystals has been determined from the lattice constants assuming Vegard's law (Vegard 1921).

The procedure for obtaining the integrated intensities of the Bragg reflections is the same as described by Subhadra and Sirdeshmukh (1977). A Phillips PW 1140 diffractometer with CuKα radiation and Ni filter was used to obtain the integrated intensities of Bragg relfections from powder samples. A xenon-filled proportional counter was used as detector to collect the intensity data. All measurable peaks

corresponding to an angular range of 2θ values between 20 and 130° were obtained. The observed intensities were corrected for temperature diffuse scattering (TDS). All measurements were made at room temperature.

3. Results and discussion

The integrated intensity (I_0) is given by:

$$I_0 = C I_c \exp(-2Bs^2), \tag{1}$$

where I_c is the calculated intensity for static lattice, $s = \sin\theta/\lambda$, B the mean Debye-Waller factor and C the scale factor. The mean Debye-Waller factor (B_{obs}) is thus obtained from a least squares treatment of $\log(I_0/I_c)$ against $(\sin\theta/\lambda)^2$. However,

$$B_{obs} = B_{thermal} + B_{static}, \tag{2}$$

B_{static}, which is due to disorder because of the presence of atoms of different radii at lattice points otherwise occupied by atoms of a given type in pure crystals is estimated based on the model of Dernier *et al* (1976). The Debye temperature θ_M is obtained from the relation

$$B_{thermal} = (6h^2/\bar{m}kT)\, W(x), \tag{3}$$

where $\bar{m}$ is mean mass, T the temperature at which the intensities are measured. $W(x)$ is the function given by

$$W(x) = \{\phi(x)/x^2\} + (1/4x), \tag{4}$$

where $x = \theta_M/T$ and $\phi(x)$ is an integral. The values of $W(x)$ for a wide range of x are tabulated by Benson and Gill (1966).

The observed Deybe-Waller factors (B_{obs}) for different compositions are given in table 1. The mean Debye-Waller factor of KBr is $2{\cdot}23 \pm 0{\cdot}05$ Å^2 which is comparable with the x-ray value (2·14 Å^2) obtained by Baldwin *et al* (1965) and with the neutron diffraction value ($2{\cdot}33 \pm 0{\cdot}09$ Å^2) obtained by Butt *et al* (1976). Similarly the value of B for RbBr is $2{\cdot}18 \pm 0{\cdot}09$ Å^2 which is comparable with the x-ray value ($2{\cdot}08 \pm 0{\cdot}10$ Å^2) obtained by Subhadra (1976).

Table 1. Values of mean Debye-Waller factors (B_{obs}, B_{static} and $B_{thermal}$) and the Debye temperature (θ_M) for $K_xRb_{(1-x)}Br$ mixed crystals.

Mole fraction of KBr in RbBr (x)	B_{obs}(Å^2)	B_{static}(Å^2)	$B_{thermal}$(Å^2)	θ_M(°K)	θ(°K) (Kopp-Neumann equation)
0	$2{\cdot}18 \pm 0{\cdot}09$	0	2·18	139 ± 3	139
0·22	$2{\cdot}30 \pm 0{\cdot}07$	0·088	2·21	142 ± 3	143
0·37	$2{\cdot}40 \pm 0{\cdot}07$	0·120	2·28	143 ± 3	146
0·51	$2{\cdot}42 \pm 0{\cdot}07$	0·144	2·27	147 ± 3	149
0·57	$2{\cdot}36 \pm 0{\cdot}09$	0·142	2·22	150 ± 4	150
0·77	$2{\cdot}38 \pm 0{\cdot}07$	0·102	2·28	153 ± 3	155
1·0	$2{\cdot}23 \pm 0{\cdot}05$	0	2·23	162 ± 2	162

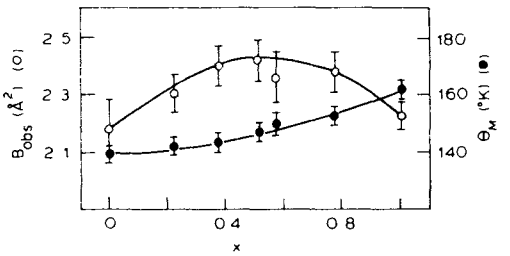

Figure 1. Plot of B_{obs} and θ_M against the molar fraction x of KBr in RbBr.

The values of B_{obs} are plotted against mole composition x in figure 1. It can be seen that the composition dependence of B_{obs} is not linear and shows positive deviation from linearity with a maximum nearabout equimolal composition. In fact, for intermediate compositions, the value of B_{obs} is greater than that for either end member.

The values of B_{static} and $B_{thermal}$ are also given in table 1. The composition dependence of $B_{thermal}$ is slightly non-linear but the deviations from linearity are of the same order as the error.

The Debye temperatures calculated from $B_{thermal}$ are given in table 1 and are also shown in figure 1. The present x-ray Debye temperatures vary with composition in a slightly non-linear fashion with a negative deviation from linearity. No other data on Debye temperatures is available for this system for comparison. The Debye temperatures are estimated from the Kopp-Neumann equation (Swalin 1962)

$$\theta^{-3} = x\theta_{KBr}^{-3} + (1-x)\theta_{RbBr}^{-3}$$

These values (included in table 1) agree with the experimental values within the limits of error.

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