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X-ray determination of the mean Debye-Waller factors and Debye temperatures of KCl-RbCl mixed crystals

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Abstract. Integrated intensities of Bragg reflections have been measured for KCl-RbCl mixed crystals with various compositions and the data used to evaluate the mean Debye-Waller factors and the Debye temperatures. The composition dependence of the Debye-Waller factor is highly nonlinear with positive deviations from linearity while that of the Debye temperature is slightly nonlinear with negative deviations from linearity. Using an empirical relationship between the Debye temperature and the molar volume, the average values of the Gruneisen parameter for some mixed crystal systems are obtained.

Keywords. Alkali halides; mixed crystals; Debye-Waller factors; Debye temperature; Gruneisen constant.

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1. Introduction

The results of X-ray determination of Debye-Waller (D-W) factors and Debye temperatures of mixed crystal systems $K_xRb_{(1-x)}Br$ and $RbCl_xBr_{(1-x)}$ were reported earlier (Srinivas and Sirdeshmukh 1985a; Srinivas *et al* 1987 hereinafter referred to as I and II). Similar results on the $K_xRb_{(1-x)}Cl$ mixed crystal system are now reported in this paper.

Using an empirical relation between Debye temperatures and molar volumes, the Gruneisen parameters of a number of mixed crystal systems are estimated.

2. Experimental

Mixed crystals were prepared from pure chemicals supplied by E Merck. The method of preparation and characterization of mixed crystals has been described in I and II. Diffractograms were obtained using a Phillips powder diffractometer equipped with a proportional counter; copper radiation was employed. Lattice constants were determined from the reflections at highest angles. The various corrections applied to the measured integrated intensities and the method of analysis of intensity data for the determination of mean D-W factor and Debye temperature are as discussed by Subhadra and Sirdeshmukh (1977) and in I and II.

3. Results and discussion

3.1 *Composition dependence of parameters*

The experimentally determined values of the mean D-W factor (B_{exp}) for the $K_xRb_{(1-x)}Cl$ system are given in table 1. The values obtained for the end members KCl and RbCl are consistent with literature values (Patomaki and Linkoaho 1969; Jarvinen and Inkinen 1967).

The composition dependence of the D-W factor (figure 1) is highly nonlinear with positive deviations from linearity with a maximum around the equimolar composition. This is similar to what has been observed in the related mixed crystal systems (I, II). The Debye temperatures (θ_M) calculated from the D-W factors are given in table 1 and shown in figure 1. The Debye temperatures of the mixed crystals have been calculated after correcting the experimental values of the D-W factor for the static displacement (Dernier *et al* 1976, I, II). The composition dependence of the Debye temperature is slightly nonlinear with negative deviations from linearity.

3.2 *Debye temperatures and Gruneisen parameters of mixed crystals*

The Gruneisen parameter is an important solid state parameter as it is directly related to the anharmonicity of atomic vibration in crystals. In a recent review, Sirdeshmukh and Srinivas (1986) pointed out that data on thermal expansion of crystals are too sparse and as a consequence no information is available regarding the Gruneisen parameters of mixed crystals. Bansigir (1968) pointed out empirically that the plot of $\log\theta$ vs $\log V$ (V being the molar volume) for a family of related crystals is linear and its slope equals the average Gruneisen parameter for the family of crystals. Subramaniam (1980) employed this method to estimate the Gruneisen parameter for the $KCl_xBr_{(1-x)}$ system using data on Debye temperatures calculated from the elastic constants. We have employed the same method to estimate the Gruneisen parameter of the $K_xRb_{(1-x)}Cl$ system and also for a few other mixed crystal systems for which Debye-temperatures have been measured in this laboratory by the X-ray method (I, II Srinivas 1981; Srinivas and Sirdeshmukh 1985b). The $\log\theta$-$\log V$ plots are shown in figure 2 and the values of the Gruneisen parameters for the mixed crystal systems are given in table 2 along with values for the pure crystals obtained from thermal expansion data.

Table 1. Values of the Debye-Waller factors (B_{exp}) and Debye temperatures (θ_M) for the $K_xRb_{(1-x)}Cl$ system.

x	B_{exp} (nm^2)	θ_M(K)
0	0·0211 ± 0·0006	165·0 ± 3
0·26	0·0220 ± 0·0008	174·6 ± 3
0·43	0·0230 ± 0·0006	178·2 ± 3
0·52	0·0229 ± 0·0009	182·4 ± 4
0·66	0·0216 ± 0·0007	194·5 ± 3
0·87	0·0207 ± 0·0007	207·6 ± 3
1·0	0·0198 ± 0·0008	217·8 ± 3

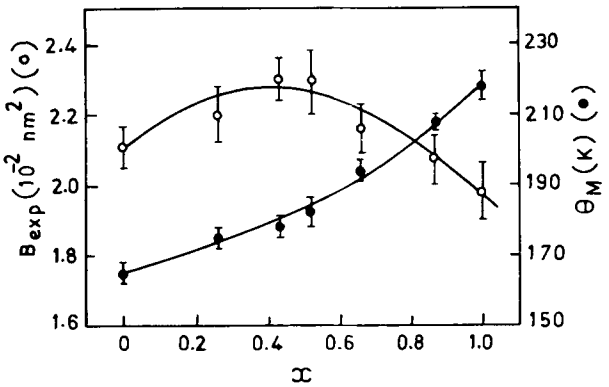

Figure 1. Plot of B_{exp} and θ_M against the composition x for the $K_xRb_{(1-x)}Cl$ system.

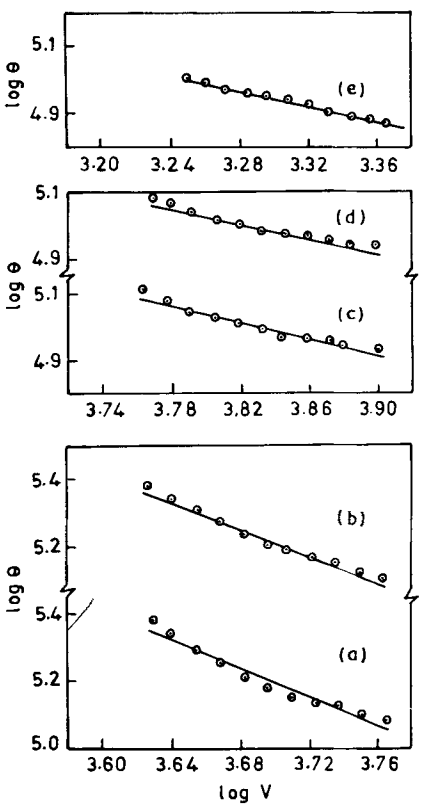

Figure 2. Plot of $\log\theta$ against $\log V$ for (a) KCL-KBr, (b) KCl-RbCl, (c) RbCl-RbBr, (d) KBr-RbBr and (e) AgCl-AgBr systems.

Table 2. Gruneisen parameters (γ) of some mixed crystal systems.

System A-B	γ for end members† *A*	*B*	Average γ for mixed crystal system from figure 2
KCl-KBr	1·49	1·50	2·07
KCl-RbCl	1·49	1·39	2·00
KBr-RbBr	1·50	1·42	1·16
RbCl-RbBr	1·39	1·42	1·22
AgCl-AgBr	1·98	2·36	1·09

†Shanker and Singh (1982a, b).

The data given in table 1 show that there is an order-of-magnitude agreement between the average Gruneisen parameters of mixed crystals and the Gruneisen parameters of the corresponding end members obtained from thermal expansion data. Subramaniam (1980) observed that the Gruneisen parameters for the $KCl_xBr_{(1-x)}$ system had a value of 1·9 which is larger than those for either of the end members. On this basis, Subramaniam concluded that the anharmonicity in mixed crystals is greater than in pure crystals. Our values for the $KCl_xBr_{(1-x)}$ system are consistent with the values obtained by Subramaniam. Further, the same trend is seen in the values of the Gruneisen parameters of the $K_xRb_{(1-x)}Cl$ system. However, in the three other systems, the trend is reversed i.e. the average Gruneisen parameter for the mixed crystal system is less than that for the end members. Thus, the data available at the moment are not sufficient for drawing a generalized conclusion about the relative anharmonicity in mixed crystals and pure crystals. Data on Gruneisen parameters for more systems and from more direct methods are required.

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