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Temperature variation of the Debye-Waller factors of metal and halide ions in CsCl and CsBr powders by X-ray diffraction. II. Debye-Waller factors of Cs^+ and Br^- ions in CsBr from room temperature to 78·2°K

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Abstract. The temperature variation of the Debye-Waller factors of Cs^+ and Br^- ions in CsBr powder has been studied using powder X-ray diffraction. The integrated intensities of the Bragg peaks at different temperatures have been obtained. These results have been verified by structure factor least squares refinement program. Theoretical shell model lattice dynamical calculations have been done using a 7-parameter model in the harmonic approximation and the values compared with the present X-ray measurements. The observed intensities have been corrected for first order thermal diffuse scattering.

Keywords. Cryostat; powder diffraction; Debye-Waller factors; SFLS program; lattice dynamics; caesium bromide; thermal diffuse scattering correction.

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1. Introduction

Caesium bromide is one of the simplest inorganic compounds and its lattice dynamics has been studied theoretically and experimentally. The phonon dispersion relations in CsBr were studied by neutron inelastic scattering (Rolandson and Raunio 1971) and the parameters for a shell model fit of the dispersion relations have been reported by Lal and Verma (1972) using the three-body force shell model (VSM) of Verma and Singh (1969). The thermal expansion has also been measured earlier by interferometric (Bailey and Yates 1967; Krishnan and Srinivasan 1956) and X-ray diffraction methods (Ganesan and Girirajan 1986) over the temperature range 78·2–298°K. Data on the Debye-Waller (D-W) factors of the metal and bromide ions in this compound and their temperature variation are however not available and it was considered worthwhile to calculate the temperature variation of the D-W factors of this compound by analysing the powder X-ray diffractograms and by using the theoretical lattice dynamics to obtain a comparison between theory and experiment.

2. Analysis of experimental data

The experimental details for getting the diffractograms over a temperature range of 78·2–298°K and data analysis are the same as described in our previous paper on CsCl

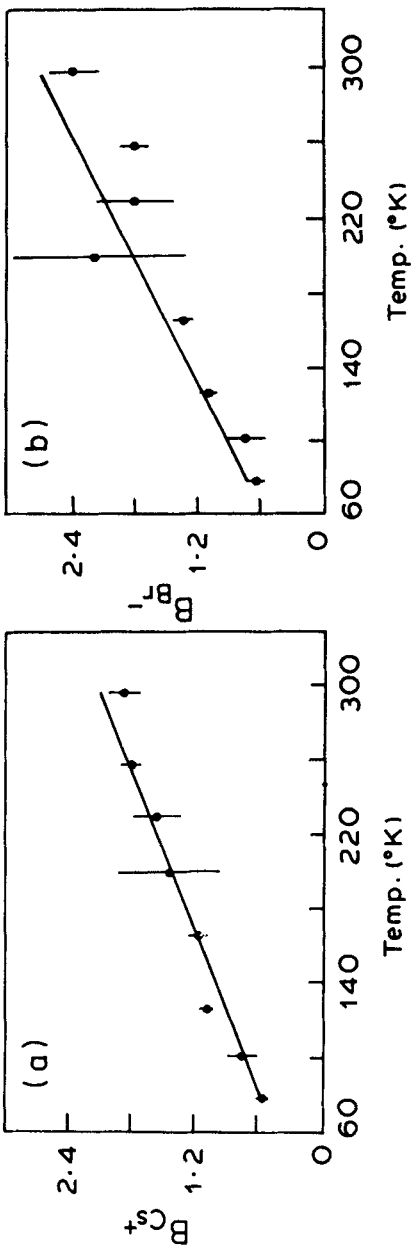

Figure 1. Temperature variation of the *B*-factors in CsBr. Dots represent experimental points and line represents theory. **a.** Cs^+ ion. **b.** Br^- ion.

Table 1. Temperature variation (°K) of the Debye-Waller factors (Å^2) of Cs^+ and Br^- in CsBr.

	Warren's method		SFLS (without TDS)		SFLS (with TDS)		Theory	
Temperature	Cs^+	Br^-	Cs^+	Br^-	Cs^+	Br^-	Cs^+	Br^-
78·2	0·50	0·76	0·58(5)	0·66(8)	0·56(4)	0·63(7)	0·56	0·71
101·0	0·72	0·78	0·72(11)	0·77(18)	0·75(12)	0·73(20)	0·72	0·92
125·8	1·13	1·32	1·18(5)	1·29(8)	1·08(3)	1·08(5)	0·89	1·14
166·1	1·30	1·70	1·22(7)	1·67(13)	1·17(5)	1·35(8)	1·18	1·51
200·2	1·69	1·98	1·57(49)	2·33(88)	1·47(48)	2·15(85)	1·42	1·82
230·8	1·84	2·08	1·70(20)	1·95(35)	1·57(22)	1·79(37)	1·64	2·10
258·7	1·84	2·32	1·98(17)	2·34(29)	1·82(8)	1·79(13)	1·84	2·35
298·0	2·09	2·41	2·06(16)	2·52(28)	1·90(14)	2·38(25)	2·12	2·71

TDS, thermal diffuse scattering; ESDs are given in parantheses.

(Ganesan and Girirajan 1988, paper I) and are therefore not repeated here. Since CsBr also exhibits the same lattice structure as CsCl, the procedure as described in paper I was used to get the D-W factors of Cs^+ (B_{Cs^+}) and Br^- (B_{Br^-}). The values thus obtained were verified by subjecting the structure factors to regular crystallographic refinement procedure using the SFLS program (see paper I). The thermal expansion results on CsBr in the temperature range reported earlier (Ganesan and Girirajan 1986) provided the correct lattice parameter to be used during refinement.

3. Theoretical calculations of B-factors in CsBr using the shell model

The phonon dispersion relations in CsBr have earlier been measured by Rolandson and Raunio (1971). Theoretical lattice dynamical calculations have also been done earlier (see paper I as well as Karo and Hardy 1968). All these models reproduce the phonon dispersion relations reasonably well. Lal and Verma (1972) have used a three-body force shell model and calculated the phonon dispersion relations. The same model was used for the present calculations in the range of temperatures of measurement. The D-W factor for ion type μ is as given in paper I. Table 1 compares the experimental values of the temperature variation of the D-W factors of Cs^+ and Br^- in CsBr with the theoretically calculated values using the shell model lattice dynamics. Figure 1 gives a graphical display of this comparison. As can be seen from these results the agreement between theory and experiment is good.

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