

## Temperature variation of the Debye-Waller factors of metal and halide ions in CsCl-Br solid solutions between room temperature and 90°K by powder X-ray diffraction

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**Abstract.** Solid solutions of CsCl-Br in different molal concentrations were prepared and X-ray diffractograms taken. The integrated intensities of the Bragg peaks have been estimated and structure factors were obtained. The crystal lattice in each of these solid solution samples is made up of a random distribution of  $\text{Cs}^+$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  ions depending upon the molal concentration. A pseudo-atom model has been proposed in which the  $\text{Cs}^+$  ions occupy (000) position and a pseudo-atom occupies  $(1/2, 1/2, 1/2)$  position. The presence of incoherence scattering in these solid solutions has been considered by applying the necessary correction to the atomic scattering factors. The integrated intensities have been analysed and the temperature variation of the Debye-Waller factors of the metal ( $\text{Cs}^+$ ) ion and the pseudo ion ( $\text{CB}^-$ ) have been estimated.

**Keywords.** Cryostat; powder X-ray diffraction; Debye-Waller factors; pseudo atom model; thermal diffuse scattering correction; structure factor least squares.

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### 1. Introduction

Studies pertaining to solid solutions and their mechanical, thermal and electrical properties are gaining importance. The physical properties of alkali halide mixed crystals have been reviewed by Hari Babu and Subba Rao (1984) and by Sirdeshmukh and Srinivas (1986). The present authors (Ganesan and Girirajan 1987) had earlier reported the thermal expansion and precise lattice parameter measurements in five different molal concentrations of CsCl-Br solid solution between room temperature and 90°K. However, experimental data on the temperature variation of the Debye-Waller (D-W) factors of the individual ions are not available. It was therefore considered worthwhile to attempt such a study and analyse the integrated intensities of the various Bragg peaks. The crystal lattice in each concentration of the solid solution contains a random distribution of  $\text{Cs}^+$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  ions and retains the parental structure of  $\text{Pm}\bar{3}\text{m}$  symmetry like CsCl or CsBr. A pseudo-atom model has been proposed in which the  $\text{Cs}^+$  ion occupies (000) position and a pseudo-atom made up of  $\text{Cl}^-$  and  $\text{Br}^-$  occupies  $(1/2, 1/2, 1/2)$  position. The presence of the pseudo-atom (ion) however depends on the molal concentration of solid solutions in which the two salts were mixed. The D-W factors and their temperature variation of the metal and pseudo-ions in all these samples have been estimated from the observed structure factors of the various Bragg reflections using the method of Warren (1969) and the crystallographic

least squares refinement program, the later to verify the results of the former method. The atomic scattering factors of the constituent atoms have been corrected for the presence of incoherent scattering by following the procedure of Willis (1973). The temperature variation of the D-W factors of  $\text{Cs}^+$  and the pseudo-atom (ion)  $\text{CB}^-$  obtained after correction for first order thermal diffuse scattering is also determined. Section 2 describes the sample preparation and experimental details for getting the diffractograms and § 3 presents the experimental data analysis and the temperature variation of the D-W factors of metal ion and the pseudo atom (ion). Section 4 gives the results.

## 2. Preparation of samples and experiment

Analar pure CsCl and CsBr compounds (BDH and Fluka) were ground to a fine powder, passed through a 325 mesh and dried at 420°K for several hours to form solid solutions. Each compound was then weighed in proper molal ratios in a microbalance to form solid solutions of concentrations CsCl-Br (0.8–0.2, 0.6–0.4, 0.5–0.5, 0.4–0.6 and 0.2–0.8). These were mixed homogeneously and filled in five different quartz tubes which were later evacuated and sealed. The sealed tubes were heated to 1123°K for 6–8 h and quenched to RT. The quartz tubes were then broken to retrieve the resulting mixture. They were again ground to a fine powder and passed through a 325 mesh and labelled for X-ray work. X-ray diffractograms were taken for each sample at eight different temperatures between RT and 90°K using a powder diffractometer (YPC 50 NM) and a continuous flow cryostat designed for this unit (Srinivasan and Girirajan 1982).  $\text{CuK}_\alpha$  radiation with nickle filter was used for all the measurements. The scanning speed of the sample was 1/4° per minute. Diffractograms were taken atleast twice for each sample to ensure reproducibility.

## 3. Analysis of experimental data

In most substitutional solid solutions, the atoms are generally arranged at random on the atomic sites of the lattice. The only major effect of a change in temperature is to increase or decrease the amplitude of thermal vibration. In one of our earlier studies it was noticed that only the composition of (0.8–0.2) of CsCl-Br resembles qualitatively as CsCl or CsBr. In the remaining four concentrations the lattice parameters did not show a steady decreasing behaviour as temperature is lowered and evidently there are regions in which thermal expansion coefficients become negative thus suggesting the possibility of an isostructural phase transformation. A study of the temperature variation of the D-W factors of the independent ions constituting these solid solutions might throw some light on the anomalous behaviour of the lattice parameters with temperature. This study was therefore undertaken. A model of the crystal lattice was found necessary for this purpose. It was observed that these solid solution samples generally exhibit a random distribution of  $\text{Cs}^+$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  ions but possess the parental Pm3m structure like CsCl or CsBr. In this context a pseudo-atom model for the crystal lattice has been found to be useful to analyse the integrated intensities of the Bragg peaks. In this pseudo-atom model all the metal ions ( $\text{Cs}^+$ ) were assumed to occupy (000) position and a pseudo-atom (ion)  $\text{CB}^-$  made up of  $\text{Cl}^-$  and  $\text{Br}^-$  occupies

(1/2 1/2 1/2) position. This means that while the scattering from the (000) position would be entirely due to metal ions ( $\text{Cs}^+$ ), the scattering from (1/2 1/2 1/2) position would be due to a combination of  $\text{Cl}^-$  and  $\text{Br}^-$  ions. The amount of scattering however would depend on the amount of Cl and Br ions present in that particular concentration. This feature reflects on the atomic scattering factors to be used for the pseudo-atom (ion) present at the (1/2 1/2 1/2) site. Another point to be considered is the presence of incoherent scattering due to all these scatterers. Willis (1973) described the method of dealing with incoherent scattering. Following his procedure two assumptions were made in the present study, (i) all the metal ions occupying (000) site do not create an incoherent scattering which varies as a function of  $\sin \theta/\lambda$  and hence contribute a uniform background in the diffraction pattern; (ii) the pseudo-atom (ion) made up of both  $\text{Cl}^-$  and  $\text{Br}^-$  ions whose atomic scattering factors denoted by  $f_{\text{CB}^-}$  could be thought of giving rise to an incoherent scattering which varies as a function of  $\sin \theta/\lambda$ . Therefore, the net atomic scattering factor for the pseudo-atom (ion) at (1/2 1/2 1/2) position can be written as

$$f_{\text{CB}^-} = [(x f_{\text{Cl}^-})^2 + (y f_{\text{Br}^-})^2]^{1/2}, \quad (1)$$

where  $f_{\text{Cl}^-}$  and  $f_{\text{Br}^-}$  are the atomic scattering factors of the  $\text{Cl}^-$  and  $\text{Br}^-$  ions and  $x$  and  $y$  the molal fraction of the chlorine and bromine ions present in the sample. The structure factor for each  $hkl$  and at each temperature would be

$$F_{hkl}^T = K \left[ f_{\text{Cs}^+} \exp\left(-B_{\text{Cs}^+} \frac{\sin^2 \theta}{\lambda^2}\right) \pm f_{\text{CB}^-} \exp\left(-B_{\text{CB}^-} \frac{\sin^2 \theta}{\lambda^2}\right) \right]. \quad (2)$$

Using this equation the integrated intensities have been analysed and the temperature variation of the D-W factors determined by the method of Warren (1969, see Ganesan and Girirajan 1988a for details). These results were verified by using the structure factor least squares (SFLS) refinement program. The thermal expansion results reported earlier (Ganesan and Girirajan 1987) provided the correct lattice parameters to be used in the refinement. Table 1 gives the lattice parameter values for all the concentrations at different temperatures of measurement. The integrated intensities

**Table 1.** Temperature vs lattice parameter for CsCl, CsBr and CsCl-Br solid solutions. Lattice parameter (Å).

Temperature (°K)	CsCl	CsCl-Br (0.8-0.2)	CsCl-Br (0.6-0.4)	CsCl-Br (0.5-0.5)	CsCl-Br (0.4-0.6)	CsCl-Br (0.2-0.8)	CsBr
78.2	—	4.10947(3)	—	—	—	—	4.25726(3)
90.0	4.09048(2)	—	—	—	—	—	—
92.0	—	—	4.20359(3)	4.13283(3)	4.19342(3)	4.22649(5)	—
101.0	4.09202(2)	4.11236(3)	4.20564(2)	4.16307(3)	4.19796(3)	4.23180(3)	4.26085(2)
125.8	4.09574(2)	4.11518(4)	4.20208(3)	4.16183(3)	4.18838(3)	4.23520(3)	4.26449(3)
166.1	4.10210(2)	4.12148(3)	4.15438(3)	4.18223(3)	4.20735(3)	4.24242(3)	4.27178(3)
200.2	4.10783(2)	4.12952(3)	4.16282(2)	4.16688(2)	4.19947(3)	4.24452(3)	4.27775(3)
230.8	4.11329(2)	4.13504(3)	4.17437(2)	4.17918(3)	4.21884(4)	4.25360(4)	4.28348(3)
258.7	4.11841(4)	4.13994(3)	4.18639(3)	4.18667(2)	4.20111(2)	4.25918(3)	4.28843(2)
298.0	4.12599(2)	4.14846(3)	4.18803(3)	4.20899(2)	4.23342(2)	4.27141(3)	4.29645(2)

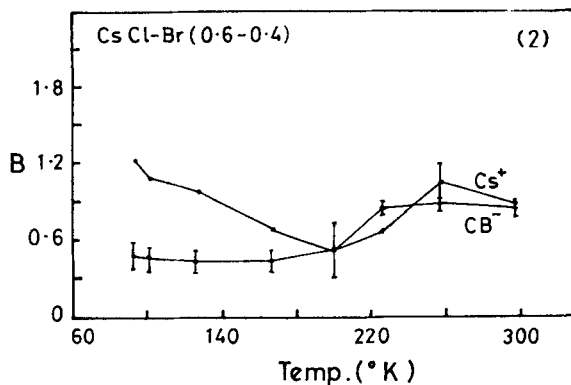
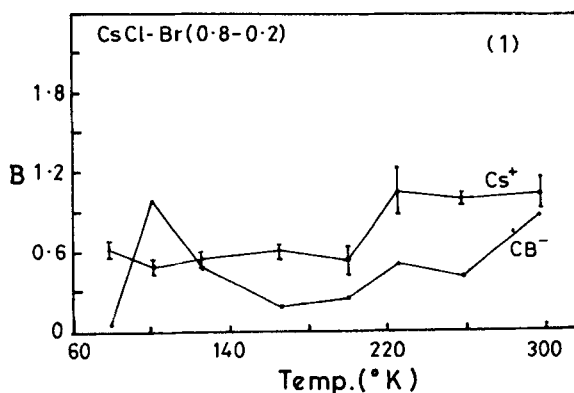
ESDs are given in parentheses.

were corrected for first order thermal diffuse scattering by using the Chipman and Paskin (1959) correction. The final  $R$  factor is  $< 6\%$  for all temperatures of measurement and concentrations.

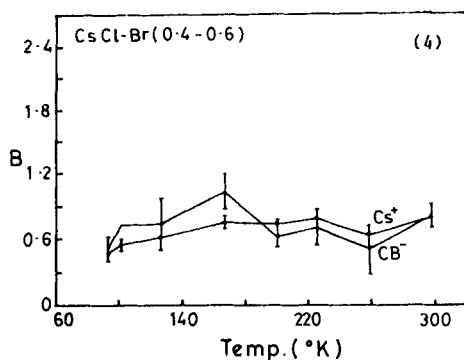
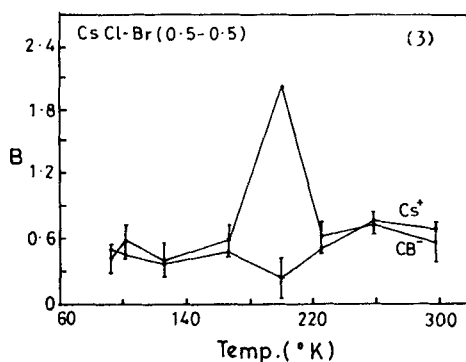
Figures 1–5 display the temperature variation of the D-W factors of the metal ( $B_{Cs^+}$ ) and the pseudo-atom ( $B_{CB^-}$ ) for each concentration. Tables 2–6 give the estimated D-W factors of the metal and the pseudo-atom (ion) as a function of temperature for all the five concentrations.

#### 4. Discussion

As stated earlier, in CsCl-Br based solid solutions, the lattice parameters in all the concentrations do not report a steady decreasing value as the temperature is lowered and there are regions of temperature in which the thermal expansion coefficients become negative. In CsCl-Br (0.8–0.2) however the sample behaved like CsCl or CsBr with regard to the lattice parameter as the temperature is lowered. This kind of anomalous behaviour has been found to occur in solid solutions formed by samarium, yttrium and sulphur. Dernier *et al* (1976) found that in  $Sm_{0.7}Y_{0.3}S$  a negative thermal expansion occurs around  $400^\circ K$ . They have also estimated the rms displacements of the



**Figures 1 and 2.** Temperature variation of the  $B$ -factors for  $Cs^+$  and  $CB^-$  ions in CsCl-Br. 1. 0.8–0.2. 2. 0.6–0.4.



Figures 3 and 4. Temperature variation of the  $B$ -factors for Cs<sup>+</sup> and Br<sup>-</sup> ions in CsCl-Br. 3. 0.5-0.5. 4. 0.4-0.6.

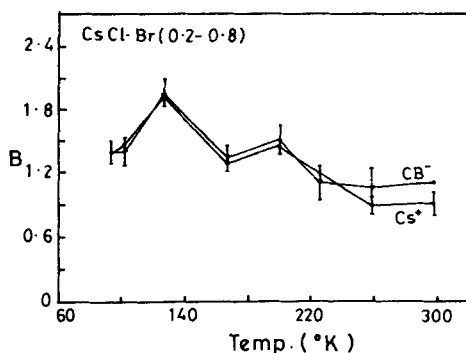


Figure 5. Temperature variation of the  $B$ -factors for Cs<sup>+</sup> and Br<sup>-</sup> ions in CsCl-Br (0.2-0.8).

atoms in this compound and plotted the individual atoms as a function of temperature. This gradual expansion in cell edge with decrease in temperature has been attributed by them to a shift in valence in Sm towards Sm<sup>2+</sup>. They have suggested the possibility of an iso-structural transition from a semiconducting NaCl phase to a denser metallic phase, also of the NaCl structure. They have also argued that this may be due to the softening of optic phonons but not of acoustic phonons.

The contributions to the mean square displacements of the atoms in an alloy or solid solution arise from both static and dynamic disorder. The two effects are

**Table 2.** Temperature variation ( $^{\circ}\text{K}$ ) of the D-W factors ( $\text{\AA}^2$ ) of  $\text{Cs}^+$  and  $\text{CB}^-$  in CsCl-Br (0.8-0.2) solid solution.

Temperature ( $^{\circ}\text{K}$ )	Warren's method		SFLS	
	$\text{Cs}^+$	$\text{CB}^-$	$\text{Cs}^+$	$\text{CB}^-$
78.2	0.55	0.03	0.60(8)	0.03(0)
101.0	0.48	1.01	0.46(6)	0.99(0)
125.8	0.58	0.42	0.51(7)	0.41(0)
166.1	0.55	0.20	0.59(6)	0.19(0)
200.2	0.51	0.22	0.51(12)	0.23(0)
230.8	1.01	0.49	1.04(19)	0.49(0)
258.7	0.95	0.41	0.98(6)	0.40(0)
298.0	1.04	0.83	1.03(13)	0.87(0)

ESDs are given in parentheses.

**Table 3.** Temperature variation ( $^{\circ}\text{K}$ ) of the D-W factors ( $\text{\AA}^2$ ) of  $\text{Cs}^+$  and  $\text{CB}^-$  in CsCl-Br (0.6-0.4) solid solution.

Temperature ( $^{\circ}\text{K}$ )	Warren's method		SFLS	
	$\text{Cs}^+$	$\text{CB}^-$	$\text{Cs}^+$	$\text{CB}^-$
92.0	0.45	1.17	0.46(10)	1.22(0)
101.0	0.52	1.04	0.45(9)	1.08(0)
125.8	0.49	0.98	0.42(9)	0.97(0)
166.1	0.47	0.69	0.42(8)	0.68(0)
200.2	0.55	0.51	0.52(10)	0.50(22)
230.8	0.83	0.65	0.84(6)	0.65(0)
258.7	0.86	1.01	0.88(7)	1.05(15)
298.0	0.86	0.89	0.84(6)	0.89(0)

ESDs are given in parentheses.

approximately additive so that

$$\bar{u}^2 = \langle u_{\text{eff}}^2 \rangle = \langle u_{\text{stat}}^2 \rangle + \langle u_{\text{dyn}}^2 \rangle. \quad (3)$$

The first term on the right side of (3) can be written for our CsCl-Br solid solution system in the pseudo-atom model as

$$\langle u_{\text{stat}}^2 \rangle = (r_A - r_B)^2 x(1-x), \quad (4)$$

where  $x$  is the molal fraction of the concentration,  $r_A$  the ionic radius of the metal ion and  $r_B = ((\sqrt{3}/2)a - r_A)$  where  $a$  is the lattice parameter of that concentration. The overall D-W factors can be obtained by an initial Wilson plot of  $F(\text{obs})$  vs  $\sin^2 \theta / \lambda^2$  and from this if the static contribution estimated using (4) is subtracted, the contribution to

**Table 4.** Temperature variation ( $^{\circ}\text{K}$ ) of the D-W factors ( $\text{\AA}^2$ ) of  $\text{Cs}^+$  and  $\text{CB}^-$  in CsCl-Br (0.5–0.5) solid solution.

Temperature ( $^{\circ}\text{K}$ )	Warren's method		SFLS	
	$\text{Cs}^+$	$\text{CB}^-$	$\text{Cs}^+$	$\text{CB}^-$
92.0	0.49	0.42	0.50(6)	0.41(13)
101.0	0.50	0.72	0.45(4)	0.59(13)
125.8	0.42	0.44	0.36(5)	0.40(16)
166.1	0.48	0.49	0.47(4)	0.58(13)
200.2	0.45	0.66	0.24(18)	2.05(0)
230.8	0.61	0.71	0.50(4)	0.62(14)
258.7	0.80	0.77	0.77(3)	0.74(10)
298.0	0.60	0.53	0.69(6)	0.56(17)

ESDs are given in parentheses.

**Table 5.** Temperature variation ( $^{\circ}\text{K}$ ) of the D-W factors ( $\text{\AA}^2$ ) of  $\text{Cs}^+$  and  $\text{CB}^-$  in CsCl-Br (0.4–0.6) solid solution.

Temperature ( $^{\circ}\text{K}$ )	Warren's method		SFLS	
	$\text{Cs}^+$	$\text{CB}^-$	$\text{Cs}^+$	$\text{CB}^-$
92.0	0.48	0.55	0.46(4)	0.51(11)
101.0	0.55	0.76	0.55(6)	0.73(0)
125.8	0.60	0.69	0.61(9)	0.74(24)
166.1	0.72	0.98	0.76(6)	1.05(17)
200.2	0.73	0.58	0.74(3)	0.63(9)
230.8	0.79	0.77	0.79(7)	0.72(17)
258.7	0.63	0.60	0.64(9)	0.51(23)
298.0	0.83	0.87	0.81(4)	0.83(12)

ESDs are given in parentheses.

the rms displacement and the D-W factor arising from the lattice dynamics of the crystal can be obtained. Tables 7–9 give the contribution from static and dynamic part and the overall  $B$  factors as a function of temperature for all concentrations. Figures 6 to 8 graphically displays these values.

A study of figures 1–8 shows that in none of these concentrations the  $B$  factors can be said to have a smooth decreasing value as the temperature is lowered contrary to what was found in CsCl and CsBr (Ganesan and Girirajan 1988, papers I & II). This is probably due to the static disorder which indeed was the case in CsCl-Br (0.6–0.4); thus the phonon frequencies and the mean square displacements arising from the lattice vibrations do not explain for such an anomalous behaviour. The dynamic effects holds out dramatically in CsCl-Br (0.2–0.8) and not so profoundly in other concentrations. The reason for studying the dynamic effects is to find out how far the lattice phonons

**Table 6.** Temperature variation ( $^{\circ}\text{K}$ ) of the D-W factors ( $\text{\AA}^2$ ) of  $\text{Cs}^+$  and  $\text{CB}^-$  in CsCl-Br (0.2-0.8) solid solution.

Temperature ( $^{\circ}\text{K}$ )	Warren's method		SFLS	
	$\text{Cs}^+$	$\text{CB}^-$	$\text{Cs}^+$	$\text{CB}^-$
92.0	1.42	1.49	1.38(5)	1.40(10)
101.0	1.45	1.43	1.46(7)	1.40(13)
125.8	1.92	1.97	1.93(6)	1.96(13)
166.1	1.31	1.35	1.29(6)	1.35(12)
200.2	1.53	1.56	1.47(7)	1.53(14)
230.8	1.14	1.12	1.20(8)	1.11(17)
258.7	0.93	1.07	0.91(9)	1.08(18)
298.0	0.96	1.14	0.93(11)	1.13(0)

ESDs are given in parentheses.

**Table 7.** Temperature variation ( $^{\circ}\text{K}$ ) of B (static) ( $\text{\AA}^2$ ) for CsCl-Br solid solutions.

Temperature ( $^{\circ}\text{K}$ )	Concentration				
	0.8-0.2	0.6-0.4	0.5-0.5	0.4-0.6	0.2-0.8
78.2	0.13	—	—	—	—
92.0	—	0.43	0.26	0.40	0.33
101.0	0.14	0.43	0.33	0.41	0.34
125.8	0.14	0.42	0.33	0.39	0.35
166.1	0.15	0.30	0.39	0.44	0.36
200.2	0.16	0.32	0.34	0.42	0.37
230.8	0.17	0.35	0.38	0.47	0.39
258.7	0.18	0.38	0.40	0.42	0.40
298.0	0.19	0.39	0.46	0.52	0.43

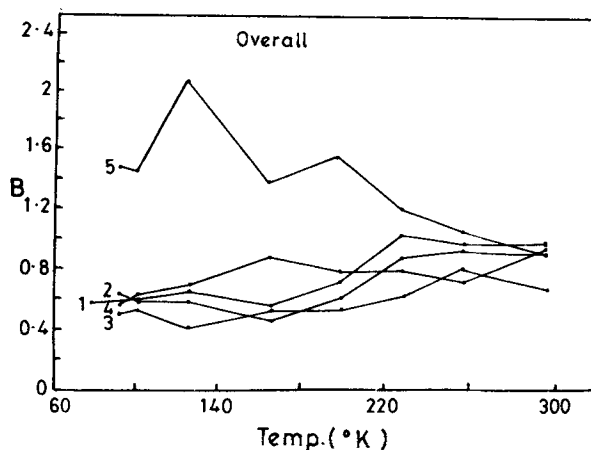
**Table 8.** Temperature variation ( $^{\circ}\text{K}$ ) of B (dynamic) ( $\text{\AA}^2$ ) for CsCl-Br solid solutions.

Temperature ( $^{\circ}\text{K}$ )	Concentration				
	0.8-0.2	0.6-0.4	0.5-0.5	0.4-0.6	0.2-0.8
78.2	0.44	—	—	—	—
92.0	—	0.20	0.24	0.16	1.14
101.0	0.45	0.15	0.19	0.21	1.09
125.8	0.50	0.15	0.07	0.29	1.70
166.1	0.40	0.15	0.12	0.42	0.99
200.2	0.53	0.26	0.17	0.34	1.15
230.8	0.83	0.50	0.22	0.29	0.77
258.7	0.76	0.51	0.37	0.27	0.62
298.0	0.75	0.48	0.18	0.37	0.44

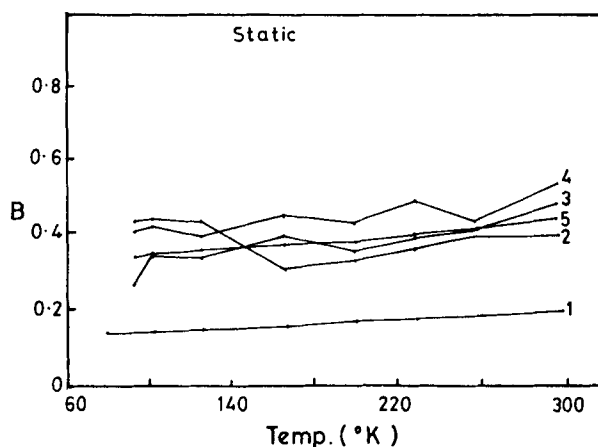


**Table 9.** Temperature variation ( $^{\circ}\text{K}$ ) of  $B$  (overall) ( $\text{\AA}^2$ ) for CsCl-Br solid solutions.

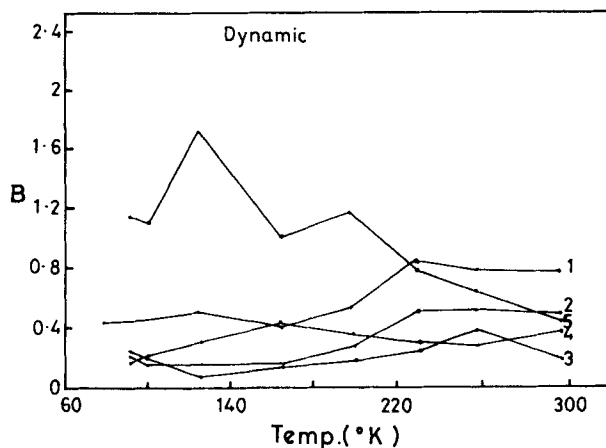
Temperature ( $^{\circ}\text{K}$ )	Concentration				
	0.8-0.2	0.6-0.4	0.5-0.5	0.4-0.6	0.2-0.8
78.2	0.57	—	—	—	—
92.0	—	0.63	0.50	0.56	1.47
101.0	0.59	0.58	0.52	0.62	1.43
125.8	0.64	0.57	0.40	0.68	2.05
166.1	0.55	0.45	0.51	0.86	1.35
200.2	0.69	0.58	0.51	0.76	1.52
230.8	1.00	0.85	0.60	0.76	1.16
258.7	0.94	0.89	0.77	0.69	1.02
298.0	0.94	0.87	0.64	0.89	0.87

**Figure 6.** Temperature variation of the overall  $B$ -factors ( $B_{\text{overall}}$ ) in CsCl-Br solid solutions. 1. 0.8-0.2. 2. 0.6-0.4. 3. 0.5-0.5. 4. 0.4-0.6. 5. 0.2-0.8.

and the phonon spectrum are responsible and can adequately explain the anomalous behaviour encountered in the behaviour of the lattice parameter and the D-W factors as the temperature is lowered. At this point it will not be out of place to point out the role played by the occupancy factor at each atomic sites. Barring the concentrations CsCl-Br (0.6-0.4) and CsCl-Br (0.5-0.5) for all the three remaining concentrations at all temperatures of measurement no refinement was necessary with regard to the occupancy factors. In CsCl-Br (0.6-0.4) at two temperatures of measurements viz 258.7 $^{\circ}\text{K}$  and 200 $^{\circ}\text{K}$  it was necessary to refine the occupancy factor and consequently the atomic scattering factor at site (000) for the metal ion  $\text{Cs}^+$  had to be multiplied by a factor of 0.85. In order to compensate for this decrease, the atomic scattering factor from the pseudo-atom had to be added by 0.15 fold. Similarly for pseudo-atom at site (1/2 1/2 1/2), the atomic scattering factor of  $\text{Cs}^+$  had to be added 0.15 times and 0.85 times for  $\text{CB}^-$ . This could mean that overlapping of atoms at these atomic sites occurs both with regard to the metal and the pseudo-atom (ion). A similar thing had to be done



**Figure 7.** Temperature variation of the static contribution for the  $B$ -factors ( $B_{\text{static}}$ ) in CsCl-Br solid solutions. 1. 0.8-0.2 2. 0.6-0.4. 3. 0.5-0.5. 4. 0.4-0.6. 5. 0.2-0.8.



**Figure 8.** Temperature variation of the dynamic contribution for the  $B$ -factors ( $B_{\text{dynamic}}$ ) in CsCl-Br solid solutions. 1. 0.8-0.2. 2. 0.6-0.4. 3. 0.5-0.5. 4. 0.4-0.6. 5. 0.2-0.8.

during refinement for CsCl-Br (0.5-0.5) at 92°K, the numbers being 0.95 and 0.05. It is clear from the present study that isostructural phase transitions might be a possible reason due to softening of some phonon modes in the case of CsCl-Br (0.2-0.8) and CsCl-Br (0.4-0.6) where the dynamic effects are appreciable. However with the present set of data available it is difficult to confirm whether the softening is due to optic or acoustic phonons. In other cases it can be said that within the errors of measurement, the static disorder effects might have caused the apparent anomalous behaviour and when the contribution to the  $B$  factors due to this are subtracted from the total  $B$  factor the resulting dynamic disorder effects do not show any appreciably strong anomalies.

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## References

- Chipman D R and Paskin A J 1959 *J. Appl. Phys.* **30** 1998  
Dernier P D, Weber W and Longinotti L D 1976 *Phys. Rev.* **B14** 3635  
Ganesan V and Girirajan K S 1987 *Pramana - J. Phys.* **28** 1 73  
Ganesan V and Girirajan K S 1988a *Pramana - J. Phys.* **30** 331  
Ganesan V and Girirajan K S 1988b *Pramana - J. Phys.* **30** 337  
Hari Babu V and Subba Rao K V 1984 *Prog. Crystallogr. Growth Charact.* **8** 189  
Sirdeshmukh D B and Srinivas K 1986 *J. Mater. Sci.* (in Press)  
Srinivasan R and Girirajan K S 1982 *Pramana - J. Phys.* **19** 203  
Warren B E 1969 *X-ray diffraction* (New York: Addison-Wesley)  
Willis B T M 1973 *Chemical application of thermal neutron scattering* Harwell series (Oxford: University Press)