Precise lattice parameter measurements 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 five different concentrations were prepared in sealed quartz tubes by heating the mixture to 1123°K for 6–8 hr and quenching to room temperature. X-ray diffractograms were taken at eight different temperatures between room temperature and 90°K for these solid solutions using the YPC50NM powder diffractometer and a continuous flow cryostat. The observed lattice parameters for each sample at each temperature obtained from the powder diffractograms were then extrapolated to give the true lattice parameters using the least square method with Nelson-Riley extrapolation scheme. The values of the true lattice parameters at each concentration and at each temperature were tabulated and the results discussed. It is shown that the lattice parameters vs temperature for some concentrations exhibit an anomalous behaviour.

1. Introduction

Study of mechanical, electrical and thermal properties of solid solutions is very important in solid state physics and in the recent past a number of people have started work in this area (Shukla *et al* 1976; Natarajan *et al* 1970; and Beg and Kobbelt 1982). In some of these solid solutions of alkali halides it has even become possible to grow single crystals for inelastic neutron scattering work to measure phonon dispersion relations (Beg and Kobbelt 1982). Shukla *et al* (1976) and Natarajan *et al* (1970) have claimed good success in forming solid solutions other than KCl-KBr systems. They were able to prove that CsCl forms good solid solutions with other alkali halides and crystallize in Pm3m structure and retain the structure throughout the concentration range in which the salts were mixed. They substantiated their results in the case of CsCl based solid solutions by heat of solution and heat of mixing measurements and by testing the homogeneity of the samples by x-ray lattice parameter measurements. Hence it was considered worthwhile to take CsCl-Br system as a case study in order to (i) obtain the lattice parameter shifts as a function of concentration and as a function of temperature and (ii) look how the lattice parameter behaves for each concentration at low temperatures down to 90°K as there is no experimental data available for these salts in this temperature range.

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2. Preparation of samples and experiment

Analar pure CsCl and CsBr compounds supplied by BDH and Fluka were first ground to a very fine powder and passed through a 325 mesh. They were dried at 420°K for several hours before forming the 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]. The two accurately weighed samples of CsCl and CsBr for each concentration were mixed homogeneously and were filled in five different quartz tubes which were later evacuated and sealed. These sealed quartz tubes were heated in a furnace upto 1123°K for 6–8 hr and quenched to room temperature (RT). These quartz tubes containing the samples were then broken to retrieve the resulting mixture. Each of them were then ground to fine powder which will pass through a 325 mesh and labelled properly for x-ray work. For each sample x-ray diffractograms were taken at eight different temperatures between RT and 90°K using the YPC50NM powder diffractometer available in the department and the continuous flow cryostat designed for this unit (Srinivasan and Girirajan 1982). Copper radiation was used in all these measurements with nickel filter. The scanning speed of the sample for all these measurements was 1/4° per minute. The diffractograms were taken in each sample at least two times to ensure reproducibility.

3. Analysis of experimental data

The diffractograms for each concentration taken at eight different temperatures between RT and 90°K were analyzed in the following way. Bragg peak positions in 2θ scale were obtained from the diffractograms for each Bragg reflection for each concentration and each temperature after properly indexing the Bragg peaks. These Bragg angles along with the h, k, l and the x-ray wavelengths where α_1 and α_2 resolutions showed up were used to obtain the observed lattice parameters from the Bragg formula. These observed lattice parameters were subjected to a least square analysis using the extrapolation function of Nelson-Riley (1945) $[\cos^2\theta/\sin\theta + \cos^2\theta/\theta]$ described in Ganesan and Girirajan (1986) and the true lattice parameters were obtained. The prominent higher angle reflections from $2\theta = 70°$ to $2\theta = 130°$ were used for extrapolation. Figure 1 gives a sample plot of the observed lattice parameter a_T(obs) vs Nelson-Riley extrapolation function for the room temperature measurement of CsCl-Br(0·8-0·2). Table 1 presents the true lattice parameters obtained by the least square method along with the error estimate in obtaining them for each concentration and each temperature of measurement. Figure 2 gives a plot of the true lattice parameter vs concentration at RT along with the values of Natarajan *et al* (1970). Figure 3 gives a plot of the true lattice parameters vs temperature for each of the samples. A look at the behaviour of the true lattice parameters with temperature from figure 3 indicates that (i) not in all concentrations the lattice parameters could be fitted into a single polynomial of T and (ii) the samples other than CsCl-Br(0·8-0·2) molal concentration indicates a tendency to behave anomalously with temperature. The sample with CsCl-Br(0·8-0·2) molal concentration only behaves in a systematic fashion with respect to temperature like either CsCl or CsBr and in this case the true lattice parameters were fitted to a cubic polynomial as given below. (a_T (true) $= a_0 + C_1 T + C_2 T^2 + C_3 T^3$ where a_0, C_1, C_2 and C_3 are constant coefficients.) The values of the constant coefficients for this
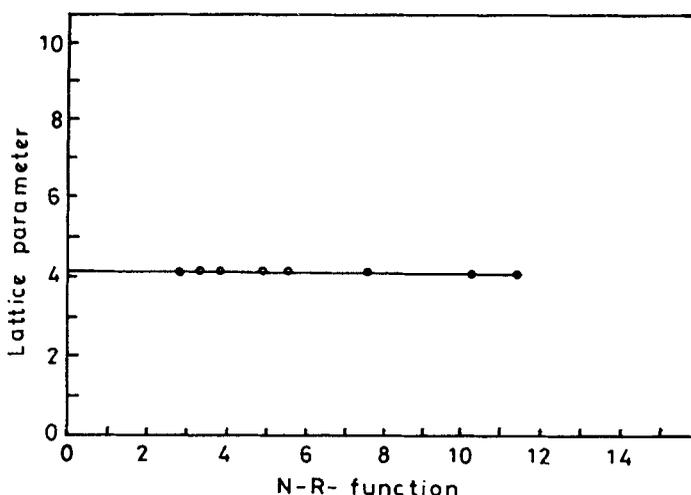
﹐**Figure 1.** Plot of lattice parameter vs N-R function at room temperature for CsCl-Br(0·8-0·2) solid solution.

concentration were $a_0 = 4·10767$, $C_1 = -5·156 \times 10^{-5}$, $C_2 = 1·091 \times 10^{-6}$ and $C_3 = -1·546 \times 10^{-9}$. The thermal expansion coefficient α_T for this concentration was obtained by differentiating a_T(true) with respect to temperature and dividing by a_0. Table 2 presents the thermal expansion coefficients of CsCl-Br(0·8-0·2) solid solution at eight different temperatures of measurement along with the values obtained for CsCl and CsBr for comparison.

4. Discussion

In CsCl-Br solid solutions system Shukla *et al* (1976) and Natarajan *et al* (1970) have done an exhaustive study of the lattice parameters at RT and higher temperatures and their aim was to look for the effects of concentrations near the phase transformation which the CsCl or CsBr individually undergoes from Pm3m to Fm3m. They have done for six different molal concentrations from CsCl-Br(0·95-0·05) to CsCl-Br(0·5-0·5) at two different temperatures RT and 560°K. However, they have not gone below (0·5, 0·5) molal concentrations. Besides there are no low temperature measurements available for these samples on the lattice parameters. Hence it was considered worthwhile to pursue this study to (i) provide values of the true lattice parameters in these solid solutions system below RT down to 90°K and (ii) to report any anomalous behaviour of these lattice parameters in this temperature range. It is found from our measurements that the solid solution composition CsCl-Br(0·8-0·2) has a behaviour which resembles qualitatively either CsCl or CsBr with the difference that in this case the thermal expansion coefficient increases às temperature is lowered from RT to 230°K and then falls off as the temperature is further lowered down to 90°K. The situation is not as simple in the remaining four concentrations where the lattice parameters themselves do not report a steady decreasing behaviour as the temperature is lowered. This is a clear indication of the fact that in the remaining four concentrations there are evidently

Table 1. Temperature vs lattice parameter for CsCl, CsBr, CsCl:CsBr solid solutions (Temperature in degree K and lattice parameter in angstroms).

No.	Temp.	CsCl	$CsCl_{0.8}Br_{0.2}$	$CsCl_{0.6}Br_{0.4}$	$CsCl_{0.5}Br_{0.5}$	$CsCl_{0.4}Br_{0.6}$	$CsCl_{0.2}Br_{0.8}$	CsBr	Lattice parameter
1.	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)		
2.	101·0	4·09202(2)	4·11236(3)	4·20564(2)	4·16307(3)	4·19796(3)	4·23180(3)	4·26085(2)	
3.	125·8	4·09574(2)	4·11518(4)	4·20208(3)	4·16183(3)	4·18838(3)	4·23520(3)	4·26449(3)	
4.	166·1	4·10210(2)	4·12148(3)	4·15438(3)	4·18223(3)	4·20735(3)	4·24242(3)	4·27178(3)	
5.	200·2	4·10783(2)	4·12952(3)	4·16282(2)	4·16688(2)	4·19947(3)	4·24452(3)	4·27775(3)	
6.	230·8	4·11329(2)	4·13504(3)	4·17437(2)	4·17918(3)	4·21884(4)	4·25360(4)	4·28348(3)	
7.	258·7	4·11841(4)	4·13994(3)	4·18639(3)	4·18667(2)	4·20111(2)	4·25918(3)	4·28843(2)	
8.	298·0	4·12599(2)	4·14846(3)	4·18803(3)	4·20899(2)	4·23342(2)	4·27141(3)	4·29645(2)	

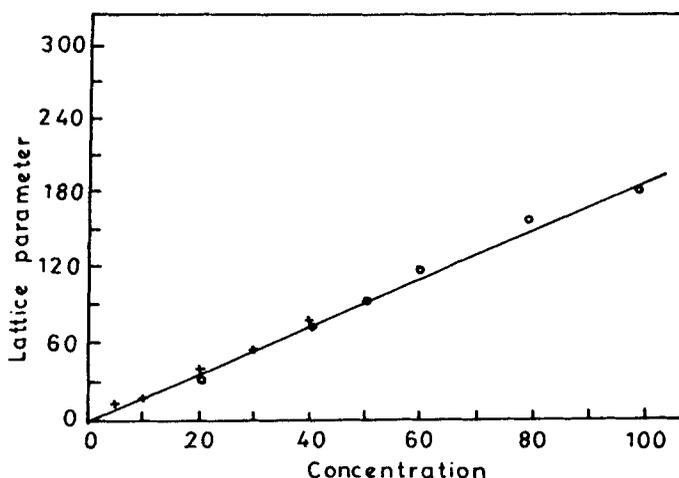(E.S.D's are given in parantheses)

Figure 2. Plot of $[a_T(\text{true}) - 4\cdot12] \times 1000$ vs concentration at room temperature for CsCl-Br solid solutions. Dots represent values and "+" marks represent Natarajan *et al* (1970) values.
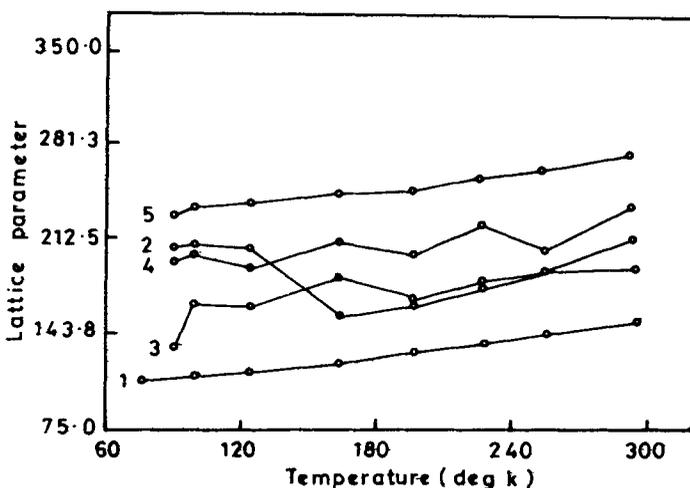

Figure 3. Plot of $[a_T(\text{true}) - 4\cdot0] \times 1000$ vs temperature for CsCl-Br solid solutions. (1) CsCl-Br(0·8-0·2) (2) CsCl-Br(0·6-0·4) (3) CsCl-Br(0·5-0·5) (4) CsCl-Br(0·4-0·6) and (5) CsCl-Br(0·2-0·8) compositions.

regions of temperatures in which the thermal expansion coefficients become negative. This was found to be true from an estimate of the average thermal expansion coefficients for these concentrations and not by fitting the true lattice parameters into a cubic polynomial. There are a number of cases in literature in which certain solids exhibit this negative thermal expansion. This is generally said to be arising from the vibrational free energy of the lattice at low temperatures. Glass and crystals having

Table 2. Thermal expansion coefficients of $CsCl_{0.8}Br_{0.2}$ solid solution (Temp. in deg. K and (α_T) is expressed in $10^{-6}/K$).

No.	Temperature	CsCl	$CsCl_{0.8}Br_{0.2}$	CsBr
1.	78·2		22·1	35·8
	90·0	34·4		
	92·0			
2.	101·0	35·2	29·6	37·2
3.	125·8	37·2	36·4	38·7
4.	166·1	40·1	44·5	41·0
5.	200·2	42·4	48·5	42·8
6.	230·8	44·4	49·9	44·2
7.	258·7	46·1	49·3	45·4
8.	298·0	48·4	45·3	46·9

diamond structures are examples of this type. Blackmann (1957, 1958, 1959) discussed this in a series of papers adopting Barron's (1955) theoretical treatment and attributed this anomalous behaviour due to the low-lying transverse acoustic branch at low temperatures is predominant in absorbing energy. However, in the present case as the temperature at which this negative thermal expansion coefficients occur is fairly high one cannot attribute the same reasons as was specified by Blackmann (1957, 1958, 1959) for the diamond structure. In certain anisotropic solids like FeF_2 and RuO_2 one finds a negative thermal expansion coefficient along one of the principal directions at high temperatures. In these cases Kirby and Rao (1967) suggested that this behaviour arises from the contributions of the acoustic and optic modes such that the optic modes are more effective in the C direction whereas the acoustic modes are predominant along directions normal to C axis. In the present case even this argument fails because the isotropic nature of the system is retained as is evident from the indexing of the x-ray data. The one reason we can attribute for this anomalous behaviour of the thermal expansion coefficients for the four concentrations is that there may be a phase transformation similar to the one encountered in NH_4Cl at 242·6°K. More work is needed to confirm this by measuring the thermal expansion and specific heats in these systems well near the regions of temperatures at which this anomalous behaviour occurs and this is in progress.

Acknowledgements

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