

## Lattice parameter and thermal expansion of CsCl and CsBr by x-ray powder diffraction. I. Thermal expansion of CsCl from room temperature to 90° K

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**Abstract.** The thermal expansion coefficients of CsCl at eight different temperatures between room temperature and 90° K are presented. The lattice parameters obtained from the observed Bragg angles with the use of Bragg formula were extrapolated to 90° using the Nelson-Riley extrapolation scheme to minimize the systematic errors. The true lattice parameters thus obtained at each temperature were used to obtain the thermal expansion coefficients and these results are compared with earlier interferometric measurements.

**Keywords.** Nelson-Riley extrapolation; thermal expansion; caesium chloride; powder diffraction; lattice parameter; cryostat.

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### 1. Introduction

Caesium chloride is one of the simplest inorganic compounds crystallizing in the cubic system with bcc lattice. Bailey and Yates (1967) measured the thermal expansion coefficients ( $\alpha_T$ ) in caesium halides from 60°K to 240°K by an interferometric method. The x-ray diffraction measurements of ( $\alpha_T$ ) in this temperature range are not available. A continuous flow cryostat was constructed for the YPC50NM powder diffractometer whose working principle was described in detail by Srinivasan and Girirajan (1982) in their report on the temperature variation of Debye-Waller factors in BaF<sub>2</sub> from room temperature (RT) to liquid nitrogen temperature (LNT). This cryostat was used in the present work for recording the Bragg reflections of CsCl powder at eight different temperatures between RT and 90°K. From the positions of Bragg reflections in the  $2\theta$  scale, the wavelength of x-ray used and the  $h, k, l$ , indices, using the Bragg formula, the lattice parameters  $a_T(\text{obs})$  were obtained at each temperature. As it usually happens, in diffractometer measurements these observed lattice parameters contained systematic errors and were minimized by an extrapolation method suggested by Nelson and Riley (1945) and the true lattice parameter was obtained at each temperature. From these true lattice parameters  $a_T(\text{true})$  the thermal expansion coefficients were obtained by a fit of the  $a_T(\text{true})$  into a cubic polynomial involving temperature  $T$  and differentiating  $a_T(\text{true})$  with reference to  $T$ . The results of ( $\alpha_T$ ) thus obtained were compared with the interferometric values of Bailey and Yates (1967) and the agreement was found to be good.

## 2. Experimental details

The description of the continuous flow cryostat and its working principle was described in detail by Srinivasan and Girirajan (1982). With this cryostat the experiment was carried out in the following way.

Analar pure CsCl powder supplied by (BDH) was ground to a very fine powder which is passed through a 325 mesh screen. After applying a little vacuum grease uniformly in the slot of the copper plate of the cryostat to improve thermal contact the powdered CsCl was filled in to the slot and pressed to get a smooth surface. The cryostat was then assembled and mounted on the central spindle of the diffractometer. The sample was properly centred by using the adjustable mount and by looking at the correct position of the largest peak for CsCl which occurs at  $2\theta = 30^{\circ}40'$  at ASTM standards. Then the vacuum chamber was evacuated to a vacuum better than  $10^{-4}$  torr before the experiment was started. Copper  $K_{\alpha}$  radiation was used with nickel filter for this work. The diffractograms of the various reflections were recorded at least two to three times to check the reproducibility. The diffractograms were recorded at six different temperatures between RT and  $90^{\circ}\text{K}$ . A standard copper constantan thermocouple was used to measure the temperature of the sample and by a manual control of the valves provided near the suction end of the cryostat it was possible to keep the specimen temperature at a constant value to within  $\pm 0.1^{\circ}\text{K}$  at any particular temperature of recording between RT and LNT throughout the course of the experiment.

## 3. Analysis

The diffractograms at eight different temperatures between RT and  $90^{\circ}\text{K}$  were collected and the position in  $2\theta$  scale for each Bragg peak at each temperature was obtained. It was noticed that except for the first five Bragg peaks, the remaining Bragg peaks beyond  $2\theta = 60^{\circ}$ , showed two distinct but close peaks due to  $K_{\alpha_1}$  and  $K_{\alpha_2}$ . The correct position in  $2\theta$  scale for peaks showing  $\alpha_1$  and  $\alpha_2$  resolution was also obtained at each temperature and after ascertaining that the  $hkl$ 's do not change at each temperature of measurement the following procedure was adopted to obtain the true lattice parameter which is used in the evaluation of thermal expansion coefficients.

### 3.1 Least squares method and extrapolation

The lattice parameters  $a_T(\text{obs})$  obtained from the  $2\theta$  values, the wavelength of x-rays and  $h, k, l$ , values using the formula

$$a_T(\text{obs}) = \frac{\lambda}{2 \sin \theta_{\text{obs}}} (h^2 + k^2 + l^2)^{1/2} \quad (1)$$

contained random and systematic errors in measurements which had to be minimized and the true lattice parameter had to be evaluated by extrapolation. In counter diffractogram measurements the usual systematic errors encountered are (i) misalignment of the instrument i.e. the centre of the incident beam must intersect the diffractometer axis and the zero position of the counter slit; (ii) use of a flat specimen instead of a curved specimen; (iii) absorption in the specimen; (iv) displacement of the specimen from the diffractometer axis which is the largest single source of error and

(v) vertical divergence of the incident beam. Error number (5) was minimized by decreasing the vertical opening of the counter slit of the diffractometer. For errors (2) and (3)  $\Delta a/a_T$  (where  $\Delta a$  is the error in the observed lattice parameter) varies as  $\cos \theta$  and varies as  $\cos^2 \theta / \sin \theta$  for error (4). Therefore no single extrapolation can be completely satisfactory. The various sources of error particularly absorption have been analyzed earlier (Nelson and Riley 1945; Taylor and Sinclair 1945) more rigorously and the following relation

$$\frac{\Delta a}{a_T} = K \left[ \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right] \quad (2)$$

holds quite accurately not only at high angles but also at very low values of  $\theta$ . Therefore in the present work the bracketed terms in (2), sometimes known as the Nelson-Riley function, were used for error minimization and extrapolation. In addition to the five errors listed, there are errors arising out of (i) spectral distribution of the wavelength of x-rays and (ii) Lorentz-polarization correction (Parrish and Wilson 1959). These errors have large contribution beyond  $2\theta = 125^\circ$  and do not vanish upon extrapolation (Ladell *et al* 1959). Owing to the fact that there are only a few feeble reflections in the region beyond  $2\theta = 125^\circ$ , the reflections beyond this region were not traced. The positional shift of the Bragg peaks in  $2\theta$  upto  $125^\circ$  are almost zero because of these last mentioned two errors and therefore corrections for these errors were not considered. The most obvious and straightforward method of extrapolation is to use the least squares method to find the best straight line on a plot of the observed lattice parameters  $a_T(\text{obs})$  against  $[(\cos^2 \theta / \sin \theta) + (\cos^2 \theta / \theta)]$  and this has been used in the present work. Typical results of the least squares analysis are shown graphically in figures 1 and 2 for RT and  $90^\circ\text{K}$ . The prominent higher angle reflections from  $2\theta = 70^\circ$  to  $2\theta = 125^\circ$  were used for extrapolation.

In table 1 the true lattice parameter  $a_T(\text{true})$  obtained by the extrapolation procedure described above along with the estimated standard deviations are given for each temperature. The true lattice parameters thus obtained were subjected to a polynomial fitting to evaluate the thermal expansion coefficients.

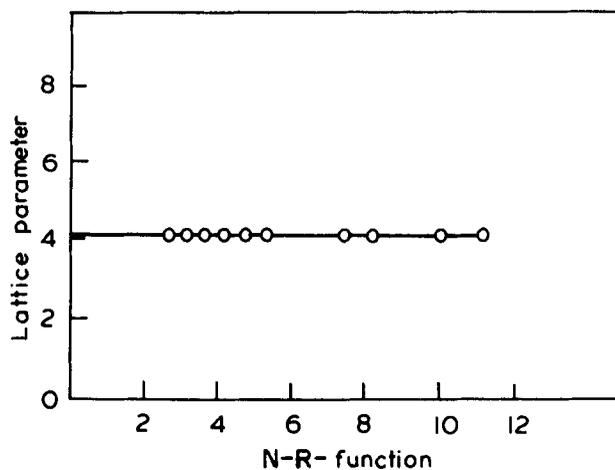


Figure 1. Plot of lattice parameter vs N-R function at room temperature for CsCl.

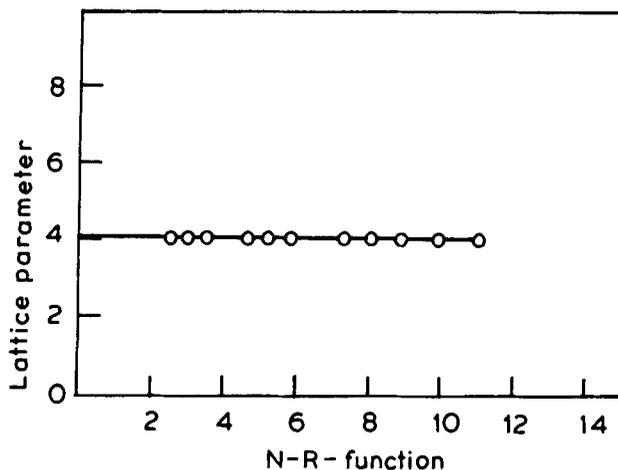


Figure 2. Plot of lattice parameter vs N-R function at 90°K for CsCl.

### 3.2 Estimation of thermal expansion coefficients

If  $a_T(\text{true})$  represents the true lattice parameter at  $T^\circ\text{K}$  then  $a_T(\text{true})$  can be written in a cubic polynomial involving temperature  $T$  of the form,

$$a_T(\text{true}) = a_0 + C_1 T + C_2 T^2 + C_3 T^3, \quad (3)$$

where  $a_0$ ,  $C_1$ ,  $C_2$  and  $C_3$  are constant coefficients, from which  $\alpha_T$ , the thermal expansion coefficient can be found by differentiating  $a_T(\text{true})$  with respect to  $T$  and dividing by  $a_0$ . By this,

$$\alpha_T = \frac{1}{a_0} \frac{d}{dT} [a_T(\text{true})] = \frac{C_1}{a_0} + \frac{2C_2 T}{a_0} + \frac{3C_3 T^2}{a_0}. \quad (4)$$

The values of the constant coefficients  $a_0$ ,  $C_1$ ,  $C_2$  and  $C_3$  are  $a_0 = 4.07925$ ;  $C_1 = 1.096E - 4$ ;  $C_2 = 1.817E - 7$  and  $C_3 = -7.723E - 11$ . In figure 3 the plot of  $a_T(\text{true})$  vs  $T$  is shown in which the continuous curve represents the cubic polynomial and the dots represent the experimental points. Table 2 gives the thermal expansion coefficients  $\alpha_T$  of CsCl,

Table 1. Temperature vs lattice parameter for CsCl (Temp. in °K and  $a_T(\text{true})$  the lattice parameter in Å (E.S.D's are in brackets).

No.	Temp.	$a_T(\text{true})$
1	90.0	4.09048 (2)
2	101.0	4.09202 (2)
3	125.8	4.09574 (2)
4	166.1	4.10210 (2)
5	200.2	4.10783 (2)
6	230.8	4.11329 (2)
7	258.7	4.11841 (4)
8	298.0	4.12599 (2)

obtained by using (4) and the constant coefficients given above along with the smoothed values of the interferometric measurements of Bailey and Yates (1967) for comparison. The absolute error in the values of  $\alpha_T$  in the interferometric measurements are 2% in this temperature range.

#### 4. Discussion

From table 2 it is seen that the true lattice parameters at various temperatures obtained by the least squares method fit very well with the cubic polynomial of the type represented by (3) and the constants of the polynomial when used to estimate  $\alpha_T$  are found to give values which agree with the previous interferometric measurements of Bailey and Yates (1967).

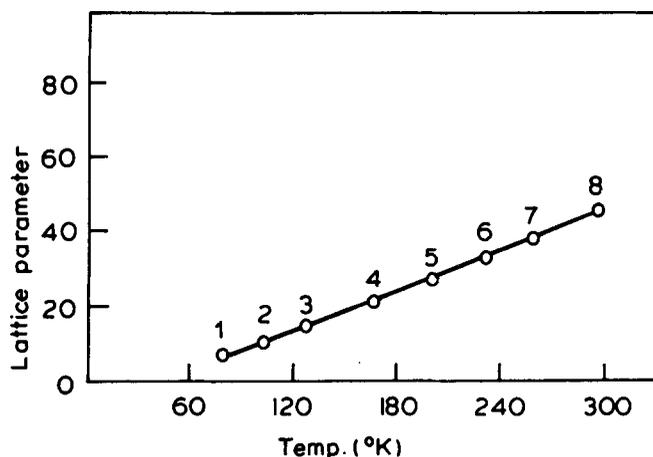


Figure 3. Plot of  $[a_T(\text{true}) - 4.08] \times 1000$  vs temperature. Dots represent experimental points and the continuous curve, the cubic polynomial.

Table 2. Thermal expansion coefficients of CsCl.

No.	Temp. °K	$\alpha_T \times 10^{-6}/^\circ\text{K}$	
		Present values	Bailey and Yates (1967) values
1	90.0	34.4	34.3
2	101.0	35.2	35.1
3	125.8	37.2	37.2
4	166.1	40.1	40.2
5	200.2	42.4	42.5
6	230.8	44.4	44.4
7	258.7	46.1	45.9
8	298.0	48.4	47.8

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