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Lattice parameter and thermal expansion of CsCl and CsBr by x-ray powder diffraction. II. Thermal expansion of CsBr from room temperature to 78·2 °K

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Abstract. The lattice parameters of CsBr at eight different temperatures from room temperature to 78·2 ° K were measured and the true lattice parameters were obtained by the least squares method using the Nelson-Riley extrapolation function. Using these parameters the thermal expansion coefficients of CsBr were estimated at each temperature by fitting them into a cubic polynomial involving temperature T. The α_T thus obtained were compared with the values of earlier workers who used an interferometric technique and the agreement was found to be good.

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

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1. Introduction

Caesium bromide is one of the simplest inorganic compounds having a CsCl structure. Three terminal capacitance measurements of thermal expansion for CsBr are available only for the near extreme temperatures of the presently considered range (White 1965; White and Collins 1973). Interferometric measurements of thermal expansion in the temperature range considered are available for CsBr (Krishnan and Srinivasan 1956; Bailey and Yates 1967). However, the thermal expansion from x-ray powder diffraction has not been attempted yet. The lattice parameters of CsBr were measured at eight different temperatures from room temperature (RT) to 78·2 ° K using the continuous flow cryostat described by Srinivasan and Girirajan (1982). These lattice parameters were subjected to the least square method using the Nelson-Riley extrapolation function to arrive at the true lattice parameters at each temperature. The parameters thus obtained were fitted into a cubic polynomial of temperature T and the thermal expansion coefficients were evaluated and compared with earlier measurements of Krishnan and Srinivasan (1956) and Bailey and Yates (1967) who used an interferometric technique.

2. Experimental details

The experimental procedure adopted here is essentially the same as in paper I (Ganesan and Girirajan 1986). AR pure CsBr supplied by Fluka was ground to a fine powder and was passed through a 325 mesh. This powder was used to record the diffractograms at eight different temperatures from RT to 78·2° K using the continuous flow cryostat described earlier (Srinivasan and Girirajan 1982). The temperature control was maintained to within ±0·1° K throughout the experiment by adjusting the liquid nitrogen flow by using the needle valve provided at the suction end of the cryostat. The scanning speed of the sample was $\frac{1}{4}$°/min and the Bragg peaks were recorded at each temperature at least two to three times to ensure reproducibility of the peak positions on the 2θ scale. Copper radiation was used in this work with nickel filter.

3. Analysis of experimental data

The Bragg peak positions at each temperature for all the reflections were obtained from diffractogram charts. These Bragg positions along with the *h*, *k*, *l* and the correspond-

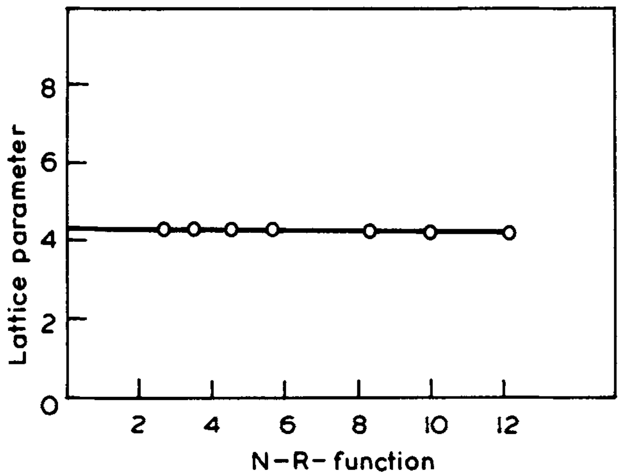

Figure 1. Plot of lattice parameter vs N-R function at room temperature for CsBr.

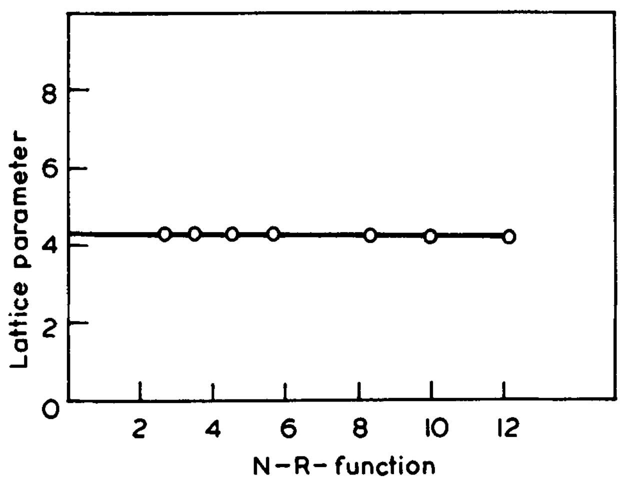

Figure 2. Plot of lattice parameter vs N-R function at 78·2° K for CsBr.

ing x-ray wavelengths ($CuK\alpha_1$ and $CuK\alpha_2$) in the case of higher angle Bragg peaks beyond 70° which showed α_1 and α_2 resolutions were used in the Bragg formula to arrive at the observed lattice parameters a_T(obs). These parameters were then subjected to the least squares method (paper I) using Nelson-Riley (1945) extrapolation function and the true lattice parameter at each temperature was obtained. Two typical plots of a_T(obs) vs Nelson-Riley extrapolation function are shown graphicaliy in figures 1 and 2 for RT and 78·2° K. The prominent higher angle reflections from $2\theta = 70°$ to $2\theta = 125°$ were used for extrapolation. Table 1 gives the true lattice parameters thus obtained for each temperature along with the error estimates. These true lattice parameters were subjected to a cubic polynomial fitting in T and the thermal expansion coefficient α_T was obtained for each temperature as described in paper I. Figure 3 gives a plot of the true lattice parameter vs temperature showing the cubic polynomial fitting. The values of the constant coefficients are a_0, C_1, C_2, C_3 are $a_0 = 4{\cdot}24630$, $C_1 = 1{\cdot}283E-4$, $C_2 = 1{\cdot}620E-7$ and $C_3 = 9{\cdot}559E-11$. In table 2 the thermal expansion coefficients of CsBr obtained in the present method using these constant coefficients and the

Table 1. Temperature vs lattice parameter for CsBr.

Temperature (°K)	a_T(true) (Å)
78·2	4·25726 (3)
101·0	4·26085 (2)
125·8	4·26449 (3)
166·1	4·27178 (3)
200·2	4·27775 (3)
230·8	4·28348 (3)
258·7	4·28843 (2)
298·0	4·29645 (2)

E. S. D. values are given in brackets.

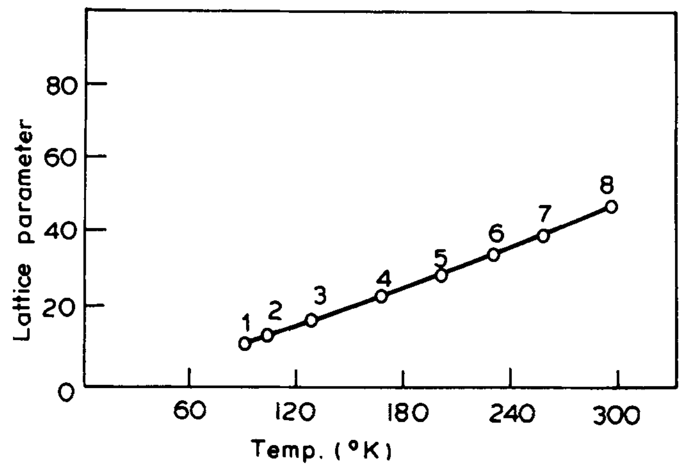

Figure 3. Plot of $[a_T(\text{true}) - 4{\cdot}25] \times 1000$ vs temperature. Dots represent experimental points and the continuous curve, the cubic polynomial.

Table 2. Thermal expansion coefficients of CsBr.

Temperature (°K)	$\alpha_T \times 10^{-6}$/°K Present values	Bailey & Yates (1967)	Krishnan & Srinivasan (1956)
78·2	35·8	36·8	36·8
101·0	37·2	38·2	38·0
125·8	38·7	39·9	39·3
166·1	41·0	42·2	41·4
200·2	42·8	44·1	43·1
230·8	44·2	45·6	44·6
258·7	45·4	46·9	45·9
298·0	46·9	48·5	47·8

interferometric values of Bailey and Yates (1967) and Krishnan and Srinivasan (1956) at each temperature are given.

4. Discussion

From table 2 it is found that the thermal expansion coefficients α_T of CsBr obtaind by the present method agree very well with the measurements of Krishnan and Srinivasan (1956) and Bailey and Yates (1967). It is also seen that the extrapolation of the observed lattice parameter a_T (observed) using the least squares method yields true lattice parameters which when used to estimate the thermal expansion coefficients give values which agree with α_T.

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