Pramāṇa – J. Phys., Vol. 30, No. 4, April 1988, pp. 331–336. © Printed in India.

Temperature variation of the Debye-Waller factors of metal and halide ions in CsCl and CsBr powders by X-ray diffraction. I. Debye-Waller factors of Cs^+ and Cl^- ions in CsCl from room temperature to 90°K

V GANESAN and K S GIRIRAJAN

Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600 025, India

MS received 16 February 1987; revised 29 December 1987

Abstract. The temperature variation of the Debye-Waller factors of Cs^+ and Cl^- ions in CsCl powder has been studied using X-ray powder diffraction. A continuous flow cryostat has been used to record the diffractograms and the integrated intensities of the Bragg peaks at different temperatures have been obtained. The integrated intensities of the odd and even reflections have been analysed following the structure of the CsCl compound and the Debye-Waller factors of the Cs^+ and Cl^- ions have been estimated. The results have been verified by structure factor least squares refinement. 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.

Keywords. Cryostat; powder diffraction; Debye-Waller factor; structure factor least square; lattice dynamics; caesium chloride; thermal diffuse scattering correction.

PACS Nos 61·60; 65·90

1. Introduction

Lattice dynamics of caesium chloride has been studied in the past both theoretically and experimentally. The phonon dispersion relations in CsCl have been studied by neutron inelastic scattering (Ahmed *et al* 1972) and the parameters for a shell model fit of the dispersion relations are given by Jindal and Mahesh (1975). Thermal expansion in this compound has been measured by interferometric (Bailey and Yates 1967) and X-ray diffraction (Ganesan and Girirajan 1986) methods over the temperature range 90–298°K. The Debye-Waller (D-W) factors of the metal and chlorine atoms in this compound and their temperature variation have not been measured and it was therefore considered worthwhile to undertake this study by analysing and calculating the powder X-ray diffractograms by employing theoretical lattice dynamics techniques. Section 2 describes the experiments for getting the diffractograms of CsCl and § 3 deals with an analysis of the experimental data and the results on the temperature variation of the D-W factors of caesium and chloride ions. Section 4 details the theoretical calculations on a shell model lattice dynamics and a comparison between theory and experiment.

2. Experimental details

Srinivasan and Girirajan (1982) had earlier described a continuous flow cryostat to record powder diffractogram charts at various temperatures between 78°K and room temperature. This cryostat was used for the present work. Analar pure CsCl powder (BDH chemicals) was ground to a fine powder and passed through a 325 mesh screen. To improve thermal contact, the slot provided for the sample holder on the copper plate of the cryostat was vacuum-greased and the CsCl powder was filled in the slot and pressed to get a smooth surface.

The cryostat was then assembled and mounted on the centre spindle of the powder diffractometer (YPC 50 NM) for which the cryostat was designed. The sample was centred using an adjustable mount. The chamber was evacuated (vacuum better than 10^{-4} torr) before starting the experiment. Copper K_α radiation was used with nickel filter. Diffractograms of the various Bragg reflections were recorded using a speed of rotation of the specimen of 1/4° per minute. The diffractograms were recorded at six different temperatures between RT and 90°K and at each temperature atleast two to three times to check reproducibility.

3. Analysis of experimental data

CsCl is one of the simplest inorganic compounds which crystallizes in the Pm3m structure. The integrated intensity of the Bragg peaks at each recorded temperature was obtained by measuring the areas occupied by each Bragg peak. These areas (A) of the different Bragg reflections were corrected for Lorentz-polarization [$L_p = (1+\cos^2 2\theta)/(2\sin^2\theta\cos\theta)$], where θ is the Bragg angle by dividing the uncorrected areas by the product of the multiplicity (m) of hkl and L_p. The square root of A/mL_p thus obtained gives the observed structure factors (F_o^T) at any temperature T. The values of F_o^T for any Bragg reflection at any temperature of measurement T are related to the atomic scattering factors f_n (corrected for anomalous disperson wherever necessary) of the atoms constituting the compound, the position x_n, y_n, z_n of the atoms in the crystal lattice, the D-W factor of the atoms B_n and the Bragg angle of hkl by the following equation

$$F_o^T = K \sum_{n=1}^{2} f_n \exp\left[2\pi i(hx_n + ky_n + lz_n)\right] \cdot \exp\left[-B_n \frac{\sin^2\theta}{\lambda^2}\right], \tag{1}$$

where K is a constant scale factor and the summation is over the number of atoms present in the crystal, which in the present case is 2. Dividing the total number of reflections into odd and even depending on whether $h+k+l$ is odd or even and noting the position of the caesium atom (000) and the chlorine atom (1/2 1/2 1/2) the structure factors F_o^T for odd and even reflections can be written as

$$Q(\text{odd}) = K\left[f_{\text{Cs}^+} \exp\left(-B_{\text{Cs}^+}\frac{\sin^2\theta}{\lambda^2}\right) - f_{\text{Cl}^-} \exp\left(-B_{\text{Cl}^-}\frac{\sin^2\theta}{\lambda^2}\right)\right] \tag{2}$$

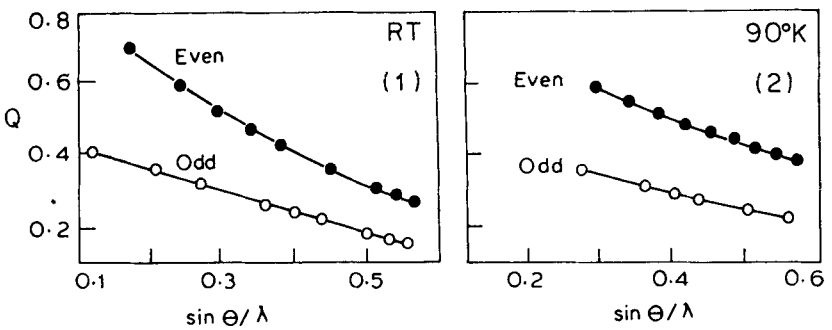
$$Q(\text{even}) = K\left[f_{\text{Cs}^+} \exp\left(-B_{\text{Cs}^+}\frac{\sin^2\theta}{\lambda^2}\right) + f_{\text{Cl}^-} \exp\left(-B_{\text{Cl}^-}\frac{\sin^2\theta}{\lambda^2}\right)\right]. \tag{3}$$

By plotting the measured values of Q(odd) and Q(even) against $\sin\theta/\lambda$, one can treat the Q's as continuous functions of $\sin\theta/\lambda$. As a result the following equations can be obtained.

$$\ln([Q(\text{odd}) + Q(\text{even})]/2f_{Cs^+}) = \ln K - B_{Cs^+}\sin^2\theta/\lambda^2, \tag{4}$$

$$\ln([Q(\text{even}) - Q(\text{odd})]/2f_{Cl^-}) = \ln K - B_{Cl^-}\sin^2\theta/\lambda^2. \tag{5}$$

The left side plots of (4) and (5) against $(\sin^2\theta/\lambda^2)$, give the values of B_{Cs^+} and B_{Cl^-} at any temperature of measurement. The values thus obtained can be verified by subjecting these observed structure factors to regular crystallographic refinement procedure. Figures 1 and 2 give sample plots of Q(odd) and Q(even) against $(\sin\theta/\lambda)$ at the two extreme temperatures of measurement (viz) RT and 90°K. Figures 3a to 3d give sample straight line plots at RT and 90°K. Many crystallographic refinement programs are available and we chose the structure factor least squares (SFLS) refinement program to refine the structure factors and verify the results. The thermal expansion results on CsCl in this temperature range reported earlier (Ganesan and Girirajan 1986) provided the correct lattice parameter. The B factors deduced above ignored the correction due to thermal diffuse scattering. However from the B values so determined the approximate



Figures 1 and 2. Plots of Q(even) and Q(odd) vs $\sin\theta/\lambda$ for CsCl. **1.** Room temperature. **2.** 90°K.

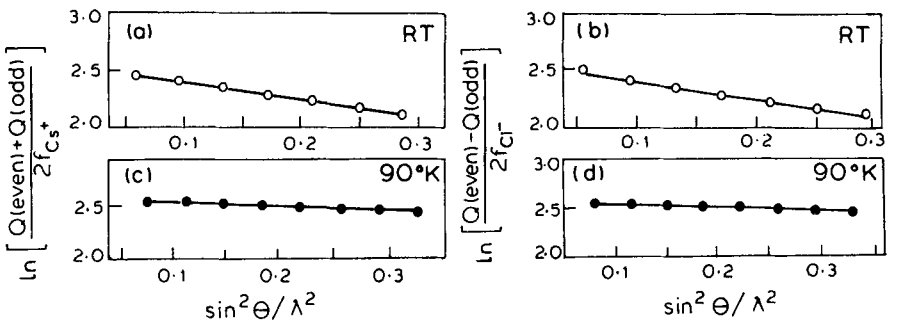


Figure 3. a, c. Plots of $\ln[Q(\text{even}) + Q(\text{odd})]/2f_{Cs^+}$ vs $\sin^2\theta/\lambda^2$ for CsCl. **b, d.** Plots of $\ln[Q(\text{even}) - Q(\text{odd})]/2f_{Cl^-}$ vs $\sin^2\theta/\lambda^2$ for CsCl.

correction for the first order thermal diffuse scattering (Chipman and Paskin 1959) can be obtained as

$$\sigma_{hkl} = (4\pi/3)^{1/3}(a/\lambda^3)(\Phi/2)B\cos\theta_{hkl}\sin^2\theta_{hkl}, \tag{6}$$

where a is the lattice parameter, λ is the weighted average of X-ray wavelength, B is the overall value obtained from the initial Wilson plot, and Φ is the background line covering a range of 2° (0.035 radian) on the diffractometer tracing. After applying this correction to measured intensities the analysis can be redone to give refined values of the B factors. The final R factor is $< 6\%$ for all temperatures of measurement.

4. Theoretical calculations of B-factors in CsCl using the shell model

The phonon dispersion relations in CsCl have been measured by Ahmed *et al* (1972). Theoretical lattice dynamical calculations have been done by several authors using different models iike the point ion model (Sharan and Tiwari 1964), the five-parameter shell model (Srivastava and Dayal 1967; Haridasan and Krishnamurthy 1968), the nine-parameter shell model (Carabatos and Prevot 1972), the modified rigid ion model (Vetelino *et al* 1973), the deformation dipole model (Agarwal and Hardy 1974) and the three-body force shell model (Lal and Verma 1972). All these models reproduce the phonon dispersion relations reasonably well. Jindal and Mahesh (1975) used the both ion-polarizable simple shell model and calculated the phonon dispersion relations and temperature variation of the D-W factors in the temperature range 296°K to 573°K. The agreement between theory and experiment quoted by them for the D-W factors of caesium and chlorine atoms is good and the same model was used for the present calculations. A Fortran program was written for the IBM 1130 computer to calculate the phonon normal mode frequencies $\nu\begin{pmatrix} q \\ j \end{pmatrix}$ and the eigenvectors $e\left(\mu\middle|\begin{matrix} q \\ j \end{matrix}\right)$ in the harmonic approximation. The D-W factors for ion type μ is given by

$$B_\mu = (2\pi/3)\frac{\hbar}{Nm(\mu)}\sum_{q,j,\alpha}\frac{\left|e_\alpha\left(\mu\middle|\begin{matrix} q \\ j \end{matrix}\right)\right|^2}{\nu\begin{pmatrix} q \\ j \end{pmatrix}}\left[2n\begin{pmatrix} q \\ j \end{pmatrix}+1\right], \tag{7}$$

where N is the number of equally distributed wave vectors q in the Brillouin zone for which calculations are made, $m(\mu)$ is the mass of ion μ, j is the branch index, α the component index and

$$n\begin{pmatrix} q \\ j \end{pmatrix} = \left[\exp\frac{\left(h\nu\begin{pmatrix} q \\ j \end{pmatrix}\right)}{k_B T} - 1\right]^{-1} \tag{8}$$

where h is the Planck's constant and k_B the Boltzmann's constant.

The temperature variation of the D-W factors was calculated using the above equations in the harmonic approximation in which the frequencies of the lattice modes are assumed to be independent of the temperature.

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

	Warren's method		SFLS (without TDS)		SFLS (with TDS)		Theory	
Temperature	Cs^+	Cl^-	Cs^+	Cl^-	Cs^+	Cl^-	Cs^+	Cl^-
90·0	0·43	0·46	0·44(2)	0·50(6)	0·40(2)	0·50(7)	0·40	0·51
101·0	0·47	0·50	0·44(2)	0·61(7)	0·41(2)	0·54(8)	0·50	0·61
125·8	0·51	0·55	0·71(3)	0·76(0)	0·58(3)	0·60(0)	0·61	0·72
166·1	0·85	0·88	0·80(3)	0·83(10)	0·69(2)	0·81(9)	0·80	0·91
200·2	0·94	0·98	0·93(2)	1·10(0)	0·92(3)	1·08(0)	0·96	1·00
230·8	1·06	1·07	1·01(2)	1·12(7)	0·99(2)	1·16(6)	1·10	1·23
258·7	1·19	1·22	1·17(2)	1·29(9)	1·10(1)	1·11(5)	1·23	1·37
298·0	1·44	1·53	1·43(2)	1·54(8)	1·37(2)	1·38(8)	1·41	1·57

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

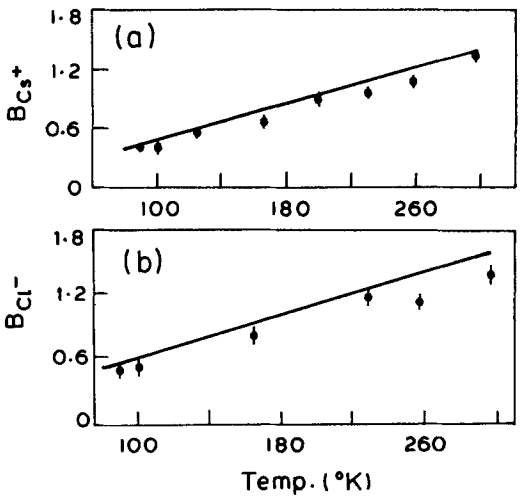


Figure 4a, b. Temperature variation of the *B* factors for Cs^+ ion and Cl^- ion respectively in CsCl. Dots represent the experimental points and the line represents the theory.

Table 1 compares the experimental values of the temperature variation of the D-W factors of Cs^+ and Cl^- in CsCl with the theoretically calculated values using the shell model lattice dynamics. Figure 4 gives a graphical display of this comparison.

In the present study the isotropic temperature factors for Cs^+ and Cl^- in CsCl have been measured using powder X-ray diffraction over the temperature range 90°K to 298°K. The agreement between theory and experiment is found to be good.

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