

X-ray determination of the mean Debye-Waller factors, amplitudes of vibration and Debye temperatures of six crystals with CsCl structure

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MS received 20 February 1978

Abstract. From the integrated intensities of Bragg reflections measured at room temperature with an x-ray powder diffractometer, the mean Debye-Waller factor B , the average r.m.s. amplitude of vibration $(\bar{u}^2)^{1/2}$ and the Debye temperature θ , have been determined for six crystals with the CsCl structure.

The energy of formation of a Schottky pair in these crystals has been estimated from an empirical relation between the x-ray Debye temperature and the energy of formation.

Keywords. Lattice dynamics; Debye-Waller factors; Debye temperature; crystals with CsCl structures.

1. Introduction

The Debye-Waller factors, amplitudes of atomic vibration and the Debye characteristic temperature of a solid are properties of lattice dynamical interest. Values of these parameters obtained from different techniques are available for a large number of crystals with NaCl structure. However, there is meagre information about these properties in the case of crystals with the CsCl structure. Literature survey revealed that while there are over a hundred reports on the x-ray and neutron diffraction determination of these parameters for about forty crystals with NaCl structure, there are just five published reports for three crystals with the CsCl structure viz. CsCl, CsI and NH_4Cl . Beaver (1974), (quoted by Agrawal *et al* 1975) is reported to have determined the Debye-Waller factors of CsCl, CsBr and CsI, but his results are not available in published form.

As a part of continuing programme on the x-ray determination of properties of lattice dynamical interest, the mean Debye-Waller factors, the amplitudes of atomic vibration and the Debye characteristic temperatures have been determined for six crystals with the CsCl structure viz. CsBr, CsI, TiCl , TlBr , NH_4Cl and NH_4Br . The results are reported here.

2. Experimental

2.1. Measurement of intensities

Room temperature measurements of the integrated intensities of Bragg reflections

from powder samples were made with a Phillips PW 1051 diffractometer. Filtered Cu radiation was used and a 2θ scan was adopted.

The method followed for sample preparation and the recording of intensities has been explained in an earlier paper (Subhadra and Sirdeshmukh 1977; hereinafter referred to as paper I). The observed intensities were corrected for dead time according to an approximate method suggested by Chipman (1969). A value of $150 \mu\text{s}$ was used for the dead time. The intensities were also corrected for TDS by the method of Chipman and Paskin (1959).

2.2. Analysis of data

The integrated intensity of a Bragg reflection may be written as

$$I_0 = C(LP) J F^2 \exp(-2B \sin^2 \theta / \lambda^2) \quad (1)$$

where I_0 is the observed intensity, C the scale factor, LP the Lorentz-polarisation factor, J the multiplicity factor, F the structure factor, B the Debye-Waller factor, θ the Bragg angle and λ the wavelength of the radiation used. As discussed in paper I, a common Debye-Waller factor is assumed for the two atoms. For CsCl structure, the structure factors are given by

$$F = (f_M \pm f_N) \quad (2)$$

where f_M and f_N are the atomic scattering factors for the two atoms. The plus sign applies to reflections with even values of $(h + k + l)$ and the minus sign to those with odd values of $(h + k + l)$.

For the calculation of the structure factors, the atomic scattering factors for Cs^+ , Br^- , I^- and Tl^+ were taken from Cromer and Waber (1965), and for Cl^- from the International Tables for X-ray Crystallography following Cromer's (1965) recommendation.

There was some difficulty in the choice of the scattering factors for the ammonium ion in the ammonium halides. Davies *et al* (1966) have given the scattering factors for the NH_4^+ ion. These scattering factors pertain to the rotating model of the NH_4^+ ion. It is an established fact that in the room temperature form of NH_4Cl and NH_4Br , the ammonium ion is not rotating. However, a comparison of the scattering factors for NH_4^+ given by Davies *et al* with the scattering factors for nitrogen, shows that the two sets become nearly equal at about $\sin \theta / \lambda = 0.25 \text{ \AA}^{-1}$. This implies that differences in the models of the NH_4^+ ion, cease to have any effect on the scattering factors for $\sin \theta / \lambda$ values greater than about 0.25 \AA^{-1} . This is also seen from the structure factors obtained by Vahavaselka and Kurki-Suonio (1975) for the different models of NH_4^+ and for N^+ . As such we have excluded the reflections with $\sin \theta / \lambda < 0.25 \text{ \AA}^{-1}$ for both NH_4Cl and NH_4Br , and for the structure factors of the other reflections scattering factors of Davies *et al* have been used.

The scattering factors for Cs^+ , Br^- , I^- , Tl^+ and Cl^- were corrected for anomalous dispersion, the dispersion terms being taken from Cromer and Liberman (1970). The dispersion correction for the ammonium ion is not known. Though the correction term for anomalous dispersion for the lighter atoms and ions is very small, an

attempt to allow for this correction is made for the NH_4^+ ion by using the value corresponding to Ne which has an equivalent number of electrons.

The procedure adopted for obtaining the mean Debye-Waller factor, the mean r.m.s. amplitude of vibration and the Debye temperature is similar to that described in paper I.

3. Results and Discussion

The values of the mean Debye-Waller factor, the average value of the r.m.s. amplitude of vibration and the values of the Debye temperature obtained in this work are given in table 1. The value of the Debye-Waller factor $2.316 \pm 0.23 \text{ \AA}^2$ for CsBr obtained in this work agrees within limits of error with the mean value $2.09 \pm 0.07 \text{ \AA}^2$ calculated from Beaver's data (quoted by Agrawal *et al* 1975). In the case of CsI, the value of the Debye-Waller factor $2.592 \pm 0.12 \text{ \AA}^2$ obtained in this work agrees reasonably with the mean value $2.15 \pm 0.15 \text{ \AA}^2$ calculated from Beaver's data. The value of the Debye-Waller factor $1.823 \pm 0.16 \text{ \AA}^2$ for NH_4Cl agrees well with the mean value 2.00 \AA^2 calculated from the data given by Kurki-Suonio *et al* (1974). The value of the Debye temperature $101 \pm 2^\circ\text{K}$ obtained in this work for CsI is intermediate between the values 96°K and 112°K obtained by Wasastjerna (1946) and Kouchkovsky (1974). In table 1, the values of the Debye temperature calculated from high temperature specific heats and room temperature elastic constants are included. It can be seen that in general the x-ray values of the Debye temperature are lower than the values from specific heats and elastic constants, conforming to the trend observed earlier (paper I). Cleavelin *et al* (1972) observed that in the alkali halides with NaCl structure the Debye temperature decreases in the sequence chloride-bromide-iodide for a given cation. A similar effect is observed in the θ values for the halides with the CsCl structure studied in this work. Mukherji

Table 1. Values of the mean Debye-Waller factor B (\AA^2), r.m.s. amplitude of vibration $(\bar{u}^2)^{1/2}$ (\AA), the Debye temperature θ ($^\circ\text{K}$) and the Schottky formation energy E_s (eV) for six halides with the CsCl structure.

Crystal	B	$(\bar{u}^2)^{1/2}$	$\theta(\text{x-ray})$	θ (Specific heat)	θ (Elastic)	E_s (Calc. from eq. 3)	E_s (Calc. by Murthy and Murti 1971)	E_s (expt.)
CsBr	2.316 ± 0.23	0.297 ± 0.02	118 ± 6	134^a	136^c	1.56	1.74	2.0^d
CsI	2.592 ± 0.12	0.314 ± 0.01	101 ± 2	101^a	115^c	1.58	1.41	1.9^d
TlCl	2.790 ± 0.08	0.325 ± 0.01	101 ± 2	157^a	125^c	1.03	1.27	1.3^d
TlBr	2.718 ± 0.09	0.321 ± 0.01	95 ± 2	118^a	114^c	1.16	1.20	—
NH_4Cl	1.823 ± 0.16	0.263 ± 0.01	268 ± 11	285^b	270^c	1.65	1.20	1.23^e 0.8^d
NH_4Br	2.605 ± 0.21	0.314 ± 0.01	164 ± 7		177^c	1.24	1.17	1.37^e

(a) Redmond and Yates (1972)

(b) Nakamura (1972)

(c) Joshi and Mitra (1960)

(d) Quoted by Murthy and Murti (1971)

(e) Murty and Prasad (1975)

(1965), March (1966) and Glyde (1967) have pointed out that the energy of formation of vacancies in metals can be estimated from a simple relationship between the energy of formation and the Debye temperature. Sastry and Mulimani (1969) and Pathak and Trivedi (1969) calculated the energy of formation of a Schottky pair from the values of the Debye temperature for a number of alkali halides with NaCl structure from the relation

$$\theta = \text{constant} (E_s/MV^{2/3})^{1/2} \quad (3)$$

where E_s is the energy of formation of a Schottky pair, M is the molecular weight and V the molar volume. We have made similar calculations for crystals with CsCl structure studied in this work as such calculations do not seem to have been made earlier. The value of the constant in eq. 3 is obtained by using a value of 151°K for the Debye temperature of CsCl (Barnea and Post 1966), and the experimentally obtained value of 1.86 eV for E_s obtained by Harvey and Hoodless (1967). The value of E_s calculated from eq. 3 is given in table 1 together with values calculated by the Mott and Littleton method (Murthy and Murti 1971) and the experimental values. Considering the empirical nature of eq. 3 and the uncertainties in the experimental values of the formation energy (as can be seen in the case of NH_4Cl) the values obtained from eq. 3 appear satisfactory. Equation 3 thus provides a simple method for estimating the values of E_s from the Debye temperatures of crystals for which experimental values of E_s are not available.

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