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The Debye–Waller factors of sodium chloride.

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The Debye–Waller temperature factors B_{Na} and B_{Cl} for NaCl have been measured by powder neutron diffraction at 4·2 and 295°K. The values obtained at room temperature agree with those given by earlier X-ray determinations, but are slightly higher than the calculated values of Reid & Smith [*J. Phys. Chem. Solids.* (1970). **31**, 2689–2697].

Introduction

The Debye–Waller factors of sodium chloride have been calculated recently by Reid & Smith (1970) using a shell model in which the force-constant parameters were fitted to the observed phonon dispersion curves. The values are smaller than the most recent experimental determinations at room temperature by X-ray diffraction (Table 1). In this note we report values of B_{Na} and B_{Cl} obtained from a powder neutron diffraction study of NaCl at 4·2 and 295°K.

Experimental

Powder neutron-diffraction data for NaCl (BDH Ltd., Analar Reagent) were collected using the PANDA diffractometer at A.E.R.E., Harwell. A neutron wavelength of 1·087 Å was obtained by reflexion from the (311) planes of a copper monochromator at a take-off angle of 59°. This high take-off angle gave good resolution of most reflexions up to $2\theta = 100°$.

Results

The intensities at 295°K were corrected for first-order thermal diffuse scattering (TDS) using the approximate method of Chipman & Paskin (1959). Only the acoustic modes contribute to the TDS correction whereas both acoustic and optic modes contribute to the Debye–Waller factors. Consequently, the B factor used in the correction formula was taken as two-thirds of the average B factor (see Suortti, 1967). The TDS correction required for the present experiment is the same as that calculated from the X-ray formula, since the neutron velocity in our experiment was greater than the mean elastic-wave velocity in NaCl (Willis, 1970).

Observed and calculated intensities were compared using the Harwell *TAILS* computer program (Rouse, 1973) which includes a correction for absorption ($\mu R = 0·14$). Neutron scattering lengths of $0·351 \times 10^{-14}$ m and $0·958 \times$ were used for sodium and chlorine respectively (Neutron Diffraction Commission, 1969). The variable parameters for each refinement were a scale factor and isotropic temperature factors for sodium (B_{Na}) and chlorine (B_{Cl}).

The observed intensities and R value $[=\sum(I_o-I_c)/\sum I_o]$ for each experiment are given in Table 2. The values of the temperature factors are summarized in Table 3, which also includes the theoretical values of Reid & Smith.

Table 2. *Data at* 4·2 *and* 295°K

Observed and calculated counts (I_o & I_c respectively) are given in hundreds.

(i) 4·2°K $a_0 = 5·5945$ Å

hkl	I_o	I_c
111	118	118
200	312	307
220	300	308
311	98	98
222	145	137
400	77	77
331	56	58
420	251	249
422	206	209
333/511	56	55
440	85	79
531	66	65
600/442	183	178
620	127	130

$R(I) = 2·0\%$

(ii) 295°K $a_0 = 5·639$ Å

hkl	I_o	I_c
111	136	140
200	358	355
220	326	329
311	104	101
222	140	136
400	66	71
331	52	52
420	216	212
422	163	164
333/511	44	44
440	57	54
531	45	45
600/442	121	111
620	74	75
533/622	82	81
444	20	18
711/551/640	77	73
642	79	84
731/553	28	30

$R(I) = 2·6\%$

Table 1. *Room-temperature B values of* NaCl

(Standard deviations are given in parentheses)

B_{Na} (Å^2)	B_{Cl} (Å^2)	Method	Reference
1·84	1·44	X-ray, powder	Merisalo & Paakkari (1967)
1·89	1·61	X-ray, single crystal	Göttlicher (1968)
1·81 (0·03)	1·49 (0·03)	X-ray, powder	Linkoaho (1969)
1·56	1·35	Shell-model calculation	Reid & Smith (1970)

Table 3. *Observed and calculated temperature factors of* NaCl

(Standard deviations are given in parentheses)

Temperature (°K)		$B_{\rm Na}$ (Å^2)	$B_{\rm Cl}$ (Å^2)
4.2	Experiment	0·35 (0·08)	0·27 (0·04)
	Reid & Smith	0·40	0·30
295	Experiment–TDS corr.	1·70 (0·10)	1·44 (0·03)
	Reid & Smith	1·56	1·35

Discussion

The observed B factors at 4·2 °K are in approximate agreement with the theoretical values of Reid & Smith; on the other hand, at room temperature the observed values are higher than those given by the calculations but in better agreement with recent X-ray determinations (Table 1). Linkoaho (1969) has suggested that the discrepancy between observed and calculated B values is due to the difficulty in making a reliable correction for thermal diffuse scattering (the correction increases the values of the observed B factors). A further possibility is that the discrepancy between experimental and calculated B values stems from the neglect of anharmonicity in the lattice dynamical calculations. Third-order and fourth-order anharmonic terms are ignored in the theory, although experimental evidence for a fourth-order (quartic) term in the Debye–Waller factors of both NaCl (Butt & Sölt, 1971) and KCl (Sölt, Butt & O'Connor, 1973) has been obtained by using Mössbauer γ-ray diffraction.

If we examine the present results in the light of the anharmonic treatment of Willis (1969), the quartic anharmonic coefficient in the potential expansion

$$V = V_0 + \tfrac{1}{2}\alpha r^2 + \gamma r^4$$

[Willis, 1969, equation (4·8)] is as given in Table 4. The Table also includes corresponding values for KCl deduced by Willis (1969) and the anharmonic parameters for NaCl and KCl obtained by Viswamitra & Jayalakshmi (1972) from single-crystal X-ray diffraction measurements close to the melting points.

Table 4. *Potential parameters for* NaCl *and* KCl

	NaCl	KCl
γ/α^2	$-0·11\ .\ 10^{12}$ erg^{-1}	$-0·14\ .\ 10^{12}$ erg^{-1}
α	$2·25\ .\ 10^{-12}$ erg Å^{-2}	$1·64\ .\ 10^{-12}$ erg Å^{-2}
γ	$-0·56\ .\ 10^{-12}$ erg Å^{-4}	$-0·38\ .\ 10^{-12}$ erg Å^{-4}
γ*	$-0·99\ .\ 10^{-12}$ erg Å^{-4}	$-0·215\ .\ 10^{-12}$ erg Å^{-4}

* Taken from Viswamitra & Jayalakshmi (1972).

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On the interpretation of anisotropic temperature factors. II.

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A discussion of how the interatomic thermal coupling is expressed in the anisotropic temperature factors was given in a preceding paper. Here a further aspect of this question is treated.

In a preceding paper (Scheringer, 1972) we discussed how the interatomic thermal coupling is expressed in the anisotropic temperature factors although these factors do not contain explicit coupling terms. We gave a lattice-dynamical formulation of the anisotropic temperature factors which showed that the mean-square amplitude matrix of the atoms of the unit cell is proportional to the sum of the inverse dynamical matrices of the crystal. On inversion of the dynamical matrices, the information which is contained in the off-diagonal blocks of these matrices is transferred into the diagonal blocks of the mean-square amplitude matrix. In the quoted paper, however, we did not take into account the fact that information on the interatomic coupling is also transferred into the mean-square amplitude matrix from the so-called 'self terms', which occur in the diagonal blocks of the dynamical matrices. The self terms also contain information on the interatomic interactions, and it is the purpose of this note to show how the self terms contribute to the anisotropic temperature factors.

The elements of the dynamical matrix of wave vector **q**

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