although each type of unit cell, when considered separately, is primitive.

The standard deviations of the atomic coordinates were less than 0.002 Å for iron atoms and less than 0.004 Å for aluminum atoms, with the exception of atom Al(9) for which $\sigma(x) = 0.020$ Å. In the absence of more accurate data no detailed understanding of the occupation of sites in the alloy can be obtained. The existence of the sites listed in Table 1 does, however, appear to be well established.

The atomic environments in both types of unit cell can be described in similar terms to those in α(AlMnSi) which have been discussed by Cooper & Robinson (1966). The transition metal coordination polyhedra contain one extremely short manganese or iron to aluminium bond. In α(AlMnSi) these bonds were 2.43 and 2.27 Å long for the 10-fold and 9-fold coordinated polyhedra respectively; in α(AlFeSi) the equivalent bond is 2·34 Å in both polyhedra. Abnormally short bonds are a well-known feature of transition metal-aluminium polyhedra and have been discussed elsewhere (*cf.* Black & Taylor 1958).

A more detailed account of the structure of this alloy, together with tables of observed and calculated structure factors, will appear in a dissertation to be submitted to the University of Cambridge by the author.

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Structure factors and Debye–Waller factors of sodium chloride at 300°K, 202°K and 78°K.

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Structure factors of sodium chloride have been measured by the X-ray powder diffraction method. The values of Debye–Waller factors were determined and compared with results of theoretical calculations by Buyers and Smith, and with earlier experimental results.

Introduction

Sodium chloride is the ionic crystal subjected to the most extensive studies by the X-ray diffraction method. However, the results of Renninger (1952), Witte & Wölfel (1955), Schoknecht (1957) and Vihinen (1960), which have been usually considered to be very accurate, differ considerably from those of more recent experimental and theoretical studies by Levy, Agron & Busing (1963), Abrahams & Bernstein (1965), Buyers & Smith (1964) and Pryor (1966). These discrepancies urged us to make an independent study of the structure factors of sodium chloride. In this work the measurement was extended to lower temperatures and the temperature dependence of Debye-Waller factors was also studied.

Experimental conditions

Intensity measurements were performed with a relative method with monochromatized Cu $K\alpha$ radiation. The integrated intensities at low temperatures were measured relatively to the room temperature values. High purity sodium chloride powder was ground until the particle size became about 1–2μ. By preliminary measurements it was proved that under a moulding pressure of 30 kp.cm^{-2} the integrated intensities were independent of specimen preparation. At higher pressures, there occurred appreciable increase in the ratio of integrated intensities, $I(h00)/I(hh0)$, apparently due to the preferred orientation. For final measurements the samples were packed into a sample holder applying pressures between 5 and 30 kp.cm^{-2}. By the texture goniometry, these samples were shown to be free from preferred orientation to one per cent.

The line broadening due to the strain in heavily ground particles may cause errors in the estimation of background. To study this, high angle reflexions of ground samples were compared with those of a sample made of a very fine sedimented powder, and it was shown that the integrated intensities were not affected by heavy grinding.

Results and discussion

The measured integrated intensities were corrected for temperature diffuse scattering (TDS) (Suortti, 1967). The scale factor was determined by putting the value of the structure factor, $F(220)$, at room temperature equal to the absolute value 16.85 measured by Witte & Wölfel (1955). The results obtained are given in Table 1, together with estimated errors, δF, due to the intensity measurements.

The Debye–Waller factors, B(Na) and B(Cl), of the individual ions at each temperature were determined on the assumption that the experimental and calculated structure factors coincided at high values of $\sin\theta/\lambda$, by employing

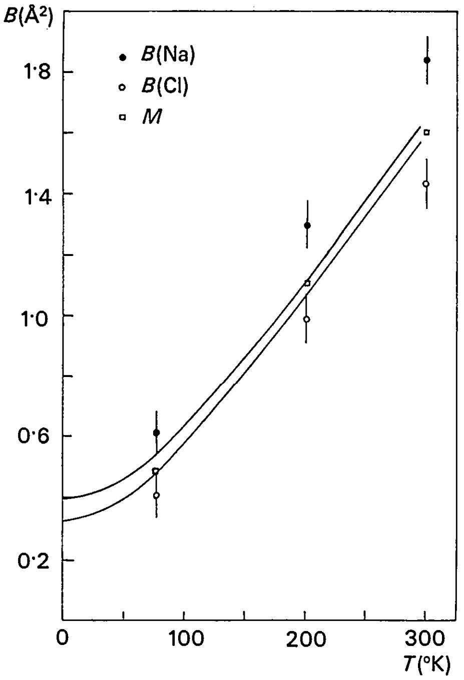

Fig. 1. Comparison of theoretical B values of sodium chloride with present data; upper curve for sodium ion, lower curve for chlorine ion. The errors given for B values are mainly due to the estimated uncertainty of 1·5% in the scale factor.

the difference Fourier method presented by Kurki-Suonio & Fontell (1963).

Table 2 presents the results of some recent measurements, together with our room temperature values. It is to be noted that our results alone have been corrected for TDS. For single crystals, the TDS correction in M value is approximately 0.15 Å^2 (Nilsson, 1957), where M is the average Debye–Waller factor obtained from the individual B values by weighting linearly by the atomic masses. This would bring the results of Abrahams & Bernstein (1965) and the neutron diffraction data of Levy *et al.* (1963) into excellent agreement with the present work. For powder, on the other hand, the TDS correction (Suortti, 1967) of M is only 0.03 Å^2, and with this the low values of earlier determinations can not be accounted for.

Fig. 1 gives a comparison of present results with those calculated by Buyers & Smith (1964) from the normal mode data of Karo & Hardy (1963). Our M values are in excellent agreement with the theoretical result, while the difference between B(Na) and B(Cl) exceeds considerably that due to the theory.

This difference is not affected essentially by the TDS correction. In this connection, it may be worth mentioning the following. (1) The values of B for individual ions may depend on the method adopted. However, the difference Fourier method gives essentially the same values as the method of least-squares. This fact was proved by comparing the result of Abrahams & Bernstein (1965) with that obtained by Kurki-Suonio & Fontell (1964) by the analysis based on the experimental data of Vihinen (1960). (2) It was proved that the error in the scale factor does not

Table 1. *Measured and calculated structure factors for a molecular unit of sodium chloride*

The experimental values, F_{meas}, have been corrected for anomalous dispersion (Cromer, 1965). Values, F_{calc}, have been calculated by the use of theoretical ionic scattering factors of Freeman (1959) and Debye–Waller factors evaluated in the present work.

	T=300°K			T=202°K			T=78°K		
hkl	F_{meas}	δF	F_{calc}	F_{meas}	δF	F_{calc}	F_{meas}	δF	F_{calc}
111	4·68	0·04	4·52	4·71	0·04	4·54	4·81	0·04	4·56
200	20·75	0·10	20·34	21·03	0·15	20·62	21·27	0·10	20·99
220	16·40	0·08	16·45	16·91	0·08	16·90	17·57	0·08	17·55
311	2·61	0·03	2·54	2·64	0·03	2·59	2·74	0·05	2·66
222	13·70	0·08	13·89	14·46	0·08	14·50	15·17	0·08	15·35
400	12·22	0·10	12·07	12·96	0·10	12·78	13·88	0·13	13·80
331	2·51	0·05	2·39	2·48	0·05	2·50	2·75	0·06	2·65
420	10·64	0·08	10·66	11·42	0·08	11·45	12·52	0·08	12·60
422	9·39	0·07	9·52	10·27	0·07	10·38	11·31	0·07	11·64
511 333	2·36	0·05	2·40	2·49	0·06	2·58	2·97	0·07	2·83
440	7·64	0·06	7·75	8·65	0·08	8·71	10·22	0·08	10·15
531	2·33	0·05	2·34	2·60	0·04	2·58	2·86	0·06	2·92
600 442	7·03	0·05	7·05	8·07	0·07	8·03	9·65	0·09	9·54
620	6·53	0·05	6·44	7·47	0·05	7·44	9·12	0·07	9·00
533	2·22	0·07	2·22	2·58	0·08	2·52	—	—	—
622	5·96	0·07	5·89	6·96	0·06	6·91	8·59	0·09	8·52

Table 2. *Comparison of the experimental Debye–Waller factors* (Å^2) *for sodium chloride at room temperature*

B(Na)	B(Cl)	M	Reference
1·84	1·44	1·60	Present work
1·64	1·33	1·45	Single-crystal, X-rays (Abrahams & Bernstein, 1965)
1·63	1·42	1·50	Single-crystal, neutrons (Levy *et al.*, 1963)
1·29	1·15	1·20	Polycrystal, X-rays (Vihinen, 1960)
1·25	1·00	1·10	Single-crystal, X-rays (Witte & Wölfel, 1955)
1·25	1·12	1·17	Single-crystal, X-rays (Renninger, 1952)

significantly affect the observed difference between B(Na) and B(Cl). (3) The reliability of X-ray B values depends on the reliability of theoretical scattering factors used. However, since the effect due to crystal environment appears only at lower values of $\sin\theta/\lambda$, the B values obtained in this study do not much depend on the choice of theoretical scattering factors. (4) A difficulty which is special to this crystal is that the odd reflexions are all weak. To check the influence due to the errors in these weak reflexions, the individual B values were determined with various combinations of odd structure factors. The resultant values were found to be consistent within 0.02 Å^2.

Further theoretical consideration seems to be wanted in order to explain the too large difference as observed between B(Na) and B(Cl).

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A note on the *a priori* estimation of *R* factors for constant-count-per-reflexion diffractometer experiments.

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To obtain data capable of yielding an R factor of 10% the total number of counts per reflexion need not exceed 25, for low background reflexions, rising to 125 for a peak to background ratio of 1·5. An equation required to develop a constant-agreement analysis is derived which is based on a constant-count type experiment.

It has been shown (Killean, 1967) that a constant-count, as distinct from a constant-time-per-reflexion diffractometer experiment, has certain advantages. In view of the high capital cost of automatic diffractometers it is relevant to consider what numerical value this constant count should be to achieve a given reliability index and, for the purposes of this paper, an ideal diffractometer experiment in which the errors in the data are due only to counting statistics is considered.

A constant count experiment gives

$$|F_o(\mathbf{h})|^2 = \frac{K\{N(\mathbf{h})-B(\mathbf{h})\}}{\mathrm{Lp}t(\mathbf{h})},$$

where Lp is the Lorentz-polarization factor. $N(\mathbf{h})$ the number of counts integrating through the peak, $B(\mathbf{h})$ the accumulated background counts, $t(\mathbf{h})$ the time taken to achieve the constant count $\{N(\mathbf{h})-B(\mathbf{h})\}=C$, and K is a scale factor required to place the structure factors on an absolute scale. In an actual experiment it will not be possible to achieve $\{N(\mathbf{h})-B(\mathbf{h})\}$ constant but small departures from constancy will not alter the subsequent order of magnitude analysis. It follows that

$$\sigma\{|F_o(\mathbf{h})|\} = \tfrac{1}{2}\,\frac{|F_o(\mathbf{h})|}{C}\,\{N(\mathbf{h})+B(\mathbf{h})\}^{\frac{1}{2}},$$

and by making the usual assumption that

$$\sigma\{|F_o(\mathbf{h})|\} \simeq \sigma\{|F_o(\mathbf{h})|-|F_c(\mathbf{h})|\}$$

the expected R value as a percentage is given by

$$R \lesssim \frac{\Sigma\,\sigma\{|F_o(\mathbf{h})|-|F_c(\mathbf{h})|\}\,.\,100}{\Sigma\,|F_o(\mathbf{h})|}$$

$$= \frac{50}{C}\left\{\frac{\Sigma\,\{N(\mathbf{h})+B(\mathbf{h})\}^{\frac{1}{2}}|F_o(\mathbf{h})|}{\Sigma\,|F_o(\mathbf{h})|}\right\}$$

$$= \frac{50}{C^{\frac{1}{2}}}\left\{\frac{\Sigma\left\{1+\dfrac{2B(\mathbf{h})}{C}\right\}^{\frac{1}{2}}|F_o(\mathbf{h})|}{\Sigma\,|F_o(\mathbf{h})|}\right\}.$$

It is usual in a diffractometer experiment to define a peak to background ratio below which a reflexion is considered to be unobserved. Let this ratio be τ. Then

$$N(\mathbf{h})/B(\mathbf{h}) \geq \tau$$

and

$$0 \leq \frac{2B(\mathbf{h})}{C} \leq \frac{2}{\tau-1},$$

which leads immediately to upper and lower limits for R.

Table 1. *Numerical values of* $C(\tau)$ *and* $N(\tau)$ *giving a theoretical R factor of the order of* 10 %

$1/\tau$	0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
$C(\tau)$	25	31	38	47	58	75	100	142	225	475	∞
$N(\tau)$	25	34	47	67	97	150	250	473	1125	4750	∞