Acta Cryst. (1974). A30, 299

The root-mean-square vibrational displacements of sodium and fluorine ions in sodium fluoride.

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(*Received* 24 *August* 1973; *accepted* 27 *September* 1973)

From the X-ray diffraction data from a single crystal of sodium fluoride at room temperature, the root-mean-square vibrational displacements of sodium and fluorine ions were determined to be 0·181 ± 0·001 Å and 0·183 ± 0·005 Å respectively. These values are compared with the values of 0·202 ± 0·007 Å for the two ions obtained by Meisalo & Merisalo [*Ann. Acad. Sci. Fenn.* A VI (1966). **211**, 3–9] from powder data.

The values of the Debye–Waller factors for the sodium and fluorine ions were determined by Meisalo & Merisalo (1966) [B (sodium) = B (fluorine) = $1·08 \pm 0·07$ Å^2], using a powder sample of sodium fluoride and Cu $K\alpha$ radiation. However, as the X-ray intensities from the powder sample for the $h00$ reflexions were affected by systematic errors like preferred orientation arising from the conditions of sample preparation and moulding pressures, it was felt necessary to reinvestigate the results using a single crystal and β-filtered Mo $K\alpha$ radiation ($\lambda = 0·7107$ Å). In addition, their intensity data may be affected by extinction, the magnitude of which was unknown in their analysis.

In the present work, a single crystal of sodium fluoride was ground into a sphere (radius 0·10 mm approx.) and the integrated intensities of 61 independent reflexions measured on a computer-controlled Siemens four-circle diffractometer using ω–2θ scan. The counting statistics on most of the reflexions were kept below 1% of the integrated intensities. As the integrated intensities for the reflexions with odd indices are dependent upon the difference of scattering factors between the sodium and fluorine ions, which is very small, a counting statistics of 5% was maintained on their integrated intensities in order to spend a justifiable time on the four-circle diffractometer. To minimize the lost counts to less than 0·5% at the peak maxima, one of a set of six attenuators was automatically inserted in the main beam before the measurement of each reflexion. All reflexions having $\sin\theta < 0·94$ were measured.

From the integrated intensities a set of relative observed structure factors was deduced. The observed structure factor for each reflexion was taken as the mean of its measured symmetry equivalents, its standard deviation being the standard error in the mean. The calculated structure factors were obtained using the atomic form factors determined by Boys (1962). The temperature factors were refined by the usual least-squares refinement technique using unit weights. However, the temperature factors did not change significantly regardless of whether unit weights or the weights based upon the standard deviations of individual reflexions were employed. After the refinement, a comparison of the observed and the calculated structure factors showed that a few low-order observed structure factors were systematically smaller than the calculated

Table 1. *Observed* (*extinction-corrected*) *and calculated structure factors*

h	k	l	$F_o(\mathbf{h})$	$F_c(\mathbf{h})$
2	0	0	58·52	57·42
2	2	0	42·92	44·02
2	2	2	34·27	35·23
4	0	0	29·11	29·07
4	2	0	24·48	24·55
4	2	2	20·97	21·10
4	4	0	16·00	16·24
4	4	2	14·42	14·48
6	0	0	14·64	14·48
6	2	0	13·03	13·02
6	2	2	11·81	11·80
4	4	4	10·64	10·76
6	4	0	9·87	9·87
6	4	2	9·05	9·10
8	0	0	8·00	7·82
8	2	0	7·36	7·28
6	4	4	7·30	7·28
6	6	0	6·73	6·81
8	2	2	6·84	6·81
6	6	2	6·36	6·37
8	4	0	5·99	5·89
8	4	2	5·65	5·62
6	6	4	5·27	5·29
8	4	4	4·72	4·71
8	6	0	4·50	4·45
10	0	0	4·57	4·45
10	2	0	4·33	4·21
8	6	2	4·23	4·21
10	2	2	4·05	3·99
6	6	6	4·02	3·99
8	6	4	3·55	3·58
10	4	0	3·58	3·58
10	4	2	3·43	3·40
8	8	0	3·07	3·06
10	4	4	2·87	2·91
8	8	2	2·91	2·91
8	6	6	2·68	2·76
10	6	0	2·72	2·76
10	6	2	2·61	2·62
12	0	0	2·52	2·50
8	8	4	2·50	2·50
12	2	0	2·29	2·37
1	1	1	4·45	4·56
3	1	1	6·33	6·41
3	3	1	5·00	5·13
3	3	3	3·74	3·81
5	1	1	3·72	3·81
5	3	1	2·72	2·81
5	3	3	1·98	2·08
7	1	1	1·49	1·56
5	5	1	1·46	1·56
7	3	1	1·07	1·20
5	5	3	1·03	1·19
7	3	3	0·91	0·94
7	5	1	0·77	0·75
5	5	5	0·82	0·75
7	5	3	0·63	0·61
9	1	1	0·66	0·61
9	3	1	0·59	0·50
7	5	5	0·50	0·43
9	3	3	0·53	0·43

structure factors indicating extinction in the data. Extinction corrections to the observed structure factors were made by the method of Zachariasen (1967). The thermal diffuse scattering (TDS) corrections to the observed structure factors were then made by the method of Cooper & Rouse (1968). The elastic constants used for this purpose were those quoted by Cottrell (1964). The TDS-corrected observed structure factors were fitted to the calculated structure factors by allowing small variations in the temperature factors of the sodium and fluorine ions only. The final values of the temperature factors which gave the best agreement between the observed and the calculated structure factors were

$$B\ (\text{sodium}) = 0{\cdot}860 \pm 0{\cdot}010\ \text{Å}^2$$
$$B\ (\text{fluorine}) = 0{\cdot}880 \pm 0{\cdot}050\ \text{Å}^2.$$

These values are about 4% higher than those obtained by using the observed structure factors not corrected for TDS and correspond to the root-mean-square vibrational displacements of $\sqrt{\overline{U^2}}$ (sodium) $= 0{\cdot}181 \pm 0{\cdot}001$ Å and $\sqrt{\overline{U^2}}$ (fluorine) $= 0{\cdot}183 \pm 0{\cdot}005$ Å as compared to the values quoted by Meisalo & Merisalo (1966) of $\sqrt{\overline{U^2}}$ (sodium) $=$ $\sqrt{\overline{U^2}}$ (fluorine) $= 0{\cdot}202 \pm 0{\cdot}007$ Å for the two ions.

It can be seen from the above that our values of the root-mean-square vibrational displacements for the two ions are significantly different from those given by the above authors. This is possibly due to the systematic errors in their intensity data arising from extinction and preferred orientation, for which no corrections were made and which gave rise to unrealistic temperature factors. However, it may be noted that the present values agree almost exactly with the values of 0·182 Å at room temperature, deduced from the Debye–Waller factors of 0·8685 Å^2 and 0·8671 Å^2 respectively for the two ions obtained by Reid & Smith (1970), using force constants derived by fitting a shell model to the measured dispersion curves.

Table 1 shows the extinction-corrected observed structure factors $F_o(\mathbf{h})$ and the calculated structure factors $F_c(\mathbf{h})$. The R index of 0·0135 based upon an agreement between the observed and the calculated structure factors reflects the accuracy with which the diffracted intensities were measured on the four-circle diffractometer.

The author's thanks are due to the referee for his useful comments.

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Acta Cryst. (1974). A**30**, 300

An analytical method of determining cubic crystal orientation from {111} surface traces. Corrections and comments.

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(*Received* 21 *August* 1973; *accepted* 18 *September* 1973)

Attention is drawn to printing errors and an item of oversight in an earlier paper [Fong, H. S. (1973). *Acta Cryst.* A**29**, 176–182]. An item of improvement is also put forward.

In a paper of the above title (Fong, 1973) equation (25) should correctly read:

$$y = -(b+m) \pm \sqrt{\{(b+m)^2 - c - n - 2z\}}$$

and the sentence containing equation (26) should read:

For each acceptable solution for y there may be two possible values for θ and φ:

Also in the paper the directions CP, AP, and BP of the pyramidal figure $ABCP$ were taken to be [110], [$0j_21$], and [j_10j_3] respectively. It was overlooked that this selection was, when $j_1 = -1$, a set of directions actually belonging to a left-handed crystal coordinate system so that the crystal orientations obtained in this case were in fact reflexions in the OXZ or OYZ plane of the actual orientations. Correction for this oversight is easily made by slight alteration of the rotation matrix M_j to:

$$\mathsf{M}_j = \begin{pmatrix} \dfrac{j_2v_2 - v_3}{j_1w_1} & \dfrac{-j_2v_1 - v_3}{j_1w_1} & \dfrac{v_1+v_2}{j_1w_1} \\ \dfrac{1+v_1w_2}{w_1} & \dfrac{-1+v_2w_2}{w_1} & \dfrac{-j_2+v_3w_2}{w_1} \\ jv_1 & jv_2 & jv_3 \end{pmatrix}.$$

It is however recommended that CP, AP, and BP be taken instead to be respectively the directions j_3[110], j_1[011], and j_2[101] which are always a right-handed set of directions whatever the values of j_1, j_2, and j_3 and which lead to somewhat neater expressions for (v_1, v_2, v_3) and M_j:

$$v_1 = (-j_1 \cos\sigma_1 + j_2 \cos\sigma_2 + j_3 \cos\sigma_3)/\sqrt{2}$$
$$v_2 = (j_1 \cos\sigma_1 - j_2 \cos\sigma_2 + j_3 \cos\sigma_3)/\sqrt{2}$$
$$v_3 = (j_1 \cos\sigma_1 + j_2 \cos\sigma_2 - j_3 \cos\sigma_3)/\sqrt{2}$$

$$\mathsf{M}_j = \begin{pmatrix} \dfrac{v_2 - v_3}{w_1} & \dfrac{-v_3 - v_1}{w_1} & \dfrac{v_1+v_2}{w_1} \\ \dfrac{1+v_1w_2}{w_1} & \dfrac{-1+v_2w_2}{w_1} & \dfrac{-1+v_3w_2}{w_1} \\ jv_1 & jv_2 & jv_3 \end{pmatrix}$$

where $w_1 = \sqrt{[2(1 + v_1v_2 + v_1v_3 - v_2v_3)]}$
$w_2 = v_2 + v_3 - v_1$.

Reference

Fong, H. S. (1973). *Acta Cryst.* A**29**, 176–182.