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Debye-Waller Factors and Extinction in Sodium Fluoride

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From consideration of the normal crystal strain in real crystals it is deduced that the value of mean domain size of a small sphere of sodium fluoride obtained by the application of Zachariasen's theory of extinction is physically meaningless and that no physical significance can be given to domain size so obtained. The values of Debye–Waller factors for the sodium and fluorine ions [B(Sodium) = 0·860 + 0·010 Å^2; B(fluorine) = 0·880 ± 0·050 Å^2] agree well with the theoretical values of 0·8685 Å^2 and 0·8671 Å^2 respectively for the two ions, recently reported by Reid & Smith [*J. Phys. Chem. Solids* (1970). **31**, 2689–2697].

Introduction

It has already been proven by Killean, Lawrence & Sharma (1972) that Zachariasen's theory for secondary extinction (Zachariasen, 1967) when applied to a small sphere of lithium fluoride gives a value of mean domain size which is physically unreasonable. These results are further supported by the application of Zachariasen's theory to a small sphere of sodium fluoride which is shown to exhibit secondary extinction.

Experimental

Small cubes of sodium fluoride single crystal were ground into spheres and a sphere of approximate radius 0·10 mm chosen for intensity-data collection. A total of 61 independent reflexions were measured on a computer-controlled Siemens four-circle diffractometer using Mo $K\alpha$ radiation [$\lambda(K\bar{\alpha}) = 0{\cdot}7107$ Å]. A five-point measuring cycle was employed using θ–2θ scan. Measurement of three standard reflexions at regular intervals showed no significant changes in the intensities of these reflexions over a data collection period of three days. The counting statistics on most of the reflexions were kept below 1 % of the integrated intensities. To minimize the lost counts to fewer than 0·5 % at the peak maxima one of a set of six attenuators was inserted in the main beam before the measurement of each reflexion.

The integrated intensities were corrected for Lorentz and polarization factors and a set of relative observed structure factors deduced. No corrections were applied for photoelectric absorption and anomalous dispersion. The observed structure factors were adjusted to the calculated structure factors in the least-squares process using only high-order reflexions which were not suspected to be affected by extinction. The reflexions 200, 220, 222, 400, 420, 422, 440, 442 and 600 were excluded from the least-squares refinement. The least-squares minimization process was carried out using two thermal parameters and a scale factor and the atomic form factors used for the computation of calculated structure factors were those given in *International Tables of X-ray Crystallography* (1962). After the least-squares refinement, a comparison of the observed structure factors and the calculated structure factors showed that the observed structure factors were systematically smaller than the calculated structure factors for a few low-order reflexions, indicating extinction in the data.

From a knowledge of the calculated structure factors and the extinction-affected observed structure factors values of r^* were obtained for each of the extinguished reflexions using the method of Zachariasen (1967). A fairly constant value of r^* for each of the highly extinguished reflexions suggested that the extinction was of the secondary type only. From the values of r^* thus obtained a weighted mean value of $r^* = (5{\cdot}6 \pm 0{\cdot}4) \times 10^{-6}$ cm was obtained. This value of r^* was used for applying the secondary extinction corrections to the extinction-affected observed structure factors by the method of Zachariasen (1967). After the application of extinction corrections a close agreement was obtained between the extinction-corrected observed structure factors and the calculated structure factors. The G index obtained was 0·0190.

Table 1 shows the observed structure factors $F_o'(\mathbf{h})$, the extinction-corrected structure factors $F_o(\mathbf{h})$ and the calculated structure factors $F_c(\mathbf{h})$. The values of thermal parameters obtained from the least-squares refinement process for sodium and fluorine ions were 0·860 ± 0·010 and 0·880 ± 0·050 Å^2 respectively.

The crystal type

In the case of the sodium fluoride sample used in this experiment it was not felt necessary to perform a diffractometer experiment with another wavelength to decide about the crystal type. This was in view of the closely matching half widths of the rocking curves observed for the lithium fluoride sample used in the

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experiments of Killean, Lawrence & Sharma (1972) and the sodium fluoride sample used in the present experiments. The rocking-curve experiments using the two samples were performed on a Lang camera for the same reflexion under identical experimental conditions. From these experiments it was concluded that the mosaic spread which in turn determines the crystal type as well as the dislocation density must be of the same nature both in the original sample of lithium fluoride used by Killean, Lawrence & Sharma (1972) and the sodium fluoride sample used in the present experiments. As it has already been established that the lithium fluoride sample is a type II crystal (Killean, Lawrence & Sharma, 1972), it can be concluded that sodium fluoride, which has the same mosaic property, is also a type-II crystal. Therefore for a type-II crystal $r^* = r$, Zachariasen (1967).

Discussion

Assuming one-to-one correspondence between a dislocation and the mosaic domain size (Gay, Hirsch & Kelly, 1953), the dislocation density in our spherical sample of sodium fluoride corresponding to its mean domain size of ($5{\cdot}6 \times 10^{-6}$ cm) can be taken as approximately 4×10^{10} cm^{-2}. Identical half widths of the rocking curves obtained for the original sample of lithium fluoride used in the experiments of Killean, Lawrence & Sharma (1972) and for the sodium fluoride sample used in the present experiments suggest a dislocation density in the original sample of sodium fluoride which is of the same order ($\simeq 10^6$ cm^{-2}) as that in the original sample of lithium fluoride, Killean, Lawrence & Sharma (1972). Furthermore, since the stiffness constants for sodium fluoride are nearly half the values of those for lithium fluoride [except for c_{11} for which $c_{11}(\text{LiF}) \simeq c_{11}(\text{NaF})$ and which is entirely in our favour] it is reasonable to assume that Johnston & Gilman's (1959) experimental relationship $n = 10^9\,\varepsilon$ between the strain ε and the dislocation density n for lithium fluoride crystal is still valid. Now, given that the average strain in a normal sodium fluoride lattice is of the order of 10^{-3} which using Johnston & Gilman's relation gives a dislocation density of about 10^6 cm^{-2} in the original sample, it is clear that in our sphere of sodium fluoride there is an increase in the internal strain of the order of 4×10^4 simply after grinding the original sample. This is impossible as such a large strain would have possibly shattered the crystal and reduced it to a very fine powdered form. It is concluded therefore that Zachariasen's theory when applied to a small sphere of sodium fluoride gives a value of mean domain size which has little physical meaning, a result which conforms to an earlier result deduced for a small sphere of lithium fluoride (Killean, Lawrence & Sharma, 1972). This result does not seem surprising when consideration is given to the fact that Zachariasen's theory of extinction is based upon a hypothetical model and many mathematical assumptions and approximations are made which may not be valid for real crystals. However, the values of the Debye–Waller factors for the sodium and fluorine ions [$B(\text{sodium}) = 0{\cdot}860 \pm 0{\cdot}010$ Å^2; $B(\text{fluorine}) = 0{\cdot}880 \pm 0{\cdot}050$ Å^2] agree almost exactly with those calculated

Table 1. *Experimentally observed, $F'_o(\mathbf{h})$, extinction corrected, $F_o(\mathbf{h})$, and calculated, $F_c(\mathbf{h})$, structure factors*

h	k	l	$F'_o(\mathbf{h})$	$F_o(\mathbf{h})$	$F_c(\mathbf{h})$
2	0	0	50·92	58·52	57·42
2	2	0	40·19	42·92	44·02
2	2	2	33·07	34·27	35·23
4	0	0	28·50	29·11	29·07
4	2	0	24·15	24·48	24·55
4	2	2	20·78	20·97	21·10
4	4	0	15·93	16·00	16·24
4	4	2	14·39	14·42	14·48
6	0	0	14·61	14·64	14·48
6	2	0	13·02	13·03	13·02
6	2	2	11·81	11·81	11·80
4	4	4	10·64	10·64	10·76
6	4	0	9·87	9·87	9·87
6	4	2	9·05	9·05	9·10
8	0	0	8·00	8·00	7·82
8	2	0	7·36	7·36	7·28
6	4	4	7·30	7·30	7·28
6	6	0	6·73	6·73	6·81
8	2	2	6·84	6·84	6·81
6	6	2	6·36	6·36	6·37
8	4	0	5·99	5·99	5·98
8	4	2	5·65	5·65	5·62
6	6	4	5·27	5·27	5·29
8	4	4	4·72	4·72	4·71
8	6	0	4·50	4·50	4·45
10	0	0	4·57	4·57	4·45
10	2	0	4·33	4·33	4·21
8	6	2	4·23	4·23	4·21
10	2	2	4·05	4·05	3·99
6	6	6	4·02	4·02	3·99
8	6	4	3·55	3·55	3·58
10	4	0	3·58	3·58	3·58
10	4	2	3·43	3·43	3·40
8	8	0	3·07	3·07	3·06
10	4	4	2·87	2·87	2·91
8	8	2	2·91	2·91	2·91
8	6	6	2·68	2·68	2·76
10	6	0	2·72	2·72	2·76
10	6	2	2·61	2·61	2·62
12	0	0	2·52	2·52	2·50
8	8	4	2·50	2·50	2·50
12	2	0	2·29	2·29	2·37
1	1	1	4·45	4·45	4·56
3	1	1	6·33	6·33	6·41
3	3	1	5·00	5·00	5·13
3	3	3	3·74	3·74	3·81
5	1	1	3·72	3·72	3·81
5	3	1	2·72	2·72	2·81
5	3	3	1·98	1·98	2·08
7	1	1	1·49	1·49	1·56
5	5	1	1·46	1·46	1·56
7	3	1	1·07	1·07	1·20
5	5	3	1·03	1·03	1·19
7	3	3	0·91	0·91	0·94
7	5	1	0·77	0·77	0·75
5	5	5	0·82	0·82	0·75
7	5	3	0·63	0·63	0·61
9	1	1	0·66	0·66	0·61
9	3	1	0·59	0·59	0·50
7	5	5	0·50	0·50	0·43
9	3	3	0·53	0·53	0·43

at 295°K by Reid & Smith (1970), [B(sodium) = 0·8685; B(fluorine) = 0·8671 Å^2], using force constants derived by fitting a shell model to measured dispersion curves. This shows that the treatment of the extinction-affected reflexions in the least-squares refinement was entirely satisfactory.

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Numerical Evaluation of *N*-Beam Wave Functions in Electron Scattering by the Multi-slice Method

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A method for the numerical evaluation of *N*-beam diffraction amplitudes and intensities which has been successfully employed over the last few years is described. This derives from the multi-slice formulation of Cowley and Moodie. The physical basis of the method and practical approaches to calculation are described.

1. Introduction

The present paper is intended to serve both as a practical guide to calculation of electron-diffraction intensities, and to give a summarized account of the physical basis of the multi-slice method. For the first purpose §§ 1 and 3 to 5 may be read alone.

The feasibility of numerical evaluation of diffraction intensities from the *N*-beam solution for a parallel-sided crystal was demonstrated by Sturkey (1962) using a scattering matrix, and by Wagenfeld (1958) and Howie & Whelan (1961), using Bethe's eigenvalue method (Bethe, 1928).

An analytical solution was obtained by Cowley & Moodie (1957) by applying the slice method to electron diffraction. The solution itself is not suited to direct numerical evaluation, but a numerical method based on the finite-slice approximation (Moodie, 1965) called here the multi-slice method, was tested by Goodman & Lehmpfuhl (1967) and has been since greatly expanded and applied to a large range of problems, including the study of large and complicated unit cells by Lynch & O'Keefe (1972).

Most, if not all, published calculations made for comparison with experimental work have used either this method, or Bethe's eigenvalue method (recent examples of the latter: Lehmpfuhl, 1972; Ayroles & Mazel, 1970; Lally, Humphreys, Metherell & Fisher, 1972). Sturkey's method has been used recently to a limited extent (*e.g.* Melvin, Morris & Bottoms, 1971). It will be shown in § 5 of this paper that economical numerical evaluation by means of the scattering matrix is identical to the multi-slice calculation. Here the term 'scattering matrix' is used to denote Sturkey's formulation, and not a theoretically trivial though convenient rewriting of the eigenvalue method in matrix notation. Leaving aside for the moment the question of computation times, the eigenvalue method appears to be useful for calculations involving a limited number of beams and for some special cases involving symmetry reduction (*e.g.* Blume, 1966). However, this utility is not maintained for large numbers of beams; the size of the computer memory required increases as N^2, and, more seriously, the probability of near coincidence of eigenvalues is increased. As against this, the multi-slice method has proved useful for calculation with several hundred beams, the memory requirement expanding roughly as N. This, and the fact that absorption, faulting and other three-dimensional effects are easily introduced, and that the calculation is not self-normalizing, have combined to make it a useful crystallographic technique.