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Extinction in a Large Crystal of Lithium Fluoride

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The integrated intensities from a large, parallel-sided crystal of lithium fluoride have been measured and it is deduced that these intensities are affected by primary extinction only, there being only one mosaic block diffracting at any time. The estimated average size of the mosaic blocks, $2{\cdot}8\times10^{-3}$ cm, is shown to substantiate this deduction. When extinction corrections are made using the general theory of X-ray diffraction [Zachariasen (1967). *Acta Cryst.* **23**, 558], excellent agreement between the corrected and the calculated results is obtained provided the extinction is less than 20%, but for more severe extinction, the corrections are found to be inadequate.

Introduction

The degree of accuracy with which integrated intensities can be measured has been increased by the advent of automatic and semi-automatic diffractometers, but even with highly accurate intensities there remains the problem of relating these to the structure factors when systematic errors such as thermal diffuse scattering, multiple reflections and extinction are present. The problem of applying exact extinction corrections has proved particularly intractable and there has been little experimental investigation of this phenomenon. This work describes the experimental investigation of extinction in a large crystal of lithium fluoride.

A recent general theory of X-ray diffraction in crystals (Zachariasen, 1967) deals with the problem of primary and secondary extinction and the corrections suggested there are now widely used and appear to be successful in many cases. Similar correction terms, applied specifically to a large crystal in both the Laue and the Bragg diffracting cases, are given by Weiss (1966).

For a particular reflexion, the extinction factor, y, defined as

$$y=\left(\frac{F_o}{F_k}\right)^2$$

where F_o and F_k are the observed and kinematic structure factors respectively, can be written as the sum of an infinite series

$$y=1+\sum_{i=1}^{\infty}(-1)^i a_i x^i$$

where a_i are constants and x represents the primary and secondary extinction, given by

$$x=AF_k^2\bar{t}^2+r^*Q\bar{T}.$$

A and r^* are constants, $\bar{t}$ is the mean path length through a single crystal block and $\bar{T}$ is the mean path length through the crystal.

According to Zachariasen, the constant r^* depends on $\bar{t}$ and g, the parameter which describes the Gaussian spread of the normals to the diffracting planes of the mosaic blocks in the crystal. The values of these quantities are not readily obtained. The normal procedure in using the extinction correction equation seems to be to assume primary extinction negligible, calculate r^* from the most extinguished reflexions assuming that the kinematic structure factor can be replaced by the calculated structure factor and then apply the nescesary corrections to all reflexions.

The effective mean path length through the crystal, $\bar{T}$, is difficult to determine in the case of an arbitrarily shaped crystal. Zachariasen suggests that the value $\bar{T}$ used should be $\frac{1}{A_C}\frac{\mathrm{d}A_C}{\mathrm{d}\mu}$ where μ is the absorption coefficient and A_C is the transmission factor.

Previous studies of extinction in lithium fluoride have been carried out by Zachariasen (1968) and Killean, Lawrence & Sharma (1972). Small, spherical crystals completely immersed in the X-ray beam, were used and different conclusions were reached with regard to the secondary extinction, *i.e.* whether lithium fluoride approximates to a type I or a type II crystal (Zachariasen, 1967).

In the experimental study of extinction the use of small spherically ground crystals has certain disadvantages. The amount of extinction tends to be small, resulting in uncertainties in the extinction parameters, and further uncertainties in these parameters can arise due to errors in the calculated structure factors which may be quite significant if the extinction is small. Also, the variation of extinction with path length through the crystal cannot be adequately studied for a spherical crystal.

The investigation of extinction is therefore best carried out on a large crystal of regular geometry and it was decided to use a thick, parallel-sided crystal whose cross-sectional area was much greater than that of the incident beam. Similar experiments have been carried out by Bragg, James & Bosanquet (1921), Bragg & West (1928) and by others. A crystal of lithium fluoride was considered very suitable for a study of extinction since its calculated structure factors are known to a fair degree of accuracy (Killean, Lawrence & Sharma, 1972), its small absorption coefficient enables thick crystals to be used, it has many planes of high reflecting power and, because of its very high symmetry, a large number of symmetry-equivalent reflexions are available.

Experimental

A large lithium fluoride crystal of thickness (0·139 ± 0·002) cm and cut along the [100], [010], [001] directions was used. The integrated intensities were measured on a Siemens AED four-circle diffractometer, controlled on-line by an IBM 1130 computer, using Mo $K\alpha$ filtered radiation (λ=0·7107A). The moving-crystal, moving-counter technique was employed, (θ–2θ) scan, with a 2θ scan range of 1·0° using a very narrow source collimator (diameter 0·4 mm) and the largest possible detector collimator. Each reflexion was measured for a period of five minutes, including background, and this resulted in a standard deviation due to counting statistics of the lowest intensity measured of 3%. To reduce lost counts, one of a set of six calibrated attenuators was placed in the main beam during the measurement of each reflexion, this attenuator being chosen on the basis of a 0·50 sec count at the peak centre using the thickest attenuator. All reflexions in a hemisphere of reciprocal space having $\theta < 70°$ were measured.

Data processing

Absorption corrections were applied to the data (μ= 3·40 cm^{-1}). The transmission coefficient applicable to each reflexion depended on whether the reflexion is of the Laue or Bragg type.

For a Laue reflexion,

$$A_c = \frac{\exp(-\mu t\sec(\theta+\varphi)) - \exp(-\mu t\sec(\theta-\varphi))}{\mu\left[1-\frac{\sec(\theta+\varphi)}{\sec(\theta-\varphi)}\right]}$$

where t=thickness of the crystal, φ=angle between the normal to the crystal face and the reflecting planes.

However, when the reflexion is of the symmetrical Laue type,

$$A_c = t \sec\theta \exp(-\mu t \sec\theta).$$

For a Bragg type reflexion

$$A_c = \frac{1-\exp\{-\mu t(\operatorname{cosec}(\theta+\varphi)+\operatorname{cosec}(\theta-\varphi))\}}{\mu\left[1+\frac{\sin(\theta+\varphi)}{\sin(\theta-\varphi)}\right]}.$$

When the reflexion is of the symmetrical Bragg type,

$$A_c = \frac{1-\exp(-2\mu t \operatorname{cosec}\theta)}{2\mu}.$$

It should be noted that the transmission coefficient A_c takes into account the different volumes of crystal irradiated for different reflexions as well as the absorption. The observed relative structure factors F_o were obtained from the measured integrated intensity ϱ from

$$\varrho = F_o^2 \,\mathrm{Lp}\, A_c$$

where Lp was the Lorentz-polarization factor.

The Siemens AED diffractometer was not designed to measure integrated intensities from such a large crystal and for some reflexions, although the incident beam width was small, the width of the diffracted beam was greater than that of the detector collimator. All such reflexions were ignored as were those reflexions where the diffracted beam emerged at grazing incidence to the crystal face since, in these cases, part of the beam was emitted from the side of the crystal.

Results

It was assumed that the kinematic structure factor, F_k, for each reflexion could be replaced by the calculated structure factor F_c. The F_c values obtained by Killean, Lawrence & Sharma (1972) using the scattering factors published in the *International Tables for X-ray Crystallography* (1962) were used.

For high sin θ, small F_c reflexions, the observed structure factors were found to be approximately proportional to the calculated structure factors and thus a scale factor for the observed data was calculated. This scale factor was only approximate since, if extinction was present, it must have affected all reflexions and small corrections would have to be applied to those reflexions used in the scaling.

After scaling, the remainder of the observed structure factors were found to be less than the calculated structure factors, the y value falling rapidly as sin θ decreased, the lowest y value being less than 0·2. It was believed that the apparent reduction in the observed structure factors was due to extinction for the following reasons:

(1) It was unlikely that there was a significant loss of counts due to experimental errors. Although, with a large crystal it is possible that the diffracted beam may be quite wide and some part of the beam may not enter the receiving collimator, this effect, if present, should be apparent at all values of θ and one would not have expected it to disappear at high θ values.

(2) Although systematic errors arising from thermal diffuse scattering and anomalous scattering might be present, these would have produced smaller effects.

(3) Those reflexions whose Miller indices were odd tended to be less diminished than those reflexions of even Miller indices. Since the structure factors for the even reflexions, being made up of the sum of the scattering from the fluorine and the lithium ions, are greater than those of the odd reflexions, being made up of the difference, the effect was seen to be dependent on the scattering power of the plane, characteristic of extinction.

It is generally accepted that, for a mosaic crystal, a formula of the type

$$\left(\frac{F_o}{F_c}\right)^2 = 1 - r^* Q \bar{T}$$

represents the extinction correction provided the extinction is not large and is of the secondary type. Symmetry equivalent reflexions, which have quite different path lengths, net counts and transmission factors were found, nevertheless, to give the same value of observed structure factor. Table 1 shows a sample of ϱ, A_c and F_o^2 values for a set of symmetry equivalents of two reflexions, the standard deviation $\sigma(F_o^2)$ being taken to be the standard error in the mean of the F_o^2 values. Consequently, no constant value of r^* could be obtained from the above equation assuming $\bar{T}$ to be $\frac{1}{A_c}\frac{dA_c}{d\mu}$ the values of r^* obtained varying within a set of symmetry equivalent reflexions by a factor of more than two.

Table 1. *The integrated intensities, transmisson factors and $(F_o)^2$ values for two sets of symmetry equivalent reflexions*

{331} reflexions			Lp = 1·053		F_c^2 = 33·64
h	k	l	ϱ	A_c	F_o^2
−3	1	−3	2·528	0·0869	27·61
−3	3	−1	1·993	0·0689	27·45
3	1	3	3·135	0·1065	27·96
3	3	1	4·915	0·1629	28·61
−3	1	3	2·601	0·0869	28·39
−3	3	1	2·032	0·0689	27·97
3	1	−3	3·083	0·1065	27·50
3	3	−1	4·898	0·1629	28·53
				Average =	(27·99 ± 0·17)

Table 1 (*cont.*)

{622} reflexions			Lp = 0·5787		F_c^2 = 27·77
h	k	l	ϱ	A_c	F_o^2
−2	2	−6	1·065	0·0805	22·87
−2	6	−2	1·027	0·0723	24·54
−6	2	−2	1·090	0·0807	23·34
2	2	6	1·998	0·1519	22·68
2	6	2	2·816	0·2083	23·36
6	2	2	1·772	0·1288	23·77
−2	2	6	1·102	0·0805	23·65
−2	6	2	0·990	0·0723	23·67
−6	2	2	1·086	0·0807	23·26
2	2	−6	1·986	0·1519	22·56
2	6	−2	2·886	0·2083	23·96
6	2	−2	1·732	0·1288	23·24
				Average =	(23·40 ± 0·16)

One of the assumptions made in the derivation of the above equation is that the crystal consists of a large number of small, perfect crystals blocks, the normals to whose diffracting planes form a Gaussian distribution. There must be, however, a sufficient number of these blocks so that many of them will diffract a parallel, monochromatic beam of X-rays simultaneously, secondary extinction being caused by energy being removed from the incident beam by blocks close to the X-ray source, resulting in less scattering by the blocks further from the X-ray source. When symmetry-equivalent reflexions undergo diffraction such that different lengths of crystal are irradiated, different amounts of extinction would be expected since different numbers of blocks would be diffracting simultaneously. The observed structure factors of all symmetry equivalents appeared to suffer the same amounts of extinction and, therefore, the extinction could not be of the secondary type.

Primary extinction in lithium fluoride

It must be concluded, therefore, that the extinction observed here is the primary type. The extinction must be taking place within a single block and only one block can be diffracting at one time; otherwise, the extinction would depend on the number of blocks diffracting, that is, on the length of crystal irradiated.

Consider a real crystal made up of small, independent blocks, each of thickness L. The width of the diffracted beam from each block is given by

$$\Delta(2\theta) = \frac{\lambda}{L\cos\theta}$$

$$\simeq \frac{10^{-8}}{L} \text{ radians.}$$

Assuming the incident beam passes through a length z of composite crystal which has a mosaic spread M, then, at any one time, a total number of $\frac{z\,10^{-8}}{L^2 M}$ blocks will be diffracting a parallel monochromatic beam of X-rays.

Assuming $M=0{\cdot}005$ radians and $z=0{\cdot}2$ cm, then to have on average only one block diffracting, the size of each block must be approximately 6×10^{-4} cm and, therefore, for primary extinction only to be present in this sample of lithium fluoride, the block size must be significantly greater than 6×10^{-4} cm.

When the incident beam has a natural width and is slightly divergent, the condition for having only one block diffracting at any one time has to be replaced by the condition that the very small ranges of wavelength of the main beam diffracted by each block do not overlap.

The total integrated intensity from the large crystal is the sum of the integrated intensities from all blocks and is therefore dependent on the size and shape of each block. Following Zachariasen (1967), it was assumed that the relationship between the observed and kinematic structure factors is

$$y=\left(\frac{F_o}{F_k}\right)^2=(1+2x)^{-1/2}=1-x+\tfrac{3}{2}x^2-\tfrac{5}{2}x^3+\cdots. \quad (1)$$

where $x=\dfrac{r_o^2F_k^2K^2\lambda^2}{V^2\sin 2\theta}[f(\theta)t]^2$, r_o = radius of an electron, K = polarization factor $=\dfrac{1+\cos^4 2\theta,}{1+\cos^2 2\theta}$ V = volume of unit cell of the crystal, t = dimension of each block, and $f(\theta)$ depends on the shape of the crystal.

The above equation assumes all blocks to have the same shape and size and, since the shape and size are unknown, it could not be used to calculate F_k but, assuming F_k to be equal to the calculated structure factor F_c, $[f(\theta)t]$ could be determined and tested as to whether the block size was sufficiently large that only primary extinction was present.

A value of $[f(\theta)t]$ was calculated for each reflexion having $\theta<50°$, the F_o^2 value in each case being taken as the average of the F_o^2 values over all symmetry equivalent reflexions. The values of $[f(\theta)t]$ were found to be fairly constant for values of y greater than 0·80. Using the average value of $[f(\theta)t]$, corrected structure factors, F_o^1, were obtained and since the reflexions which had been used in the scaling received small correction, a new scale factor was required. This produced slight changes in the $[f(\theta)t]$ values and the process was repeated until a constant scale factor was obtained, the scale factor being chosen such that the sum of the squares of the observed, corrected structure factors was equal to that of the calculated structure factors for those reflexions having $y>0{\cdot}975$.

The average value of $[f(\theta)t]$ for reflexions having values of y in the range $0{\cdot}950>y>0{\cdot}80$ was $(2{\cdot}77\pm{\cdot}06)\times10^{-3}$ cms. Table 2 shows the observed structure factors F_o with the standard deviations $\sigma(F_o)$, the corrected and calculated structure factors, F_o^1 and F_c, along with the y value for each reflexion and the $[f(\theta)t]$ values for those reflexions having $y<0{\cdot}950$.

Table 2. *The standard deviation, observed, corrected and calculated structure factors and the y and* $[f(\theta)t\times10^3]$ *values for each reflexion*

h	k	l	$\sigma(F_o)$	F_o	F_o^1	F_c	y	$f(\theta)t$
1	1	1	0·08	9·42	19·64	19·80	0·227	2·81
2	0	0	0·10	12·48	30·48	29·73	0·176	2·63
2	2	0	0·09	11·64	22·06	21·09	0·305	2·50
3	1	1	0·03	7·20	9·29	8·87	0·659	2·37
2	2	2	0·04	10·65	17·08	16·19	0·432	2·43
4	0	0	0·05	10·14	14·46	13·05	0·604	2·06
3	3	1	0·02	5·29	5·92	5·80	0·832	2·43
4	2	0	0·02	9·03	11·85	10·90	0·686	2·09
4	2	2	0·04	7·96	9·83	9·32	0·729	2·25
5	1	1	0·02	4·30	4·59	4·52	0·904	2·40
4	4	0	0·02	6·47	7·43	7·18	0·812	2·31
5	3	1	0·01	3·62	3·80	3·82	0·900	2·96
6	0	0	0·02	5·85	6·56	6·42	0·830	2·44
4	4	2	0·02	5·84	6·54	6·42	0·828	2·47
6	2	0	0·01	5·29	5·82	5·79	0·835	2·67
5	3	3	0·01	3·20	3·32	3·36	0·907	3·19
6	2	2	0·01	4·85	5·26	5·27	0·847	2·79
4	4	4	0·01	4·47	4·80	4·82	0·860	2·84
5	5	1	0·01	2·90	2·99	3·01	0·928	3·07
7	1	1	0·01	2·91	3·00	3·01	0·934	2·96
6	4	0	0·01	4·16	4·43	4·43	0·882	2·75
6	4	2	0·01	3·89	4·10	4·09	0·905	2·68
8	0	0	0·01	3·38	3·52	3·52	0·922	2·74
7	3	3	0·01	2·41	2·47	2·47	0·952	
8	2	0	0·01	3·17	3·29	3·28	0·934	2·61
6	6	0	0·01	2·98	3·07	3·06	0·948	2·56
8	2	2	0·01	2·99	3·08	3·06	0·954	
7	5	1	0·01	2·20	2·24	2·24	0·964	
6	6	2	0·01	2·80	2·86	2·86	0·958	
8	4	0	0·01	2·65	2·71	2·68	0·978	
7	5	3	0·01	2·02	2·05	2·03	0·990	
9	1	1	0·01	2·01	2·04	2·03	0·980	
8	4	2	0·01	2·47	2·52	2·51	0·968	
6	6	4	0·01	2·32	2·36	2·35	0·974	
9	3	1	0·01	1·82	1·84	1·84	0·978	
8	4	4	0·01	2·06	2·09	2·08	0·980	
7	5	5	0·01	1·66	1·67	1·66	1·000	
7	7	1	0·01	1·66	1·67	1·66	1·000	
10	0	0	0·01	1·94	1·96	1·97	0·970	
8	6	0	0·01	1·94	1·96	1·97	0·970	
10	2	0	0·01	1·80	1·82	1·84	0·957	
8	6	2	0·01	1·82	1·84	1·84	0·978	
9	5	1	0·01	1·47	1·48	1·51	0·948	
7	7	3	0·01	1·48	1·49	1·51	0·960	
10	2	2	0·01	1·70	1·72	1·74	0·955	
6	6	6	0·01	1·71	1·73	1·74	0·966	

The agreement between the calculated and the corrected structure factors was excellent for those reflexions having $y>0{\cdot}80$. The G index (Kitaigorodskii, 1961) defined as

$$G=\left[\frac{\sum|\Delta(h)|^2}{\sum|F_o^1(h)|^2}\right]^{1/2}$$

was 0·0071, the conventional R index being 0·0053. The theoretical G index, defined as

$$G=\left[\frac{\sum\sigma^2(F_o)}{\sum|F_o^1(h)|^2}\right]^{1/2}$$

was 0·0034, suggesting that some systematic errors still existed in the corrected data.

For reflexions having $y<0{\cdot}80$, the corrected structure factors were greater than the calculated values and two other suggested forms of y.

$$y=\frac{\tanh\sqrt{(3x)}}{\sqrt{(3x)}}=1-x+\frac{6}{5}x^2-\frac{51}{35}x^3\ldots \quad (2)$$

$$y=\frac{\tan^{-1}\sqrt{3x}}{\sqrt{3x}}=1-x+\frac{9}{5}x^2-\frac{27}{7}x^3\ldots \quad (3)$$

did not produce an improved agreement between the calculated and corrected structure factors. Table 3 shows the corrected structure factors, $F_o^1(1)$, $F_o^1(2)$ and $F_o^1(3)$, obtained using equations (1), (2) and (3) respectively for reflexions with $y<0{\cdot}90$.

Table 3. *The calculated structure factors and the corrected structure factors obtained using equations* (1), (2) *and* (3) *for reflexions with* $y<0{\cdot}90$

h	k	l	F_c	$F_o^1(1)$	$F_o^1(2)$	$F_o^1(3)$
1	1	1	19·80	19·64	21·45	18·26
2	0	0	29·73	30·48	33·49	27·98
2	2	0	21·09	22·06	23·94	20·69
3	1	1	8·87	9·29	9·55	9·10
2	2	2	16·19	17·08	18·20	16·30
4	0	0	13·05	14·46	15·13	13·99
3	3	1	5·80	5·92	5·96	5·89
4	2	0	10·90	11·85	12·22	11·58
4	2	2	9·32	9·83	10·04	9·68
4	4	0	7·18	7·43	7·50	7·37
6	0	0	6·42	6·56	6·60	6·52
4	4	2	6·42	6·54	6·59	6·50
6	2	0	5·79	5·82	5·85	5·80
6	2	2	5·27	5·26	5·28	5·25
4	4	4	4·82	4·80	4·81	4·79
6	4	0	4·43	4·43	4·44	4·42

Concluding remarks

It has been shown that very accurate integrated intensities can be measured on a conventional four-circle diffractometer using a large crystal whose cross-sectional area is much larger than the incident X-ray beam. All measured intensities suffered from extinction and it was shown that this extinction was of the primary type.

The values of $[f(\theta)t]$ are fairly constant for reflexions having $0{\cdot}975>y>0{\cdot}80$ and there is no evidence that $[f(\theta)t]$ varied with θ. Assuming $f(\theta)$ to be about unity. the size of the mosaic block is about 3×10^{-3} cm, far larger than the minimum size of block required to ensure that only one block is diffracting a parallel, monochromatic beam of X-rays at any one time, thus justifying the assumption that only primary extinction is taking place.

The good agreement between the corrected and calculated structure factors for reflexions having $y>0{\cdot}80$ reflected the accuracy of Zachariasen's equation for small amounts of extinction. For these reflexions, the x values were sufficiently small that only the first two terms of the series, $1-x$, had any sufficient contribution to y and any of the suggested forms of y give the same corrected structure factors. For larger amounts of extinction, all forms of y tended to oversetimate the extinction and it must be concluded that none of the suggested forms of y give satisfactory corrections. The problem of finding a suitable closed form of y is made extremely difficult by the very slow convergence of the power series.

Certain assumptions made in the derivation of equation (1) must, of course, impose some limit on the possible agreement between theory and experiment. The blocks in the mosaic crystal will not be of the same size and shape and, as has been pointed out by Werner (1969), Zachariasen's treatment can take no account of the coherent nature of the wave inside the crystal, which must have an effect on the amount of primary extinction. However, it may be that the discrepancies between theory and experiment are mainly due to the inadequacies of the mosaic block model of a crystal.

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