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Large Extinction Effects in Magnesium Oxide

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Integrated intensities from a large crystal of magnesium oxide are shown to be affected by primary extinction. The intensities are found to fit the solutions of the dynamic theory of X-ray diffraction for both the Laue and the Bragg cases. A mosaic block size of $3{\cdot}56\times10^{-3}$ cm has been found.

Introduction

Many authors, *e.g.* Weiss (1966), have pointed out the importance of investigating extinction experimentally and experimental studies have been carried out by varying the wavelength of the incidental radiation (Zachariasen, 1968*a*, *b*); the degree of polarization of the incident beam (Chandrasekhar, 1960); and the crystal size (Cochran, 1953; Denne, 1972). Recently, Lawrence (1972) has investigated extinction in a large crystal of lithium fluoride which allows a variation in the incident and diffracted path lengths in the crystal, and similar experiments carried out on magnesium oxide are described here.

Magnesium oxide has the sodium chloride-type structure and therefore the positions of the ions in the structure are known. The thermal parameters were obtained from a separate experiment (Lawrence, 1973), using high-order structure factors measured from a small single crystal using molybenum $K\alpha$ radiation. They were found to be 0·30 and 0·34A^2 for the magnesium and oxygen ions respectively. Depending, therefore, on the accuracy of the theoretical scattering factors, the calculated structure factors are known and can be assumed to be equal to the kinematic structure factors.

Following Zachariasen (1967), the extinction factor y can be defined as

$$y=(F_o/F_K)^2$$

where F_o and F_K are the observed and kinematic structure factors respectively. Four equations for y have been suggested, each of which can be expanded as an infinite series. They are

$$y=(1+2x)^{-1/2} \tag{1}$$

$$y=\frac{\tan h\sqrt{3x}}{\sqrt{3x}} \tag{2}$$

$$y=\frac{\tan^{-1}\sqrt{3x}}{\sqrt{3x}} \tag{3}$$

$$y=\frac{\sum J_{2n+1}(2\sqrt{3x})}{\sqrt{3x}}\,. \tag{4}$$

These equations represent Zachariasen's solution for a small spherical crystal (1) and the solution for dynamic theory for the Bragg and Laue cases, (2) and (4). (3) is an equation whose behaviour is similar to the others.

The parameter x is the sum of the primary and secondary extinction and is 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, Q is the reflectivity of the plane and $\bar{T}$ is the effective path length through the crystal.

For small values of x, the four equations for y are the same, giving $y=1-x$, but for large x, y tends to different values. On theoretical grounds, all solutions for y are likely and it was decided to test the validity of the equations experimentally using a large crystal of magnesium oxide, magnesium oxide being chosen since it was known to exhibit large extinction effects.

Experimental

A large magnesium oxide crystal of thickness (0·151 ± 0·002) cm, cut along the [100], [010] and [001] directions, was used. The observed structure factors were obtained as in the study of lithium fluoride, Lawrence (1972 *a*).

When large extinction effects are present, difficulty is experienced in putting the data on an absolute scale. It had been found that the Bragg-type reflexions from a large plate of sodium chloride exhibited no extinction, comparison between the observed and calculated structure factors giving an R index of less than 0·02. Since the crystals in both cases were much larger than the cross section of the X-ray beam, the incident intensity was the same for each crystal. The scale factor for the sodium chloride data, after taking into account the difference in the unit-cell dimensions, was used to scale the magnesium oxide data. Due to possible errors in the scattering factors for the sodium and chlorine ions and in the calculated thermal parameters, the accuracy of this scale factor was not considered to be better than 5%.

Results

A study of the observed structure factors and comparison between them and the calculated structure factors showed:

(1) All observed structure factors were extinguished. The y values ranged from 0·025 to 0·722 for the reflexions with even indices and from 0·394 to about unity for the weaker reflexions with odd indices.

(2) The observed structure factors for a set of symmetry-equivalent reflexions whose planes diffracted with Laue-type geometry were the same, as were those with Bragg-type, the Laue-type structure factors being less than the Bragg-type in each case. The structure factors for the five planes of highest reflectivity in the Laue case were not significantly different, these structure factors having approximately two thirds of the value of the corresponding Bragg reflexions.

The extinguished structure factors being the same, regardless of the path length through the crystal, implied that the extinction was mainly of the primary type and that only one mosaic block was diffracting a parallel monochromatic beam at one time. A similar effect had been found in lithium fluoride; symmetry equivalent Laue and Bragg reflexions gave the same structure factors in that case.

In the four equations listed above, the value of x was therefore

$$x = \frac{r_0^2 |F_K|^2 \lambda^2 K^2 \bar{t}^2}{V^2 \sin 2\theta}$$

where

r_o = radius of electron,

λ = wavelength,

K = polarization factor

and

V = volume of unit cell.

To determine which of the equations for y gave the best agreement between the known y values and x, each equation was solved for $\bar{t}$ for each structure factor to find which equation gave the most consistent value of $\bar{t}$. The value of each structure factor was taken to be the average value of its symmetry equivalents, Laue and Bragg-type reflexions being considered separately.

Laue-type reflexions

There was a large range of y values for these reflexions and none of the equations gave a consistent value of $\bar{t}$ over the whole range of y. However, for the y values $0{\cdot}80 > y > 0{\cdot}36$, equation (4) gave very consistent $\bar{t}$ values, the average value of $\bar{t}$ over this range being $(3{\cdot}51 \pm 0{\cdot}03) \times 10^{-3}$cm. For values of y down to 0·136, the values of $\bar{t}$ increased, the equation overestimating the amount of extinction. For values of y below 0·136, the function oscillates and it was therefore impossible to find unique values of $\bar{t}$ which satisfied the equation. There was no evidence of these oscillations in the observed data, the value of y decreasing monotonically as the reflectivity of the planes increased.

The other three equations failed to give consistent values of $\bar{t}$, even in the range $0{\cdot}80 > y > 0{\cdot}36$ where the $\bar{t}$ values varied from their mean value by as much as 30% for all equations. For large extinction, these equations underestimated the amounts of extinction, giving small values of $\bar{t}$.

Equation (4) represents the results of the dynamic theory for a parallel plate of thickness $\bar{t}$ in the Laue case and this sample of magnesium oxide behaves as a large number of thin sheets of perfect crystal of approximate thickness $3{\cdot}5 \times 10^{-3}$ cms, only one perfect crystal diffracting a parallel beam of X-rays at one time.

When the observed structure factors were corrected using equation (4), an R index of 0·015 was obtained for equations having $y > 0{\cdot}36$. Table 1 shows the observed, calculated and corrected structure factors and the y and $\bar{t}$ values. The $\bar{t}$ values are not given for reflexions having very large extinction, $y < 0{\cdot}150$, since no unique solutions of $\bar{t}$ exist in this region and no $\bar{t}$ or y values are given for small amounts of extinction, *i.e.* $y > 0{\cdot}80$, since these values are very susceptible to errors in the scale factor. The agreement between the observed and calculated structure factors is less good for values of $y < 0{\cdot}36$, the observed data apparently not matching the oscillatory nature of the function in this region.

Bragg reflexions

The Bragg reflexions were less extinguished than the corresponding Laue reflexions and again none of the equations gave a consistent value of $\bar{t}$ over the whole range of y. However, apart from the most extinguished reflexions, equation (2) gave a consistent value of $\bar{t}$, the average value being $(3{\cdot}61 \pm 0{\cdot}04) \times 10^{-3}$cm. The $\bar{t}$ values from the other three equations varied from their mean value by as much as 25%.

As for the Laue reflexions, the most consistent value

Table 1. *The observed, calculated and corrected structure factors and the y and t̄ (×10³) values for each Laue-type reflexion*

h k l	F_o	F_c	F_{corr}	y	t̄
2 0 0	8·32	52·32	43·21	0·025	
2 2 0	8·37	41·25	39·47	0·041	
2 2 2	8·36	34·08	29·76	0·060	
4 0 0	8·34	29·00	29·45	0·082	
4 2 0	8·40	25·23	22·40	0·110	
4 2 2	8·24	22·33	21·40	0·136	
4 4 0	8·28	29·00	24·20	0·205	2·56
6 0 0	7·73	16·70	21·77	0·214	2·78
4 4 2	8·09	16·70	22·79	0·234	2·69
6 2 0	7·65	15·51	19·77	0·243	2·87
6 2 2	7·44	14·34	17·52	0·269	2·99
4 4 4	7·58	13·41	16·48	0·319	2·97
6 4 0	7·40	12·63	14·76	0·342	3·05
6 4 2	7·03	11·89	13·14	0·349	3·19
8 0 0	6·45	10·73	10·79	0·361	3·46
8 2 0	6·37	10·21	10·23	0·389	3·49
6 4 4	6·36	10·21	10·22	0·388	3·49
6 6 0	6·54	9·75	10·01	0·450	3·36
8 2 2	6·64	9·75	10·10	0·463	3·30
6 6 2	6·33	9·36	9·36	0·457	3·47
8 4 0	6·17	8·98	8·83	0·471	3·56
8 4 2	6·18	8·62	8·58	0·514	3·51
6 6 4	6·00	8·29	8·11	0·524	3·60
8 4 4	6·04	7·70	7·80	0·616	3·39
10 0 0	5·67	7·41	7·17	0·584	3·69
8 6 0	5·89	7·41	7·45	0·631	3·44
10 2 0	5·69	7·15	7·09	0·632	3·54
8 6 2	5·77	7·15	7·19	0·650	3·44
10 2 2	5·65	6·91	6·98	0·668	3·41
10 4 0	5·29	6·48	6·50	0·667	3·46
10 4 2	5·03	6·27	6·20	0·642	3·62
3 3 1	5·97	9·51	9·80	0·394	3·36
5 1 1	5·38	7·23	6·87	0·554	3·76
5 3 1	4·69	5·47	5·36	0·735	3·75
5 3 3	3·81	4·23	4·21	0·811	3·70
7 1 1	3·14	3·33	3·18		
5 5 1	3·16	3·33	3·19		
7 3 1	2·58	2·67	2·66		
5 5 3	2·57	2·67	2·66		
7 3 3	2·17	2·22	2·21		
7 5 1	1·84	1·91	1·87		
9 1 1	1·66	1·67	1·68		
7 5 3	1·70	1·67	1·72		
9 3 1	1·45	1·49	1·47		
7 7 1	1·30	1·34	1·31		
9 3 3	1·34	1·34	1·35		

Table 2. *The observed, calculated and corrected structure factors and the y and t̄ (×10³) values for each Bragg-type reflexion*

h k l	F_o	F_c	F_{corr}	y	t̄
2 0 0	12·12	52·32	46·79	0·053	
4 0 0	11·08	29·00	26·33	0·145	
4 4 0	9·99	29·00	17·58	0·298	3·92
6 0 0	9·63	16·70	16·13	0·332	3·89
6 2 0	9·32	15·51	15·04	0·361	3·87
6 2 2	9·22	14·34	14·34	0·413	3·62
6 4 0	8·51	12·63	12·52	0·453	3·69
6 4 2	8·31	11·89	11·95	0·488	3·58
8 0 0	7·51	10·72	10·37	0·490	3·92
8 2 0	7·44	10·21	10·08	0·531	3·74
6 6 0	7·40	9·75	9·85	0·576	3·53
8 2 2	7·14	9·75	9·50	0·536	3·88
8 4 4	6·41	7·70	7·82	0·692	3·43
10 0 0	6·18	7·41	7·47	0·696	3·52
10 2 0	6·02	7·15	7·23	0·709	3·51
8 6 2	6·06	7·15	7·27	0·719	3·44
10 2 2	5·88	6·91	6·99	0·722	3·48
10 4 0	5·54	6·48	6·56	0·731	3·45
10 4 2	5·29	6·27	6·28	0·710	3·62
5 1 1	6·00	7·23	7·28	0·689	3·52
5 3 1	4·87	5·47	5·47	0·790	3·62
7 1 1	3·22	3·33	3·37		
5 5 1	3·21	3·33	3·36		
7 3 1	2·66	2·67	2·74		
7 3 3	2·22	2·22	2·27		
9 3 1	1·48	1·49	1·49		
7 7 1	1·33	1·34	1·34		
9 3 3	1·34	1·34	1·35		
7 5 5	1·31	1·34	1·32		
9 5 1	1·25	1·24	1·26		
7 7 3	1·22	1·24	1·23		
9 5 3	1·15	1·17	1·15		
11 1 1	1·08	1·10	1·08		
7 7 5	1·07	1·10	1·07		

of t̄ was obtained using the equation which represents the solution of the dymamic theory. Also, the value of t̄ was the same for the two types of reflexions.

The observed structure factors were corrected using equation (2) and an R index of 0·017 was obtained for all the reflexions except the two most extinguished. Table 2 shows the observed, calculated and corrected structure factors and the y and t̄ values. The y and t̄ values are again not given for reflexions having $y > 0{\cdot}80$.

Concluding remarks

It has been shown that the integrated intensities from the sample of magnesium oxide used were affected only by primary extinction. The observed structure factors have been found to fit the solutions of the dynamic theory of X-ray diffraction in both the Laue and Bragg cases. Only one mosaic block can be diffracting a parallel beam of X-rays at one time and each block seems to behave as a perfect crystal of thickness $3{\cdot}56 \times 10^{-3}$cm.

In making extinction corrections, it is usually assumed that primary extinction can be neglected. The results from magnesium oxide and from lithium fluoride have shown that in the samples used, primary extinction predominated. While such large crystals are not normally used in intensity measurements and while treatment by cutting or grinding may induce an increase in the dislocation density and, hence, a decrease in the mosaic block size, these results show that such an assumption may be unjustified.

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