Acta Cryst. (1972). A28, 405

Extinction in Lithium Fluoride - A Comment on Zachariasen's Theory of Extinction

BY R. C. G. KILLEAN, J. L. LAWRENCE AND V. C. SHARMA

School of Physical Sciences, The University, St. Andrews, Scotland

(*Received* 17 *March* 1972)

Zachariasen's theory of extinction is used to obtain the mean radius of the mosaic domain of a spherical lithium fluoride crystal. From consideration of the mosaic domain size obtained for a large thick crystal from the same specimen batch and of the crystal strain, it is deduced that this radius is physically unreasonable.

Introduction

Zachariasen (1967) has derived intensity formulae for X-ray diffraction in real crystals and these formulae are widely used for correcting observed diffraction data for extinction. Zachariasen has pointed out that the application of his theory to small crystals involves mathematical approximations and Werner (1969) has commented that Zachariasen's theory is likely to have serious shortcomings when primary extinction is important although Zachariasen states that primary extinction should on the basis of his theory and experiments be negligible even for the strongest reflexions of most crystal specimens.

Zachariasen (1968) has supported the application of his theory to small crystals by examining extinction effects in a small lithium fluoride sphere. He concludes that the crystal he used was a type I mosaic crystal in which the width of the mosaic spread is much greater than that of the diffraction from a single domain and that the mean domain radius was $1{\cdot}14\times10^{-5}$ cm, an order of magnitude smaller than that required for the presence of primary extinction (Zachariasen, 1967).

This paper is concerned with a reinvestigation of the results obtained by Zachariasen (1968) using a lithium fluoride sphere that had been ground from a block of the material. These results, denoted by (Z) and (KLS) respectively, are also compared with the results obtained by Lawrence (1972), for a large parallel sided crystal from the same batch of material as used by (KLS).

Experimental

Small fragments of lithium fluoride were cut from a large single crystal and ground into spheres. A spherical crystal of radius 0·21 mm was chosen and mounted on a goniometer in an arbitrary setting. The intensities were measured on a Siemens' four-circle diffractometer, controlled on-line by an IBM 1130 computer. A five-point measuring cycle was employed using a θ–2θ scan. To minimize lost counts to less than 0·5% at maximum counting rate and to maximize the total intensities, one of a set of six attenuators was placed in the main beam before the measurement of each reflexion, this attenuator being chosen on the basis of a 0·5 sec trial experiment at the peak centre with the thickest attenuator. Three standard reflexions were measured after every thirty reflexions and no statistically significant change in intensities of these was recorded over the data collection period. The time between measurements of groups of standard reflexions was approximately three hours.

All reflexions, having $\theta<70°$, in a hemisphere of reciprocal space were measured in such a way that the standard deviation for all integrated intensities due to counting statistics was less than 0·1% of the intensity. The observed structure factor for each reflexion was taken to be the mean of all equivalent reflexions and the corresponding standard deviation, $\sigma(\mathbf{h})$, was defined as the standard error in that mean. For all structure factors, this error was never greater than 0·6% of the structure factor, this error occurring for the 111 reflexion. The average error was 0·25% which compares with an average error due to counting statistics alone of less than 0·1%. It is clear that other residual errors exist in the data.

Two data sets were obtained; one using molybdenum $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å), the (Mo) set, the other using copper $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å), the (Cu) set. In both cases β filters were used.

There were 52 independent reflexions in the (Mo) set and nine in the (Cu) set. No corrections were made for anomalous dispersion or thermal diffuse scattering but absorption corrections were applied [μR(Cu)$=0{\cdot}68$; μR(Mo)$=0{\cdot}071$].

(Mo) Data set

The (Mo) data set was initially scaled to the molybdenum radiation data of (Z) using the reflexions in the range $0{\cdot}7<\sin\theta/\lambda<1{\cdot}3$ and those reflexions which appeared to bc affected by extinction were eliminated from the least-squares minimizing process. The reflexions 200, 220, 222, 400, 420 and 111 were therefore omitted. The weights $\omega(\mathbf{h})$ used were

$$\omega(\mathbf{h})=\frac{1}{\sigma^2(\mathbf{h})}$$

but it was found that the final parameters were not significantly different whether these weights or unit weights were employed. The least-squares minimization of the function $\sum\omega(\mathbf{h})|\Delta(\mathbf{h})|^2$ was carried out with respect to the two thermal parameters and the scale factor using the form factors of Cromer & Waber (1965).

From a knowledge of the calculated values of the structure factors for the extinguished reflexions, these reflexions were corrected for extinction using the method of Zachariasen (1967). The calculated structure factor is expressed in terms of the observed structure factor, $F_o(\mathbf{h})$, by

$$F_c(\mathbf{h})=F_o(\mathbf{h})\,(1+2px_0)^{1/4}$$

where p is the polarization factor $=\dfrac{1+\cos^4 2\theta}{1+\cos^2 2\theta}$

and

$$x_0=r^*\frac{\bar{T}Q_0}{\lambda}$$

$$r^*=r\left[1+\left(\frac{r}{\lambda g}\right)^2\right]^{-1/2}.$$

Q_0 and λ have their usual meaning, r is the mean radius of each mosaic block in the crystal, g is a function of the width of the mosaic spread distribution and $\bar{T}$ is the effective mean path length through the crystal.

An estimate of r^* was obtained for each extinguished reflexion together with an estimated standard deviation obtained from $\sigma(\mathbf{h})$. The weighted mean value of r^* was $(1{\cdot}5\pm0{\cdot}3)\times10^{-6}$ cm and the observed, $F'_o(\mathbf{h})$, extinction-corrected, $F_o(\mathbf{h})$, and calculated structure factors using the thermal parameters ($B_{Li}=0{\cdot}96$, $B_F=0{\cdot}66$) obtained from the initial least-squares process are given in Table 1 along with $\sigma(\mathbf{h})$ for the observed structure factors.

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

$\sigma(\mathbf{h})$ is the standard deviation of the experimentally observed structure factor.

h k l	$\sigma(\mathbf{h})$	$F'_o(\mathbf{h})$	$F_o(\mathbf{h})$	$F_c(\mathbf{h})$
2 0 0	0·08	28·47	29·89	29·92
2 2 0	0·03	21·49	21·90	21·73
2 2 2	0·02	16·44	16·60	16·84
4 0 0	0·04	13·60	13·62	13·61
4 2 0	0·04	11·45	11·46	11·34
4 2 2	0·02	9·78	9·78	9·68
4 4 0	0·02	7·51	7·51	7·44
4 4 2	0·02	6·69	6·69	6·64
6 0 0	0·04	6·72	6·72	6·64
6 2 0	0·02	6·04	6·04	5·99
6 2 2	0·03	5·44	5·44	5·45
4 4 4	0·04	4·94	4·94	4·99
6 4 0	0·02	4·57	4·57	4·59
6 4 2	0·02	4·21	4·21	4·23
8 0 0	0·02	3·66	3·66	3·64
8 2 0	0·02	3·42	3·42	3·40
6 4 4	0·01	3·36	3·36	3·40
8 2 2	0·01	3·18	3·18	3·18
6 6 0	0·02	3·17	3·17	3·18
6 6 2	0·01	2·98	2·98	2·97
8 4 0	0·01	2·80	2·80	2·78
8 4 2	0·01	2·62	2·62	2·61
6 6 4	0·02	2·44	2·44	2·45
8 4 4	0·01	2·19	2·19	2·17
10 0 0	0·01	2·06	2·06	2·06
8 6 0	0·01	2·04	2·04	2·06
10 2 0	0·01	1·91	1·91	1·93
8 6 2	0·01	1·91	1·91	1·93
10 2 2	0·01	1·81	1·81	1·82
6 6 6	0·02	1·82	1·82	1·82
1 1 1	0·12	19·82	20·32	19·73
3 1 1	0·02	9·23	9·23	9·47
3 3 1	0·02	6·08	6·08	6·19
3 3 3	0·02	4·64	4·64	4·77
5 1 1	0·02	4·80	4·80	4·77
5 3 1	0·01	4·02	4·02	3·99
5 3 3	0·02	3·48	3·48	3·49
5 5 1	0·02	3·07	3·07	3·12
7 1 1	0·02	3·13	3·13	3·12
7 3 1	0·01	2·82	2·82	2·81
5 5 3	0·01	2·80	2·80	2·81
7 3 3	0·01	2·55	2·55	2·55
7 5 1	0·01	2·31	2·31	2·31
5 5 5	0·01	2·31	2·31	2·31
9 1 1	0·01	2·15	2·15	2·10
7 5 3	0·02	2·11	2·11	2·10
9 3 1	0·01	1·93	1·93	1·91
9 3 3	0·01	1·72	1·72	1·73
7 7 1	0·02	1·73	1·73	1·73
7 5 5	0·02	1·73	1·73	1·73
9 5 1	0·02	1·55	1·56	1·57
7 7 3	0·02	1·58	1·58	1·57

(Cu) Data set

There was no direct way of correcting the (Cu) data set for extinction since all the reflexions were affected by extinction and, hence, the data could not be put on an absolute scale. However, from the weighted mean value of r^* obtained for the (Mo) data set the pairs of extreme r^* values for the (Cu) data set were calculated assuming the crystal was either of type I or of type II and the (Cu) data corrected for both cases. The data was scaled such that the sum of the calculated structure factors was equal to the sum of the extinction-corrected observed structure factors. Table 2 shows the absorption-corrected observed structure factors with their standard deviations, the structure factors corrected for extinction assuming the crystal to be of both types, and the calculated structure factors. Inspection of Table 2 shows that this specimen approximates more to a type II crystal than a type I crystal. Hence

$$r^*=r$$

and the estimated mean radius of the mosaic domain is $1{\cdot}5\times10^{-6}$ cm.

This procedure of finding r^* was repeated by using three more sets of scattering factors (Freeman, 1959; Berghuis, Haanoppel, Potters, Loopstra, MacGillavry & Weenendaal, 1955; *International Tables for X-ray Crystallography*, 1962). No significant changes in r^* values were obtained and the crystal still approximated closely to type II of the two crystal types. However,

Table 2. *Experimentally observed, F_o'(h), extinction corrected, F_o(h), and calculated F_c(h), structure factors, for the* (Cu) *data set assuming type* I *or type* II *crystal*

σ(h) is the standard deviation of the experimentally observed structure factor.

			Type I extinction					Type II extinction		
h	*k*	*l*	σ(h)	F_o'(h)	F_o(h)	F_c(h)	σ(h)	F_o'(h)	F_o(h)	F_c(h)
2	0	0	0·15	26·45	31·12	29·92	0·15	27·43	29·96	29·92
2	2	0	0·02	19·93	21·52	21·73	0·02	20·68	21·48	21·73
2	2	2	0·04	15·77	16·63	16·84	0·04	15·02	16·75	16·84
4	0	0	0·02	12·93	13·32	13·61	0·02	13·42	13·61	13·61
4	2	0	0·02	10·79	11·00	11·34	0·02	11·20	11·30	11·34
4	2	2	0·02	9·05	9·22	9·68	0·02	9·39	9·47	9·68
1	1	1	0·10	18·66	20·55	19·73	0·10	19·33	20·32	19·73
3	1	1	0·02	9·00	9·14	9·47	0·02	9·34	9·41	9·47
3	3	1	0·02	5·86	5·89	6·19	0·02	6·08	6·10	6·19

as is expected, small changes in least-squares parameters were observed in the four refinements.

The analysis described here applied to the (*Z*) data confirms that the (*Z*) crystal conformed more to a type I crystal than a type II crystal although small changes in the least-squares parameters were obtained. (In this analysis $B_{Li}=1·02$; $B_F=0·68$; scale=0·96: *cf.* (*Z*) $B_{Li}=0·90$; $B_F=0·63$; scale 1·00). By the method of analysis described here it is impossible to obtain *r* for a type I crystal.

Discussion

Johnston & Gilman (1959) have deduced an experimental relationship between the strain, ε, in a lithium fluoride crystal and the density of dislocations *n*,

$$n=10^9\varepsilon\,.$$

Lawrence (1972) has deduced a mean radius for the mosaic domain in a large thick crystal of lithium fluoride of $2·5\times10^{-3}$ cm which assuming one to one correspondence between the mosaic domain size and a dislocation gives a dislocation density of about 10^5 cm^{-2}. The dislocation density of the original sample as quoted by the manufacturers is about 10^5 cm^{-2}. The present analysis of a small fragment of this material ground into a sphere has, applying Zachariasen's theory to a small crystal, given a mean radius for the mosaic domain of $1·5\times10^{-6}$ cm and consequently a dislocation density of 2×10^{11} cm^{-2}, which, on the basis of the strain equation gives an increase in the internal strain of ($\times2\times10^5$) simply after grinding the crystal. Clearly this is impossible as the average strain in the normal crystal lattice is between 10^{-3} and 10^{-4}. It is concluded therefore that even although the strain equation may not hold good for large strains, Zachariasen's theory when applied to small crystals does not successfully account for extinction and gives a value of r^* which is physically unreasonable.

It is also concluded that the widely accepted practice of including an extinction parameter in a least-squares analysis has little validity and that no physical deductions can be made from a consideration of the differences between observed and calculated structure factors affected by extinction, when such a parameter has been included in the analysis.

We would like to thank the referee for his constructive criticism and, in particular, for pointing out the importance of the strain equation to a proper understanding of the experimental results.

References

BERGHUIS, J., HAANOPPEL, I. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.

FREEMAN, A. J. (1959). *Acta Cryst.* **12**, 261.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

JOHNSTON, W. G. & GILMAN, J. J. (1959). *J. Appl. Phys.* **30**, 129.

LAWRENCE, J. L. (1972). *Acta Cryst.* A**28**, 400.

WERNER, S. A. (1969). *Acta Cryst.* A**25**, 639.

ZACHARIASEN, W. H. (1967). **23**, 558.

ZACHARIASEN, W. H. (1968). *Acta Cryst.* A**24**, 324.