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Extinction in an Extended-Face Crystal of Zinc Selenide

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Abstract

X-ray intensity measurements from an extended-face single crystal of cubic zinc selenide obtained by McIntyre, Moss & Barnea [*Acta Cryst.* (1980), A**36**, 482–490] have been reanalysed with a view to explaining the unresolved discrepancies between theory and experiment present in the original analysis of the most severely extinguished reflections. The results obtained are shown to complement the recent findings of a wavelength-dependent study using the same crystal specimen [Stevenson & Barnea (1983). *Acta Cryst.* A**39**, 538–547] and foreshadow the need to allow for the presence of the Borrmann effect.

Introduction

In interpreting their X-ray diffraction intensity data from an extended-face crystal of zinc selenide, McIntyre, Moss & Barnea (1980) (hereafter referred to as MMB) were primarily concerned with the thermal vibrations of the atoms allowing for cubic anharmonic effects. This emphasis is reflected in their weighting scheme, which downgrades the importance of reflections affected by extinction.

In this paper we attempt to reconcile the data of MMB with calculations based on alternative models of extinction. This is particularly important because very few studies of extinction in extended-face imperfect crystals are available (*e.g.* Mair & Barnea, 1975).

The extinction factor used by MMB was that defined by Zachariasen (1967) for secondary extinction and required the refinement of the effective domain radius

$$r^* = r/\{1 + [r/(\lambda g)]^2\}^{1/2}, \quad (1)$$

where r is the mean radius of the perfect-crystal domains, λ is the wavelength of the incident radiation and g is the quantity in the isotropic Gaussian distribution law describing the misalignment of the domains:

$$w(\Delta) = \sqrt{2}\, g \exp(-2\pi g^2 \Delta^2),$$

where Δ measures the angular deviation from the mean orientation. The standard deviation of the distribution is given by

$$\sigma_w = 1/(4\pi g^2)^{1/2}. \quad (2)$$

The extinction models explored here include allowance for primary extinction, the Borrmann effect and the additional angle dependence predicted by Becker & Coppens (1974*a*,*b*).

Analysis

The reader is directed to MMB for the details of the experimental procedure and conditions used in the collection of the room-temperature data with Mo $K\alpha$ X-radiation.

The observed (background-corrected) intensities I_{oi} ($i = 1,2,\ldots,138$) were taken from MMB directly, where I_{oj} represents the average of equivalent reflection intensities (at least two) for the jth reflection after correction for anisotropic thermal diffuse scattering effects, the only systematic effect for which the correction was applied to the observed rather than the calculated intensities.

The calculated kinematic intensities I_{ki} were obtained using the relativistic Hartree–Fock spherical X-ray atomic scattering factors of Doyle & Turner (1968) and the anomalous dispersion corrections of Cromer & Liberman (1970). The lattice parameter was taken to be 5·6670 Å (ASTM file, 1953).

The normal linear absorption coefficient (μ_0) has been calculated using the photoelectric cross sections of Veigele (1973), giving a value of 337·6 cm^{-1}. (The authors believe that the value used by MMB was 357·7 cm^{-1}.) The normal linear absorption coefficient is used in the extinction models. In particular, the mean path length through the crystal is given by

$$\bar{T} = -A^{-1}\, \mathrm{d}A/\mathrm{d}\mu_o,$$

where $A \equiv A(\mu_0)$ is the transmission factor. In the case of extended-face crystals A is the product of $1/(2\mu_0)$ and a geometrical term, and so $\bar{T} = 1/\mu_0$. In the formula for the extinction factor used by MMB $\bar{T}$ multiplies r^* and so any changes in $\bar{T}$ will be absorbed by the refined value of r^*, with no other changes resulting. (Indeed, in this instance $r^*\bar{T}$ is an equally good parameter for refinement.)

The least-squares refinement program, written especially for this analysis, uses the IMSL (1975) library subroutine *ZXSSQ* to minimize the difference

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between observed and calculated intensities. The quantity minimized is

$$M = \sum_i w_i(I_{oi} - I_{ci})^2, \quad (3)$$

where w_j is the weight given to $(I_{oj} - I_{cj})$ and

$$I_{cj} = I_{kj} y_j,$$

where y_j is the extinction factor for the jth observation. The parameters which can be refined are: the two isotropic temperature parameters B_{Zn} and B_{Se}; the effective cubic anharmonic temperature parameter β' (Cooper, Rouse & Fuess, 1973; MMB); the scale factor s; the extinction parameters r and/or g (or r^* if appropriate).

ZXSSQ uses a modification of the Levenberg–Marquardt algorithm, for solving non-linear least-squares problems, which eliminates the need for explicit derivatives. The program used by MMB (*LSEFC5*) employs the method of normal equations (*International Tables for X-ray Crystallography*, 1959) and derivatives are calculated explicitly. Thus a comparison of the final results of MMB with those obtained by simulating the original refinement is of interest and provides an independent test of the performance of our program.

A correlation matrix is calculated in order to assess the interactions of the refined parameters, as are estimated standard deviations for the refined parameter values (Geller, 1961; Rollett, 1965). Hamilton's R factor (R_H) and the goodness-of-fit parameter (GFIT) are also calculated.

The weights w_i, appearing in (3), were taken directly from MMB. These weights had been calculated as follows:

$$w_j = 1/[\sigma^2(I_{oj}) + \sigma^2(I_{cj})], \quad (4)$$

where $\sigma^2(X)$ is the variance for quantity X. The calculation of $\sigma^2(I_{oj})$ has been discussed in detail by McIntyre (1977) and represents the summation of a variety of error sources including counting statistics, population statistics and the thermal diffuse scattering correction. The variance in I_{cj} is due to the uncertainty in the extinction correction and is of the form

$$\sigma^2(I_{cj}) = [\varepsilon(I_{kj} - I_{cj})/100]^2, \quad (5)$$

where ε is the percentage error assigned to the quantity $(1 - y_j)$. MMB used $\varepsilon = 20\%$ since their primary concern was that of characterizing the thermal motion of the atoms and it was evident that the extinction correction being applied was too severe for the most extinguished reflections. The change of emphasis in this study and the improved agreement between theory and experiment as a result of using other models of extinction led us to use $\varepsilon = 10\%$, a change of little or no consequence for all but the lowest-angle reflections. (Refinements of the data aimed at simulating those of MMB will, of course, retain $\varepsilon = 20\%$.)

As well as calculating GFIT for the entire data set, it is calculated in each of several equal intervals in the magnitude of the scattering vector. In this way the correctness of the weighting scheme can be gauged.

The form of the calculated kinematic intensity is

$$I_{kj} = s|F_{kj}|^2 L_j P_j,$$

where F_{kj} is the structure factor, L_j is the Lorentz factor and P_j is the polarization factor (for the jth observation). The square of the scattering amplitude, $|F_{kj}|^2 = F^*_{kj}F_{kj}$, is calculated using equations (3) of MMB, neglecting terms higher than first order in the antisymmetric components of the temperature factor and using the effective anharmonic temperature factor (in terms of β'). The antisymmetric components of the atomic scattering factor (bonding effects) are also neglected. These approximations, made in calculating $|F_{kj}|^2$, are those made by MMB originally and their effect on the low-angle reflections [with the exception of the weak 200, 222 and 22$\bar{2}$ reflections, which are affected by bonding (Moss, 1977)] is negligible.

No attempt will be made in this paper to allow for the possible anisotropic nature of extinction.

Discussion and results

The values of the refined parameters obtained by MMB (*Refinement* 1) are listed, for convenience, in Table 1 (column *A*) together with the values obtained by simulating that refinement with our program (column *B*) (we ignore, for the moment, the last three columns). The values of R_H and GFIT, and the extinction factors for three selected reflections are also included in Table 1. These two sets of results are almost identical and if $\mu_0 = 357{\cdot}7$ cm^{-1} had been used the value of r^* would

Table 1. *Values of parameters, and extinction factors for three selected reflections, for different extinction models*

The models are based on: *A* equation (1); *B* equation (1); *C* equation (8); *D* equation (8) with allowance for the presence of the Borrmann effect; *E* kinematic. The results in column *A* are from MMB, the results in column *B* are from a simulation of that original refinement.

	A	*B*	*C*	*D*	*E*
B_{Zn} (Å^2)	1·021 (4)	1·021 (4)	1·025 (4)	1·026 (4)	1·000 (6)
B_{Se} (Å^2)	0·743 (6)	0·743 (6)	0·758 (6)	0·759 (6)	0·695 (6)
β' ($\times 10^{-19}$ J Å^{-3})	−5·6 (9)	−5·7 (8)	−5·3 (7)	−5·2 (7)	−7·7 (1·5)
s	118·2 (1·2)	118·3 (1·3)	122·3 (1·4)	122·8 (1·5)	107·6 (9)
r (μm)	—	—	0·96 (11)	1·15 (14)	—
r^* (μm)	0·51 (7)	0·49 (7)	—	—	—
R_H (%)	2·81	2·80	2·63	2·64	4·24
GFIT	1·32	1·34	1·28	1·29	2·16
y(111)	0·458	0·455	0·618	0·609	1·000
y(400)	0·649	0·646	0·656	0·663	1·000
y(533)	0·933	0·932	0·906	0·901	1·000

be 0·52 (8) μm. A simulation of MMB's *Refinement* 2 also produced nearly identical results.

Becker & Coppens (1974*a*,*b*) have shown that a sin 2θ factor (θ being the Bragg angle) has been omitted from the expression for the diffraction cross section in a perfect crystallite given by Zachariasen (1967). The main consequence of this additional angle dependence is that the differentiation between type I and type II crystals (Zachariasen, 1967) becomes less distinct for severe extinction. The two crystal 'types' represent limiting cases of (1):

$$\text{type I: } r/(\lambda g) \gg 1 \rightarrow r^* = \lambda g, \tag{6}$$

$$\text{type II: } r/(\lambda g) \ll 1 \rightarrow r^* = r. \tag{7}$$

When the sin 2θ factor is included in (1), by replacing r by $r \sin 2\theta$, (6) remains unchanged (provided that sin 2θ is not too small) and (7) becomes

$$\text{type II: } r/(\lambda g) \ll 1 \rightarrow r^* = r \sin 2\theta. \tag{8}$$

If $r/(\lambda g) \gg 1$ but sin 2θ is sufficiently small then $r \sin 2\theta/(\lambda g) \sim 1$, with r^* depending on both r and g, and if sin 2θ is very small the crystal may even be classified as type II. The authors are not aware of any studies with extended-face crystals where the sin 2θ factor has been included in the extinction model [with the exception of Stevenson & Barnea (1983) – hereafter referred to as SB], making its inclusion of particular interest.†

When primary extinction effects are important Zachariasen (1967) predicts that r^* should be replaced by

$$r_p^* = r^* + 3r[r - r^*]/(2\bar{T}). \tag{9}$$

To include the sin 2θ factor in (9) the expression for r^* given by (1) is altered as before and the r within the square brackets is replaced by $r \sin 2\theta$. It should be noted that if the crystal is of type II (7) and (9) imply $r_p^* = r^* = r$ and (8) and the analogue of (9), obtained when the sin 2θ factor is included, imply $r_p^* = r^* = r \sin 2\theta$, even when primary extinction effects are significant (Pryor & Sanger, 1970; Cooper & Rouse, 1976).

From the point of view of least-squares refinement there is no difference in our case between (1), (6), (7) and (9) because the data were collected at a single wavelength and so only the effective extinction parameter (r^* or r_p^*) can be refined, *i.e.* the differences lie in the interpretation of the refined value of the effective extinction parameter. For example, if the ZnSe specimen in question is of type I the interpretation of the value of r^* given in column B of Table 1 [according to (6)] is that $g = r^*/\lambda = 6{\cdot}9\ (1{\cdot}0)$ mrad^{-1}, but if the crystal is of type II then (7) implies $r = r^* = 0{\cdot}49\ (7)$ μm.

† It should be pointed out that the secondary extinction models of Becker & Coppens (1974*a*,*b*, 1975) are themselves not applicable to the special geometric conditions of extended-face crystals.

The extinction models which were investigated include: (i) using (1) with the inclusion of the sin 2θ factor; (ii) using (8); (iii) using (9) with the inclusion of the sin 2θ factor. The use of (ii) requires the refinement of r alone, whereas the use of (i) or (iii) requires the refinement of both r and g. The refinement of r and g for data collected at a single wavelength is possible because the inclusion of the sin 2θ factor in (1) and (9) makes these expressions, in general, different for different reflections.

Testing these three models of extinction we found that (ii) produced the best agreement between theory and experiment, as reflected by the values of R_H. The refinement using (i) produced a large value for g, indicating that $r \ll \lambda g$ and thereby advocating the use of (ii). The refinement using (iii) proved to be unsuccessful in that the refined values of r and g were unrealistic and had very large estimated standard deviations. The details from the refinement using (ii) are given in Table 1 (column C). We see that the refined values of B_{Zn} and β' have not changed significantly, while the value of B_{Se} has changed by approximately two standard deviations, mainly due to its interaction with s and r (for which the correlation coefficients are 0·95 and 0·79 respectively). The change in s is attributed to its interaction with r (Lander & Mueller, 1970; Stevens & Coppens, 1975), for which the correlation coefficient is 0·88 (as well as the interaction with B_{Se}). [MMB demonstrated the reliability of their values of the thermal parameters, whose determination relies primarily on the refinement of the high-angle data, by removing from the refinement those reflections for which the reduction in the kinematic intensity due to extinction had been predicted (Zachariasen, 1967) to exceed 2%. The three reflections most affected by bonding (Moss, 1977) were also excluded and no corrections for extinction were made. The resulting values of the thermal parameters were all well within the estimated standard deviations of the values from the full refinement.]

The ratio of the values of R_H in columns B and C is 1·067 and corresponds to a rejection of the hypothesis that the original model of extinction [using (1)] should be used in preference to (ii), at the 0·5% significance level (Hamilton, 1965), which is 'highly significant' (Hamilton, 1964). The value of GFIT shows slight improvement, the optimum value being unity. The most severely extinguished reflection (111) now has an extinction factor which represents a 38% reduction of the kinematic intensity rather than the original 54% reduction. The values of GFIT, when calculated for six equal intervals in sin θ/λ, vary from 1·10 to 1·67, indicating the suitability of the weighting scheme.

The next model of extinction to be tested was the same as (ii), but allowance was also made for the presence of the Borrmann effect (Borrmann, 1941; Zachariasen, 1968*a*,*b*). This inclusion was prompted by

the results of a recent wavelength-dependent study of Bijvoet ratios in the same crystal (SB). SB showed that allowance for the Borrmann effect considerably reduced the discrepancy between observed and calculated Bijvoet ratios between the K-absorption edges of Se (0·9798 Å) and Zn (1·283 Å). The Borrmann effect is not expected to be as prominent for the data under consideration here because μ_0 is smaller for Mo $K\alpha$ radiation and the large Bijvoet ratios observed by SB between the absorption edges, due to large differences between the values of the imaginary dispersion corrections, made their effect more conspicuous. However, this crystal seems to meet the requirements stated by Zachariasen (1968*a*) for the Borrmann effect to be significant (strong reflections; type II crystal; $r \gtrsim 1$ μm; $\mu_0 \bar{T} \geq 1$).

For a description of the extinction model with allowance for the presence of the Borrmann effect the reader is referred to Zachariasen (1968*a*) and SB, the latter describing how to modify Zachariasen's original model to allow for the noncentrosymmetric nature of ZnSe. The sin 2θ factor omitted by Zachariasen (1967) is included by using (8). A minor point of interest is that the inclusion of cubic anharmonic effects in the structure-factor expressions required for the extinction-factor calculations cannot be made in terms of the effective cubic anharmonic temperature parameter mentioned earlier, because of the form of these structure-factor expressions (they depend on F_{kj} rather than $F^*_{kj} F_{kj}$). Thus, to achieve this use was made of an approximation suggested by Moss, McMullan & Koetzle (1980), namely

$$\beta_{\mathrm{Zn}} = -\beta_{\mathrm{Se}}, \qquad (10)$$

in the notation of MMB. Equation (10) is used only for the extinction-factor calculations and results in β' being of a simpler form, suitable for our needs.

The details from this refinement are given in Table 1 (column D). Comparison of columns C and D in Table 1 shows that only the refined value of r has changed appreciably, by approximately two standard deviations. The ratio of the values of R_H in columns D and C is 1·005 and implies that the hypothesis that the model of extinction with the inclusion of the Borrmann effect should be used in preference to the model without it cannot be rejected at the 25% significance level (Hamilton, 1965) and rejection at a level greater than 5% is 'not significant' (Hamilton, 1964).

The authors believe that the reason why the introduction of the Borrmann effect in this analysis has not resulted in any improvement in the agreement between theory and experiment is most aptly given by Dawson (1975): 'Zachariasen's successful treatment of the situation posed by his CaF_2 specimen is an important demonstration of the basic power of his new extinction formalism. It can be argued, however, that there is a sufficient similarity between the forms of $y_B(\mathbf{S})$ and $y_0(\mathbf{S})$ for explicit consideration of the Borrmann modification to be warranted only if dual values of r_i^* are being sought so as to derive reliable estimates of $\bar{r}$ and η for the specimen at hand. And that for a single wavelength study where extinction treatment of intensity is the only aim, and where conditions conducive to strong Borrmann effects are consciously avoided, then any minor onset of such effects can be neglected through the capacity of $y_0(\mathbf{S})$ to simulate $y_B(\mathbf{S})$ in terms of a slightly erroneous value of r^*.' By way of explanation: Zachariasen (1968*b*) reports on the testing of his theory of extinction with allowance for the Borrmann effect (Zachariasen, 1968*a*) for a small sphere of CaF_2; $y_B(\mathbf{S})$ and $y_0(\mathbf{S})$ represent the extinction factor with and without allowance for the presence of the Borrmann effect, respectively, with $\mathbf{S}$ being the scattering vector; the subscript on r_i^* distinguishes between values of r^* obtained at different wavelengths; $\bar{r}$ and η represent r and σ_w [see (2)], respectively. The ability of the extinction model used for column C of Table 1 to simulate the model used for column D is evident from the results. The Borrmann effect causes an apparent reduction of extinction and so the slightly erroneous value of r in column C is, as expected, lower than the value in column D (by approximately 17%) [*cf.*the results for the CaF_2 sphere, where $r^*_{\mathrm{Mo}} = 2{\cdot}2$ and $r^*_{\mathrm{Cu}} \simeq 1{\cdot}0$ μm using $y_0(\mathbf{S})$, and $r^*_{\mathrm{Mo}} = 2{\cdot}5$ and $r^*_{\mathrm{Cu}} = 3{\cdot}0$ μm using $y_B(\mathbf{S})$, so that the requirement $r^*_{\mathrm{Cu}} \geq r^*_{\mathrm{Mo}}$ is satisfied (Zachariasen, 1968*b*; Dawson, 1975)].

Whereas the analysis of the single-wavelength data of MMB can be carried out quite satisfactorily without making allowance for the Borrmann effect, the multi-wavelength data of SB revealed the necessity of including it in the extinction model. A similar observation was made by Zachariasen (1968*b*) for his CaF_2 data, collected with Mo $K\alpha$ and Cu $K\alpha$ radiation. As emphasized by Cooper, Rouse & Fuess (1973), there is a 'danger associated with the derivation of r and g values from data obtained at two wavelengths only'. The uncertainty in these values, which are not indicated in Zachariasen's various analyses using Mo $K\alpha$ and Cu $K\alpha$ radiation [summarized by Zachariasen (1969)], may be quite significant (Cooper & Rouse, 1976). It is for these reasons that we advocate the use of multiwavelength studies to characterize the extinction effects of a given crystal specimen, and in so doing test the extinction theory.

The value of r obtained by SB using the same model as that for column D in Table 1 was 0·46 (13) μm [*cf.* 1·1 (1) μm in the present study]. SB list values of r and g obtained for various crystals, showing that these values of r are quite typical.

The last column in Table 1 (E) lists the results in the absence of any extinction correction (kinematic case), to demonstrate the importance of this correction. Since $I_{kj} = I_{cj}$ for all the data, $\sigma^2(I_{cj}) = 0$ and w_j depends only on $\sigma^2(I_{oj})$ [see (4) and (5)]. All four refined parameter

Table 2. *The observed intensity (I_{oi}) and the calculated intensities (I_{ci}) corresponding to columns B, C, D and E in Table 1, for those reflections where there is more than 10% extinction, as calculated for C*

$h\,k\,l$	I_{oi}	$I_{ci}(B)$	$I_{ci}(C)$	$I_{ci}(D)$	$I_{ci}(E)$
1 1 1	8979884	5845374	8206695	8105040	11700607
1 1 $\bar{1}$	8715469	5689996	7957190	7869115	11191343
2 2 0	7365934	5126443	6074961	6227024	9491132
3 1 1	2610770	2490350	2719421	2694131	3285178
3 1 $\bar{1}$	2710633	2592645	2835589	2804721	3469499
4 0 0	3225753	2977248	3118710	3160372	4229746
3 3 1	1510830	1494911	1533794	1521319	1723243
3 3 $\bar{1}$	1416589	1426681	1464012	1454181	1627992
4 2 2	1856639	1892509	1892197	1909141	2330396
4 2 $\bar{2}$	1845555	1892401	1892093	1909040	2330207
3 3 3	915284	890853	895346	891657	946530
3 3 $\bar{3}$	954510	936620	940412	935443	1002172
5 1 1	951534	932689	936610	931467	996873
5 1 $\bar{1}$	887003	886870	891486	887630	941231
4 4 0	1174704	1251328	1229618	1238432	1414786
5 3 1	584580	578793	578179	576716	590624
5 3 $\bar{1}$	615703	610349	608900	606783	625954
6 2 0	840865	850187	831601	836720	911946
4 4 4	593593	591213	578749	581807	613596
4 4 $\bar{4}$	587805	591042	578590	581651	613380
6 4 2	413086	419965	412269	414092	426888
6 4 $\bar{2}$	411937	419866	412177	414002	426768

values have changed significantly and both R_H and GFIT have increased dramatically.

Table 2 gives the observed intensity (I_{oi}) and the calculated intensities (I_{ci}) corresponding to columns *B*, *C*, *D* and *E* in Table 1, for those reflections where there is more than 10% extinction, as calculated using model (ii). Comparisons of the observed intensities and the calculated intensities in columns $I_{ci}(C)$ and $I_{ci}(D)$ reveal that a systematic discrepancy between theory and experiment still remains at low angles, but it has been considerably diminished [*cf.* column $I_{ci}(B)$]. The remaining discrepancy is most likely due to inherent limitations of the extinction models tested (SB).

Conclusions

We have shown that the inclusion, in the extinction-factor expression, of the additional angle dependence predicted by Becker & Coppens (1974*a*,*b*) results in a significant improvement in the agreement of observed and calculated intensities for the most severely extinguished reflections observed with an extended-face crystal. When allowance is made for the presence of the Borrmann effect the accompanying change in the value of R_H is insignificant, but the change in the refined value of r foreshadows the necessity of using this model at other wavelengths, as reported elsewhere (SB).

The conclusions reached by MMB regarding the reliability of their refined thermal parameter values in spite of the presence in the data of moderate to high extinction effects have received further confirmation.

The analysis of MMB's data with various extinction models has been particularly instructive because that data was collected from an extended-face crystal. The advantages of the extended-face-crystal technique (Mair, Prager & Barnea, 1971*a*,*b*) for accurate measurement of integrated intensities render further investigation of the treatment of extinction in such crystals highly desirable.

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