

Absorption and Extinction Corrections: Calculation Methods and Standard Tests

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The results are presented of a series of standard calculations of absorption correction factors, covering a range of recording conditions and absorption coefficients. Similar results are given for extinction correction factors. Errors affecting the analytical method for absorption correction are discussed, with suggestions for their removal.

Cahen & Ibers (1972) point out the need for standardized calculations with which absorption correction programs can be checked, and present a small group of such calculations. However, their examples specify the ray directions and crystal orientations explicitly rather than calculating them from the reflexion indices, and thus leave a major section of a complete program unchecked. In this paper, a more extended series is given, starting from data as it would be presented in a real calculation, with comments on some further aspects of absorption calculations. For the main set (Table 1) a crystal lacking any mor-

phological symmetry is used (*cf.* Cahen & Ibers, 1972) so that errors involving ray reversal or crystal rotation can be discovered. It is also useful to check that equivalent reflexions give identical results, and Table 2 contains a more limited set for a crystal of *mmm* symmetry.

The sequence of calculation is significant at two points. In the description of the crystal, the face planes are defined by their Miller indices and the direction cosines are calculated from these. For diffractometer recording, the crystal position is defined by the direction cosines of the vectors \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* on laboratory-

Table 1. *Irregular crystal*

Unit cell: $a=10.0$, $b=11.0$, $c=12.0$ Å; $\alpha=95.80$, $\beta=101.31$, $\gamma=106.80^\circ$; $\lambda=1.542$ Å.

Crystal definition [Miller indices or direction cosines of the normals on axes a^* , b^* , c^* , and perpendicular distance from origin]

h	k	l	OX	OY	OZ	D (arbitrary units)
1	0	0	1.0	0	0	1.0
0	1	1	0.3644	0.7150	0.5967	1.5
0	-2	1	-0.2057	-0.8829	0.4216	0.5
-3	0	1	-0.9637	0.0270	0.2658	0.3
1	1	-4	0.1645	0.1676	-0.9720	1.3

Transmission factors ($\times 10^4$)

μ (units as D)			1.0	0.15	0.01	1.0	1.0	1.0	1.0	1.0
Method			Equi-inc.	Equi-inc.	Equi-inc.	Equi-inc.	Normal beam	Oscillation 15° inclination	Precession 30° angle	Four-circle diffractometer
Rotation axis			X	X	X	Y	Y	Y	X (precession axis)	*
h	k	l					Upper Side	Lower Side		
0	1	1	2049	7529	9807	3300	3235	3055	2830	3349
0	0	1	2202	7670	9820	3261	3261	2859	2804	3397
0	0	-1	2202	7670	9820	3261	3261	3431	2804	3397
1	2	3	2349	7663	9818	3187	3066	3090	2651	3200
1	2	-3	1874	7409	9796	2735	2661	2678	2473	1680
1	-2	3	1851	7384	9794	3193	3137	2779	3013	2563
1	-2	-3	2095	7598	9813	3020	2819	3355	2957	3358
-1	2	3	2128	7601	9813	3020	2782	2812	Not	3358
-1	2	-3	1905	7389	9793	3192	3137	3304	observable	2658
-1	-2	3	1874	7409	9796	2773	2688	2601	observable	1773
-1	-2	-3	2169	7647	9818	3163	3047	3051	observable	3175

* Diffractometer Recording: $-90 \leq \chi \leq 90$; $\varphi=0.0$ if $\chi=0.0$. Direction cosines (circles at zero)

	to X	to Y	to Z
a^*	0.1000	0.8543	-0.5100
b^*	0.7500	0.5239	0.4038
c^*	0.7219	-0.2025	-0.6616

Table 2. *Regular crystal*

Unit cell: $a=10.0$, $b=11.0$, $c=12.0$ Å; $\alpha=\beta=\gamma=90.0^\circ$; $\lambda=1.542$ Å

Crystal definition

All forms of {111} at a distance of 1.0 from the origin. These have direction cosines: ± 0.6298 ; ± 0.5726 ; ± 0.5249 . Equi-inclination recording; Rotation axis X; $\mu=1.0$

Reflexion	Transmission factor ($\times 10^4$)
$0 \pm 1 \pm 1$	1823
$0 \ 0 \pm 1$	2338
$\pm 1 \pm 2 \pm 3$	2009

fixed right-handed axes with (when all circles are at zero) Z parallel to the φ axis, leaving the crystal on the opposite side to the goniometer head, Y in the direction of the primary beam (leaving the crystal) and X orthogonal to them. The interaxial angles given by these cosines should correspond precisely to those of the specified unit cell, but the direction cosines take precedence.

A further important aspect of many absorption correction programs is the calculation of \bar{T} , the mean path length, required for secondary-extinction correction (Larson, 1970)

$$\bar{T} = \frac{1}{A(\mu)} (T_1 + T_2) \exp[-\mu(T_1 + T_2)d\tau] \quad (1)$$

with $d\tau$ indicating integration over the whole crystal and T_1 and T_2 as the path lengths for a particular ray before and after diffraction, *i.e.* [Zachariasen, 1967, equation (42)]

$$\bar{T} = \frac{-1}{A(\mu)} \frac{dA(\mu)}{d\mu} \quad (2)$$

$A(\mu)$ is the transmission factor for a particular reflexion, and μ is the linear absorption coefficient. For simple transmission through a plane plate or in any other situation where the path length is constant for all rays, it is also true that

$$A(\mu) = \exp(-\bar{T}\mu) \quad (3)$$

$$i.e. \quad \bar{T} = \frac{1}{\mu} \cdot \ln [A(\mu)] \quad (4)$$

However, this relationship does not hold generally, because of the different weighting of the various portions of the path in the crystal. Examples show that \bar{T} is generally systematically smaller than values calculated from equation (4).

The quantity \bar{T} enters into the equations for extinction correction as δ (Larson, 1970)

$$\delta = \left(\frac{e^2}{mc^2V} \right)^2 \cdot \frac{\lambda^3}{\sin 2\theta} \cdot \frac{P_2}{P_1} \cdot \bar{T} \quad (5)$$

where V is the unit-cell volume, P_2 and P_1 are polarization factors ($P_n = 1 + \cos^{2n} 2\theta$ normally) and the other quantities have their usual significance. It is convenient to calculate δ during the absorption-correction calculation, and save it for each reflexion. Some complications arise if crystal-monochromated radiation is being used, when P_n takes on a more complex form. With α as the Bragg angle of the monochromator (assumed ideally mosaic) and β as the dihedral angle ($\geq 90^\circ$) between the plane containing the incident and monochromated beams and the plane containing the monochromated and diffracted beams, then the components of the monochromated beam can be resolved along and across the diffracted beam to give

$$P_n = 0.5 [(\cos \beta + \sin \beta \cos^2 \alpha) + (\sin \beta + \cos \beta \cos^2 \alpha) \cos^{2n} 2\theta] \quad (6)$$

For neutrons, P_n is invariably 1.0.

When data are recorded with a four-circle diffractometer β is invariant: 0 and 90° for parallel and perpendicular geometry respectively. For photographic or two-circle recording β changes from reflexion to reflexion, and has to be calculated for each one. With a laboratory-fixed set of axes defined with Y along the monochromated X-ray beam, leaving the crystal, X along the camera or diffractometer rotation axis (zero

Table 3. *Extinction correction*

			Equi-inclination Crystal 1, Rotation axis X	Diffractom- eter as Table 1		Diffractometer as Table 1 No mono- chromator $\alpha=35^\circ \beta=0^\circ$		
h	k	l	$\mu=1.0$ \bar{T}	$\mu=0.15$ \bar{T}	$\mu=0.01$ \bar{T}	$\mu=1.0$ \bar{T}	$10^6 \delta / \bar{T}$	$10^6 \delta / \bar{T}$
0	1	1	1.235	1.834	1.948	0.987	1781	1777
0	0	1	1.219	1.719	1.810	0.964	2916	2913
0	0	-1	1.219	1.719	1.810	0.964	2916	2913
1	2	3	1.089	1.711	1.835	0.999	577	566
1	2	-3	1.308	1.937	2.056	1.387	749	740
1	-2	3	1.311	1.957	2.078	1.102	749	740
1	-2	-3	1.253	1.780	1.885	0.981	720	711
-1	2	3	1.225	1.755	1.887	0.981	720	711
-1	2	-3	1.261	1.947	2.082	1.069	749	740
-1	-2	3	1.308	1.937	2.056	1.301	749	740
-1	-2	-3	1.229	1.739	1.838	1.017	577	566

inclination) and \mathbf{Z} orthogonal, the geometry can be specified by the angle γ ($0 \leq \gamma \leq 180$) between the \mathbf{X} axis and the normal (\mathbf{N}) to the monochromated beam and the beam incident on the monochromator. \mathbf{N} lies in the \mathbf{XZ} plane and is taken on the same side of the \mathbf{XY} plane as \mathbf{Z} . The angle calculations (Alcock, 1969) for each reflexion produce the direction cosines on the crystal-fixed axes of the incident (\mathbf{I}) and reflected (\mathbf{O}) rays; the direction cosines (\mathbf{R}) of the crystal rotation axis are also known. With Weissenberg geometry, inclination of the rotation axis does not move it out of the \mathbf{XY} plane and so the direction cosines (\mathbf{ZC}) of the laboratory \mathbf{Z} axis on the crystal-fixed axes can be found by

$$\mathbf{ZC} = \mathbf{R} \wedge \mathbf{I}.$$

This is not correct for precession geometry, but it is not likely that the error introduced by using it will be significant for photographic data. Then for the laboratory X axis

$$\mathbf{XC} = \mathbf{ZC} \wedge \mathbf{I}$$

and the direction cosines (\mathbf{N}) for the normal to the plane containing the incident and diffracted beam are given by

$$\mathbf{N} = \mathbf{I} \wedge \mathbf{O}.$$

The required angle β is given by the difference between γ and $\widehat{\mathbf{XC}\mathbf{N}}$. Values to illustrate the calculation of these extinction corrections are given in Table 3.

The calculations described here have been carried out with the program *ABSCOR* (Alcock, 1970) which employs the analytical method for absorption correction (de Meulenaer & Tompa, 1965), with identical results on three different computers, ATLAS, ICL 1906A (both with 48-bit floating-point word length) and IBM 360/75 (using REAL*8, *i.e.* 64-bit floating-point word length – see below). The program has also been checked on the data of Cahen & Ibers, 1972, giving results identical to their 'correct answers'. They report erroneous results with the analytical method in the unacceptably high proportion of 1% of the calculations. However, careful consideration of all such errors has led to a reduction of the error rate to an undetectably small proportion with *ABSCOR*, certainly less than 1 in 10000 reflexions.

The sources of error are threefold: calculation of volume, of transmission and of $dA/d\mu$. For the transmission factor, errors arise from the evaluation of $h(x) = [1 - \exp(-x)]/x$ and related functions (de Meulenaer & Tompa, 1965) when x is small, and can be avoided by using a series expansion if x is smaller than some limit ϵ (Alcock, 1970). Errors in the transmission factor also affect $dA/d\mu$ (which is evaluated by simple numerical differentiation) particularly if μ is small. With the limited accuracy of the 32-bit floating-point word length of the IBM 360, ϵ must be taken as the rather large value of $1 \cdot 10^{-2}$ to avoid the calculation of some negative transmission factors; even then some

values of $dA/d\mu$ are wrong and some transmission factors are inaccurate. The use of 48 or 64-bit real word length removes all these problems.

In the volume calculation† errors arise in two ways, failure to find all the auxiliary points (de Meulenaer & Tompa, 1965), and failure to calculate the volume of individual Howells polyhedra correctly. The first arises because various test criteria for an auxiliary point to be real are of the form

$$0 \leq \alpha \leq 1$$

and the test function α may be systematically equal to 0 or 1 and therefore may fall slightly outside this range by computational inaccuracy. Tolerances of $1 \cdot 10^{-6}$ proved satisfactory for 48-bit floating-point word length. Failures at this point in the program are most likely with high-symmetry crystals in symmetrical orientations.

A more serious and general cause of failure lies in the calculation of the volume of each Howells polyhedron, which is done by subdividing each polyhedron into irregular tetrahedra (de Meulenaer & Tompa, 1965; Alcock, 1970); these tetrahedra are found by starting from one tetrahedron formed from an arbitrarily selected set of four points, and adding other tetrahedra on each face of the original and of the added tetrahedra, until the whole polyhedron is included. Errors arise if the original tetrahedron has a very small volume. This will be negligible in itself, but the volume of a tetrahedron formed by a further point and one face of the original tetrahedron can be large, leading to large (perhaps 50%) errors in the total crystal volume. To accept any tetrahedron, however small, as genuine is not satisfactory, because the volume defined by four coplanar points should be zero, but can be increased by rounding errors.

The resolution of this problem involves an addition to the original program of de Meulenaer and Tompa. After the selection of those auxiliary points which are vertices of the particular Howells polyhedron being considered, their coordinates are checked to remove any points which are essentially identical to others in the list (whether true or accidental coincidences). This also has the advantage of speeding up the volume calculations. Two points are considered identical if none of their coordinates differ by more than δ , which is chosen partly to cover the spread given to the coordinates of identical points by rounding errors and partly for reasons given below. For 48-bit precision $\delta = 1 \cdot 10^{-5}$ was satisfactory. Then, the volume (ξ) of the smallest tetrahedron which is accepted as genuine is set to be rather larger than that for four points which just fail to coincide. This volume must also be larger than the volume of a tetrahedron formed by four coplanar points which have random computational errors in their coordinates. It may be necessary to in-

† All crystals are normalized so that their largest coordinate is set to 1.0.

crease δ so that the minimum volume which is likely to be calculated exceeds this maximum erroneous volume. A value of $\xi = 1 \cdot 10^{-9}$ was satisfactory for 48-bit word length.

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The Effect of Surface Damage on the Intensity of X-rays Diffracted by Ground Spherical Single Crystals

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Integrated intensities from ground spherical single crystals of silicon, zinc sulphide, and calcium fluoride before and after etching are compared. The surface damage of the unetched crystals, apparent on scanning electron micrographs, is shown to give rise to a very appreciable enhancement of the X-ray Bragg intensities. A possible explanation for physically unrealistic phenomenological extinction parameters reported in the literature is suggested.

Introduction

The crystalline character of abraded surfaces of flat crystals treated in various ways and the effect of such treatment on the diffracted X-ray intensity has been investigated by Gay & Hirsch (1951).

A recent multi-wavelength investigation of extinction (Prager & Barnea, 1974) has suggested that ground spherical crystals may consist of a rather perfect 'core' surrounded by a less perfect 'skin'. With such a possibility clearly raising important issues for the applicability of Zachariasen's extinction theory, in which the central assumption is one of imperfectional homogeneity of the specimen, we now report on experiments designed to test this speculation.

Experimental procedures and results

Scanning electron micrographs of a single crystal of semiconductor-quality silicon ground to spherical shape with a Bond-type grinder (Bond, 1951), whose grinding surface was impregnated with 800-mesh diamond dust, are shown in Figs. 1 and 2. Figs. 3 and 4 show micrographs of a similarly prepared sphere of silicon after brief etching in a solution consisting of

16 parts of 48% hydrofluoric acid, 44 parts of glacial acetic acid, and 100 parts of fuming nitric acid. To facilitate the microscopy, a thin layer of gold was evaporated onto both crystals. The ground crystals were rinsed vigorously in acetone before the gold was deposited. The micrographs of the unetched crystals reveal considerable surface roughness, fine cracks, and possibly some detached particles. The etched crystals are comparatively smooth; some faceting of the etched surface is apparent.

Integrated intensities of a number of Bragg reflexions of silicon were measured on a manual Picker four-circle diffractometer using nickel-filtered copper $K\alpha$ radiation detected by a scintillation counter. The measurements were carried out in the following sequence. A silicon sphere was ground and then rinsed in acetone; integrated intensities of a number of reflexions were then measured. The crystal was then detached from the glass fibre on which it was mounted, briefly etched, and remounted. The measurements were repeated with the same settings of the X-ray generator and detector electronics.

The integrated intensities of equivalent reflexions differed by no more than 4%. The peak heights of the two measured equivalent reflexions were compared with those of other equivalent reflexions and no discrepancies outside the above limits were observed.

In order to exclude the possibility that the very appreciable decrease in the intensities observed with the etched crystal was due to a peculiar intensity distribu-

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