Let us assume a frequency stability of

$$K_\omega = 10^{-3} .$$

If our top frequency in 50 kHz, and the longest wavelength we detect is 10 Å, we will have $\omega\tau/n \lesssim 794$, and

$$\varepsilon \simeq 0{\cdot}08 .$$

Such a chopper system would be adequately described by equations (9*a*) and (9*b*).

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Absorption and Volume Corrections for a Cylindrical Sample, Larger than the X-ray Beam, Employed in Eulerian Geometry

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A treatment of the absorption and volume corrections for a cylindrical sample, which is larger than the X-ray beam and which is employed in 'Eulerian cradle' geometry, is described. The procedure described here is strictly correct only for a one-dimensional X-ray beam, but it has given satisfactory results for a beam of finite cross section. The calculation is easily done by computer and requires only the radius of the sample, the 2θ and χ values for each reflection, and the zeros of Legendre polynomials and their weights if Gaussian integration is used.

Introduction

Although procedures for absorption corrections have been extended to crystals of arbitrary shape and to diffraction geometries currently in use, most of these treatments assume that the crystal is completely irradiated by the primary X-ray beam (see, for example, Wuensch & Prewitt, 1965). However, Skertchly (1957) has pointed out that in the investigation of metallic and fibrous substances it is often convenient to use a cylindrical specimen having a diameter larger than that of the X-ray beam. He treated the case of a cylindrical specimen irradiated with a fine beam at perpendicular incidence.

A situation arose in our laboratory involving a large cylindrical crystal and 'Eulerian cradle' geometry (Coyle, Schroeder & Ibers, 1970) where the incident beam and the crystal are not necessarily perpendicular. An absorption and volume correction for such a geometry is developed in this paper. The treatment developed is subject to two limitations. A minor restriction is that the axis of the cylindrical crystal be coincident with the φ (polar) axis of the 'Eulerian cradle' (Furnas, 1957). This should be easily achieved in most experimental situations. The second limitation is that our treatment is exact only for a one-dimensional beam. Thus, it is desirable that the ratio of the beam diameter to the diameter of the cylinder be as small as is experimentally feasible.

When a crystal is not totally bathed in an X-ray beam the volume of that crystal seen by the beam is not necessarily constant for various reflections, and the amount of variation depends on the geometry of

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the crystallographic method used. Both the intensity of the reflected radiation, and also its absorption by the sample, are functions of the 'irradiated volume'; the former is a monotonic increasing function since more reflecting planes are encountered, while the transmission due to absorption is monotonic decreasing since the radiation will on the average pass through more crystalline material. Equations (1) may serve to illustrate how the effects combine.

$$\frac{I}{I_0^0} = \frac{I}{I^0} \cdot \frac{I^0}{I_0^0} = \frac{\int_v \exp[-\mu(t_0+t)]\mathrm{d}v'}{\int_v \mathrm{d}v'} \cdot \frac{\int_v \mathrm{d}v'}{\int_{v_0} \mathrm{d}v'}$$

$$= \frac{\int_v \exp[-\mu(t_0+t)]\mathrm{d}v'}{\int_{v_0} \mathrm{d}v'} \quad (1)$$

where

I_0^0 is the intensity corrected for both volume and absorption;
I^0 is the intensity corrected for absorption only;
I is the intensity observed (uncorrected);
μ is the linear absorption coefficient;
t_0 is the length of the incoming beam within the crystal;
t is the length of the diffracted beam within the crystal;
v' is an umbral integration variable;
v is the volume seen by the beam;
v_0 is the standard volume to which correction is made.

I/I^0 is therefore the correction due to the absorption and I^0/I_0^0 that due to the varying volume. The absorption correction, of course, should be carried out over the volume v and not over v_0, and the volume correction represents a change in the normalization quotient from v to v_0. Thus the volume correction should be applied to I^0 and not to I, and the absorption correction to I and not to I^0* so that the corrections are not simply commutative.

General description of the problem

Fig. 1 shows the 'Eulerian cradle' geometry that we are considering. The axis of the cylindrical crystal is coincident with the φ axis and makes an inclination (Furnas, 1957) angle χ with its projection on the plane of the incident and diffracted beams (represented by the vectors $\mathbf{S}_0$ and $\mathbf{S}$). Both of these beams make the Bragg angle θ with their projections on the plane of the χ circle so that the diffraction vector $\mathbf{S}-\mathbf{S}_0$ is always in the plane of the χ circle as is the axis of the cylinder.† The intersection of the plane $\mathbf{S}_0,\mathbf{S}$ with the cylinder results in an elliptical cross section as shown in Fig. 2. The minor axis of the ellipse is simply the diameter of the cylinder because the axis of the χ circle is coincident with this diameter (since the cylinder axis and the φ axis are coincident). The length of the major axis is equal to $2R/\cos\chi$ (R is radius of the crystal). Fig. 2 shows the direction of the incident beam which always makes the Bragg angle with the minor axis of the ellipse.

Volume correction

Fig. 1 shows that the volume of crystal available for diffraction (shown by dotted lines) varies with the angle between the crystal axis (φ axis) and the direction of the incident beam. The angle between the cylinder axis and the incident beam is denoted by α in Fig. 1. It is convenient to follow Parkes & Hughes (1963) and write the volume of crystal seen by the X-ray beam as $v=v_0/\sin\alpha$, where v_0 is the minimum volume corresponding to perpendicular incidence. This is the standard volume to which the correction will be made.

† In the case of a four-circle diffractometer, this treatment is applicable to reflections measured in the θ–2θ (bisecting) mode.

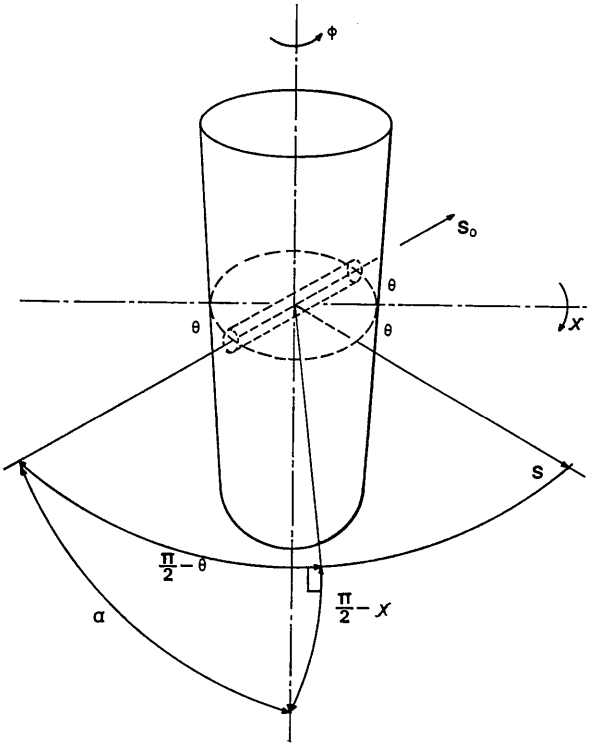

Fig. 1. The experimental arrangement for 'Eulerian cradle' geometry. The axis of the cylindrical crystal is coincident with the φ axis. The vectors $\mathbf{S}_0$ and $\mathbf{S}$ represent the incident and diffracted beams.

* Otherwise I/I_0, the volume correction, is equal to

$$\int_v \exp[-\mu(t_0+t)]\mathrm{d}v' \Big/ \int_{v_0} \exp[-\mu(t_0+t)]\mathrm{d}v' .$$

$\cos\alpha=\sin\theta\sin\chi$ by spherical trigonometry according to our convention for the sense of angle χ. Then $\sin\alpha=(1-\cos^2\alpha)^{1/2}=(1-\sin^2\theta\sin^2\chi)^{1/2}$ and the volume correction ratio I^0/I_0^0 is thus simply equal to $(1-\sin^2\theta\sin^2\chi)^{-1/2}$.

Absorption correction

In Fig. 2, NON' is the incoming beam. Diffraction occurs from a volume element dv (denoted by P) and the diffracted beam meets the crystal surface at Q. By taking $dv=\pi r^2\,dz$ (where z is in the direction of the incident beam whose radius is r) we replace the usual form for the correction

$$\frac{I}{I^0}=\frac{1}{v}\int_v \exp\left[-\mu(t_0+t)\right]dv' \tag{2}$$

by a single integration over line elements dz:

$$\frac{I}{I^0}=\frac{1}{2\varrho}\int_0^{2\varrho}\exp\left[-\mu(t_0(z)+t(z)\right]dz\,, \tag{3}$$

where $t_0(z)=NP$ and $t(z)=PQ$ as denoted in Fig. 2.

Then the path length t_0 is just the value of integration variable z and all that remains is to calculate the path t as a function of z. The incoming elliptic radius ϱ can be calculated from the equation of the ellipse. Choosing x along the minor axis and y along the major, the equation of the ellipse becomes $x^2+y^2\cos^2\chi=R^2$ and since the point $(\varrho\cos\theta,\ \varrho\sin\theta)$ lies on this curve, then

$$\varrho=R(1-\sin^2\theta\sin^2\chi)^{-1/2} \tag{4}$$

The outgoing elliptical radius σ can be calculated in a similar manner, as follows.

Let ψ be the angle between OQ and the minor axis, and since $OP=\varrho-z$, then

$$\sigma=R/(1-\sin^2\psi\sin^2\chi)^{1/2}$$

and from the triangle OPQ,

$$\sigma/\sin 2\theta=(\varrho-z)/\sin(\psi-\theta)\,.$$

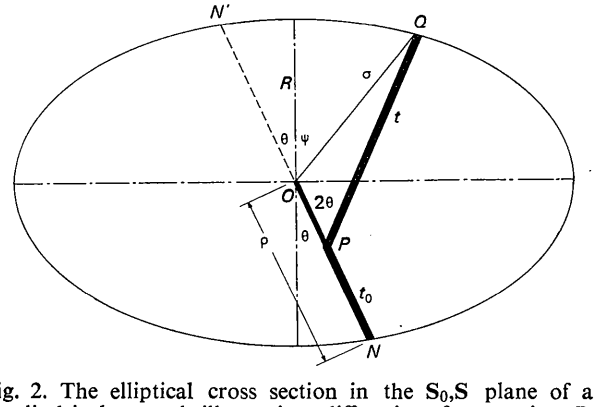

Fig. 2. The elliptical cross section in the S_0,S plane of a cylindrical crystal illustrating diffraction from point P.

ψ may be eliminated from these two equations to give a quadratic in σ^2:

$$A\sigma^4+B\sigma^2+C=0\,, \tag{5}$$

where

$$A=(1-\sin^2\theta\sin^2\chi)^2,$$

$$B=-2R^2(1-\sin^2\theta\sin^2\chi)$$
$$-2(\cos^2\theta-\sin^2\theta\cos^2\chi)\cdot\sin^2 2\theta\sin^2\chi\,(\varrho-z)^2,$$

$$C=R^4+\sin^4 2\theta\sin^4\chi\,(\varrho-z)^4$$
$$+2R^2\sin^2 2\theta\sin^2\chi\,(\varrho-z)^2\cos 2\theta\,.$$

One can show that the discriminant $B^2-4AC\geq 0$ provided the following equation holds for the ranges of z, θ and χ relevant to the physical problem

$$\left|\frac{\varrho-z}{\varrho}\right|\leq\frac{1-\sin^2\theta\sin^2\chi}{\sin 2\theta\cos\chi}\,. \tag{6}$$

The right-hand side of equation (6) has a minimum value of 1 when $\cos\chi=\pm\cot\theta$, which can only occur when $\theta\geq\pi/4$, *i.e.* for back scattering. Since the range of z is $0\leq z\leq 2\varrho$, the left-hand side of equation (6) is always ≤ 1 and thus equation (6) always holds. It is easy to show that the roots of equation (5), in addition to being real, are always positive. Since A and C are always positive and B is always negative, a root could only be negative if $|B|<\sqrt{B^2-4AC}$ or $B^2<B^2-4AC$. However, $B^2\geq B^2-4AC$ because AC is always non-negative. Thus the roots of equation (5) are real and positive as they must be since they represent values of σ^2. The larger root corresponds to values of $z<\varrho$ and the smaller to $z>\varrho$.

Several special cases are of at least academic interest:

(*a*) When $z=\varrho$, reflection occurs from the origin; the discriminant vanishes, the roots of the quadratic in σ^2 are equal and $\sigma=\varrho=\dfrac{R}{(1-\sin^2\theta\sin^2\chi)^{1/2}}$.

(*b*) When $\chi=0$, the ellipse becomes a circle, $A=1$, $B=-2R^2$, $C=R^4$; the discriminant vanishes, the roots of the quadratic in σ^2 are equal and $\sigma=R$.

(*c*) When $\chi=\pm\pi/2$, the ellipse becomes a pair of parallel lines; then the path length $t=2\varrho-z$, and the path length between the parallel lines is $z+t=2\varrho$, which is independent of z.

t is subsequently obtained from the triangle formula

$$t^2-2t(\varrho-z)\cos 2\theta+(\varrho-z)^2-\sigma^2=0\,. \tag{7}$$

One root of this equation is always negative, so the positive root is chosen as the physically plausible solution. The equation above may be compared to that of Skertchly, who treated the special case of a circular cross section. The transmission factor for absorption is therefore

$$\frac{I}{I^0} = \int_0^{2\varrho} \exp\{-\mu[z+t(z)]\}\mathrm{d}z \Big/ \int_0^{2\varrho} \mathrm{d}z \qquad (8)$$

and that for the combined absorption and volume is

$$\frac{I}{I^0} = \int_0^{2\varrho} \exp\{-\mu[z+t(z)]\}\mathrm{d}z \Big/ \int_0^{2R} \mathrm{d}z\,. \qquad (9)$$

Discussion

Our treatment is an extension of that presented by Skertchly (1957) and as such is exact only for a one-dimensional beam. When diffraction occurs from a volume element $\pi r^2 \mathrm{d}z$ (r is the radius of the beam) instead of the line element dz, as in the treatment of the one-dimensional beam, the sum (t_0+t) is no longer constant for all points within this volume element. Thus, a one-dimensional integration does not give the true value for the transmission factor.

Skertchly stated that his equation gave the path length associated with each volume element fairly accurately when the ratio of the radius of the cylindrical sample (R) to the radius of the beam (r) is ≥ 5. Under these conditions the sum (t_0+t) for some points within a given volume element may vary by 10% (those cases where the diffracted beam occurs at 2θ angles $>75°$) from that obtained from Skertchly's treatment. However, the mean value of (t_0+t) for points within the volume element (the average over the cross section of the beam) is within 2% of that obtained from Skertchly's equation. Since $|\Delta e^{-\mu t}|/e^{-\mu t} = \mu\Delta t$, we see that the variation in the transmission factor for a given volume element becomes more serious when μ is larger. Similar conclusions are drawn from our treatment.

Since our absorption correction is approximate it is appropriate to mention the experimental conditions under which it is most accurate. Our treatment is most applicable to experiments involving a finely collimated X-ray beam of small radius that is irradiating a large cylindrical sample. These conditions make the R/r ratio large thus reducing the error in the path length for a given volume element. The fine collimation is desirable because our correction assumes that the intensity is constant throughout the portion of the sample that is being irradiated. Since the sample is larger than the diameter of the collimator (or the umbra region of irradiation by the X-ray beam) it is desirable to make the penumbra region of irradiation as small as possible because the incident intensity is lower than in the umbra.

We have applied our absorption correction to some data collected on a cylindrical crystal of $K(H_4F_5)$ that was surrounded by a concentric Kel-F (polychlorotrifluoroethylene) tube (see Appendix for details). The values of the linear absorption coefficient, μ, for the crystal and tube are 10·17 and 9·87 cm^{-1}, respectively. The outer radius of this assembly was 0·17 cm so μR was about 1·7. This case is less favorable because the radius of the sample was only 2·2 times that of the X-ray beam compared with the factor of five that Skertchly suggested. The variation in (t_0+t) from the mean value of (t_0+t) for a given volume element may approach 15% for some angles of diffraction. Also, in order not to lose diffracted intensity, we did not use the finest collimation available to us. Our collimator angle was about 40 minutes.

The crystallographic agreement factors

$$R_1 = \sum||F_{\mathrm{obs}}| - |F_{\mathrm{calc}}||/\sum|F_{\mathrm{obs}}|$$

and

$$R_2 = [\sum w(F_{\mathrm{obs}} - F_{\mathrm{calc}})^2/\sum w(F_{\mathrm{obs}})^2]^{1/2}$$

were 0·088 and 0·134 for the refinement of the $K(H_4F_5)$ structure before the absorption correction. Our absorption correction yielded transmission factors in the range 0·028 to 0·036.* Identical refinement of the corrected data yielded values for R_1 and R_2 of 0·068 and 0·082, respectively, which is a considerable improvement. Our experience, although limited to this particular case, indicates that the absorption correction presented here is capable of yielding useful results.

The correction is simple to apply in practice. It requires only the 2θ and χ values for each observation in addition to the sample radius and the absorption coefficient. If Gaussian integration is used then the zeros of the Legendre Polynomials and their weights are also required.

APPENDIX

Treatment of the case where a cylindrical crystal is enclosed in a concentric tube; use of the Gaussian quadrature

An extension of our previous theory was used to treat data obtained from a crystal of $K(H_4F_5)$ of radius R_1 which was enclosed in a concentric Kel-F tube of

* These numbers are not transmission factors in the usual sense since they include our correction due to the varying volume.

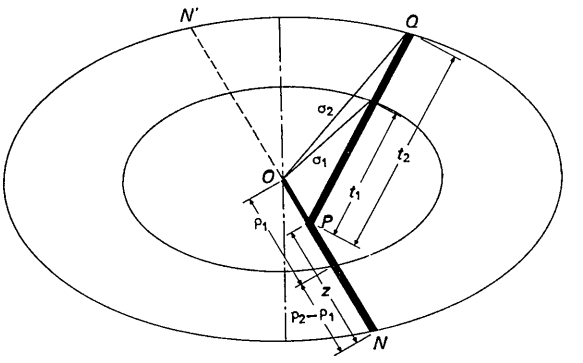

Fig. 3. Elliptical section in the S_0,S plane, showing diffraction from P in the large cylindrical crystal enclosed in a cylindrical tube. The incident beam is along NON' and the diffracted beam along PQ.

radius R_2. This extension allows for the fact that the linear absorption coefficient of the tube is likely to be different from that of the crystal and that while both media absorb the radiation, only the enclosed medium diffracts. Fig. 3 shows the cross section of the crystal and tube in the S, S_0 plane. The ellipses are concentric, and have the same eccentricity, $\sin\chi$.

In the following equations subscript 1 refers to the crystal and subscript 2 refers to the tube. ϱ_1, ϱ_2, σ_1 and σ_2 can all be calculated from equations (4) and (5) as given in the main text using both R_1 and R_2.

For any given value of z, where $\varrho_2-\varrho_1\le z\le\varrho_2+\varrho_1$, t_1 and t_2 can be computed from equation (7), using the corresponding σ_1 and σ_2 values. The absorption correction becomes

$$\frac{I}{I^0}=\int_{\varrho_2-\varrho_1}^{\varrho_2+\varrho_1}\exp\{-\mu_1(z+t_1-\varrho_2+\varrho_1)-\mu_2(\varrho_2-\varrho_1+t_2-t_1)\}\mathrm{d}z\Big/\int_{\varrho_2-\varrho_1}^{\varrho_2+\varrho_1}\mathrm{d}z \quad \text{(A1)}$$

and the correction for absorption and volume becomes

$$\frac{I}{I_0^0}=\frac{\int_{\varrho_2-\varrho_1}^{\varrho_2+\varrho_1}\exp\{-\mu_1(z+t_1-\varrho_2+\varrho_1)-\mu_2(\varrho_2-\varrho_1+t_2-t_1)\}\mathrm{d}z}{\int_{R_2-R_1}^{R_2+R_1}\mathrm{d}z}. \quad \text{(A2)}$$

The integral (A2) may be computed using any of the standard numerical methods. The most efficient of these (though not always the easiest to apply), *viz.* Gaussian quadrature, is briefly outlined as follows. The theory of Gaussian quadrature itself is given in several texts (Conte, 1965; Hartree, 1958).

The integral may be replaced by a weighted sum of the values of the function at the N zeros of the Legendre polynomial of degree N in the interval $[-1, +1]$. These zeros x_i and their corresqonding weights w_i are readily available (Abramowitz & Stegun, 1964). The linear transformation

$$z_i=(r_1 x_i+r_2)(1-\sin^2\theta\sin^2\chi)^{-1/2}: i=1\ldots N$$
$$=\varrho_1 x_i+\varrho_2 \quad \text{(A3)}$$

converts the Gaussian variable x into the beam coordinate z for each i of the N summation points.

Then the transmission expression for the combined absorption and volume correction becomes

$$\frac{I}{I_0^0}=\frac{\int_{\varrho_2-\varrho_1}^{\varrho_2+\varrho_1}\exp\{-\mu_1(z+t_1-\varrho_2+\varrho_1)-\mu_2(\varrho_2-\varrho_1+t_2-t_1)\}\mathrm{d}z}{2R_1} \quad \text{(A4)}$$

$$=\frac{\varrho_1}{2R_1}\int_{-1}^{+1}\exp\{-\mu_1(\varrho_1 x+\varrho_1+t_1)-\mu_2(\varrho_2-\varrho_1+t_2-t_1)\}\mathrm{d}x$$
$$=\tfrac{1}{2}(1-\sin^2\theta\sin^2\chi)^{-1/2}\sum_{i=1}^{N}w_i\exp\{-\mu_1(\varrho_1 x_i+\varrho_1+t_1)-\mu_2(\varrho_2-\varrho_1+t_2-t_1)\} \quad \text{(A5)}$$

where t_1 and t_2 are calculated as functions of the Gaussian variable x_i by using the linear transformation given by equation (A3). These equations are identical with equation (A2) above. This treatment can be used to solve the simpler case of the exposed crystal where $\mu_2=0$, $R_2=R_1$, $\varrho_2=\varrho_1$, and equations (A1) and (A2) reduce to equations (8) and (9). We used twenty Gaussian points to evaluate equation (A5) and processed 245 reflections in 60 seconds of CDC 6400 computer time.

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