

So we have experimental values for F_o^2 . We know that we can calculate (if we know the atom positions) the structure factors from

$$F(hkl) = \sum \{f_i \cos[2\pi (hx_i + ky_i + lz_i)] + i \sin[\dots]\}$$

What are the units of F_o^2 ?

What are the units of $F_{(hkl)}$?

(i.e. the calculated structure factor F_c)

What are the units of F_c^2 ?

How do we scale our observations into what we need?

**Data processing:
generation of F values
for structure solution**

$$F(hkl) = \sum \{f_i \cos[2\pi (hx_i + ky_i + lz_i)] + i \sin[\dots]\}$$

$$F(\bar{h}\bar{k}\bar{l}) = \sum \{f_i \cos[-2\pi (hx_i + ky_i + lz_i)] + i \sin[-\dots]\}$$

**Now look at F_c^2 as the product of F_c with F_c^*
(i.e. $F(h,k,l)$ and $F(-h,-k,-l)$)**

For x between 0 and 1

What is the sum of $\sin(2\pi hx)$ for $h= 0$ to infinity ?

What is the sum of $\cos(2\pi hx)$ for $h= 0$ to infinity?

$$\begin{aligned}
&= \left(\sum_i f_i e^{i2\pi(hx_i + ky_i + lz_i)} \right) \left(\sum_j f_j e^{-i2\pi(hx_j + ky_j + lz_j)} \right) \\
&= \sum_i \sum_j f_i f_j e^{i2\pi(h[x_i - x_j] + k[y_i - y_j] + l[z_i - z_j])}.
\end{aligned}$$

$$|F|^2 = \sum_j f_j^2 + \sum_i \sum_{\substack{j \\ i \neq j}} f_i f_j e^{i2\pi(h[x_i - x_j] + k[y_i - y_j] + l[z_i - z_j])}.$$

If either the average or the sum is taken over all hkl , the last term tends to zero since it contains as many positive as negative components, so that

Remember, the average value of any sine or cosine function tends to zero, so the average value of the F^2 in a given $\sin\theta/\lambda$ range is

$$\overline{|F|^2} = \sum_j \overline{f_j^2}.$$

Why 6 at $\sin\theta/\lambda = 0$?
Why ~ 2 at $\sin\theta/\lambda = .4$?

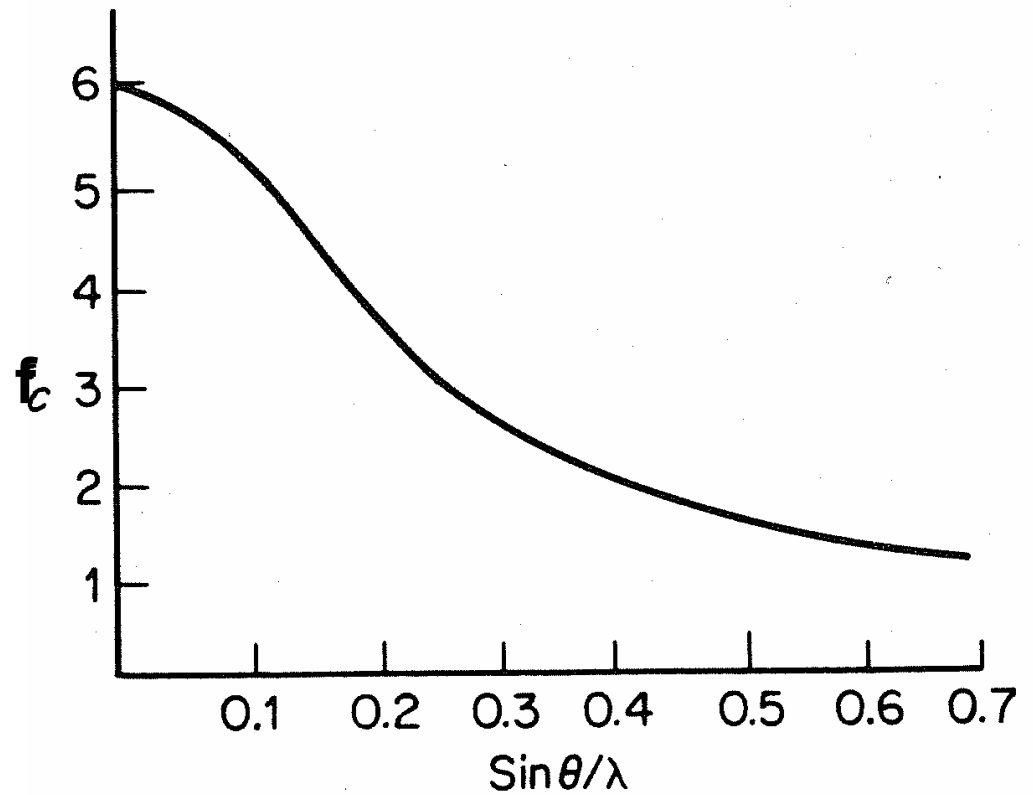


Figure 7.3. Scattering factor of carbon as a function of $(\sin \theta)/\lambda$.

$$e^{-B(\sin^2 \theta)/\lambda^2}$$

$$B = 8\pi^2 \overline{u^2}$$

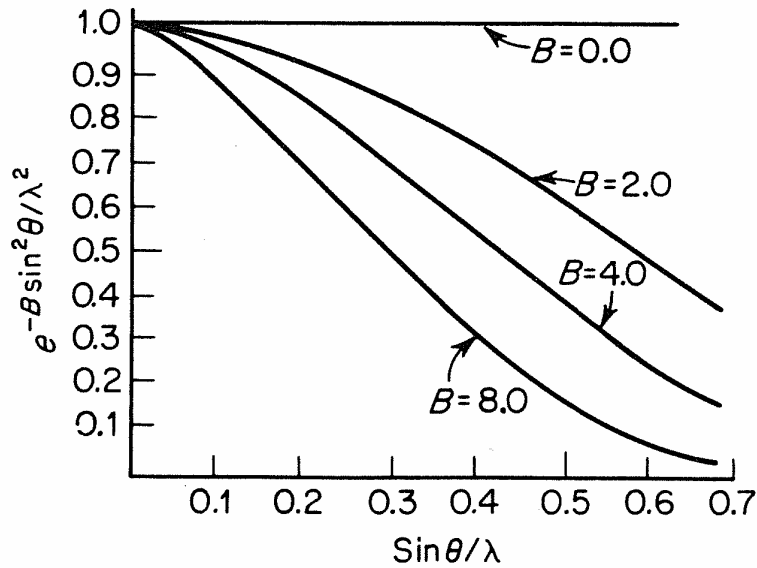


Figure 7.4. Temperature factor $e^{-B(\sin^2 \theta)/\lambda^2}$ as a function of $(\sin \theta)/\lambda$.

$$f = f_0 e^{-B(\sin^2 \theta)/\lambda^2}$$

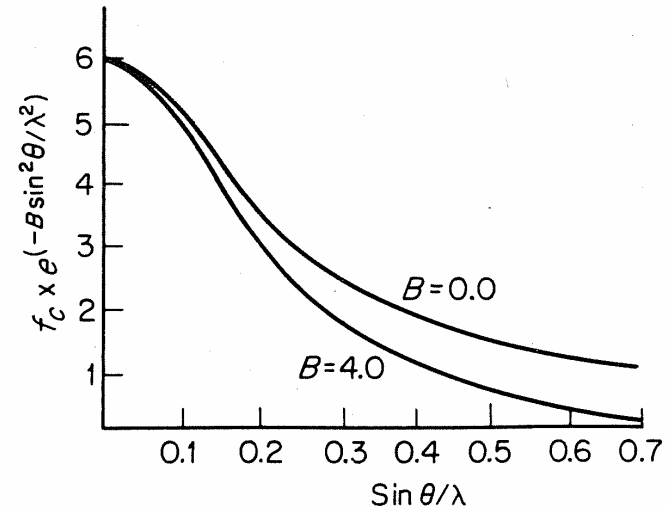


Figure 7.5. The product $f_0 e^{-B(\sin^2 \theta)/\lambda^2}$ as a function of $(\sin \theta)/\lambda$.

but within a shell of $\sin \theta / \lambda$ we can consider the f_j values constant. So average the F_0^2 values within these onion skins of the reciprocal lattice sphere

$$\bar{I}_{\text{rel}} = \langle |F_{\text{rel}}|^2 \rangle_{\text{ave}}$$

$$\bar{I}_{\text{abs}} = \sum_{i=1}^N f_i^2$$

$$\bar{I}_{\text{abs}} = \sum_{i=1}^N f_{oi}^2 e^{-2B(\sin^2 \theta)/\lambda^2}$$

$$\bar{I}_{\text{abs}} = e^{-2B(\sin^2 \theta)/\lambda^2} \sum_{i=1}^N f_{oi}^2$$

$$\bar{I}_{\text{rel}} = C \bar{I}_{\text{abs}}$$

$$\bar{I}_{\text{rel}} = C e^{-2B(\sin^2 \theta)/\lambda^2} \sum_{i=1}^N f_{oi}^2$$

$$\frac{\bar{I}_{\text{rel}}}{\sum_{i=1}^N f_{oi}^2} = C e^{-2B(\sin^2 \theta)/\lambda^2}$$

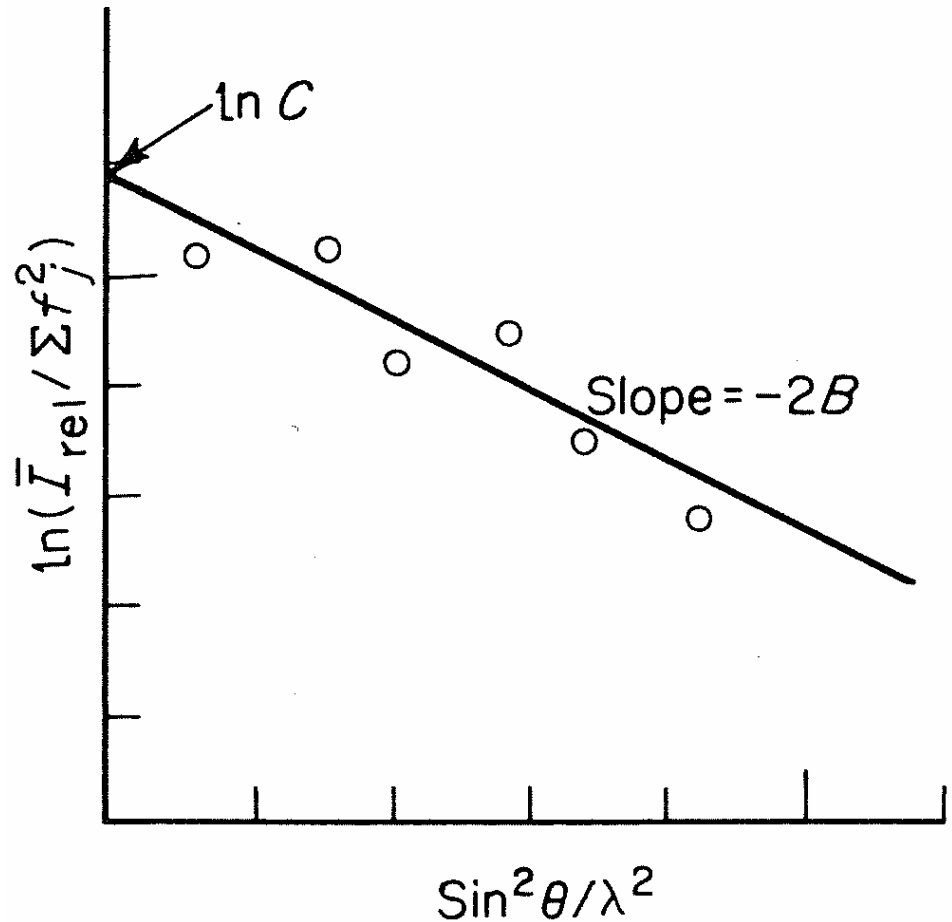


Figure 7.6. Wilson plot for determining scale and thermal parameters.

$$\ln\left(\frac{\bar{I}_{\text{rel}}}{\sum_{i=1}^N f_{o_i}^2}\right) = \ln C - \frac{2B(\sin^2 \theta)}{\lambda^2}$$

So now we have F_o in electrons

$$k = 1/\sqrt{C}$$

and F_o^2 in electrons²

$$|F_{\text{abs}}| = k|F_{\text{rel}}|$$

$$I/I_0 = e^{-\mu x} \quad \mu = \rho \sum_i g_i \mu_m^i$$

For the crystal at right the total path for the incoming and outgoing X-ray beam from one diffracting volume element is x , so increasing the size but keeping the shape constant means that

$$I_0 \propto x^3 \quad \text{and} \quad I \propto x^3 e^{-\mu x}.$$

This means that the maximum intensity will occur when

$$\frac{dI}{dx} = 3x^2 e^{-\mu x} - x^3 \mu e^{-\mu x} = x^2 e^{-\mu x} (3 - \mu x) = 0$$

$$x \approx 3/\mu.$$

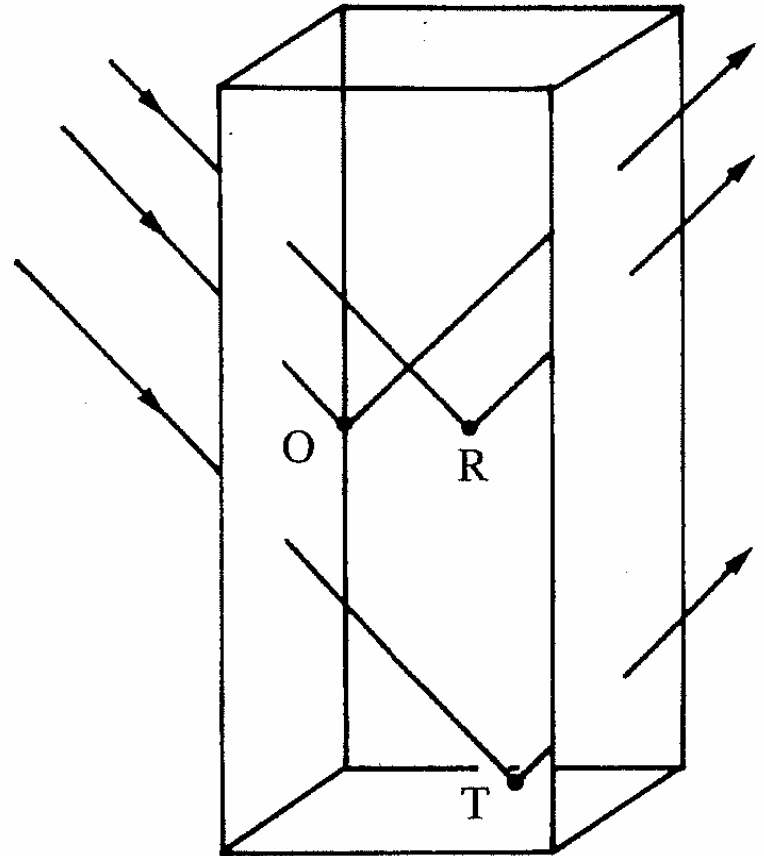


Fig. 5.41

For a given scattering angle 2θ , the path of the incident and scattered beams in the crystal depends on the position of the scattering point within the crystal.

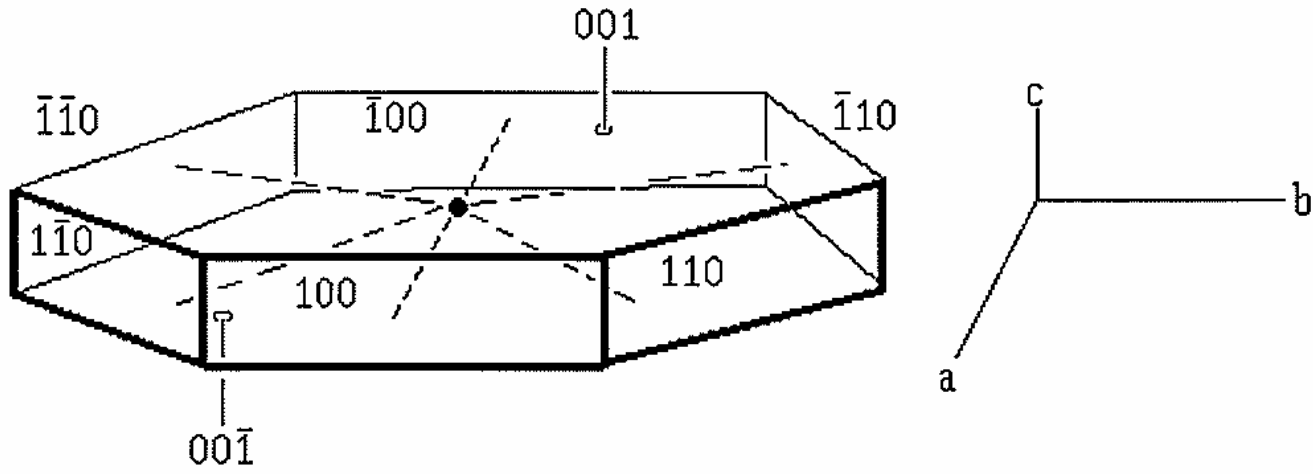


Fig. 7.17. Indexing and measurement of a crystal for an analytical absorption correction.

$$T = \frac{1}{V} \int_V e^{-\mu(p+q)} dv.$$

The Absorption Correction in Crystal Structure Analysis

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Two beams divide a plane into triangles, where all the incoming rays pass through one edge and outgoing rays pass through a second edge

for example, triangle ARB (edges AB in, AB out) , or triangle QDP (edges AD in, BC out)

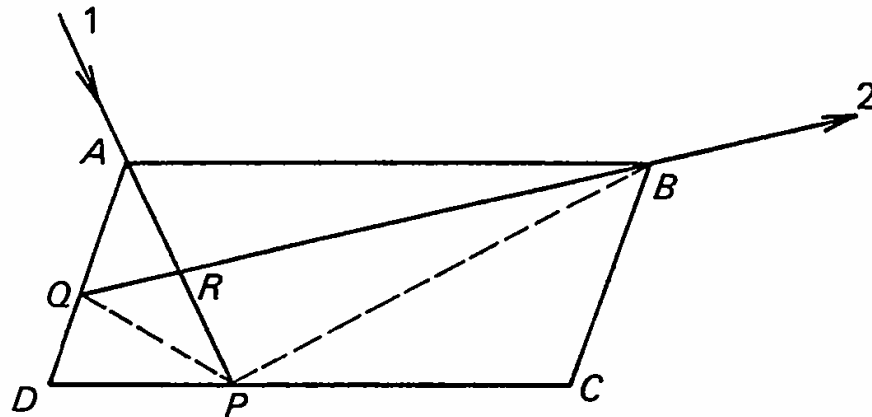


Fig.1. Decomposition of a parallelogram into Howells polygons and triangles; 1: direction of incident beam, 2: direction of diffracted beam.

The Tompa algorithm for analytically computing the transmission factor of a crystal of measured and indexed faces

Similarly, the crystal can be divided up into tetrahedra for which all of the incoming rays pass through one crystal face and outgoing through a second common face.

The incoming path length p and outgoing q can then be analytically expressed and the transmission integrated over the volume of the subunit tetrahedron.

EX is the incident beam and FU the outgoing beam. The rays from these beams are projected over the surface of the bounding planes of the crystal to generate sections. The intersection of those sections are the tetrahedra (such as EFST) that share incoming ray faces and outgoing ray faces.

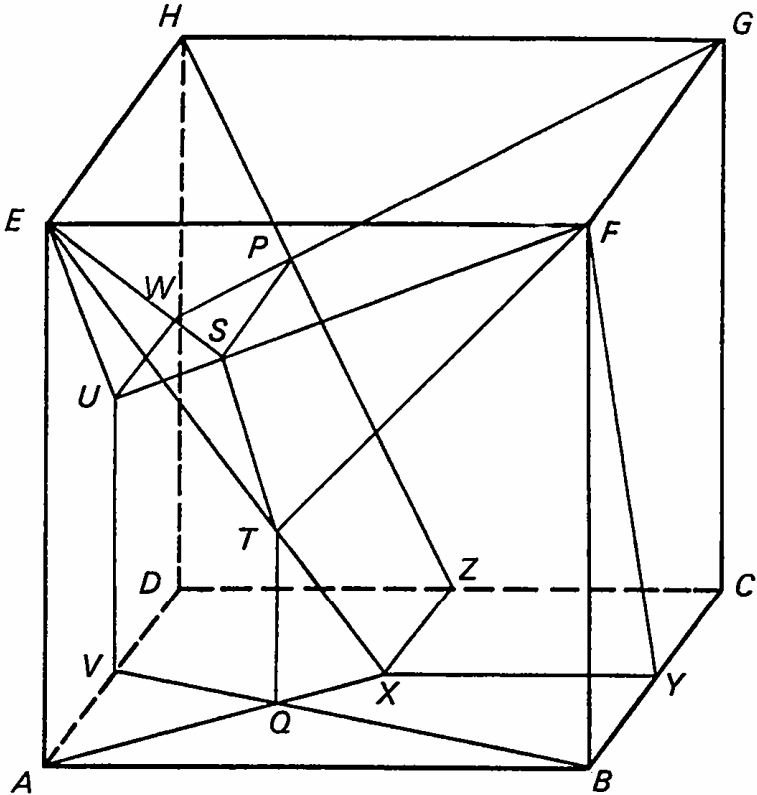


Fig. 2. Decomposition of a cube into elementary polyhedra.

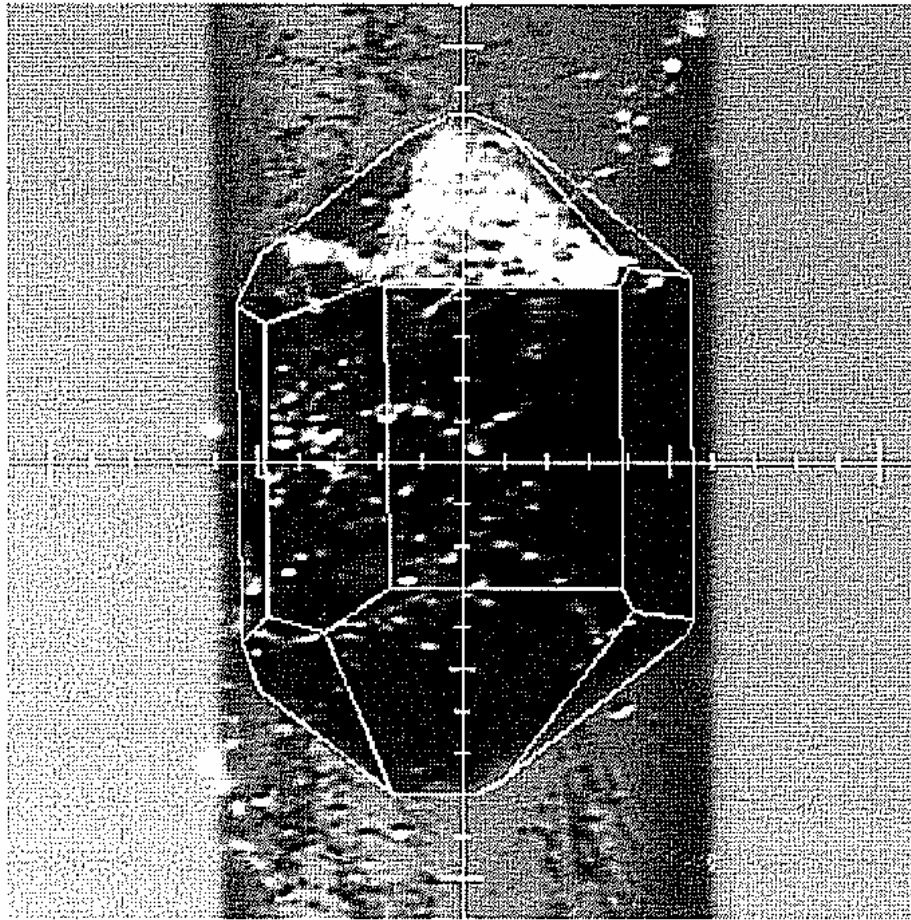


Fig. 7.18. Example of the description of a crystal by indexed faces.

too good to be easy....

A Semi-Empirical Method of Absorption Correction

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An extension of Furnas's method is described. The variation of intensity of an axial reflexion as the crystal is rotated about the goniometer axis is used to give a curve of relative transmission T against azimuthal angle φ for the corresponding reciprocal lattice level. Transmission coefficients for any general reflexion hkl are then given approximately by $T(hkl) = [T(\varphi_{inc}) + T(\varphi_{ref})]/2$ where φ_{inc} and φ_{ref} are the azimuthal angles of the incident and reflected beams. Equations are derived for φ_{inc} and φ_{ref} and the accuracy of the method is discussed.

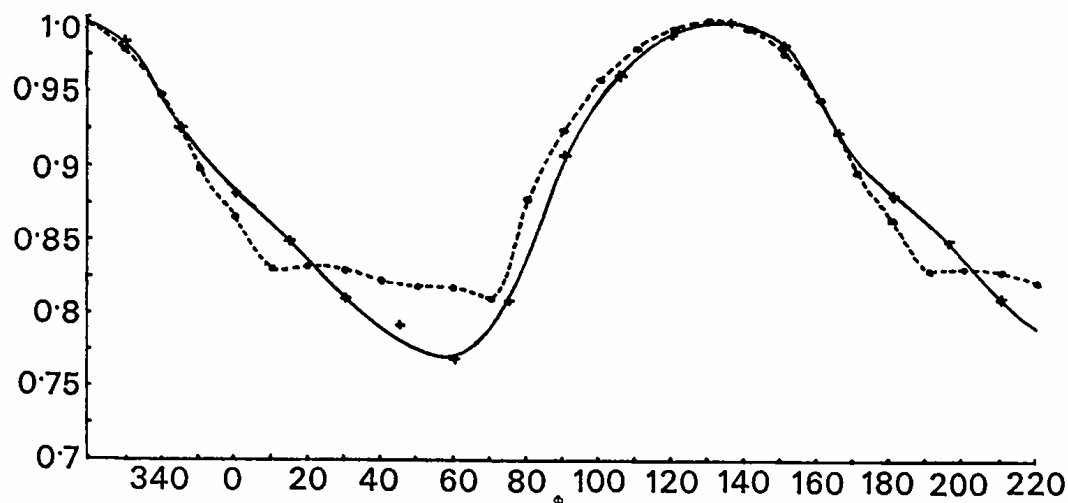
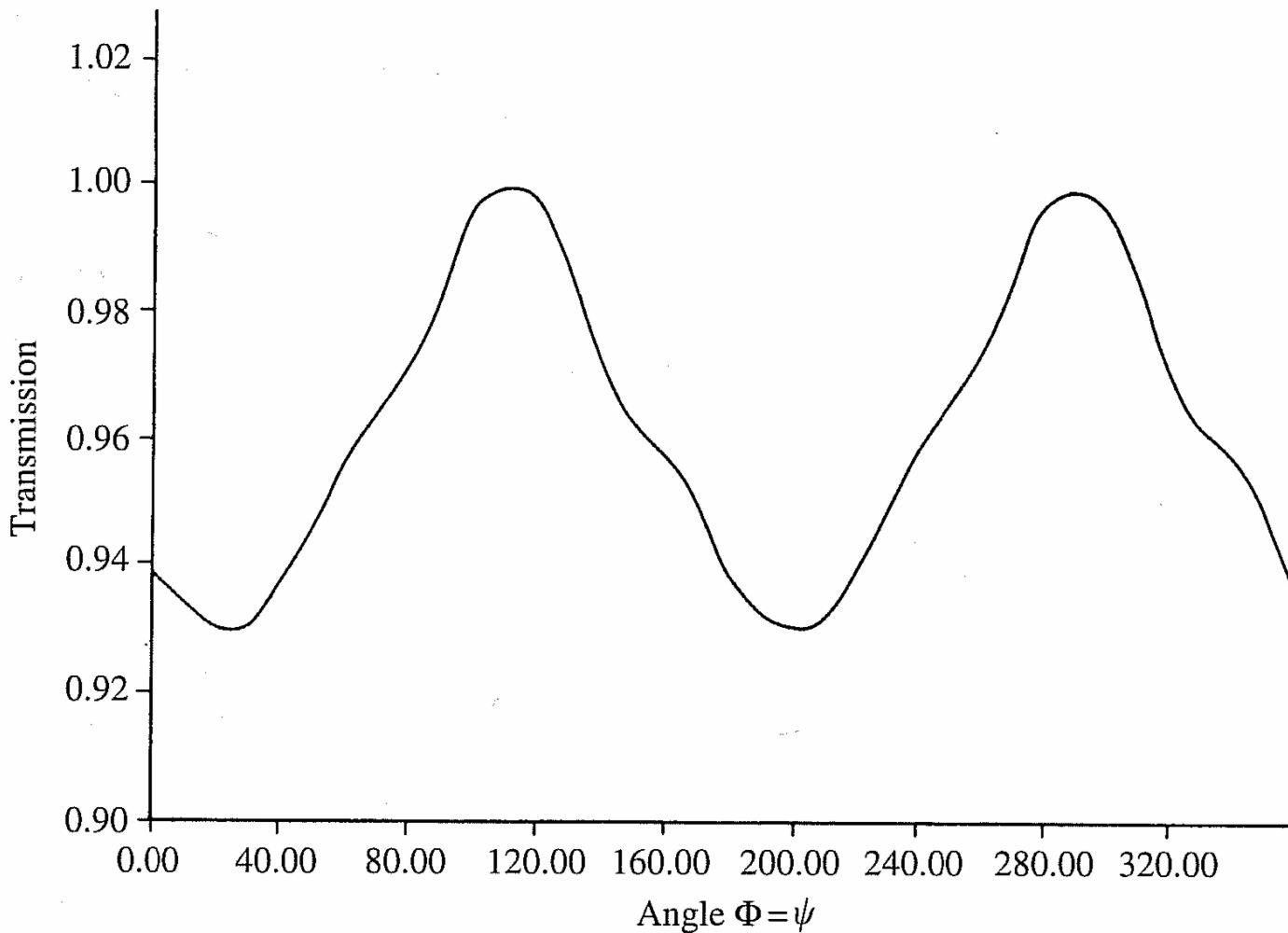


Fig. 1. Variation of relative transmission with azimuthal angle φ . Solid line, as measured; broken line, as calculated, neglecting effect of mother liquor and capillary, by the use of *ORABS*.



too easy to be good

Relative transmission factor plotted as a function of the scanning angle $\Phi = \psi$ for a reflection chosen with a χ value close to 90° . The plot can be used to apply an empirical absorption

One step
further...

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Automatic Absorption Correction using Intensity Measurements from Azimuthal Scans

BY HOWARD D. FLACK

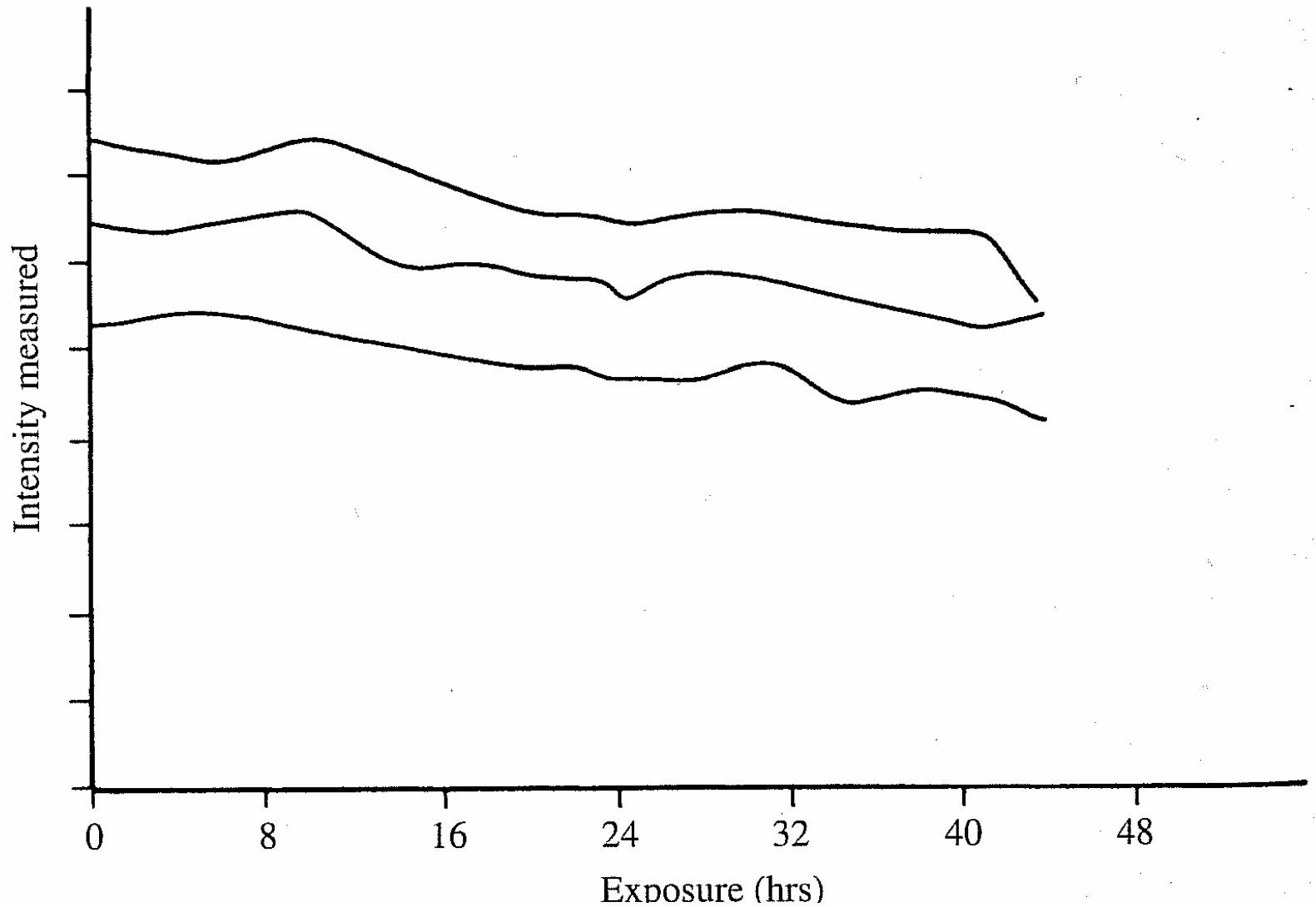
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A new method of making absorption corrections from azimuthal scans is described. The method is designed to work on an automatic four-circle diffractometer for crystals with high absorption, of arbitrary shape and having at least four general equivalent reflexions. The data are treated by a procedure which expands the transmission factor as a Fourier series in the diffractometer angles. The variation of transmission with 2θ is simulated by tabulated values for a sphere. The method has been tested by correcting for absorption in a crystal of SmAu_6 ($\mu R = 5.9$).

input is the
value of μ and
an estimate of
the average
radial path

A point of more practical consideration is how to choose the value of R to use in $A(\mu R, 2\theta)$. We suggest three simple prescriptions:

- (a) $R = (3V/4\pi)^{1/3}$ where V is the volume of the crystal. This gives the radius of a sphere of volume equal to the crystal.
- (b) $R = \frac{1}{2}(V)^{1/3}$ which gives the semidimension of a cube of volume equal to the crystal.
- (c) $R = \frac{1}{2}\bar{x}$ where \bar{x} is the mean linear dimension of the crystal.



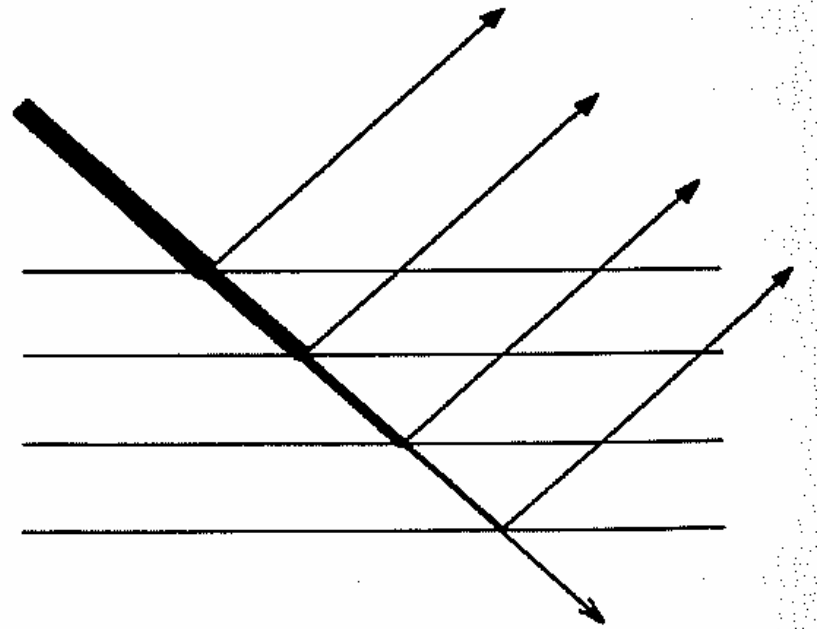
Decay of three reflections of a crystal as a function of time due to radiation. This can be approximated as a linear function and the data back corrected for both time and crystal orientation

If I_o^{ext} represents the observed integrated intensity and if I_c represents the calculated intensity on the same scale then the theory of Zachariasen predicts that secondary extinction should result in these being related by:

$$I_o^{\text{ext}} = I_c e^{-2gI_c}$$

Where g is an empirical extinction coefficient. For g small and recognizing that I_c is $F_c^2 Lp$ we can expand the exponential series and throw away higher terms to give:

$$|F_o^{\text{corrected}}| = |F_o^{\text{ext}}|(1 + g|F|^2 Lp)$$



Secondary extinction:

The diffraction weakens the primary beam, so that parts of the crystal deeper into the crystal see a weaker beam. This is usually a problem for only a few, very strong, F_{hkl} diffraction amplitudes and can be corrected in refinement

What is the percent of this correction?

Simply

$$g|F|^2 Lp$$

For what reflections will this be most important?

Very strong ones!