

**Rotation B**

Rotation by an angle  $2\theta$  about  $Y_A$  brings  $X_A$  into  $X_B$  along beam (2) (Fig. 7b). The rotation matrix is

$$\begin{bmatrix} \cos 2\theta & 0 & \sin 2\theta \\ 0 & 1 & 0 \\ -\sin 2\theta & 0 & \cos 2\theta \end{bmatrix}.$$

Beam (1) now has the direction cosines  $(\cos 2\theta_1 \cos 2\theta + \sin 2\theta_1 \sin 2\theta \cos \varphi, \sin 2\theta_1 \sin \varphi, \sin 2\theta_1 \cos 2\theta \cos \varphi - \cos 2\theta_1 \sin 2\theta)$ .

The principal vibration directions of beam (2) are along  $Y_B$  and  $Z_B$  and, if a mosaic crystal and no extinction are assumed, their amplitudes are respectively  $cE$  and  $cE \cos 2\theta$ , where  $c$  is a proportionality constant.

**Rotation C**

Rotation by an angle  $\mu$  about  $X_B$  brings  $Z_B$  into  $Z_C$  in the plane defined by  $X_B$  and the beam (1). The angle  $\mu$  is obtained from the direction cosines of beam (1) with  $Y_B$  and  $Z_B$  (Fig. 7c):

$$\begin{aligned} \tan \mu &= -\frac{\cos(1 \wedge Y_B)}{\cos(1 \wedge Z_B)} \\ &= \frac{\sin 2\theta_1 \sin \varphi}{\cos 2\theta_1 \sin 2\theta - \sin 2\theta_1 \cos 2\theta \cos \varphi}, \end{aligned}$$

and the rotation matrix is:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \mu & \sin \mu \\ 0 & -\sin \mu & \cos \mu \end{bmatrix}.$$

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**A Priori Estimates of Errors in Intensities for Imperfectly Spherical Crystals**

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**Abstract**

*A priori* estimates of errors in intensities for spheres arising from non-sphericity in crystal shape may now be readily determined from a recently published table of  $(1/A^*)(\partial A^*/\partial \mu R)$  values [Flack & Vincent (1978). *Acta Cryst.* **A34**, 489–491] using an expression given

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The direction cosines of beam (1) are  $(\cos 2\theta_{12}, 0, \sin 2\theta_{12})$  with  $\cos 2\theta_{12} = \cos(1 \wedge X_B) = \cos 2\theta_1 \cos 2\theta + \sin 2\theta_1 \sin 2\theta \cos \varphi$ . From Fig. 7(d) the radiation along beam (1) has two independent parallel components for the 2→1 reflection with amplitudes  $cE \cos \mu$  and  $cE \cos 2\theta \sin \mu$ . After reflection, the intensity with  $\sigma$  polarization is  $c_1^2 E^2 (\cos^2 \mu + \cos^2 2\theta \sin^2 \mu)$ . In the same way, the intensity with  $\pi$  polarization is  $c_1^2 E^2 \cos^2 2\theta_{12} (\cos^2 2\theta \cos^2 \mu + \sin^2 \mu)$ , where  $c_1$  is a proportionality constant.

Finally, the polarization correction appropriate to the 0→2→1 reflection is

$$\begin{aligned} P_{021} &= \frac{1}{2} [\cos^2 \mu + \cos^2 2\theta \sin^2 \mu + \cos^2 2\theta_{12} \\ &\quad \times (\cos^2 2\theta \cos^2 \mu + \sin^2 \mu)]. \end{aligned}$$

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by Jeffery & Rose [*Acta Cryst.* (1964), **17**, 343–350]. However, a new relationship between  $\sigma(R)$  and  $\sigma(r)$  is determined. The effects of crystal radius, non-sphericity and wavelength on intensity errors are discussed. The importance to the selection of crystals for electron density measurements is stressed. Universal curves of  $\sigma(r)/r$ , the error due to non-sphericity, against  $\mu r$  calcu-

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lated for a range of intensity errors at  $\theta = 0$  and  $45^\circ$  are given.

### Introduction

Jeffery & Rose (1964, hereafter referred to as JR) and Jeffery (1971) give an expression to obtain estimates of errors in intensities for crystals which are approximately spherical. The model they have used to derive the expression is based on the following arguments.

At each reflecting position the true absorption-correction factor ( $A^* + \Delta A^*$ ) for an approximately spherical crystal will differ slightly from the absorption-correction factor ( $A^*$ ) for a perfectly spherical specimen with the same volume. Thus for each reflecting position there corresponds a radius  $R$  of a perfect sphere having the same value of its absorption-correction factor as  $A^* + \Delta A^*$ . In the absence of other effects, the variation in intensities of a set of crystallographically equivalent reflections [mean  $I$  and standard deviation  $\sigma(I)$ ] gives an indirect measure of the standard deviation of the corresponding radius,  $\sigma(R)$ . The expression which relates these quantities is

$$\frac{\sigma(I)}{I} = \frac{R}{A^*} \cdot \frac{\partial A^*}{\partial R} \cdot \frac{\sigma(R)}{R}, \quad (1) \text{ [JR1]}$$

where  $\sigma(I)/I$  and  $\sigma(R)/R$  are the coefficients of variation of  $I$  and  $R$  respectively.

To obtain an estimate of  $\sigma(I)/I$  purely from measurements of the crystal shape, it is necessary to determine the relation between  $\sigma(R)/R$  and the measured variations in the crystal radius,  $\sigma(r)/r$ . Replacing  $\sigma(R)/R$  by  $\alpha\sigma(r)/r$  and  $R$  by  $r$  (assuming that for an approximately spherical crystal  $R \simeq r$ ) (1) may be written as

$$\frac{\sigma(I)}{I} = \alpha \mu r \left[ \frac{1}{A^*} \frac{\partial A^*}{\partial \mu r} \right] \frac{\sigma(r)}{r}, \quad (2)$$

where  $\mu$  is the linear absorption coefficient.

The quantity in square brackets in (2) can be found in a recently published table (Flack & Vincent, 1978) as a function of  $\mu r$  and  $\theta$ ,  $\theta$  being the Bragg angle. For a particular value of  $\mu r$ , the interpolation program *SPHCOR* (Flack & Vincent, 1978) may be used to calculate the corresponding values at intervals in  $\theta$ .  $\sigma(r)$  is estimated from measurements of the crystal radius and it only remains to determine the form of  $\alpha$ .

From a plot of  $\sigma(R)$ , the standard deviation of  $R$  derived from variations in intensities among symmetry-related reflections, against  $\sigma(r)$ , the standard deviation of the measured crystal radii of mean  $r$ , for several near-spherical specimens of variable radii, JR concluded that  $\sigma(r)$  was approximately linearly related to  $\sigma(R)$  with  $\alpha \simeq 2.8$ . In their work, values of  $\sigma(I)/I$  were determined photometrically from integrated Weissenberg films corrected for film errors and corresponding

values of  $\sigma(r)$  and  $r$  from photomicrographs of the specimens. While evidently JR took every precaution to correct, minimize or, at least, assess the contribution of other sources of error (extinction, multiple reflection *etc.*) to the total error in  $\sigma(I)/I$ , it is apparent in an approach of this kind that one must be certain that the variations in  $I$  are due to absorption errors alone. Although JR deemed these additional errors as small or non-applicable in the compounds they used, it seemed to us that the possible effects of extinction, notably anisotropic extinction, might well have been seriously underestimated in their method of determining  $\alpha$ .

Our interest in the work of JR was aroused not only because of the readiness with which  $\sigma(I)/I$  can now be calculated from the table of Flack & Vincent (1978), but also for the usefulness of their expression as an *a priori* means of selecting crystals of highly absorbing materials, such as alloy systems, suitable for electron density studies. Thus we have reinvestigated the relation between  $\sigma(R)$  and  $\sigma(r)$  using a theoretical model and analytical methods.

### Reinvestigation of the relation between $\sigma(R)$ and $\sigma(r)$

The basis of our model was a hypothetical cubic crystal (holohedral class) of unit cell such that  $\sigma(I)/I$  could be analysed at discrete values of  $\theta$  from  $\sim 0$  to  $50^\circ$  in steps of  $5^\circ$  for reflections of the general form  $\{hkl\}$ , thus taking full advantage of the equivalency of the 48 reflections of this symmetry.

Values of  $\sigma(I)/I$  were determined with a double precision (UNIVAC 1108: 36 bits/word) version of the analytical absorption program *ABSCOR* (Alcock, 1969, 1970, 1974) from the inverse of the transmission factors calculated for crystals of known habit.

Transmission factors were calculated for the hypothetical crystal for shapes corresponding to a cube  $\{100\}$ , an octahedron  $\{111\}$ , a rhombic dodecahedron  $\{110\}$  and an icositetrahedron  $\{211\}$ , these forms representing various degrees of non-sphericity. For each shape, transmission factors were calculated for  $\mu R$  values of 6.2, 2.5, 1.2 and 0.2 where  $R$  was determined from the volume of the polyhedron, taken as identical to that of an equivalent sphere.  $I$  was calculated as the mean of the inverse transmission factors of standard deviation  $\sigma(I)$  for each set of equivalent reflections. Corresponding values of  $\sigma(R)/R$  were calculated from (1) with the program *SPHCOR* which uses the  $A^*$  data of Dwiggin (1975) up to  $\mu R = 2.5$ . Beyond this value, the data of Weber (1969) were used. The  $\sigma(R)/R$  data were then averaged over the sets of reflections.

$\sigma(r)/r$  was determined analytically by fitting a sphere of equivalent volume to each crystal form and evaluating  $\sigma(r)$  by Simpson's rule. The values of  $\sigma(r)/r$  obtained in this way for the cube, octahedron, rhombic dodecahedron and icositetrahedron were 0.12440, 0.11049, 0.06495 and 0.04829 respectively.

We concluded from the variation in  $\sigma(R)/R$  that the relation between  $\sigma(R)$  and  $\sigma(r)$  was a function of  $\mu R$  ( $= \mu r$ ). Fig. 1 shows a graph of  $\alpha = \{\sigma(R)/R\}/\{\sigma(r)/r\} = \sigma(R)/\sigma(r)$  versus  $\mu r$ . A least-squares fit to a straight line gives

$$\alpha = 0.15\mu r + 0.05.$$

This form of  $\alpha$  is applicable for the range of  $\sigma(r)/r$  (0.0 to 0.124) for the polyhedra considered here. For larger values of  $\sigma(r)/r$ , such as platelets or needles,  $\alpha$  might show a dependence on  $\sigma(r)/r$ . However, these crystal habits are hardly describable as being imperfectly spherical.

### Effects of non-sphericity on intensity variations and their minimization

In view of the differences between our form of  $\alpha$  and that of JR, it is necessary to reassess some of the implications of (2). It will be clear, however, from a comparison of the relative magnitudes of  $\alpha$ , that the contributions to the intensity errors from absorption errors as estimated with (2) will be much smaller in our case than in JR's.

#### (a) Variation with $\mu$

Fig. 2,\* equivalent to JR's Fig. 6, illustrates plots of intensity errors  $[\sigma(I)/I]$  against  $\theta$  for various values of

\* For both the  $\mu = 300$  and  $500 \text{ cm}^{-1}$  plots, the tails of the curves have been smoothed owing to discontinuities in the high-angle values of  $(1/A^*)(\partial A^*/\partial \mu r)$ . This is most probably due to rounding errors in  $A^*$  at the corresponding values of  $\mu r$  taken from the tables of Weber (1969). Where appropriate, similar smoothing has been applied in other graphs involving  $(1/A^*)(\partial A^*/\partial \mu r)$ .

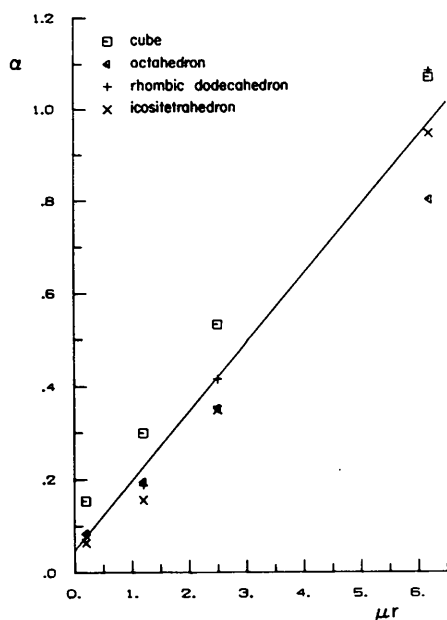


Fig. 1. Graph of  $\alpha = \{\sigma(R)/R\}/\{\sigma(r)/r\}$  against  $\mu r$  for four crystal habits of forms  $\{100\}$ ,  $\{111\}$ ,  $\{110\}$  and  $\{211\}$ .

$\mu$  calculated with the same crystal model as JR. For crystals of a given degree of non-sphericity  $[\sigma(r)/r]$  and low  $\mu$ , these errors can be small and constant over the range  $\theta = 0$  to  $90^\circ$ . As  $\mu$  increases, the errors in the low-angle region increase more rapidly than those in the high-angle region. This effect is also evident in Fig. 3 which is a graph of  $\beta$  [the ratio of  $\sigma(I)/I$  to  $\sigma(r)/r$ ] against  $\mu r$  for various values of  $\theta$  (equivalent to Fig. 4 in JR).

Unlike the results of JR, Fig. 2 shows that  $\sigma(I)/I$  continues to increase with increasing  $\mu$ . JR found that at large  $\mu$  their curves tended to converge to points at  $\theta = 0$  and  $90^\circ$ , inferring that there was an upper limit to the errors (JR's Fig. 6). This convergence may be explained as follows. At  $\theta = 0^\circ$ , the absorption-correction factor for a sphere of radius  $r$  is (*International Tables for X-ray Crystallography*, 1967)

$$A^* = \frac{2(\mu r)^3}{3} \left\{ \frac{1}{2} - \exp(-2\mu r) \left[ \frac{1}{2} + \mu r + (\mu r)^2 \right] \right\}^{-1}.$$

Differentiating with respect to  $\mu r$  gives

$$\mu r \frac{\partial A^*}{\partial \mu r} = 3A^*[1 - A^* \exp(-2\mu r)].$$

When  $\mu r$  is large,  $\exp(-2\mu r) \rightarrow 0$  and terms in  $\exp(-2\mu r)$  can be neglected. Hence

$$\frac{\mu r}{A^*} \frac{\partial A^*}{\partial \mu r} = 3. \quad (3a)$$

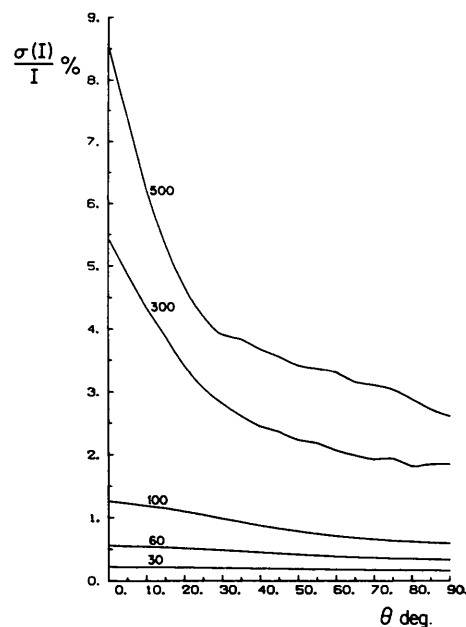


Fig. 2. Graph of  $\sigma(I)/I$  (%) against  $\theta$  ( $^\circ$ ) for five values of  $\mu$ , the linear absorption coefficient in  $\text{cm}^{-1}$ . Crystal specifications:  $r = 150 \mu\text{m}$ ,  $\sigma(r)/r = 2.5\%$ .

A similar treatment of the expression of the absorption-correction factor at  $\theta = 90^\circ$ ,

$$A^* = \frac{4\mu r}{3} \left\{ \frac{1}{2} - \frac{1}{16(\mu r)^2} [1 - (1 + 4\mu r)\exp(-4\mu r)] \right\}^{-1},$$

gives, after neglecting terms in  $\exp(-4\mu r)$ ,

$$\mu r \frac{\partial A^*}{\partial \mu r} = A^* \left\{ 1 - \left[ \frac{2}{8(\mu r)^2 - 1} \right] \right\}$$

and hence

$$\frac{\mu r}{A^*} \frac{\partial A^*}{\partial \mu r} \simeq 1 \text{ when } \mu r \text{ is large.} \quad (3b)$$

Thus, with JR's form of  $\alpha$ , when  $\mu r$  becomes greater than about 4, (2) and (3) show that  $\sigma(I)/I$  becomes independent of  $\mu$  at  $\theta = 0$  and  $90^\circ$ . Hence the curves of high  $\mu$  will converge to points for a particular value of  $\sigma(r)/r$ . However, with the form of  $\alpha$  found in the present work, the values of  $\sigma(I)/I$  at  $\theta = 0$  and  $90^\circ$  increase linearly with  $\mu r$ , and we find no upper limit to the errors  $\sigma(I)/I$ .

#### (b) Variation with $r$ and $\sigma(r)/r$

While it is always advantageous to reduce  $\sigma(r)$  if  $r$  is constant, Fig. 3 shows that it is also better to reduce  $r$  if  $\sigma(r)$  is reduced in the same ratio. The latter conclusion is contrary to the implications of JR's Fig. 4 from which they deduced that this would be only effective if  $\mu r$  was less than about 2.

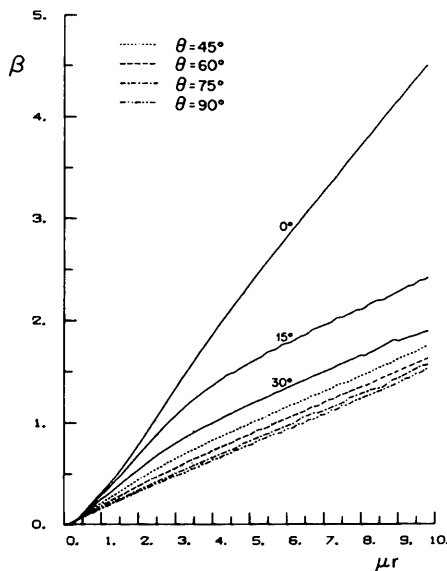


Fig. 3. Graph of  $\beta \{ = [\sigma(I)/I] / [\sigma(r)/r] \}$  against  $\mu r$  for seven values of  $\theta$  ( $^\circ$ ).

#### (c) Variation with wavelength

Apart from improvements in crystal shape, minimization of absorption errors may also be effected by reducing the linear absorption coefficient ( $\mu$ ) of the substance. For most elements a change to a shorter wavelength of radiation will achieve the required result. As an illustration, consider an approximately spherical crystal of ScSi of mean radius  $75 \mu\text{m}$  and standard deviation equivalent to a 5% variation. What magnitude of errors in intensities may be expected if data were collected with Cu  $K\alpha$ , Mo  $K\alpha$  and Ag  $K\alpha$  radiations? Fig. 4 shows the results of plotting  $\sigma(I)/I$  against  $\sin \theta/\lambda$  for the wavelengths mentioned. It is apparent that the estimated errors can be reduced by changing from Cu  $K\alpha$  to Mo  $K\alpha$  from an unacceptably high level to a more than tolerable one. Fig. 4 shows that there is a further reduction in errors if Ag  $K\alpha$  is used instead of Mo  $K\alpha$ , albeit less striking. Moreover, if a comparison between the linear absorption coefficients of a substance for Cu  $K\alpha$  and Mo  $K\alpha$  indicates no improvement in absorption errors, there will nevertheless always be an improvement between Cu  $K\alpha$  and Ag  $K\alpha$  (except for H and He).

#### Electron density studies on highly absorbing systems; an aid to selecting suitable crystals

Recently it has been shown that meaningful results can be obtained from X-ray experiments on the nature of the electronic structure of metals and alloys (Staudemann, 1976). Generally, these systems are highly absorbing and the specimens used in the investigations

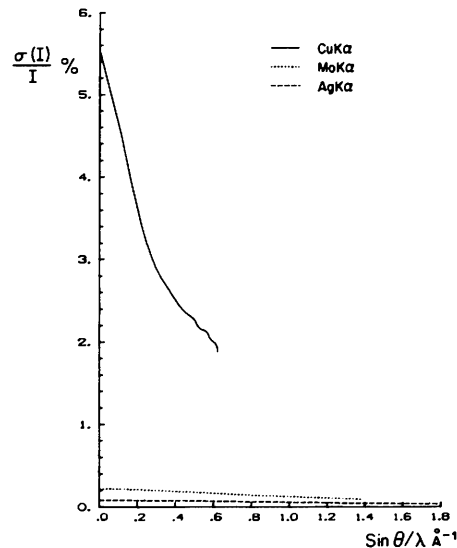


Fig. 4. Graph of  $\sigma(I)/I$  (%) against  $\sin \theta/\lambda$  ( $\text{\AA}^{-1}$ ) for three different radiations. Crystal specifications: compound ScSi,  $\mu(\text{Cu } K\alpha) = 470 \text{ cm}^{-1}$ ,  $\mu(\text{Mo } K\alpha) = 52 \text{ cm}^{-1}$ ,  $\mu(\text{Ag } K\alpha) = 26.1 \text{ cm}^{-1}$ ,  $r = 75 \mu\text{m}$ ,  $\sigma(r)/r = 5\%$ .

are, by necessity, in the form of spheres, having been ground from fragments of a crushed ingot of the prepared material.

Electron density studies on these systems demand better accuracy of the data over structure analysis, mainly because the core-electron scattering is dominant

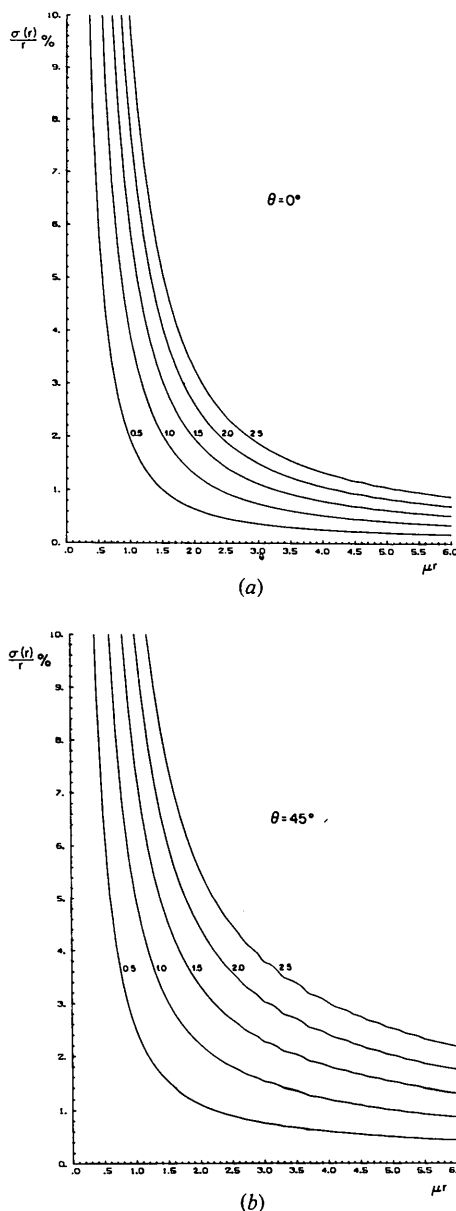


Fig. 5. Graphs of  $\sigma(r)/r$  (%) against  $\mu r$  for five values (0.5, 1.0, 1.5, 2.0, 2.5) of  $\sigma(I)/I$  (%). (a)  $\theta = 0^\circ$ . (b)  $\theta = 45^\circ$ .

in these compounds. Furthermore, it is plain from Figs. 2, 3 and 4 that the errors in intensities incurred by assuming the specimen to be perfectly spherical are greatest in the low-angle region where the contributions from the valence electrons to the scattering are most pronounced. Although the investigator is probably aware that deviations of his specimen from true sphericity will lead to errors in his data, he may not know to what extent until data-collection time. Therefore, the usefulness of an *a priori* estimate of the absorption errors from measurements of crystal shape alone, their influence on the intensity errors and their possible reduction as described previously, becomes abundantly clear when the choice of a suitable crystal has to be made.

As an aid to selecting crystals, Fig. 5 shows universal curves of  $\sigma(r)/r$  against  $\mu r$  for  $\theta = 0$  and  $45^\circ$  from which estimates of the allowed tolerances in crystal perfection corresponding to errors of 0.5, 1.0, 1.5, 2.0 and 2.5% in  $\sigma(I)/I$  can be made. The asymptotic nature of the curves in Fig. 5(a) at large  $\mu r$  is a direct consequence of the reduced form of  $(\mu r/A^*)(\partial A^*/\partial \mu r)$  at these values [equation (3)]. A more complete analysis of the errors can be made from (2) in conjunction with the program *SPHCOR* if desired.

For a given value of  $\sigma(r)/r$ , the accuracy of data as indicated by Fig. 5 appears much better than that obtained in current experimental procedures. The latter is due in part to the influence of a non-homogeneous incident X-ray beam associated with a non-spherical sample. This situation will be the subject of a future publication.

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