

to employ isotropic form factors. Then any asymmetry in the electronic distribution, the anisotropy of thermal vibrations, and all other sundry effects are lumped together into asymmetric temperature factors. In this case, the use of \bar{f} is a reasonable approximation and the \bar{f} values deduced from the Hartree-Fock radial distributions are surely superior to McWeeny's. However, the differences do not exceed 0.2 electrons and are hardly significant in most crystal-structure work. If, on the other hand, the comparatively large effects of atomic asymmetry are to be taken into account in an elaborate structure refinement, we would write:

$$f'' = \bar{f} + \frac{2}{3}\Delta, \quad (9)$$

$$f' = \bar{f} - \frac{1}{3}\Delta, \quad (10)$$

where $\Delta = f'' - f'$ can be computed from McWeeny's values. This is a sufficient approximation, since Δ is small relative to the \bar{f} value for the whole atom.

In agreement with McWeeny's work, the present work has shown that the interpolation technique of James & Brindley is unreliable. It is not unlikely that their interpolated values for other atoms as well are faulty, so that new calculations are desirable, based when possible on Hartree-Fock radial wave functions. If non-spherical effects are considered, it should be noted that, whereas (8) holds for any orbital, (4) and

(7) apply only to p electrons. Corresponding expressions for d electrons, for example, can be worked out in a similar way, provided that the shape of orbital has been previously deduced from an estimate of the bonds in which the atom is engaged.

We wish to thank Prof. Verner Schomaker for suggesting this problem and for his continued interest in the work.

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On the Visual Estimation of X-ray Reflexion Intensities from Upper-Level Weissenberg Photographs.

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Formulae are derived which govern the variations in reflexion spot area observed on upper-level Weissenberg photographs. It is shown that they can be used in a routine correction of intensities visually estimated from such photographs.

1. Introduction

The increasing use of three-dimensional methods in X-ray crystal structure analysis has stimulated interest in the measurement of reflected X-ray intensities, and it has been established that the visual estimation of intensities from photographic records is sufficiently accurate for many purposes. There are objections, however, to the general use of this simple and convenient method since the measurements do not give directly the required integrated intensities but rather the mean or peak intensities. The use of visually estimated intensities depends, therefore, on

the absence of variations in area or density distribution in the reflexion spots or on the use of proper corrections for variations which do occur. Unfortunately, quite large variations in reflexion spot area do occur in upper-level Weissenberg photographs, those on which general X-ray reflexions from single crystals are recorded most conveniently. In these photographs corresponding reflexions are extended on one side of the film and contracted on the other, the degree of distortion varying from reflexion to reflexion in a way which depends on the experimental arrangement. The effect and its general explanation are well known (Buerger, 1942); many workers, for example,

Kaan & Cole (1949), and Alexander, Fraenkel, Many & Steinberger (1953), have remarked upon it, and because of it several, including most recently Wallwork & Standley (1954), have suggested more or less complicated photometric procedures as the only satisfactory methods of intensity estimation. Nevertheless, visual estimation still is widely used, no doubt because of its attractive simplicity and because the intensities, even when uncorrected for variations in spot area, have been proved accurate enough in many structure investigations concerned only with the determination of atomic positions. Some attempts have been made to correct visually-estimated intensities for this effect. Kaan & Cole (1949) have suggested that for small differences in area the average of intensities estimated on the two halves of the film is the undistorted value; Scouloudi (1953) has used an experimentally determined ratio of extended-spot intensity to contracted-spot intensity in correcting the intensities of reflexions not observed on both halves of the film; others appear to have used a process of visual integration. In this last approach visual estimations are made of both the spot area and the density; the product of the two then is used as a measure of the integrated intensity. It is shown in the present paper that formulae can be derived which govern the variation of spot area with reflexion parameters and camera constants and that these formulae can be used in a routine correction of visually-estimated intensities.

The variation in spot areas arises from the divergence of the X-ray beam incident upon the crystal. The collimators used in single-crystal cameras generally consist of two small pin-holes separated by a comparatively large distance. Such a system, when illuminated by an X-ray source of uniform brightness and sufficient size to fill the aperture, gives an X-ray beam with a central region of uniform intensity and an outer region in which the intensity decreases with

increase of distance from the axis. The X-rays in the central region may be regarded as diverging from a point source at the centre of the first pin-hole, the finite size of which can be considered separately. The crystal should be irradiated only by the central part of the beam. Departures from this condition and the others mentioned above give rise to variations in reflexion spot characteristics which have been illustrated and discussed by Lonsdale (1945); they may be avoided by careful setting.

The production of a reflexion record on the photograph is shown diagrammatically in Fig. 1. It is con-

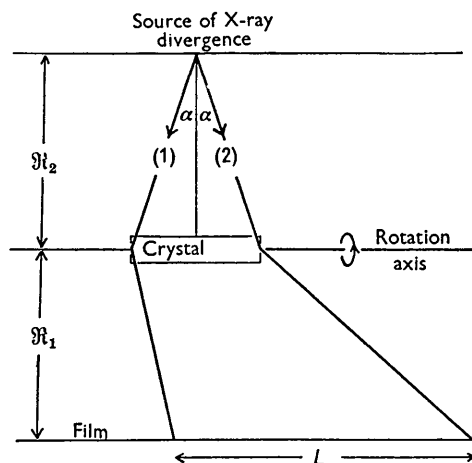


Fig. 1. Diagram illustrating the characteristics of X-ray reflexion spots when the incident beam is divergent. The extreme directions in the incident beam are numbered for comparison with Figs. 2 and 4.

venient to consider only the horizontal beam divergence, that in the plane containing the crystal axis-of-rotation, by considering a thin element of crystal parallel to that axis. Suppose the crystal to be divided

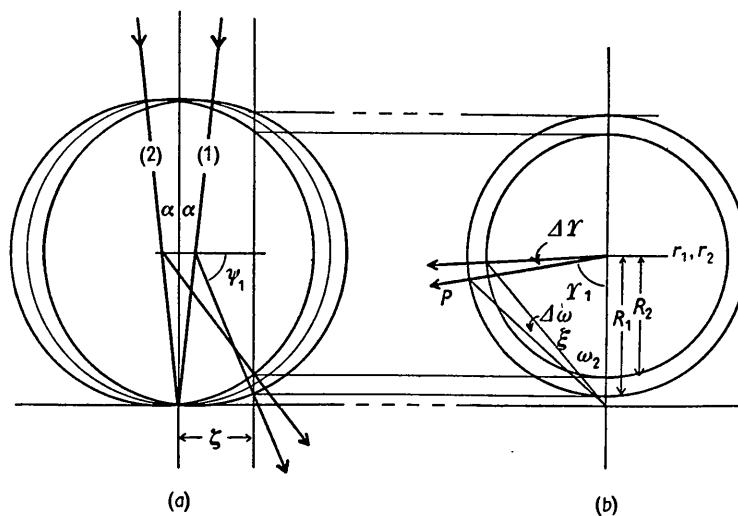


Fig. 2. Reciprocal-space diagrams showing Ewald spheres for a divergent incident X-ray beam and the genesis of reflexions in the normal-beam setting.

into elements of length. Each element receives X-rays at an angle of incidence which depends on its position in the crystal. All do not reflect at the same instant but they are brought into the reflecting position in turn as the crystal is rotated and, in fact, for upper-level reflexions the spots on the photograph grow from one end. During the time taken to complete a reflexion in this way the film is moved a distance depending on the camera constants so that the reflexion spots on the film are contracted or extended according to whether the film motion is in the same direction as the spot growth or in the opposite direction. The amount of distortion obviously depends upon the angular range through which a crystal has to be turned in order to bring each element into the reflecting position.

2. Calculation of angular range of reflexion

2.1. Normal-beam setting

The properties of Weissenberg photographs taken in all camera settings have been described in detail by Buerger (1942), whose notation is used here. Fig. 2(a) shows the plane of the reciprocal lattice defined by the incident beam and the crystal rotation-axis. The range of incident angles corresponding to beam divergence 2α is shown, together with the circles in which the limiting and mean spheres of reflexion cut this plane. Fig. 2(b) shows the reciprocal-lattice plane at height ζ which is to be photographed. We have now to calculate the angle $\Delta\omega$ through which this reciprocal-lattice plane must be turned in order that a lattice point P , distant ξ from the axis, should pass through the annulus bounded by the limiting circles of reflexion.

These circles have centres at distances from the origin

$$r_1 = r_2 = (1 - \alpha^2)^{\frac{1}{2}}; \quad r_0 = 1, \quad (1)$$

and radii given by

$$R_1^2 = 1 - (\zeta - \alpha)^2; \quad R_2^2 = 1 - (\zeta + \alpha)^2; \quad R_0^2 = 1 - \zeta^2. \quad (2)$$

In terms of polar coordinates (ξ, ω) their equations are

$$\xi^2 - 2r_1\xi \cos \omega + (r_1^2 - R_1^2) = 0 \quad (3)$$

and

$$\xi^2 - 2r_2\xi \cos \omega + (r_2^2 - R_2^2) = 0. \quad (4)$$

The lattice point P intersects the circles in turn as the crystal is rotated through the angle

$$\Delta\omega = |\omega_1 - \omega_2|.$$

From (3) and (4)

$$\cos \omega_1 - \cos \omega_2 = (R_2^2 - R_1^2)/2r_1\xi, \quad (5)$$

or, substituting from (1) and (2)

$$2 \sin \frac{1}{2}(\omega_1 + \omega_2) \sin \frac{1}{2}\Delta\omega = 2\alpha\zeta/\xi(1 - \alpha^2)^{\frac{1}{2}}. \quad (6)$$

There are five different ranges of values of ξ for which the properties of $\Delta\omega$ vary, but for the important range, defined by $(r_2 + R_2) > \xi > (r_2 - R_2)$, we may

write $\frac{1}{2}(\omega_1 + \omega_2) = \omega_0$. Then, for small values of α , we have

$$2 \sin \omega_0 \sin \frac{1}{2}\Delta\omega = 2\alpha\zeta/\xi, \quad (7)$$

or, since

$$\cos \omega_0 = (\xi^2 + 1 - R_0^2)/2\xi,$$

$$\Delta\omega \simeq 2 \sin \frac{1}{2}\Delta\omega = 4\alpha\zeta/\{4\xi^2 - (\zeta^2 + \xi^2)^2\}^{\frac{1}{2}}. \quad (8)$$

In terms of the film coordinate \mathcal{Y} ,

$$\Delta\omega \simeq \alpha\zeta/(1 - \zeta^2)^{\frac{1}{2}} \sin \mathcal{Y}. \quad (9)$$

As might be expected, this expression is very similar in form to the Lorentz factor for the same experimental arrangement (e.g. Cochran, 1948). It is clear that $\Delta\omega$ increases towards the maximum and minimum observable values of ξ and that it increases with increasing ζ . The form of the variations is apparent in Fig. 5, in which the ordinates are equivalent to $1 + \text{const. } \Delta\omega$.

Another feature of these photographs can be noticed here: there is a variation in \mathcal{Y} during each reflexion as a result of which reflexions generally are recorded not as straight lines parallel to the rotation axis but as lines inclined to that axis. Thus

$$2 \sin \frac{1}{2}(\mathcal{Y}_1 + \mathcal{Y}_2) \sin \frac{1}{2}\Delta\mathcal{Y} = \frac{1}{2}(1 + R_1^2 - \xi^2)/R_1 - \frac{1}{2}(1 + R_2^2 - \xi^2)/R_2, \quad (10)$$

or, approximating as before,

$$\Delta\mathcal{Y} \simeq 2 \sin \frac{1}{2}\Delta\mathcal{Y} = 2\alpha\zeta(\zeta^2 - \xi^2)/(1 - \zeta^2)^{\frac{1}{2}}\{4\xi^2 - (\zeta^2 + \xi^2)^2\}^{\frac{1}{2}}. \quad (11)$$

The variation of $\Delta\mathcal{Y}$ with ξ is shown in Fig. 3. Only

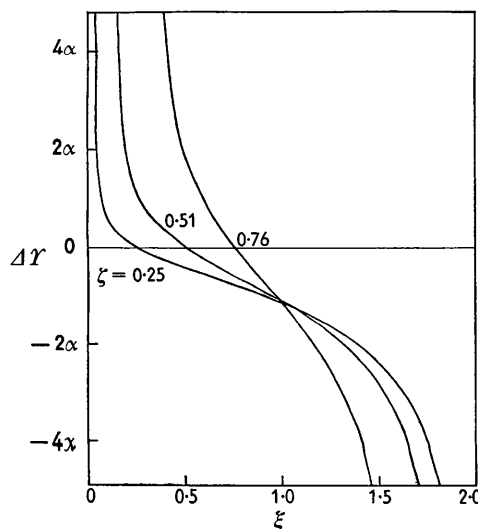


Fig. 3. Variation of $\Delta\mathcal{Y}$ with ξ and ζ in the normal-beam setting.

those reflexions for which $\xi = \zeta$ are recorded as lines parallel to the rotation axis; all others are recorded as lines inclined to that axis. This is shown clearly in Buerger's (1942) Fig. 137 and it is, of course, observable in rotation as well as Weissenberg photographs.

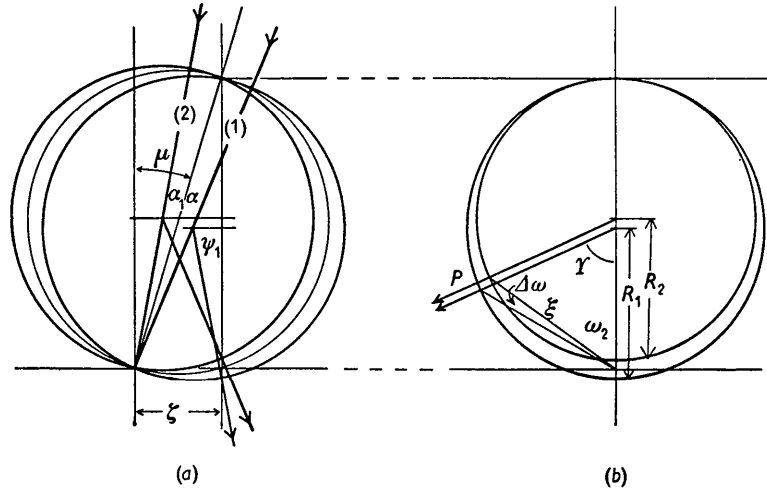


Fig. 4. Reciprocal-space diagrams showing Ewald spheres for a divergent incident X-ray beam and the genesis of reflexions in the equi-inclination angle setting.

Since, according to simple theory, there is no resultant change in spot area this effect is not considered further.

3.2. Equi-inclination-angle setting

The orientation of the limiting and mean spheres of reflexion and their relation to the reciprocal-lattice plane under examination are shown in Fig. 4. For an equi-inclination angle μ , given by $\sin \mu = -\frac{1}{2}\zeta$, we have, in the notation introduced above,

$$r_1 = \cos(\mu + \alpha_1), \quad r_2 = \cos(\mu - \alpha_1), \quad r_0 = \cos \mu \quad (12)$$

and

$$R_1^2 = 1 - \{\zeta - \sin(\mu + \alpha_1)\}^2; \quad R_2^2 = 1 - \{\zeta - \sin(\mu - \alpha_1)\}^2, \quad (13)$$

where the effective beam divergence $2\alpha_1$ is given by

$$2\alpha_1 = 2\alpha \cos \mu. \quad (14)$$

Hence, if α is small,

$$\left. \begin{aligned} R_1 &= r_2 = \cos \mu + \alpha_1 \sin \mu, \\ R_2 &= r_1 = \cos \mu - \alpha_1 \sin \mu, \\ \text{and } R_0 &= r_0 = \cos \mu. \end{aligned} \right\} \quad (15)$$

The limiting circles of reflexion again are given by (3) and (4) so that

$$2 \sin \omega_0 \sin \frac{1}{2} \Delta \omega = \frac{r_2 \{\xi^2 + (r_1^2 - R_1^2)\} - r_1 \{\xi^2 + (r_2^2 - R_2^2)\}}{2r_1 r_2 \xi}. \quad (16)$$

Then, since $r_1 + r_2 = 2r_0$ and $\sin^2 \omega_0 = (4R_0^2 - \xi^2)/(2R_0)^2$,

$$\Delta \omega \simeq 2 \sin \frac{1}{2} \Delta \omega = \frac{(r_1 + r_2)(r_1 - r_2) \left\{ \frac{(r_1 + r_2)^2}{\xi^2} - 1 \right\}^{\frac{1}{2}}}{2r_1 r_2}. \quad (17)$$

Substituting from (14) and (15), we have

$$\Delta \omega \simeq 2\alpha \sin \mu \left(\frac{\xi_m^2}{\xi^2} - 1 \right)^{\frac{1}{2}}, \quad (18)$$

where $\xi_m = (4 - \zeta^2)^{\frac{1}{2}}$ is the maximum observable value of ξ .

The angular range over which the crystal reflects thus increases as ξ decreases and as ζ increases. The form of the variation is apparent in Fig. 6.

In this setting there is no significant variation in γ during reflexion.

3. Reflexion-spot length without camera translation

3.1. Normal-beam setting

The X-rays reflected from the mean direction in the incident beam lie on a conical surface with semi-vertical angle ψ_0 such that $\cos \psi_0 = \zeta$. Similarly, $\cos \psi_1 = \zeta - \alpha$ and $\cos \psi_2 = \zeta + \alpha$ define the surfaces to which X-rays reflected from the extreme incident directions are confined. These surfaces intersect the film at

$$X_1 = \mathfrak{R}_1 \cot \psi_1 \quad \text{and} \quad X_2 = \mathfrak{R}_1 \cot \psi_2 + l, \quad (19)$$

where \mathfrak{R}_1 is the camera radius and l the length of the crystal. The length of the reflexion spot is thus

$$L = \mathfrak{R}_1 (\cot \psi_2 - \cot \psi_1) + l, \quad (20)$$

or, if α is small and since $\zeta < 1$,

$$L = 2\alpha \mathfrak{R}_1 / (1 - \zeta^2)^{\frac{3}{2}} + l. \quad (21)$$

Then, since $l = 2\alpha \mathfrak{R}_2$, where \mathfrak{R}_2 is the pin-hole to crystal distance,

$$L = 2\alpha \{ \mathfrak{R}_1 / (1 - \zeta^2)^{\frac{3}{2}} + \mathfrak{R}_2 \}. \quad (22)$$

When $\zeta = 0$, therefore,

$$L = 2\alpha (\mathfrak{R}_1 + \mathfrak{R}_2) \quad (23)$$

and L increases with ζ .

3.2. *Equi-inclination-angle setting*

The mean and limiting reflected beams lie in cones with semi-vertical angles given by

$$\cos \psi_0 = \sin \mu, \quad \cos \psi_1 = \sin (\mu - \alpha_1) \quad \text{and} \\ \cos \psi_2 = \sin (\mu + \alpha_1). \quad (24)$$

Then, from (20) we have

$$L = \mathfrak{R}_1 \{ \tan (\mu + \alpha_1) - \tan (\mu - \alpha_1) \} + l \quad (25)$$

or, for small α ,

$$L = 2\alpha \{ \mathfrak{R}_1 / (1 - \zeta^2/4)^{\frac{1}{2}} + \mathfrak{R}_2 \}. \quad (26)$$

Again $L = 2\alpha(\mathfrak{R}_1 + \mathfrak{R}_2)$ when $\zeta = 0$, but in this setting L increases only slowly as ζ increases.

3.3. *Interpretation of results*

This simple analysis makes no allowance for the additional lengthening due to extension of the effective X-ray source and to the natural length of reflexions from individual crystal elements. When the experimental arrangement fulfills the conditions mentioned in § 1 the reflexion from each element has a nearly square profile of length, when $\zeta = 0$, given by

$$S_1 \simeq S \mathfrak{R}_1 \mathfrak{R}_2, \quad (27)$$

where S is the pin-hole width. Equations (23) and (25) then give the integral lengths of the reflexions, $\int IdL/I_{\max.}$. Approximations to the lengths having peak intensity are given by subtracting S_1 , while the total lengths are given by adding S_1 . It is clear, incidentally, that maximum peak intensity in any reflexion is obtained only when $L \geq S_1$, giving reflexion lengths, measured on the film, between $L + S_1$ and $L - S_1$ according to intensity. Limits are thus established for the crystal length:

$$S > l > S \mathfrak{R}_1 / (\mathfrak{R}_1 + \mathfrak{R}_2). \quad (28)$$

4. Reflexion-spot length with camera translation

The instrumental constant C_2 relates distance travelled by the camera to angular rotation of the crystal. Thus $\Delta L = \Delta\omega/C_2$, where C_2 commonly is equal to 2 when L is measured in millimetres and ω in degrees. The lengths of corresponding reflexions on opposite sides of the film, $L + \Delta L$ and $L - \Delta L$, then give for the normal-beam setting

$$\frac{L \pm \Delta L}{L} = 1 \pm \frac{180}{\pi} \frac{\zeta}{[\{4\xi^2 - (\zeta^2 + \xi^2)^2\}^{\frac{1}{2}} \{ \mathfrak{R}_1 / (1 - \zeta^2)^{\frac{1}{2}} + \mathfrak{R}_2 \}]} \quad (29)$$

and for the equi-inclination setting

$$\frac{L \pm \Delta L}{L} = 1 \pm \frac{180}{4\pi} \frac{\zeta (\xi_{ml}^2 \xi^2 - 1)^{\frac{1}{2}}}{\{ \mathfrak{R}_1 / (1 - \zeta^2/4)^{\frac{1}{2}} + \mathfrak{R}_2 \}}. \quad (30)$$

The variations of these functions with ξ are shown in

Figs. 5 and 6 for typical values of ζ and camera dimensions $\mathfrak{R}_1 = 28.7$ mm., $\mathfrak{R}_2 = 78.0$ mm.

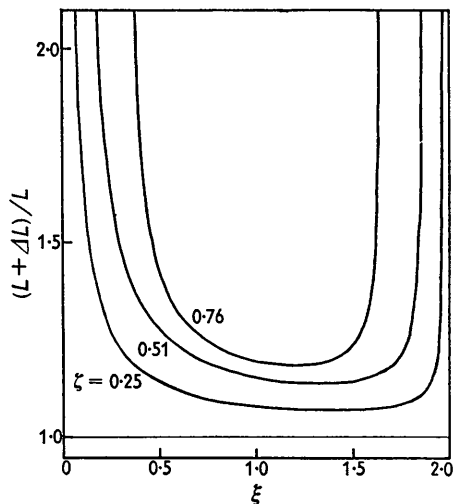


Fig. 5. Variation of $(L + \Delta L)/L$ with ξ and ζ in the normal-beam setting.

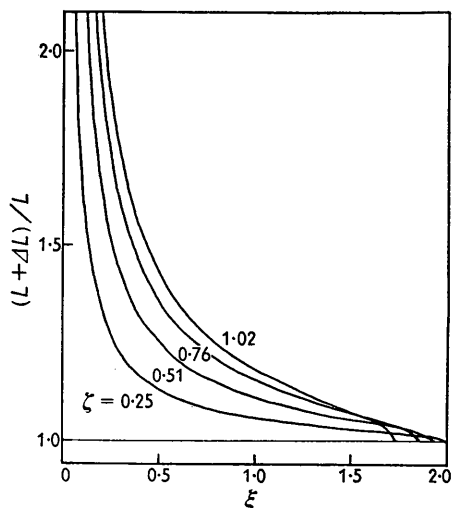


Fig. 6. Variation of $(L + \Delta L)/L$ with ξ and ζ in the equi-inclination-angle setting.

It must be noticed, however, that while the length of the extended spot can increase indefinitely, the contracted spot has a minimum length S_1 when $\Delta L = L$. For larger values of ΔL the length of the reflexion spot again increases. S_1 , furthermore, is not a constant but varies because of the camera translation in the same way as the overall reflexion length, except that it is contracted when the reflexion spot is extended and increased when the whole spot is contracted. The variation in spot size clearly cannot be eliminated by decreasing the crystal size and it is assumed here that the crystal length lies in the range defined by equation (28).

5. Visual estimation of intensities

We have considered so far a crystal element parallel to the rotation axis. If now a large number of such elements are considered together equations (29) and (30) can be taken to govern the variation in reflexion-spot area since no new asymmetry is introduced by the vertical divergence of the X-ray beam.

Visual estimation of reflexion-spot densities gives results proportional to either the mean optical density or the peak optical density. For sufficiently large crystals these are not widely different and, since the use of calibration spots makes allowance for departures from linearity in the exposure-density relationship, the process may be considered to measure the mean X-ray energy per unit area incident on the photographic film. We may suppose that the number of silver grains, N , in any spot corresponding to a particular reflexion remains constant whatever the variations in area. Then, if the densities in both the extended and contracted spots are estimated, we have, for small variations in area,

$$N = n_0 A = n_1(A + \Delta A) = n_2(A - \Delta A). \quad (31)$$

n_1 , n_2 are the observed densities and n_0 is the undistorted value to be derived from them. Obviously

$$n_0 = 2n_1n_2/(n_1+n_2), \quad (32)$$

i.e. the harmonic mean of the two observed values can be used when variations in spot area are small. When the variations are very small, this is equivalent to the arithmetic mean recommended by Kaan & Cole (1949).

When the variations in area are large, however, the method outlined above cannot be used because the area of the contracted spot then is not simply $(A - \Delta A)$. In these circumstances the best procedure is to estimate the densities of the extended spots alone, and to correct them by use of the formula $n_0 = n_1 W$, where

$$W = (A + \Delta A)/A \quad (33)$$

is given by (29) or (30).

The validity of this method has been tested by comparing visual estimations corrected in this way with photometric measurements of the intensities of the same reflexions when recorded by the integrating-Weissenberg camera* (Wiebenga & Smits, 1950). The

* Intensities may, of course, be estimated visually from properly integrated reflexion-spots (Wiebenga & Smits, 1950), but the instrument required for this solution to the problem is not available in most laboratories.

equi-inclination angle setting was used. Table 1 shows the results. The intensities are from the $h3l$ level for

Table 1. Comparison of corrected visual estimations WI_v with measured integrated intensities I_p .*

hkl	ξ	W	I_v	WI_v	I_p
131	0.190	1.96	34	67	63
032	0.228	1.82	29	53	59
132	0.282	1.64	293	480	492
231	0.326	1.56	181	282	225
232	0.382	1.48	358	530	491
133	0.388	1.47	52	76	80
034	0.456	1.40	15	21	19
233	0.470	1.38	50	69	65
234	0.494	1.36	42	57	44
135	0.606	1.29	10	13	13
236	0.774	1.22	41	50	51
237	0.804	1.21	8	10	8
137	0.830	1.20	71	85	73
237	0.884	1.18	13	15	19
038	0.912	1.18	16	19	16
138	0.942	1.17	15	18	18
239	1.102	1.13	5	6	8
2,3,10	1.130	1.13	5	6	5
2,3,11	1.242	1.10	17	19	15
2,3,14	1.578	1.06	6	6	6

* The scales of these relative intensities have been adjusted to make ΣI_v , ΣWI_v and ΣI_p nearly the same for $\xi > 1.0$.

acridine III (Phillips, 1950), and the correction curve is that shown in Fig. 6 for $\zeta = 0.76$ r.l.u. The corrected visual estimations clearly agree very well with the photometric measurements of integrated intensity.

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