The a_i's are independent of the chosen values of h, k, l and there are similar equations with constants b_i and c_i for variable k or l respectively. When $k=l=0$ one can simplify the result by using the facts that $\hat{F}_{h00}=\hat{F}_{\bar{h}00}$ and $\hat{F}_{000}=1$.

By a simple transformation an analogous equation can be written which corresponds to any set of parallel row lines in reciprocal space in the way that the given equation corresponds to rows parallel to the axis a_0^*. But there can be no more than three independent sets of constants for a crystal.

This equation can be applied only if the unit cell is large enough in one direction to show at least $(N+1)$ $\hat{F}$'s with two indices constant. This in itself is a severe limitation. The constants a_i are related to the x coordinates of the atoms through Newton's relations and for Banerjee's special case are directly related to the $\hat{F}_{h00}$'s. Since the equation is linear in the $\hat{F}$'s a scale factor may be included, so that it is applicable to relative as well as to absolute data. If enough signs are known, so that the a's can be calculated, the equation can be used to obtain other signs or sign relationships quite rapidly for other rows with k and l constant. Thus, for example, if the $h0l$ reflections have been signed they may be used to calculate the a_i's and c_i's and the equation used on the hkl data.

With a_i's calculated from the x parameters this method gave correct results on the larger $\hat{F}_{h0l}$'s for dicyandiamide (Hughes, 1940). For this projection $N=2n=12$. This, however, is not a very severe test.

With more symmetry than a symmetry center there are additional relationships between the roots and consequently further reduction in the number of the various constants. One may also use the fact that with higher symmetry the number of equivalent planes in a form is generally greater. For example, with a mirror plane perpendicular to the a_0 axis of the crystal, $\hat{F}_{hkl}=\hat{F}_{\bar{h}kl}$, with consequent simplification of an equation like that above.

If atoms occur in special positions of a space group, there will be one or more roots with special fixed values, such as ± 1. Such roots must be included in the polynomial when deriving an appropriate equation for the $\hat{F}$'s.

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The Measurement and Correction of Intensities from Single-Crystal X-ray Photographs

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An account is given of the effect of spot size in single-crystal X-ray photographs on the errors in intensity measurements made by eye estimation and by direct photometry of the negative. It is shown how direct photometry of the negative has been used to obtain intensities from equi-inclination Weissenberg photographs to within an accuracy of ± 10 %. Charts are given for the simultaneous correction of X-ray intensities for Lorentz and polarization factors for equi-inclination Weissenberg photographs and for rotation and oscillation photographs.

The measurement of X-ray intensities

Direct measurements of integrated X-ray intensities may be made on the instruments described by Robinson (1933), Dawton (1937) and Robertson & Dawton (1941), or that suggested by Wiebenga (1947). Indirect measurements may be carried out by the methods suggested by Dawton (1938). However, most single-crystal workers, in recent years, have measured X-ray intensities by eye comparison of a standard intensity scale against the series of unknown spots. The intensity scale is made by successively exposing different portions of a piece of X-ray film to a suitable reflexion for various time intervals during which the X-ray output is maintained constant.

Eye estimation of intensities is physically tiring and liable to serious error owing to the fact that the unknown spots have not the same size or variations in density as the spots of the intensity scale. Furthermore, although one observer may reproduce results to within an accuracy of 10 %, several observers may obtain quite different values because the linear dimensions of the spots are close to the limit of smallest detail visible by eye. One observer may see the spots well detailed and will therefore match maximum densities. Another observer may not be able to see the spots so well and will consequently match two spots having more or less the same mean transparency.

Eye estimation of intensities can become particularly unreliable for general *hkl* reflexions, for in the usual methods of collecting these data there are two effects which alter considerably the size of reflexions and the distribution of density in comparison with those obtained from zero-level photographs, which are normally used in making intensity scales.

The obliquity effect

This effect arises because for all reflexions, other than those from the zero level, the diffracted X-ray beam passes through the film obliquely and in so doing suffers increased absorption and covers a larger area of photographic emulsion than for normal incidence. The effect has been discussed by Cox & Shaw (1930), who published a table of factors by which the observed intensities must be multiplied to obtain the true values. However, these factors apply to integrated intensities and cannot be used when intensities are measured visually. The obliquity effect occurs in both oscillation and Weissenberg photographs.

The contraction and extension of spots on Weissenberg photographs

All Weissenberg photographs, other than those from the zero level, show a drawing out of the spots on one half of the film and a contraction of the spots on the other half. The effect has been discussed by Buerger (1942), who showed how it arose because of the divergence of the X-ray beam. It can also be shown that the change in area is not the same for a reflexion occurring on both halves of the film.

The effect of spot size on the accuracy of intensity measurements

Measurements made by the authors in the present investigation have shown that the variation in density within spots is not large and may be neglected when intensities are measured to within an accuracy of only ±10 %. Variations in size of spots, on the other hand, is a much more serious matter and can cause large errors in measurements made either by eye observations or by direct photometry of the negative, as the following analysis will show.

Let us consider what happens when an unknown spot of area A_x and density D_x is measured against an intensity scale the spots of which have an area A_t and a density D_t. The density within all spots is considered constant.

With an integrating photometer we will find that $A_x D_x = A_t D_t$, so that

$$D_x = \frac{A_t}{A_x} D_t. \tag{1}$$

With eye observation we have, for an observer viewing the spots through a hand lens and consequently matching maximum densities,

$$D_x = D_t. \tag{2}$$

With direct measurement of the negative the following analysis applies. A spot is measured with a light beam larger than its area and from the photometer measurements we can find the difference between the amount of light transmitted when the spot is under the beam of light and when the clear film base is under the same beam of light. Let the light beam cover an area A and let the unknown spot have an area A_x with a transparency t_x, leaving an area $A - A_x$ of clear film base with a transparency t'_0. Similarly, let a spot on the intensity scale have an area A_t with a transparency t_t, leaving an area $A - A_t$ of clear film base with a transparency t_0. For the unknown spot the difference in light transmission set out above is proportional to

$$t'_0 - \left\{\frac{A_x t_x}{A} + \frac{A - A_x}{A} t'_0\right\}.$$

For a spot on the intensity scale it is proportional to

$$t_0 - \left\{\frac{A_t t_t}{A} + \frac{A - A_t}{A} t_0\right\}. \tag{3}$$

These differences, reduced to the same clear film base value, must be the same, so

$$1 - \left\{\frac{A_x}{A}\frac{t_x}{t'_0} + \frac{A - A_x}{A}\right\} = 1 - \left\{\frac{A_t}{A}\frac{t_t}{t_0} + \frac{A - A_t}{A}\right\},$$

which reduces to

$$\frac{t_x}{t'_0} = \frac{A_t}{A_x}\frac{t_t}{t_0} + 1 - \frac{A_t}{A_x}.$$

But as we define $D = \log_{10}(t_0/t)$,

then
$$10^{D_x} = \frac{A_t}{A_x} 10^{D_t} + 1 - \frac{A_t}{A_x}. \tag{4}$$

By considering constant values of A_t/A_x we can plot equations (1), (2) and (4), as has been done in Fig. 1 for $A_t/A_x = 2$ and for $A_t/A_x = \frac{1}{2}$. All curves are symmetrical about $D_x = D_t$ and are true only up to a density of 0·75. Equation (4) is asymptotic, for, in the case of $A_t/A_x = \frac{1}{2}$, as D_t tends to ∞ D_x tends to 0·301. This means that if an unknown spot has a density of 0·301 and a size twice that of the spots on the intensity scale, integrating photometry would show it had the same X-ray intensity as a spot on the intensity scale having a density of 0·602, but direct photometry of the negative would give no result at all. With eye estimation it would be said that the unknown spot was formed by the same X-ray intensity as a spot on the intensity scale of density 0·301. Such a result is quite inaccurate. Direct measurement of the negative at or below a density $D_t = 0{\cdot}4$ would give greater accuracy than from eye estimation, and below a density $D_t = 0{\cdot}2$ the results are accurate to within ± 10 %.

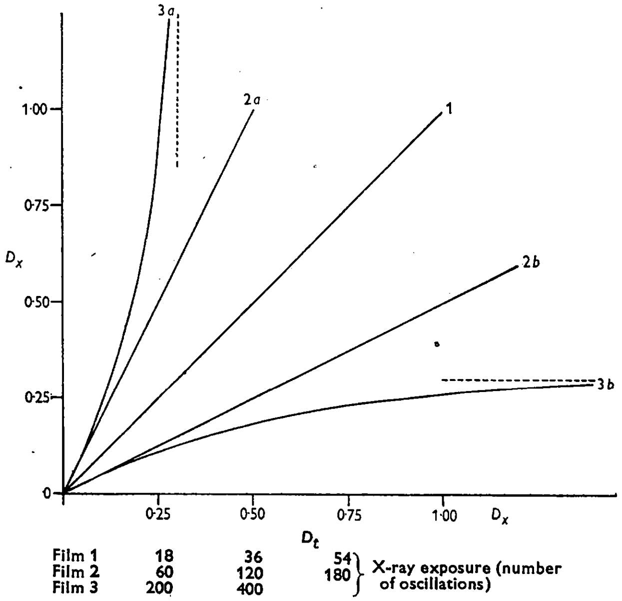

Fig. 1. Curves showing the effect of measuring unknown spots of area A_x against an intensity scale with spots of area A_t. 1, by eye estimation (equation 2); 2*a*, by integrating photometry for $A_t/A_x = 2$ (equation 1); 2*b*, by integrating photometry for $A_t/A_x = \frac{1}{2}$ (equation 1); 3*a*, by direct photometry of negative $A_t/A_x = 2$ (equation 4); 3*b*, by direct photometry of negative $A_t/A_x = \frac{1}{2}$ (equation 4).

Direct photometry of the negative in practice

The results of the previous section can be verified by plotting the film characteristic curve in the form of transparency *v.* X-ray exposure (Fig. 2). These curves show that up to a transparency of 65 %, or a density of 0·20, $(t_0 - t)$ is proportional to the X-ray exposure.

If measurements are now made on an intensity scale, as outlined in the previous section, and allowance is made for the fact that the density within a spot is not uniform, so that an area ΔA has a transparency t_t, then equation (3) becomes

$$t_0 - \left\{\sum_{A_t} t_t \frac{\Delta A}{A} + \frac{A - A_t}{A} t_0\right\},$$

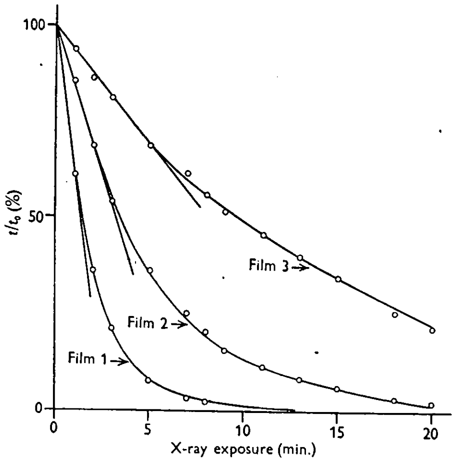

Fig. 2. Characteristic curve of Kodak Industrex films, separated by 0·210 mm. Cu foils and exposed to Mo $K\alpha$ radiation, plotted in the form of transparency *v.* X-ray exposure.

which reduces to

$$\frac{1}{A}\left\{\sum_{A_t} t_t \Delta A - t_0 A_t\right\}.$$

This is of the form $\sum_{A_x} (t_0 - t)\,\Delta A$,

and is proportional to the X-ray exposure. Results of such measurements are shown in Fig. 3, where the values have been reduced to the same clear film base value by dividing throughout by t_0. The curves show that $(t_0 - t)/t_0$ is proportional to the X-ray intensity up to an exposure of 18 for film (1), 45 for film (2) and 160 for film (3). Other measurements show that a density of 0·20, the maximum density for which linearity exists between transparency and X-ray intensity, corresponds to an exposure of 15 for film (1), 49 for film (2) and 156 for film (3).

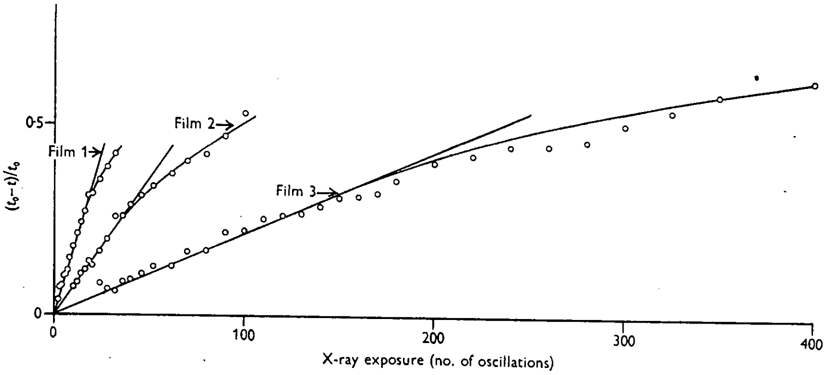

Fig. 3. Transparency *v.* X-ray exposure curve for intensity scales on Kodak Industrex films separated by 0·210 mm. Cu foils and exposed to Mo $K\alpha$ radiation. Measurements were made using a beam of light larger in area than the area of the spots on the intensity scales.

Discussion

This work arose out of difficulties encountered in trying to measure X-ray intensities accurately by eye from equi-inclination Weissenberg photographs in collecting data for (*hkl*) general reflexions. Initially it was not known how the two values for the same reflexion occurring on both halves of the film should be treated, and when a reflexion occurred on only one half of the film the position was even worse. The results show that the best way to measure such films by eye is to view them at a distance, when a mean of the values from the two halves is fairly accurate for most reflexions. However, the integration by eye is not complete and for large changes in area, and where a reflexion occurs on only one half of the film, eye estimation is inaccurate. These points are illustrated in Table 1.

Table 1. *Comparison of X-ray intensities measured on equi-inclination Weissenberg photographs by the positive-film method, by direct photometry of the negative, and by eye estimation*

						Eye estimation			
		Positive film		Negative film		(*a*) Viewed at a distance		(*b*) Viewed through a lens	
Level	Indices	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
*hk*0	040	226		239		208			
	060	270		292		232			
	080	38		34		35			
	0,10,0	35		34		32			
	0,12,0	3·5		4·5		4·5			
	0,14,0	3		3		4·5			
	0,16,0	22		22		19			
*h*8*l*	082	18·5	21·5	15	23	13	28	12	66
	083	25	28·5	25	29	20	38	16	59
	084	54	60	47	52	28	70	32	90
	$28\bar{1}$	—	—	10	—	7	—	—	—
	$28\bar{2}$	—	—	16	20	13	25	—	—
	$48\bar{1}$	—	—	—	23	—	32	—	—
	$48\bar{2}$	—	—	17	—	68	—	—	—
	$48\bar{4}$	—	—	43	43	34	80	—	—
*hk*3	043	—	—	—	92	—	150	—	—
	063	—	—	19	23	18	28	—	—
	$35\bar{3}$	—	—	46	50	46	90	—	—

In the determination of X-ray intensities from our Weissenberg photographs we finally used direct measurement of the negative up to an intensity of 160, which included most reflexions, and beyond this either positive-film technique or direct measurement of short exposures. The measurements could be made quite quickly, were free from bias, could be carried out by more than one individual, and were more accurate than estimations by eye. We prefer to use direct measurement of the film rather than of a positive film because, apart from the necessity of reprinting all the X-ray negatives, we have found the exposure and developing conditions for the positive more critical than suggested by Dawton, and one should consequently print an intensity scale with each positive to verify linearity between transparency and X-ray exposure. The curves we have obtained are very similar to those published by Wood & Williams (1948).

Finally, it will be noted that we used multiple-film technique in determining our intensities and that, in effect, we prepared three intensity scales simultaneously by making exposures with the same film and screen combination as used in the Weissenberg photographs. Thus each unknown film has its own intensity scale, and factors relating exposures on the different films of the multiple-film packet do not have to be determined.

The correction of X-ray intensities

Once the X-ray intensities have been determined they must be corrected for Lorentz and polarization factors before they can be converted into the final F values required for Fourier syntheses. Thus $I_0 \propto LpF^2$, where I_0 is the X-ray intensity, L is the Lorentz factor, p is the polarization factor and F is the structure factor for the plane under consideration. The polarization factor is independent of the method of recording and is given by $\frac{1}{2}(1+\cos^2 2\theta)$. The Lorentz factor depends on the method of recording and, as shown by Buerger & Klein (1945), can be expressed in the form of $1/(S \sin \gamma)$, where S is a level scale factor, constant for any level, and γ is the angle between the direct beam and the projection of the reflected ray on the plane, normal to that containing the reflexion and the rotation axis (Buerger, 1942). For all but rotation and oscillation photographs, S may be eliminated by suitable timing of exposures so that the Lorentz factor is a matter of applying $\sin \gamma$ to each level. The combined Lorentz and polarization factor then becomes

$$\frac{1}{Lp} = \sin \gamma \frac{2}{1+\cos^2 2\theta}. \tag{5}$$

In correcting large numbers of X-ray intensities it is advisable to have these factors in a combined form, and in the present paper charts are given whereby this can be carried out in one operation for equi-inclination Weissenberg photographs and for rotation and oscillation photographs.

Equi-inclination Weissenberg photographs

The plot of equation (5) against μ, the angle of inclination, is given in Fig. 4. For a given angle of inclination the combined correction factors are straight lines running across the film at the points of intersection of the $1/Lp$ *v.* μ curves. It will be noticed that Fig. 4 is essentially the same as Fig. 2 published by Lu (1943), who gives a plot of

$$\alpha=\frac{\cos^2\mu\sin\gamma}{1+\cos^2 2\theta} \quad \text{against} \quad \xi=2\sin\mu.$$

The present chart, which was constructed before the close similarity with that of Lu was realized, is to be used when $\cos^2\mu$ is eliminated by suitable timing of exposures. Lu also published a chart whereby the same corrections can be applied by means of the reciprocal net. A similar chart has recently been prepared by Cochran (1948) who, like ourselves, was unaware of the existence of Lu's charts.

Rotation and oscillation photographs

For these photographs

$$\frac{1}{L}=\cos\mu\sin\gamma=\frac{\sin\gamma}{(1-\xi^2)^{\frac{1}{2}}}=\sin 2\theta\,\frac{(\sin^2\rho-\sin^2\theta)^{\frac{1}{2}}}{\cos\theta}, \qquad (6)$$

where ρ is the angle between the rotation axis and the normal to the crystal plane. The expression

$$\frac{(\sin^2\rho-\sin^2\theta)^{\frac{1}{2}}}{\cos\theta}$$

has been evaluated by Cox & Shaw (1930). We have combined this expression with $\sin 2\theta\,\dfrac{2}{1+\cos^2 2\theta}$, values of which have been published by Buerger & Klein (1945), giving a chart, Fig. 5, of combined $1/Lp$ factors as they vary on rotation and oscillation photographs. This chart serves the same purpose as a similar chart, recently prepared by Cochran (1948), which expresses the same function in terms of the reciprocal net.

In practice Figs. 4 and 5 are enlarged to suit a particular camera radius. Reproductions can be supplied by the authors to suit a camera of radius 3·00 cm.

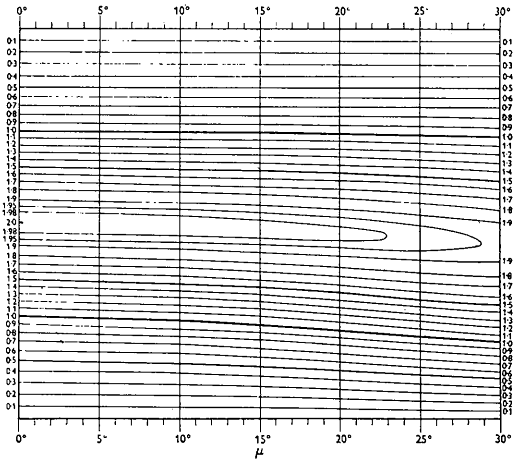

Fig. 4. Variation of combined Lorentz and polarization factors ($1/Lp$) with angle of inclination (μ) on equi-inclination Weissenberg photographs.

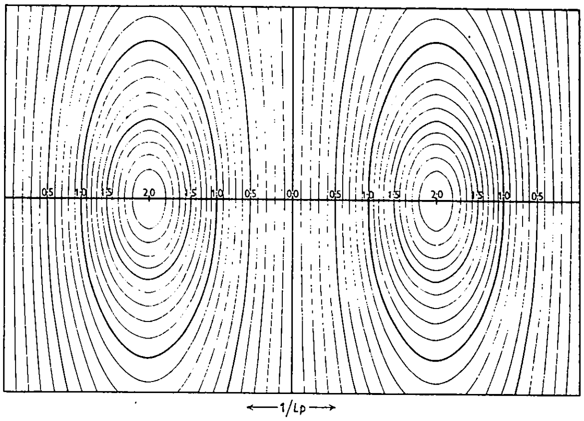

Fig. 5. Variation of combined Lorentz and polarization factors ($1/Lp$) on rotation and oscillation photographs.

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Indexing Powder Photographs of Orthorhombic Crystals

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A method for attempting to index the powder photograph of an orthorhombic substance is described and is illustrated by its successful application to the indexing of recently published data for KNO_3.

I was interested to read the paper by Hesse (1948) on the interpretation of powder photographs. Several years ago I devised rather similar methods, which, for the lack of suitable data on which to test them, were not published, although they are to be described in a book, now in the press, on the interpretation of X-ray diffraction photographs, written by Dr W. A. Wooster, Dr N. F. M. Henry and myself.

The publication of the data for KNO_3, however, led me to try out my method again and since it proved completely successful I propose to describe it in full in the present article. The method is essentially the same as that described by Hesse but is, I think, rather neater.

1. General principles

The method is based on that described by Bradley & Taylor (1937), who made use of the relation

$$q_{hkl} = \sin^2\theta_{hkl} = h^2A + k^2B + l^2C,$$

where $A = \lambda^2/4a^2$, $B = \lambda^2/4b^2$, $C = \lambda^2/4c^2$. The problem is to find values of A, B and C that account for all the observed values of q with integral values of h, k and l; the method is to examine systematically the differences between the observed values of q, in order to detect relationships such as

$$q_{0kl} - q_{1kl} = A,$$
$$q_{0kl} - q_{2kl} = 4A, \ \ldots, \text{ etc.}$$

In addition, it is useful to form some idea of the order of magnitude to be expected for the quantities A, B and C, so that one should know for what sort of difference to look.

2. Order of magnitude of A, B and C

The quantities A, B and C depend upon the cell dimensions and are larger for smaller unit cells. The larger the unit cell the larger the number of lines on the powder photograph, and hence, by examining the number of lines that appear within a given range of q, it should be possible to decide on the order of magnitude of A, B and C. So many simplifying assumptions have to be introduced that it is not possible to attain any high accuracy, but this is not necessary.

Suppose that the number of lines on the powder photograph with values of q less than q_m is M. The number of points in reciprocal space satisfying this condition is approximately

$$\frac{4\pi}{3}(2q_m^{\frac{1}{2}})^3\frac{1}{V^*},$$

where V^* is the volume of the unit cell of the reciprocal lattice.

This, however, is not equal to the number of lines on the powder photograph for several reasons: in the orthorhombic system, the reciprocal points hkl, $\bar{h}kl$, $h\bar{k}l$, etc., all represent reflexions with the same value of q, and so give only one powder line; moreover, many reflexions will be absent because their structure amplitudes are very small, or because they are forbidden by space-groups conditions. Both these effects are difficult to assess quantitatively, but as a rough approximation we may allow the factor 8—the multiplicity factor for the general reflexion in the orthorhombic system—for