

Photometry of Single-Crystal X-ray Photographs

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The derivation of intensities from single crystal X-ray photographs is discussed, and a method of direct photometry of the negative is described in detail. The errors likely to occur are examined, and it is shown that they do not usually exceed 10% in those cases where the variation in spot area is less than 2:1. An alternative photometric procedure is suggested which may prove advantageous when large variations in spot area are found.

1. Introduction

Most of the methods which have been employed hitherto for the estimation of single-crystal X-ray intensities by the photometric measurement of the blackening of a photographic film have involved some special piece of apparatus such as an integrating photometer (Robinson, 1933; Dawton, 1937; Robertson & Dawton, 1941) or a special Weissenberg camera (Wiebenga, 1947), or have necessitated a subsidiary photographic process, as in the positive-print method (Dawton, 1938). In view of the time and expense involved in constructing special equipment and the difficulties and possible errors involved in the positive-print process (Kaan & Cole, 1949), none of these methods is widely used. The visual comparison of X-ray spots with a standard calibration negative, preferably produced from the same crystal, is still widely used in spite of its recognized disadvantages of failure to take account of changes in spot area and of the subjective factor in comparison of blacknesses of two different spots.

The direct photometry of the X-ray negative would seem to be a method capable of combining reasonable accuracy with relative simplicity of apparatus, but the method was rejected by Dawton (1938) in view of the non-linear relationship between spot transparency and X-ray intensity, and it has more recently been considered and criticised by Kaan & Cole (1949). They discuss the errors involved in comparing the blacknesses of spots of the crystal diffraction pattern with those of a standard calibration negative when different spot areas occur. The exploring light beam is assumed to illuminate a constant area of film in each case. Briefly, the error is due to the insensitivity of the method when the spot area is small compared with the size of the exploring light beam. However black the spot, it cannot absorb more of the exploring beam than the fraction of the total illuminated area which

it occupies, and thus, for small spots having a wide range of blackness, the transmitted beam will show only a small variation of intensity.

A photometric method which to some extent avoids this difficulty has been in use for some time in this laboratory, a Hilger non-recording photoelectric microphotometer being employed. The method yields results certainly equal to, and in most cases more accurate than, those obtained by visual estimation, and is to be preferred to the latter method, if only on account of the absence of the subjective factors. The details of the method are given below (§ 2) together with a brief theory of its operation and a consideration of its limitations. In § 3 a photometric method is suggested which may prove to be capable of higher accuracy.

2. The direct photometric method

In this paper we have used 'transmission' to mean the total light flux falling upon the photocell from the exploring beam, after passing through the X-ray negative. The photometer reading is proportional to the transmission. 'Transparency' is defined as the ratio of light intensity (or flux per unit area) in the incident beam to that in the transmitted beam.

A standard calibration negative is prepared in the usual way by exposing a selected crystal reflexion for successively increasing periods of time, keeping the X-ray tube output constant. When the film has been processed, it is placed on the photometer and the exploring light beam and photocell aperture are arranged so that the illuminated area of the film projected on the cell is just greater than that of the spots on the calibration negative. The galvanometer sensitivity is adjusted to give full-scale deflexion for the transmission of clear film base, and then the deflexion corresponding to the transmission of each

of the spots is read off. In each case the transmission is that of the spot surrounded by a small area of film which has been exposed to weak incoherent radiation only, but since the method of preparation of the calibration negative ensures that the incoherent intensity is a constant fraction of the coherent intensity, the total transmission will vary regularly with X-ray exposure.

The blackening of a uniform area of film is specified by the optical density, D , defined in terms of the transparency t , and the transparency of clear base t_0 by $D = \log_{10}(t_0/t)$. For X-ray film, D is proportional to exposure at constant intensity if D is not too high, and thus a convenient calibration curve for a given emulsion is obtained by plotting $\log(t_0/t)$ against exposure. In fact, the graph plotted is that of exposure against the log of the ratio of the two transmissions, measured as described above, since the transparency t is not directly measured by the photometer. Such a curve may then be used to convert densities into relative X-ray intensities, since relative exposures at constant intensity and relative intensities at constant exposure time are, within wide limits, the same.

The film bearing the spots of the crystal diffraction pattern to be measured is then placed on the photometer, and again the exploring light beam and photocell aperture are adjusted until an area just larger than the largest spot is projected on to the cell. This will frequently involve a different area from that used with the calibration negative, but it ensures that the instrument is operated in the most sensitive manner. The sensitivity control is then adjusted to give full scale deflexion (P units) for clear film base, most conveniently done on Weissenberg photographs on the central clear portion of the film caused by the shadow of the beam catcher. Then for each spot two measurements are made: one of the transmission when the spot is projected on to the photocell (β units), and the other of the transmission of an adjacent patch of film corresponding to the same $\sin \theta$ value (α units). β is the transmission due to clear film base together with the coherent crystal reflexion ('spot') and the incoherent background, while α is the transmission due to clear base and background only, in the region of the spot. One then calculates $\log(P/\alpha)$ and $\log(P/\beta)$, reads off the corresponding X-ray intensities from the calibration curve and obtains, by subtraction, the intensity of the spot alone.

The theory of this method will now be considered briefly, first with regard to the calibration negative, and then in its application to the film bearing the crystal diffraction pattern.

Let I be the intensity of the light beam incident upon the film in the photometer and t_0 , b , t_s be the transparencies of clear base, background and spot respectively. Assume that the exploring beam has cross-sectional area A just greater than that of the spot on the calibration negative. The expressions for the three quantities P , α and β are as follows:

$$P = IAt_0,$$

$$\alpha = IAt_0b,$$

$$\beta = I[A_s t_0 b t_s + (A - A_s) t_0 b],$$

whence

$$t_s = \frac{A}{A_s} \left[\frac{\beta}{\alpha} + \frac{A_s}{A} - 1 \right].$$

The density of the calibration spot is

$$D = \log \frac{t_0}{t_s} = k + \log \left[\frac{A_s}{A(\beta/\alpha + A_s/A - 1)} \right],$$

where k is a constant, since we assume a constant clear-base transparency for the film. Since the areas A_s and A are unknown, this correct expression is not used in the calibration plot. Instead, $\log(P/\beta)$ is plotted against exposure. Although background transmission does not enter into this expression, this procedure may be justified in the case of the calibration spots because (i) the background density is always extremely small so that $b \simeq 1$ and $\alpha \simeq P$, and (ii) the incoherent X-ray intensity causing the background is proportional to the coherent intensity. Experimentally the procedure appears to be justified since the calibration curves for both Ilford Industrial B and Industrial G films are linear, within experimental error, at least up to the point where the spots begin to look opaque. The characteristic curves for the emulsions, kindly supplied by the makers, confirm that the linearity may be expected within this approximate density range.

In comparing the X-ray intensities of two unknown spots, the exploring light beam is adjusted to have an area X just greater than the larger of the two spots A_1 and A_2 . The true optical densities of the spots are given by equations of the type

$$D_1 = \log \frac{t_0}{t_1} = k + \log \left[\frac{A_1}{X(\beta_1/\alpha_1 + A_1/X - 1)} \right].$$

Since only α and β in these equations are known, we cannot compute D , but instead we use the calibration curve to compare X-ray intensities corresponding to $\log(\alpha/\beta)$.

It might be noted here that, since the calibration curves for Ilford Industrial B and Industrial G films are found experimentally to be straight lines passing through the origin, for transparencies greater than about 55%, it is possible to dispense with the curves for these emulsions, and to regard the values of $\log(\alpha/\beta)$ as constituting the relative X-ray intensities of the crystal reflexions.

Consideration of the equation for D_1 above shows that the errors involved in deriving relative X-ray intensities from values of $\log(\alpha/\beta)$ are twofold. First, we ignore the fact that A_1/X differs from A_s/A of the calibration spot. If all the spots on the negative are roughly similar in size, as will often be the case if the crystal specimen has been carefully chosen, A_1/X will be close to unity, as was A_s/A of the calibration spot. Thus under these favourable circumstances the

calibration curve will yield relative intensities very close to the true values. The second source of error lies in the fact that the 'integrated X-ray intensity' causing a given spot should be derived from the product of the area of the spot and its optical density. In the calibration negative all spots were of the same area and this point did not arise.

The involved nature of the complete equation for the 'integrated X-ray intensity' precludes a simple verbal argument of the errors likely to arise. We have therefore computed relative values of true and apparent X-ray intensity. The true intensity, I_T , is equal to the product of area of spot and its optical density and is therefore equal to $A_1 \log(t_0/t_1)$, while the

Table 1. Comparison of apparent and true X-ray intensities

A_1	t_1	β	I_T	$\log(\alpha/\beta)$	R
1.0	0.5	250	0.301	0.301	1.00
0.9	0.9	455	0.041	0.041	1.00
	0.7	365	0.140	0.137	1.02
	0.6	320	0.200	0.194	1.03
	0.5	275	0.271	0.260	1.04
0.8	0.9	460	0.037	0.036	1.01
	0.7	380	0.124	0.119	1.04
	0.6	340	0.178	0.168	1.06
	0.5	300	0.241	0.222	1.09
0.6	0.9	470	0.027 ₄	0.027	1.02
	0.7	410	0.093	0.086	1.08
	0.6	380	0.133	0.119	1.12
	0.5	350	0.181	0.155	1.17
0.5	0.9	475	0.023	0.022	1.02
	0.7	425	0.078	0.071	1.10
	0.6	400	0.111	0.097	1.15
	0.5	375	0.151	0.125	1.20

I_T is the true intensity calculated from (area of spot \times optical density).

$\log(\alpha/\beta)$ is proportional to the apparent intensity as given by the calibration curve.

R is the ratio $I_T/\log(\alpha/\beta)$.

apparent intensity is given by $\log(\alpha/\beta)$. The results are shown in Table 1, in the computation of which the constant parameters used were $X = 1$, $\alpha = 500$, $t_0 = 1$. The accuracy of the $\log(\alpha/\beta)$ values may be seen from the values of the ratio R of true intensity to $\log(\alpha/\beta)$. It will be observed that errors exceeding 10% occur only with spot areas, A_s , of 0.6 or less and then only with spot transparencies of 60% or less. It is to be noted that the calibration curve departs from linearity at a transparency of about 55%.

Thus we may conclude that this method of intensity estimation fulfils the accuracy requirements for all normal purposes. It is superior to the method of visual estimation in that it takes account of the incoherent background and, in part, of variation in spot area also, besides avoiding a subjective matching process.

The foregoing examples and discussion are based upon the assumption of a spot of uniform density. It is shown in the Appendix that the conclusions are not

invalidated for a non-uniform spot, so long as the variation in density across a spot is small.

3. An indirect photometric method

During the investigation into the limitations of the foregoing method, an alternative procedure was arrived at which may, in some cases, be capable of increased accuracy. It could be used only upon spots in which the variation in density is small, and, in effect, uses the photometer to measure relative areas of the spots.

In addition to the first measurements with the exploring light beam greater in area than the largest spot, similar measurements are made with the beam area just less than that of each spot. We thus obtain the following equations, where the primed quantities refer to the second set of measurements:

$$IA t_0 = P, IA t_0 b = \alpha, I[A_s t_0 b t_s + (A - A_s) t_0 b] = \beta, \\ I'A' t_0 b = \gamma, I'A' t_0 b t_s = \delta.$$

From the equations for α and β :

$$t_s = (A/A_s)(\beta/\alpha - 1) + 1$$

and from those for γ and δ :

$$t_s = \delta/\gamma.$$

Equating the values of t_s , we find

$$\frac{A_s}{A} = \frac{1 - \beta/\alpha}{1 - \delta/\gamma}.$$

If, in the first measurements, the beam area A is kept constant for all the spots, the integrated X-ray intensity, T , proportional to the product of area and optical density, is given by

$$T \propto A_s D \propto \frac{1 - \beta/\alpha}{1 - \delta/\gamma} \log \frac{t_0}{t_s} \propto \frac{1 - \beta/\alpha}{1 - \delta/\gamma} \log \frac{\gamma}{\delta},$$

since t_0 is very close to unity.

The calibration negative is used to establish the range in which a linear relationship holds between density and X-ray intensity, and relative intensities are found by computing for each spot

$$\frac{1 - \beta/\alpha}{1 - \delta/\gamma} \log \frac{\gamma}{\delta}.$$

In theory, there are no limitations imposed on the relative sizes of A and A_s , but errors will obviously occur if there is a large area of any spot over which the density varies appreciably. For small density variations, the errors are expected to be small, as in the previous method.

An experimental comparison of the two methods detailed above has not yet been carried out. However, the first method has been shown to be capable of an accuracy which is quite adequate for most general purposes, and it is felt that only in special cases will the expected increase in accuracy of the second method be such as to warrant the lengthier experimental procedure.

APPENDIX

Photometer measurements on spots of non-uniform density

In the following, the clear-base transparency is taken as unity.

Suppose the spot is divided into areas $A_1, A_2, \dots, A_r, \dots, A_n$ with corresponding transparencies $t_1, t_2, \dots, t_r, \dots, t_n$. The total X-ray intensity causing this spot is proportional to (area \times density) and is given by $T = \Sigma A_r \log(1/t_r)$, where r has the values 1 to n . Assuming that density variation across the spot is small, we may write $t_r = t_1 + \Delta_r$, where Δ_r is small.

Then

$$\log \frac{1}{t_r} = \log \frac{1}{t_1 + \Delta_r} = \log \frac{1}{t_1} - 2.3 \frac{\Delta_r}{t_1},$$

if we ignore terms in $(\Delta_r)^2$ etc. Thus

$$T = \Sigma A_r \left(\log \frac{1}{t_1} - 2.3 \frac{\Delta_r}{t_1} \right) = A \log \frac{1}{t_1} - 2.3 \Sigma \frac{A_r \Delta_r}{t_1},$$

where A is the total spot area.

The photometer reading β corresponds to an effective mean transparency for the spot given by $\bar{t} = \Sigma A_r t_r / \Sigma A_r$, and hence to a mean density $\bar{D} = \log(1/\bar{t})$.

Thus

$$\bar{D} = \log \left(\frac{\Sigma A_r}{\Sigma A_r t_r} \right) = \log \left(\frac{\Sigma A_r}{\Sigma (A_r t_1 + A_r \Delta_r)} \right),$$

which reduces on expansion, ignoring terms in $(\Delta_r)^2$ etc., to

$$\begin{aligned} \bar{D} &= \log A - \log A t_1 - 2.3 \frac{\Sigma A_r \Delta_r}{A t_1} \\ &= \log \frac{1}{t_1} - 2.3 \frac{\Sigma A_r \Delta_r}{A t_1}. \end{aligned}$$

Thus the product of total area and mean density, $A\bar{D}$, is equal to T above.

Hence, under the above conditions, the transmission reading β is based upon a mean transparency which would lead to a true value of X-ray intensity, and thus the arguments in § 2 for a uniform spot are valid also for one across which the density variation is small.

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An X-ray Study of Na_2SO_4 III

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The determination of the crystal system of Na_2SO_4 III was made directly from the powder pattern. Na_2SO_4 III was found to belong to the tetragonal system with $a = b = 13.45 \text{ \AA}$ and $c = 7.879 \text{ \AA}$, with 16 molecules in the unit cell.

Introduction

Of the five forms of Na_2SO_4 indicated by the thermal analysis, Kracek & Kasanda (1930) studied the spacing of only three by the X-ray diffraction method, namely (1) Na_2SO_4 V or thenardite, stable at ordinary temperatures, (2) Na_2SO_4 I, stable only above 245°C ., and (3) Na_2SO_4 III, stable below 185°C . Colby (1931) found Na_2SO_4 V to belong to the orthorhombic space-group $Fddd$. However, no definite information about the other two forms can be found. It was seen by us that Fravel's (1940) suggestion that Na_2SO_4 III is orthorhombic is not consistent with all the lines of the powder pattern, and Lipson's (1949) method applied by us further showed that it certainly does not belong

to the orthorhombic system. The main difficulty in finding the actual crystal class of Na_2SO_4 III lies in the fact that no single crystal of appreciable size can be obtained so that standard methods cannot be applied.

Recently Hesse (1948) suggested a novel method for indexing powder photographs. Stosick (1949) made some modifications of Hesse's idea and treated the case in the general way. He showed that if there be any equation of the type $m_1 q_1 = m_2 q_2$, where q 's are the $\sin^2 \theta$ values and m 's are integers, the crystal system must be either (a) tetragonal, (b) hexagonal or (c) cubic, of which the last can be recognized immediately from the pattern itself. When $m_1 q_1 = m_2 q_2$ one can have $m_1 M_1 = m_2 M_2$ (l being zero), where $M = h^2 + k^2$ or