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Experimental Requirements for Accurate X-ray Intensity Measurements by Photograpic Means

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The main requirements for reducing recording errors in X-ray intensity towards the goal of 1–2% in total error in relative F^2 values are discussed under the following headings: (*a*) X-ray source, (*b*) specimen preparation and mounting, (*c*) camera checks and adjustments, (*d*) film pack, (*e*) integrating limits, (*f*) equi-inclination settings with particular reference to multiple reflections and lengthened spots, (*g*) processing and photometry of films, (*h*) correlation of layers, (*i*) extinction. An X-ray shutter for photographing the direct beam is described.

Introduction

It has been shown that in many cases the errors of photographic recording using photometry of integrating Weissenberg photographs are small compared with other errors, of which the most important is that due to absorption (Jeffery & Rose, 1964; Rose & Jeffery, 1964; Jeffery, 1963; MacGillavry, 1964). However, this recording accuracy, and the reduction of other errors towards the goal of 1–2% total error in relative F^2 values, can be achieved only by careful attention to detail and the elimination or reduction of systematic errors. It may, therefore, be useful to list the main experimental requirements for achieving this accuracy, together with a brief commentary. The description applies directly to the standard Nonius integrating Weissenberg camera (Wiebenga & Smits, 1950), the Unicam rotation camera and the Phillips–Muller type sealed-off X-ray tube, but is readily interpretable for alternative arrangements. Profile photometry was done with a Joyce–Loeble–Walker photometer. In general, the methods used in this laboratory are described as they have developed up to the present, with the hope that they may serve as a basis for improvement.

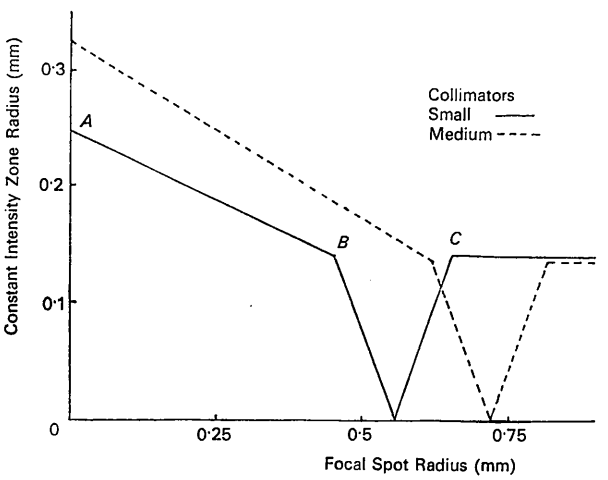

Fig. 1. Relationship between the radius of the X-ray tube focus (the projected shape is assumed to be circular) and the radius of the constant intensity zone at the specimen, for small and medium collimators.

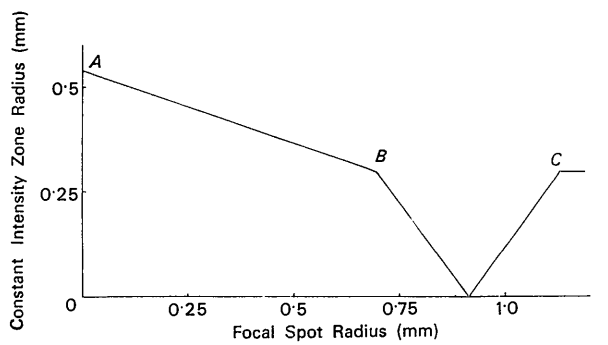

Fig. 2. Relationship between the radii of the focus and the constant intensity zone for the large collimator.

X-ray source

Whitaker (1965) has considered theoretically the relationship between the size of the X-ray tube focus, the collimator apertures and the uniform area of the X-ray beam at the specimen plane, subject to the following simplifying assumptions:

(*a*) Dimensions parallel or almost parallel to the axis of the collimator are large compared with those perpendicular to the axis.

(*b*) The focal spot shape resolved in the plane perpendicular to the collimator axis is circular and the specific emission from this area is constant.

The form of the relationship depends on the size of the tube focus relative to the collimator dimensions. For the experimental arrangement used, the relationship is shown for the small and medium collimators in Fig. 1 and for the large collimator in Fig. 2. For small focal spot size the constant intensity area is dependent only on focal spot size and the diameter of the central aperture of the collimator (*A–B* in the Figures); for medium focal spot size, it is dependent on the focal spot size and the diameter of the entrance aperture of the collimator (*B–C*); and for large focal spot size it is dependent only on the sizes of the entrance and central apertures of the collimator (beyond

C). It can be seen from the Figures that for both medium and small collimators there is a considerable range of focal spot size over which the uniform beam is at least 0·27 mm diameter. (A larger – and more intense – uniform area can be obtained with the large collimator, but the outer, non-uniform zones are also much larger and the additional X-rays cause undesirable scatter. For this reason the smallest collimator giving the required uniform area and intensity should be used). For all collimators it is possible for the uniform zone to shrink to zero (although even then the variation in a central area of 0·25 mm diameter is fairly small, the decrease of intensity at the edge compared with the centre being 8·4% and 6·3% respectively for the small and medium collimators). Fortunately the two smaller collimators are to a considerable extent complementary and there is only a small range of focal spot size which will give a zone of constant intensity too small with both these collimators. In fact, if the crystal diameter is less than 0·22 mm one is assured that a uniform beam will be obtained with one or other of the collimators. However, it is essential to take both (*a*) a pinhole photograph of the focus before deciding on the choice of collimator and (*b*) a photograph of the beam at the specimen plane to check the effect of the various departures from the assumed conditions. In particular, X-ray tube manufacturers do not appear to be able, at present, to produce a completely uniform focus and higher intensity 'wings' run along the two long sides of the focus. If these are too close together or the central area is too non-uniform the collimated beam uniformity will be adversely affected.

Ideally a highly stabilized direct-current high-tension supply should be used, but a self-rectified supply with saturated core stabilizer for the filament circuit, provided the mains supply is itself stabilized at least by a similar (though larger) saturated core transformer, has sufficient short and long term stability to keep errors in intensity from this source below 1%.

Crystal preparation

Crystal shape and size

The necessity for shaping most crystals into spheres or at least cylinders, and the intensity errors arising from departures from geometrical perfection, have been discussed elsewhere (Jeffery & Rose, 1964). The method described by Bond (1951) or its modification (Whitmore, 1954) is used for sphere grinding and cylinders are formed on a watchmaker's lathe with an Airbrasive unit as described by Pepinsky (1953). For difficult cases it may be necessary to get an approximation to a cylinder by allowing the edges of an equant prism to sublime or dissolve away. To enable the specimen to be bathed in a uniform beam, the diameter should not be greater than 0·25 mm and the practical lower limit is about 0·1 mm. A cylinder will give rise to end-effect errors if it is short or errors due to lack of uniformity of the beam over its length if it is long, and since the size of these errors has not been investigated, it is worth persevering with sphere grinding. The degree of perfection necessary depends on the final accuracy of atomic coordinates or electron density required. The residual, R, corresponding to this required accuracy should be calculated from Cruickshank's (1960) approximate relations between R and the errors in electron density or coordinates. $\sigma(I)/I$ can now be estimated in terms of R, and the corresponding shape error in the crystal, $\sigma(r)/r$, obtained from the relations given by Jeffery & Rose (1964). Whitaker (1965) gives further details of the calculation. For cylinders one can only assume, at present, that the relation is of the same order of magnitude as for a sphere. A rough calculation of this sort will prevent the use of a crystal which cannot produce sufficiently accurate results.

Crystal washing

Grinding usually leaves powder on the surface and this requires washing off by a liquid in which the crystal is slightly soluble. For a sphere this is done in a shallow dish before mounting, great care being required not to lose the tiny crystals. A cylinder is best washed on the lathe, using a brush dipped in solvent as a lathe tool (utilizing surface tension to keep the solvent round the cylinder).

Thermal shock

To improve the mosaic character of the crystal it should be dipped in liquid air (Lonsdale, 1947, 1948) contained in a shallow hemispherical Dewar flask, so that the crystal can be recovered if it comes away from the fibre. For a sphere, this should be done before final mounting.

Crystal orientation

For cylinder grinding the crystal can usually be set optically fairly accurately and final setting done by the usual X-ray methods. The arcs are then transferred to the watchmaker's lathe for the grinding process.

In the case of a sphere it is usually necessary to pick the crystal up at random on a fibre using, say, a water-soluble adhesive; find its orientation using the method described by Henry, Lipson & Wooster (1960) using a rotation camera; and bring the desired rotation axis into the horizontal plane and perpendicular to the collimator. It can be shown (Whitaker, 1965) that it is essential to mount the sphere on the tip of a fibre if significant errors due to absorption in the fibre are to be avoided. A hollow borosilicate glass fibre, 50μ in diameter, is therefore fastened by Plasticene to the front of a second microscope attached to one side of the camera. The crystal is adjusted by the translation movement of the arcs and spindle so that when this fibre is racked forward it is opposite the crystal, parallel to the desired axis of rotation. A small blob of, say, alcohol-soluble adhesive is transferred to the end of the fibre, and/or to the side of the crystal by a second fibre and

the second microscope racked forward until the mounting fibre is seen in the normal front microscope to be attached to the crystal. When the new adhesive is dry, water is applied to the original mounting adhesive by a small hand brush or a spill of paper attached to a third microscope mounted on the other side of the camera, so that surface tension keeps a drop surrounding the join until the adhesive dissolves away. The new fibre is then mounted on the arcs and the final setting obtained in the usual way.

Stability of the crystal mounting

To avoid appreciable bending of the fibre carrying the crystal there should not be more than 1 or 2 mm of unsupported fibre projecting from the mount. A check photograph should be taken at the end of the exposure under conditions identical with those of the layer line screen check photograph taken before the start, in order to make sure that no movement of the crystal has taken place during the exposure.

Camera checks and adjustments

Functioning of camera

(*a*) *Intersection of axes.* For this check and for later adjustments, a small (*ca.* 0·1 mm diameter) sphere, highly absorbing for both light and X-rays, should be mounted on arcs and centred on the Weissenberg rotation axis at its intersection with the collimator axis (*i.e.* centred in a light beam filling the collimator). Swinging the top base over its whole range of movement should not give rise to movement of the crystal (as observed in the fixed microscope) of more than one-tenth of its diameter. If greater movement is observed (or, of course, if the collimator axis does not intersect the rotation axis) the faulty adjustment must be remedied before proceeding further. If the mechanical axes intersect, this only involves adjustment of the collimator, but otherwise it is a workshop job.

(*b*) *Uniformity of traverse and rotation.* This can only be satisfactorily tested by using a *fixed* polycrystalline specimen (a simple jig can be made to hold the camera spindle stationary) and recording the small arc of a powder ring coming through the narrow layer line screen slit on the moving Weissenberg film. The circumferential integrating mechanism should be used to give a uniform central band about 1 mm wide and optical density between 0·5 and 1·0. The longitudinal integrating movement must be set at zero. Photometry of the central band should show not more than 1–2% variation of density. Most of this variation will be due to film and processing errors and variations in speed of traverse would be less than 1·0%. In this case it can be assumed that the angular rotation errors are also below 1·0%.

(*c*) *Smooth operation of integrating mechanism.* Any sticking of the integrating movement will normally show up as irregularities in the spots on the photograph but two points should be particularly inspected for wear. These are the points (one inside the platform) where the linear movement of a plunger is turned into the radial movement of an arm, and where there is therefore sliding movement between plunger and arm. The arm is liable to wear into pits and give rise to sticking on the spring or gravity loaded return movement. If the arm is not already of hardened steel, an insert should be let in where the plunger bears against it. Adequate lubrication must be provided to prevent sticking.

Alignment of camera against X-ray tube

Theoretical and experimental investigations (Whitaker, 1965) show that movements as small as 0·1 mm from the optimum position can affect the uniformity of the X-ray beam bathing the crystal. However, if the X-ray beam is symmetrical about the collimator axis, this should define the optimum position and the small sphere set previously on the axis of the collimator can be used with a fluorescent screen to align the camera in this position. A photograph of the beam containing the shadow of this sphere should be taken using the auxiliary shutter described below, and final adjustments made photographically if necessary. The sphere is then removed and a photograph of the beam taken as near to the crystal position as possible. This is photometered across the centre, vertically and horizontally, to check the uniformity.

Description of X-ray shutter

Photographs of the beam are taken with the use of an ordinary six-bladed optical shutter. This is held on a frame clamped to the film holder platform and the horizontal position can be adjusted by manual operation of the lead screw. The vertical position can be adjusted by packing under the clamp. It is essential that the axis of the shutter should coincide with the axis of the collimator, because only the central area of the shutter, where the six blades all overlap, is thick enough to prevent appreciable intensity of X-rays getting through for the second or so on either side of the exposure. A lead sheet between the shutter and the film holder is swung out of the way for the exposure. The shutter can be screwed on to the frame in two positions, one such that the shutter is almost touching the end of the collimator and the film is nearly at the specimen plane, and the other further back so that the opaque sphere can be in position in front of the shutter. A pack of about 10 nickel β filters reduces the intensity so that exposure times of 15–20 sec can be used. This means that the irregularities caused by the shutter blades leaving and re-entering the beam area are negligible but introduces irregularities due to lack of uniformity of the nickel foil. The use of a large number of foils tends to average out the irregularities and provided there are no creases in the foils the effect is small. No significant differences have been found by varying the position of the foils.

The uniformity of the beam should be checked before and after the layers about one axis have been photographed, or if there is any reason to suspect any change in tube and/or camera conditions.

Position of β filter

Results obtained by Rose & Jeffery (1964) suggest that errors arising from non-uniformity of the nickel foil are of the order of 3% when the foil is fixed over the layer line screen opening, and this is likely to be considerably greater than errors arising from an increase in background due to fluorescent radiation if the filter is put in the collimator. If there is no interference from β reflexions it is, usually, better not to have a filter at all. This assumes that background fogging is minimized by closing the layer line screen aperture to twice the spot width. The crystal must be set to better than 0·05° to avoid cutting off part of any reflexion.

Film pack

The minimum detectable optical density is about 0·005 and the maximum density which is still linearly dependent on X-ray intensity is about 1·0, so that on a single film the measurable range of intensities is 200–1. If a double film pack is used with Ilford Industrial G on top and Industrial B underneath, then the ratio of densities on the two films is about 10:1 and an overall range of 2000:1 can be obtained.

Mammi, Bardi & Bezzi (1963) claim that X-ray film (Ilford Industrial G) is non-linear even below density 1·0. Their results are confirmed by Morimoto & Uyeda (1963), but the departure from linearity is small and can be ignored except in the most favourable circumstances, when the error will be comparable to or greater than absorption errors. In such cases the densities should be corrected in the first processing of the data. Rather more serious is the claim by Mammi *et al.* that this lack of linearity leads to an error in the estimation of the film factor for a double film pack (two Industrial G films in their experiments) which is of the order of 10%. However, their assumption of a linear relationship between the film factor ($F=D_1/D_2$) and density of the top film (D_1) is not justified by their results for $D_1<1{\cdot}0$, which can equally well be interpreted as scatter about a constant value of F (Whitaker, 1965). Results in this laboratory using Industrial G as top film and Industrial B (which has negligible departure from linearity – Morimoto & Uyeda 1963) as second film, show only random departures from constant F up to $D_1=1{\cdot}0$, but this may be partly due to the better characteristics of the Industrial B film. Any departure from constancy of F is masked by the random variations due to variation in thickness of film. This effect was thought to be negligible (Rose & Jeffery 1964), but subsequent work has shown that it probably gives rise to an error of about 0·3% in D_1 and 1·5% in D_2. This would account for most of the scatter of the results for F and justifies the lower weight (corresponding to an additional error of 4%, Jeffery & Rose 1964) allocated to reflexions measured on the second film.

Integrating limits

These should be 0·6 mm greater than the largest dimension of any spot on a non-integrating Weissenberg film in the relevant direction (see below for exceptions on non-zero layers). It is important to note that an oscillation spot (*e.g.* on a layer line screen checking photo) will not be as long as the corresponding Weissenberg spot, even on the zero layer and if such spots are used to find the integration limits, the central plateau of the integrated spot will be too small for accurate photometry. It is better to have the integration limits slightly too large than too small.

Equi-inclination photographs

Equi-inclination settings. Cell parameters must be known to 0·1% in order to calculate equi-inclination settings with sufficient accuracy, and the setting of the reciprocal lattice layer accurately perpendicular to the rotation axis is of even more importance than for the zero layer, because displacement of the reflexions for a given setting error is greater. However, if a reciprocal lattice line coincides with the crystal lattice line along the rotation axis, it is also important that the equi-inclination angle should be deliberately misset (*ca.* 0·5°) so that the axial reciprocal lattice point is not in the sphere, since otherwise the condition will be fulfilled for producing multiple reflexions for all reflexions of the layer (Yakel & Fankuchen, 1956). To check that this does not occur, it is necessary to modify the layer line screen so that this axial reflexion, if it occurs, will register on the centre line of the film in a preliminary photograph.

(*b*) *Lengthened spots.* The divergence of the X-ray beam leads to the lengthening of reflexions on one side of the film, and this effect increases with the height of the layer (Phillips, 1954). The lengthening is greatest for reciprocal lattice points near the rotation axis, but a considerable increase in the lengthening may be produced by an error in the equi-inclination setting. Because the reciprocal lattice points are nearer the rotation axis, the effect is greater for Mo $K\alpha$ radiation than for Cu $K\alpha$.

If a few reflexions are very much longer than the rest they should be ignored and their intensities obtained from photographs about another axis. These reflexions will in any case be subject to serious errors in the velocity factor (MacGillavry, 1964) and should for this reason be recorded under different geometrical conditions.

Processing and photometry of films

The precautions required have been discussed elsewhere (Rose & Jeffery, 1964; Jeffery, 1963), but it should be reiterated that if the integration limits are too small, photometer errors will be larger than those

quoted. Exposures should, ideally, give a maximum density of 1·0 on the second film of the pack.

Before photometry the film should be carefully scrutinized for any signs (such as irregularities in the spots or unusual shadows in the background) that the experimental arrangements were faulty in any way.

If the photometer errors are comparable with absorption errors the films should be photometered twice, on different occasions, and any measurements which disagree by more than twice the expected standard deviation repeated until consistent results are obtained.

Correlation of layers

Correlation should be achieved by the use of data collected about two axes (Rollett & Sparks, 1960; Hamilton, Rollett & Sparks, 1965). Such data would normally be necessary in any case if all independent reflexions are to be measured. In order to get as many corresponding pairs of reflexions from the two sets as possible and also increase the accuracy of the correlation, the symmetry-related reflexions in the layers should be averaged before correlation (Whitaker, 1965) and the weights already assigned to the intensities (Jeffery & Rose, 1964) adjusted accordingly. If symmetry-related reflexions occur on different films these should be utilized in the correlation.

Extinction

Data from more than one crystal should enable extinction to be detected, but for a quantitative estimate some of the single-crystal intensity values should be compared with those measured on a diffractometer using very fine ($<1\mu$) powder, or Chandresekhar's method using polarized X-rays should be applied to the single-crystal specimen.

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The Crystal Structure of β-In_2S_3

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A structural analysis of β-In_2S_3, using Weissenberg data, has confirmed the cation-deficient spinel structure proposed by Rooymans. The absence of some of the tetrahedrally coordinated cations, found in spinel, leads to appreciable atomic displacements from idealized positions.

Introduction

On the basis of accurate powder data, Rooymans (1959) proposed that β-In_2S_3 has a spinel-type structure with ordered vacant tetrahedrally coordinated cation sites. Rooymans found a body-centred tetragonal supercell, containing 16 In_2S_3 molecules, which was related to the spinel-type cell by $a=d_{(110)}/2=7{\cdot}62$ Å and $c=3d_{(001)}=32{\cdot}32$ Å, $d_{(110)}$ and $d_{(001)}$ being planar spacings of the spinel lattice. The space group suggested by Rooymans was $I4_122$ with the four cation vacancies per cell located at the equivalent positions of the 4_1 screw axes.

A more detailed investigation of the space group was undertaken by King (1962) using a single-crystal technique. Systematically absent reflexions on Weissenberg photographs, taken about the [110] axis, suggested the more highly symmetrical space group $I4_1/amd$, which is indeed the space group of the structure proposed by Rooymans. King also calculated the unit-cell parameters from the Weissenberg data and found $a=7{\cdot}61$, $c=32{\cdot}24$ Å.

Goodyear & Steigmann (1961) carried out a single-crystal examination of twinned crystals of β-In_2S_3 and were able to explain the twinning mechanism in terms of a cation-deficient spinel model. The twin components