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THE DEVELOPMENT OF AN ACCURATE LOW ANGLE X-RAY POWDER DIFFRACTION CAMERA

LORIN HAWES, *Department of Chemistry, Canberra University College, Canberra, Australia.*

INTRODUCTION

Most attempts at increasing the degree of accuracy attainable from low powder angle powder diffraction data have hitherto been directed toward the recognition and mathematical correction of general systematic errors, toward the manual correction of collimation and recording geometry distortions and towards the construction of larger and more intricate cameras and diffractometers. There are limits to the practicability of attempting to eliminate errors entirely by these means; usually it is found that the random errors of observation become more serious at low angles than any or all of the systematic errors attributable to the nature of the recording instrument or to the specimen.

Random errors

Quantitative assessments of the effect of random errors may be obtained upon consideration of the instantaneous magnification, M_i, defined as the rate of change of measured film distance, S, with respect to the interplanar spacing, D, in the crystal. In the case of the familiar Debye-Scherrer type of camera, the measured film distance is proportional to θ, and, in the terms of Bragg's equation,

$$M_i = \frac{dS}{dD} = \frac{-4R}{n\lambda \cot\theta \csc\theta}$$

The magnitude of a random error of observation may be regarded as independent of ϕ, and its effect upon a derived lattice spacing is inversely proportional to M_i, that is,

$$\Delta \propto \frac{n\lambda \cot\theta \csc\theta}{4R}$$

Since $\cot\theta$ and $\csc\theta$ are functions which increase in value rapidly with decreasing θ, any recording device which measures in units proportional to θ must, as a corollary, produce increasingly inaccurate "D" data at low angles.

To a large extent therefore the problem of equalizing and minimizing the effects of random errors at different angles is the problem of recording the diffracted rays so that a linear relationship exists between D and the measured distance on the film; *i.e.* so that the magnification is constant and independent of θ. The geometrical surface conforming to this requirement is depicted in Fig. 1, in which the specimen is at the origin and the

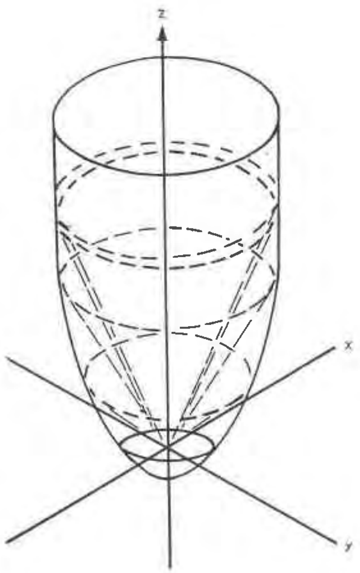

FIG. 1. The ideal surface of constant magnification.

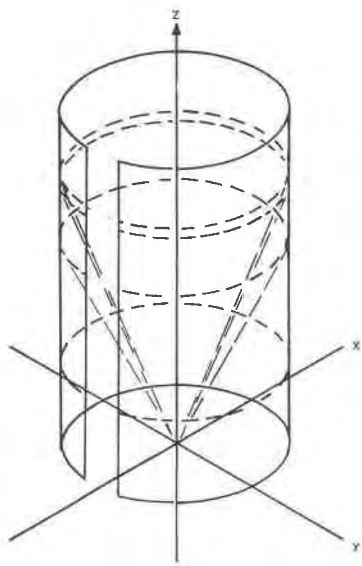

FIG. 2. The limiting cylinder.

x-ray beam is coincident with the Z axis. Such a surface unfortunately would be difficult to fabricate accurately and would be limited to a particular wavelength of x-rays.

By using the limiting circular cylinder (1) which becomes asymptotic to such a surface at low angles however, very nearly the same effect may be obtained. This arrangement is depicted in Fig. 2. The film is held in the form of a circular cylinder coaxial with the x-ray beam, the specimen is in a plane perpendicular to the beam, the diffracted rays strike the film at a distance Z above the specimen plane intercept, and the relationship between Z and D is nearly linear, the relationship being

$$D = \frac{n\lambda}{2 \sin \frac{(\text{arc cot } Z)}{2}}$$

The magnification factor for this geometry is given by the relationship

$$M_i = R\frac{dZ}{dD} = R(n\lambda \cos^3 \theta)$$

Since $\cos \phi$ approaches unity at low angles, M_i approaches a constant value.

The relative effectiveness of the arrangement of the film in a circular cylinder coaxial with the x-ray beam may be judged from Table I in which the instantaneous magnifications are compared at various angles

TABLE I. M_i AS A FUNCTION OF θ FOR DEBYE-SCHERRER AND COAXIAL FILM ARRANGEMENTS (CuKα RADIATION)

θ	M_i coaxial	M_i Debye	Ratio
45	1.835×10^8	1.835×10^8	1.00
40	1.441×10^8	1.40×10^8	1.03
35	1.180×10^8	1.04×10^8	1.13
30	0.998×10^8	0.75×10^8	1.33
25	0.874×10^8	0.51×10^8	1.71
20	0.782×10^8	0.32×10^8	2.42
15	0.720×10^8	0.18×10^8	4.00
10	0.679×10^8	0.08×10^8	8.54
5	0.656×10^8	0.02×10^8	33.1
Very small	0.648×10^8	0	—

for the circular Debye-Scherrer type of camera and for the coaxial cylinder arrangement, both of unit radius. It will be noted that the value of M_i for the coaxial arrangement is large and reasonably constant over the entire low angle range.

Systematic Errors

The major systematic errors which could affect data from a coaxial camera are essentially analogous to those encountered with other types, namely

1) absorption of diffracted x-rays by the specimen.
2) non coaxial placement of the film cylinder in relation to the x-ray beam.

In addition to these, an error which in the Debye-Scherrer type of camera is a random error of small magnitude now becomes a systematic error of some importance, *i.e.*

3) definition of the base line on the film from which all measurements are made. (In the case of the Debye camera it is the position $\theta=0°$ and/or $\theta=90°$, in the case of the coaxial it is the position of the specimen plane, $Z=0, \theta=45°$)

The elimination of each of these systematic errors will be discussed in later sections.

Construction of the Camera

In addition to minimizing, as far as practicable, the sources of systematic error of an instrumental nature, it is desirable that a camera constructed along the lines discussed should possess the following features:

1) A means for specimen rotation about the beam axis.
2) A means for printing fiducial reference marks on the film during exposure for later use in film shrinkage correction.
3) A means for accurately locating the $Z=0$ line on the film.
4) The camera should be lightproof, easy to load, easy to align in the x-ray beam, and, once so aligned, should be removable at will without requiring further adjustment.

A camera incorporating these features is illustrated in Fig. 3.

The camera body is constructed from a length of two inch copper tubing, accurately machined on the interior to form a true circular cylinder. Film is held in place by being expanded against this surface by two elliptical cams, these being spring tensioned so that a steady tangential compression is applied to the film during exposure. A series of small holes (0.009″) in the side of the camera body permits the direct printing of fiducial marks. The specimen holder provides a means for

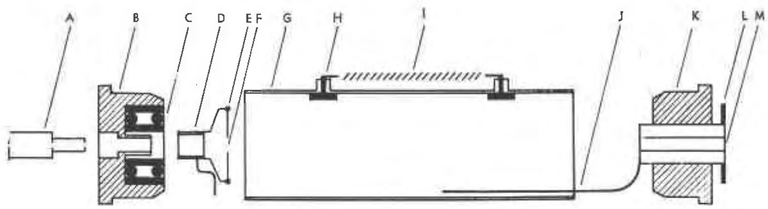

FIG. 3. A coaxial camera.

A Collimator
B Front end piece
C Double row ball race
D Specimen holder
E Rim of disc
F Specimen position
G Camera body
H Tensioning cam
I Tensioning spring
J Longitudinal rod
K Rear end piece
L Sprocket
M Black paper

positioning the powder wafer in the x-ray beam and a means* for printing the $Z=0$ line on the film. It consists of a levitated thin (0.003″) brass disc with a central hole; it is the shadow of the rim of this brass disk which defines the position of the specimen plane during exposure.

The specimen itself may be conveniently prepared and mounted by sprinkling the powdered sample onto a piece of scotch tape which is then stretched tightly across the central hole of the brass disc. The thickness of the powdered specimen need not exceed 0.001″; thus errors due to absorption are usually negligible.

The rear end piece, when in place completes the closure of the camera body and contains part of the mechanism for specimen rotation, a longitudinal rod attached to a large hollow bushing. The bushing is drilled with four small holes, 90° apart, through which a thin wire may be strung to form a crosshair for later use in alignment. The longitudinal rod rotates eccentrically about the common camera axis and engages a protruding arm on the specimen holder. The motive power for specimen rotation is transmitted from an external synchronous motor to a sprocket on the bushing by a chain drive. A lightproof exit port for the x-ray beam is provided by gluing a piece of black paper over the end of the bushing.

Alignment and Calibration of Camera

The camera is mounted opposite a point focus x-ray source and adjusted until a collimated circular beam is centered in the crosshairs in the bushing of the rear end piece. A sample of standard grating crystal, such as rocksalt or calcite, is then placed on the specimen holder and an exposure made.

Accurate values of θ can be calculated for all lines from these substances (2) and used to determine the camera radius by means of the relationship

$$R = L \tan 2\theta$$

(Only the lowest angle lines should be used in this determination; those lines for which $\tan 2\theta$ is greater than 2 are generally unsuitable because corresponding L values can be read to only two or three significant figures. Lines near $\theta=45°$ may be used to advantage in locating the $Z=0$ plane in the calibration since changes in R do not appreciably affect their position.) The calibration of the camera in this manner provides a good check on the presence of measurable systematic errors, which if present, would cause a drift in the calculated values of R at different values of θ.

* See Fisher, D. J., A modified coaxial powder x-ray camera: *Rev. Sci. Instr.* (Accepted for publication, probably Dec. 1960).

Line Breadth and Exposure Technique

The accuracy and precision of data obtained from the coaxial camera is to a certain extent limited by the breadth of the lines on the film, and this in turn can be shown to be governed by the relationship

$$B \propto t + A\frac{m}{l}\cot 2\theta + \frac{R(\sin\phi + \sin\gamma)}{\sin^2 2\theta}$$

where B is the line breadth, t the specimen thickness, A the size of the limiting collimator aperture, l the distance from the X ray source to the specimen, θ the Bragg angle, m the distance from the limiting collimator aperture to the specimen, R the camera radius, ϕ the angle of divergence

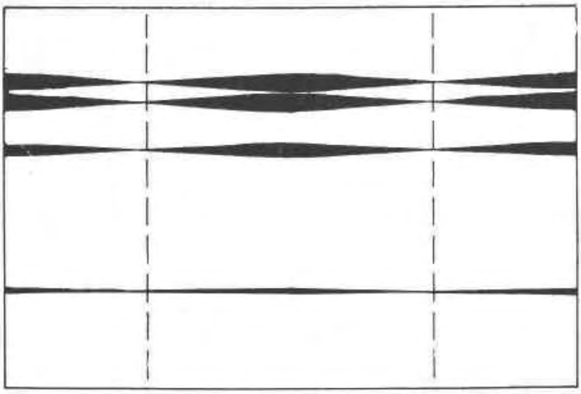

FIG. 4. High resolution trace pattern.

of the x-ray beam and γ the angular range of reflection of the crystal. A point source of x-rays is assumed.

Two essentially different exposure techniques are possible depending upon the degree of accuracy sought from the data; for photographs of the highest resolution and finest line breadth, such as for calibration or for the resolution of closely spaced doublets, a slit collimator (0.1 mm. by 0.6 mm.) is desirable. The slit should be in the same plane as the x-ray tube target, or as nearly so as possible; when this condition is fulfilled the x-ray beam has virtually no divergence normal to the plane of the tube target but great divergence in that plane, and the diffraction traces are focused sharply on two narrow areas of the film and spread out widely on all others, as shown in Fig. 4. In the terms of Fig. 2, if the plane of the x-ray tube target and the collimator slit is the XZ plane, lines will be highly resolved on the film cylinder where it is intercepted by the YZ plane.

Under these conditions of exposure the line breadth is extremely small, even at the lowest angles; the actual breadth of lines is usually smaller, in relation to resolution, than that attainable with any other type of camera in existence. Exposure times for such photographs are of the order of four hours, when the camera is sixteen centimeters from the x-ray tube.

For photographs of lesser accuracy but requiring vastly shorter exposure times, a rather large circular pinhole collimator is used and the specimen is held stationary during exposure. In this circumstance it is desirable to use a somewhat coarser specimen and to vary the camera angle so that the camera axis is no longer coplanar with the tube target,

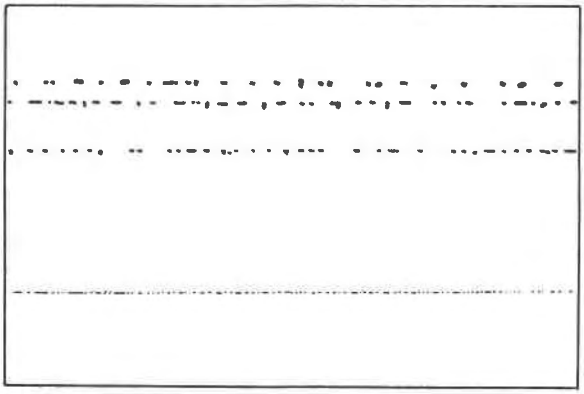

FIG. 5. Stationary spot pattern.

but so that the beam appears perfectly circular at the exit port. Photographs taken using this technique contain the diffraction spots in random array on parallel lines as shown in Fig. 5, and any flattening of the beam due to incorrect camera angle with respect to the target will be evident in that the spots may tend to form sinusoidal curves, as in the previous case.

The continuous reflection from a stationary crystal is far more effective in exposing the film than in the previous case since all of the diffracted energy is concentrated upon a small spot instead of being swept around the film, and exposure times for such photographs may be as brief as a few minutes, depending upon the size of the collimator and the nature of the specimen.

Such photographs of isolated spots can provide useful data during the study of an unknown lattice since the number of spots along a given line is proportional to the multiplicity of equivalent planes in the crystal, all other factors being the same. This makes it possible, at an early stage in the study of an unknown lattice, to differentiate between basal reflections, octahedral reflections and so forth by simply counting the number of spots having a common value of Z.

Table II. Relation of Z to Other Functions

θ	Z	$\sin^2 \theta$	D	Q
5	5.671	0.0076	8.846	0.01278
6	4.705	0.0109	7.375	0.01838
7	4.011	0.0149	6.325	0.02500
8	3.487	0.0194	5.540	0.03258
9	3.078	0.0244	4.928	0.04118
10	2.748	0.0302	4.438	0.05077
11	2.475	0.0364	4.036	0.06139
12	3.246	0.0432	3.705	0.0728
13	2.050	0.0506	3.421	0.0854
14	1.881	0.0585	3.182	0.0988
15	1.732	0.0670	2.975	0.1130
16	1.600	0.0760	2.795	0.1280
17	1.483	0.0855	2.633	0.1442
18	1.376	0.0955	2.492	0.1610
19	1.280	0.1060	2.366	0.1786
20	1.192	0.1170	2.252	0.1972
21	1.110	0.1285	2.149	0.2165
22	1.036	0.1403	2.058	0.2361
23	0.966	0.1526	1.972	0.2571
24	0.900	0.1654	1.895	0.2785
25	0.839	0.1786	1.824	0.3006
26	0.781	0.1922	1.756	0.3243
27	0.726	0.2061	1.696	0.3477
28	0.674	0.2204	1.640	0.3718
29	0.625	0.2350	1.590	0.3956
30	0.577	0.2500	1.542	0.4206
31	0.532	0.2652	1.495	0.4474
32	0.488	0.2809	1.454	0.4730
33	0.445	0.2970	1.413	0.5009
34	0.404	0.3125	1.378	0.5198
35	0.364	0.3295	1.342	0.5553
36	0.324	0.3457	1.310	0.5827
37	0.287	0.3624	1.280	0.6104
38	0.249	0.3795	1.250	0.6400
39	0.213	0.3960	1.225	0.664
40	0.176	0.4132	1.198	0.6968
41	0.141	0.4305	1.174	0.7255
42	0.105	0.4477	1.152	0.7535
43	0.070	0.4651	1.130	0.7831
44	0.035	0.4826	1.109	0.8131
45	0	0.5000	1.090	0.8417

Elimination of Systematic Errors

In a properly constructed camera defining the $Z=0$ position by fiducial spots as suggested by Fisher, and using a thin specimen and slit collimator as discussed previously, the only remaining source of error of a systematic nature is that of misalignment of the film cylinder with respect to the x-ray beam.

The effect of a coaxial misplacement of the camera axis so that it lies in the YZ plane is to tend to reduce the Z value of a given trace in one of the two areas of high resolution and to increase it in the other by the same amount. Correction therefore simply involves reading the Z values independently for each of the two areas and averaging them together, a desirable course of action in any case since it reduces random errors of observation. Misalignment of the film cylinder so that its axis lies in the XZ plane is of no consequence since it affects the film only at those positions where the lines have a maximum breadth and where precise Z values would not be expected.

Application to Lattice Parameter Determination

The use of data from the coaxial camera is an indirect process since it involves conversion to $\sin^2\theta$ or Q terms which may be used in the least squares treatment. In an earlier article (1), the application of data from the coaxial camera was used to calculate the lattice parameters of iodine by the Cohen least squares method (3). Although the Cohen method may be used with data from the coaxial camera it involves an unnecessary analytical extrapolation based upon the error characteristics of the Debye-Scherrer camera. A different least squares treatment, rigidly applicable to data from the coaxial camera, will be presented elsewhere.

Useful values relating Z to other functions are given in Table II.

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