real equations in q would be missed by rejecting coincidences between q-sums or q-differences which differ by an amount exceeding 0·0004. In the examples given above, however, the value 0·0005 was chosen.

In order to get the above accuracy with a camera of the Debye-Scherrer type the camera diameter must be large. With a diameter of 19 cm. an error of 0·1 mm. in line position will cause an error in q of 0·0005 for lines with a mean deviation (2θ) of 90°.

I wish to thank Prof. G. Hägg for his constant interest and help during the preparation of this paper.

References

Bjurström, T. (1931). *Z. Phys.* **69**, 346.

Bunn, C. W. (1945). *Chemical Crystallography*. Oxford: University Press.

Hägg, G. (1947). *Rev. Sci. Instrum.* **18**, 371.

Hägg, G. & Regnström, G. (1944). *Ark. Kemi Min. Geol.* **18** A, no. 5.

Hull, A. W. & Davey, W. P. (1921). *Phys. Rev.* **17**, 549.

Johnsen, A. & Toeplitz, O. (1918). *Phys. Z.* **19**, 47.

Kiessling, R. (1947). *Acta chem. scand.* **1**, 893.

Runge, C. (1917). *Phys. Z.* **18**, 509.

Westgren, A. (1931). *Trans. Amer. Inst. Min. (Metall.) Engrs*, **93**, 13.

Acta Cryst. (1948). **1**, 207

Multiple Guinier Cameras

By P. M. de Wolff

Technisch Physische Dienst T.N.O. en T.H., Delft, Holland

(*Received* 12 *March* 1948 *and in revised form* 2 *June* 1948)

The novel type of Guinier camera described in this paper is characterized by a combination of several cameras in a compact unit using a single focusing monochromator and a single film, and by the disposition of the camera relative to the monochromator in such a manner that α-doublet diffraction lines coincide for a θ value of, say, 15°. In this way an exceptionally high resolving power is obtained in a considerable range of glancing angles, centred about this value, which contains the most selective lines for analytical purposes. The line width in the respective cameras is discussed, and the conclusion is reached that in the significant region $\theta < 30°$ there is no appreciable difference between the outer and the middle cameras of the unit. With a view to comparison purposes, the line shift for the outer cameras is also calculated; it appears to be of little consequence. Finally, short descriptions of a twofold and of a fourfold camera are given.

Introduction

In 1939 Guinier described a new type of focusing powder camera in which a convergent X-ray beam produced by a curved crystal monochromator passes through the specimen. Diffracted rays for any glancing angle θ converge to sharp diffraction lines on a film lying on the circular cylinder which contains the focal line and the sample (Fig. 1). As advantages of the new method compared with common powder diffraction technique, Guinier (1945, p. 147) has enumerated the low background intensity arising from the absence of white radiation, the good resolving power, and the large specimen volume, yielding smooth diffraction lines.

In our opinion, Guinier in this recapitulation (duly completed with the disadvantages: restricted θ-range; rather difficult preparation of samples; exact focusing only in one plane) has by no means exhausted the merits of his achievement. In fact, after about a year of experience with Guinier cameras we think that they possess some unique features, to witness:

(*a*) The exceptionally high resolving power in the θ-range for which the Guinier camera is suited, i.e. $\theta < 30°$. The resolving power in this range is essentially much better than with a Debye-Scherrer camera of the same dispersion for two reasons: (1) The focusing pro-

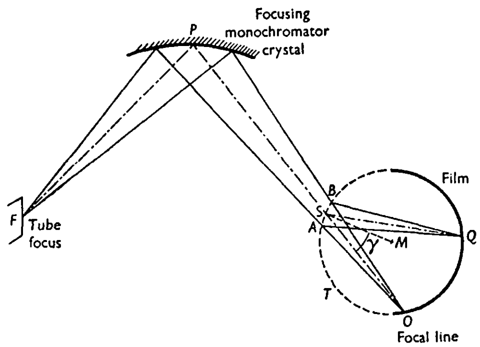

Fig. 1. Schematic plan of the Guinier camera. F, tube focus; OQ, film; S, specimen; O, focal line; P, focusing monochromator crystal.

perty eliminates to a large extent the influence of the thickness of the specimen. (2) Pairs of diffraction lines corresponding to both wave-lengths of the α-doublet can be made to coincide for any desired value of θ, while their separation is much reduced in a region extending considerably on both sides of this value.

The fact that only a restricted θ-range is covered by the Guinier camera is, of course, a handicap. On the other hand, the range in question is very important in that it contains the most characteristic lines of inorganic crystals for the most commonly used wavelengths (i.e. the strongest and the most selective lines, cf. § 2) and the greater parts of patterns yielded by organic substances. Also the Guinier camera is, in our opinion, more convenient than a Debye-Scherrer one for identification purposes.

(*b*) The possibility of taking simultaneous exposures of several samples for comparison purposes or serial work. This can be achieved by building several cameras together as a unit, using the full length of the focal line delivered by the curved crystal, so that the different patterns are neatly arranged one above the other on a single film. In §§ 3 and 4 we will show that the ensuing deformation of the patterns is negligible.

2. Resolving power

This quantity is limited by three factors, which will be considered separately.

(*a*) *Broadening due to specimen thickness*

This contribution is readily computed with the result

$$\Delta_t = 57{\cdot}3t(\sin 2\theta)/2d \cos\gamma \cos(2\theta-\gamma), \tag{1}$$

where Δ_t is expressed in degrees of θ, d is the camera diameter, t is the specimen thickness and γ is the angle MSO (Fig. 1).

(*b*) *Broadening caused by oblique rays*

If the angles of primary and secondary ray with the plane of Fig. 1 (which will be called the equatorial plane and assumed to be horizontal) are ν and μ respectively, the angle 2ϕ between their projections on this plane is given by the formula (cf. Menzer, 1932)

$$\cos 2\phi = (\cos 2\theta)/\cos\mu \cos\nu - \tan\mu \tan\nu \approx \cos 2\theta + \tfrac{1}{2}(\mu^2+\nu^2)\cos 2\theta - \mu\nu. \tag{2}$$

Supposing the sample to be irradiated homogeneously over a height h, we obtain finally for the range of possible apparent diffraction angles 2ϕ

$$\theta > \phi > \theta - \Delta_h, \quad \Delta_h = 57{\cdot}3 \tan 2\theta \frac{h^2}{16l^2}\left[\frac{(1+\lambda)^2}{\sin^2 2\theta} - 1\right] \text{ degrees,} \tag{3}$$

$$\text{with} \quad \lambda = l(\cos 2\theta)/d\cos(2\theta-\gamma), \quad l = FP + PO. \tag{4}$$

In Fig. 2 a graph is presented of Δ_t and Δ_h as functions of θ. The best compromise between sharpness and intensity of diffraction lines is reached in the region where $\Delta_t \approx \Delta_h$. Since the most efficient value of t depends only on the absorption coefficient of the sample, the optimum θ-region is entirely determined by the choice of h.

(*c*) *α-doublets*

The loss in resolving power caused by α-doublets of diffraction lines is much reduced if, as in Fig. 1, the effects of sample and monochromator are made to counteract each other. In fact, it can be shown that a value θ_0 of θ exists, given by

$$\tan\theta_0 = PO(\tan\xi)/2d\cos\gamma,$$

where ξ is the glancing angle of the monochromator crystal, for which the resulting separation vanishes. Sharp and intense single lines are obtained in this way, even with the largest cameras. The opposite camera arrangement, on the contrary, yields resolved doublets which are often inconvenient.

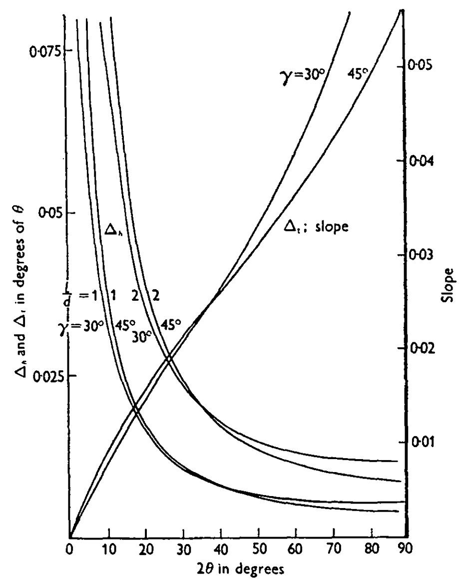

Fig. 2. *Left-hand scale*: Line broadening in degrees of θ. Δ_t is the broadening due to a sample of effective thickness $t' = t + b^2/4d + \epsilon b = d(\cos\gamma)/500$ (cf. equation (1)). Δ_h is the broadening due to a vertical divergence $h/l = \frac{1}{50}$ in the incident beam (cf. equation (3)). (These quantities have been chosen to correspond approximately to the cameras described in § 5.) *Right-hand scale*: Slope of diffraction line arising from a specimen irradiated by a direct beam having an average slope $k_0/l = \frac{1}{25}$ with respect to the equatorial plane (cf. equation (9)).

Apart from the absence of white radiation, the strength and selectivity of diffraction lines in the θ-region for which the resolving power is a maximum are very favourable circumstances. In order to illustrate what is here meant by 'selectivity', we quote the following facts of which we became aware when designing the special twofold camera described in § 5.

From a statistical investigation of 1000 substances classified by Hanawalt, Rinn & Frevel (1938) we have found the frequency of Cu $K\alpha$ diffraction lines per degree to increase slowly with increasing θ towards a maximum value reached at about $\theta = 40°$. The strongest lines, however, show a different distribution, with a maximum value at 15–20° and a rapidly decreasing frequency on both sides of this value (Fig. 3). Correspondingly, we have chosen 15° as the optimum value of θ. With $\gamma=30°$, $l=180$ mm., $d\cos\gamma=150$ mm., coincidence of the α-doublet lines takes place at $\theta=14\frac{1}{2}°$. The value of γ assures normal incidence for $\theta=15°$. Also the height of the sample was such (6 mm.) that in this region neither the line width due to horizontal dimensions nor that due to the height was dominating.

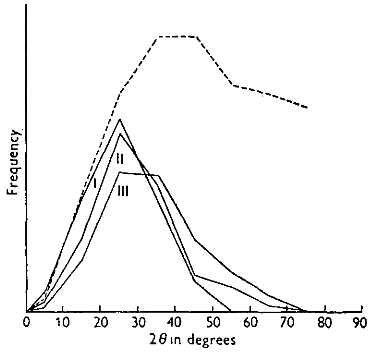

Fig. 3. Distribution of the Cu $K\alpha$ diffraction lines of 1000 substances classified by Hanawalt, Rinn & Frevel in successive intervals of 10° in 2θ. Broken line: distribution regardless of intensity; I, II, III: distribution of first, second and third strongest lines.

3. Multiple cameras

Of the cone formed by the diffracted rays for a certain θ, only a narrow portion on either side of the equator is used for measuring purposes. On the other hand, the dimension h should not exceed $d/30$ when a reasonable line sharpness for medium values of θ is demanded. The useful height of both film and sample thus being very small in comparison with the camera diameter d, the camera takes the shape of a rather thin disk.

This is an uneconomical state of affairs. In fact, the total vertical divergence of the direct beam can easily reach a value of 5°, whereas a single camera uses no more than 1–2° for the reasons given above. Moreover, the focal line is practically straight, and the line width at 20 mm. from the equator is still of no consequence (de Wolff, 1948). Hence it has occurred to us that it should be possible to use several cameras mounted one upon the other with one common focusing monochromator. It then becomes only natural to record the respective diffraction patterns on the same film and to bring the different samples in a common plane (being a sufficient and convenient approximation to a cylindrical surface), as this introduces no appreciable defocusing of the diffraction lines (§ 4d).

Both these steps towards simplification, however, cause some distortion of the pattern. Now this is not a disadvantage so long as it remains possible to find a measuring level, where the line width is not appreciably larger than the minimum width. In the following paragraph we will demonstrate that this is, indeed, the case. Also the relative displacements of the respective diffraction lines belonging to the same θ will appear to be not of a disturbing nature.

4. Distortion in the extra-equatorial patterns

In the case of a single camera where the equatorial plane of the focusing crystal forms a plane of symmetry the diffraction lines clearly have their minimum width in this plane (umbrella effect). When building several cameras together in the way described above (with one film, and with specimens in one plane), the following condition must be fulfilled for the extra-equatorial patterns to be comparable with an equatorial one and to allow uniform measurements: (a) It should be possible to choose a microphotometer track yielding line widths not appreciably larger than the equator on an equatorial pattern. (b) It is desirable for comparison purposes that there is no visible shift for lines in different patterns corresponding to the same θ. For exact measurements, checking of each separate camera with a standard substance is indispensable anyhow, so that a small shift is of no importance.

A complete analysis of the line profile as it appears in the photometer curve will not be attempted here because of the intricacy of the problem. We shall investigate each cause of line broadening separately, as has been done before (§ 2) for the single camera. Though the results are thus related only to the total line width, it is still possible to infer from them which are the dominating causes, and to estimate differences between the respective patterns.

(a) *Broadening due to specimen thickness*

It needs no proof that the contribution of the thickness of the specimen (or, generally, of the departure from the focal cylinder) is the same as in the case of § 2, given by (1).

(b) *Broadening caused by vertical divergence of the direct beam*

Suppose diffraction occurs from a crystallite situated k mm. from the equator, the diffracted ray intersecting the film at a distance k' from the same. The apparent diffraction angle 2ϕ is found in the same way as in § 2, only the slopes of the rays are now

$$\nu=k/l,\quad \mu=(k-k')/QS=(k-k')/d\cos(2\theta-\gamma). \quad (5)$$

Substituting these in (2) we obtain

$$\cos 2\phi-\cos 2\theta=\tfrac{1}{2}\cos 2\theta\left[\frac{k^2}{l^2}+\frac{(k'-k)^2}{d^2\cos^2(2\theta-\gamma)}\right]-\frac{k(k'-k)}{ld\cos(2\theta-\gamma)}. \quad (6)$$

The width does not follow directly from this, as the measuring level still has to be found. Anyhow, it is possible to calculate the minimum line width and the height k'_m where it occurs by considering Fig. 4. From this schematic drawing it appears that a minimum occurs at the intersection of the diffraction curves corresponding to top and bottom of the sample. Calling k_0 the distance from the sample centre to the equator plane, the locus of minimum width is consequently found by equating the values of (6) for $k = k_0 \pm \frac{1}{2}h$ respectively. It can be written as

$$k'_m = k_0\left[1 + \frac{\sin^2 2\theta}{\lambda+1} + \frac{\cos^2 2\theta}{\lambda}\right], \tag{7}$$

with $$\lambda = \frac{l \cos 2\theta}{d \cos (2\theta - \gamma)}.$$

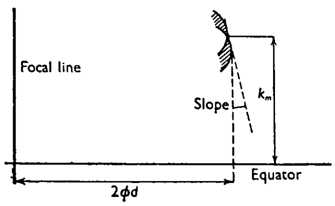

Fig. 4. Schematic drawing of the contour of a diffraction line arising from a specimen off the equator.

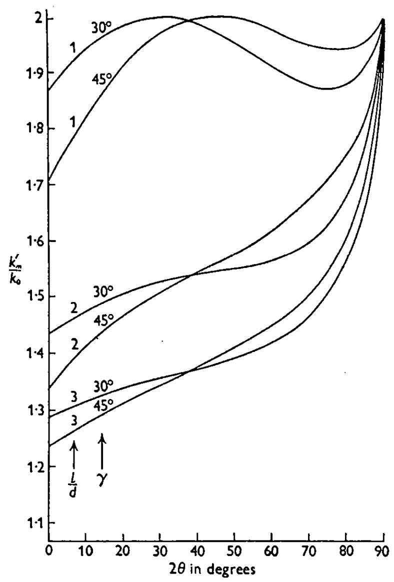

Fig. 5. Locus of minimum width of diffraction lines arising from a specimen off the equator. Vertical distance is expressed as its ratio to the distance between the centre of the specimen and the equator (cf. equation (7)).

The minimum width itself turns out to be equal to Δ_h in (3). Hence the curves of Fig. 2 are equally valid for the general case.

A graph of k'_m/k_0 for several combinations of γ and l/d is presented in Fig. 5. It appears from these curves that for $2\theta < 60°$ the locus of minimum width is practically a straight line if $l/d \geqslant 2$; for k_0 as high as 10 mm. the deviations are only a fraction of commonly used photometer slit lengths. The case $l/d = 1$ yields a more sinuous curve in this θ-range, so that k_0 should be given a lower value in order to obtain measured widths not appreciably larger than the minimum value.

For larger diffraction angles the case $l/d = 1$ seems more favourable than $l/d \geqslant 2$ because it does not show the sudden increase in slope occurring in the latter. The difference is, however, insignificant, because in this region the thickness of the sample is the dominating cause of line broadening. This is clearly shown in Fig. 2, and also by the photograph in Fig. 8, where the lines are practically straight and of constant width in this region.

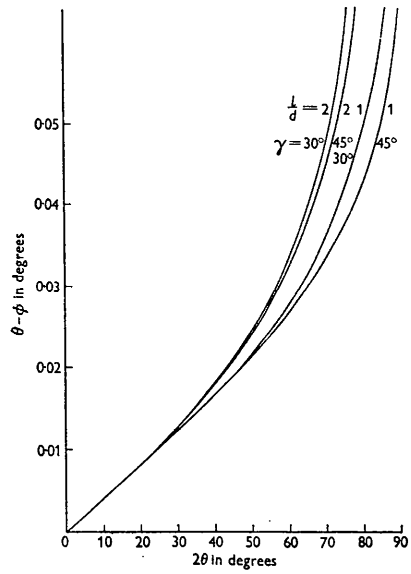

Fig. 6. Displacement of diffraction lines from their equatorial position if the direct beam has an average slope of $k_0/l = \frac{1}{25}$ with respect to the equatorial plane (cf. equation (8)).

(c) *Shift of diffraction lines*

The difference between 2θ and the apparent diffraction angle 2ϕ is directly found from (6). Inserting $k' = k'_m$, $k = k_0$, we obtain

$$\theta - \phi = \frac{57 \cdot 3}{4} \tan 2\theta \frac{k_0^2}{l^2}\left[1 - \frac{\sin^2 2\theta}{(\lambda+1)^2}\right] \text{degrees}, \tag{8}$$

of which a graphical representation is given in Fig. 6 with $k_0/l = \frac{1}{25}$, which is the largest value occurring in our cameras (§5). Even then, the shift in the important region $2\theta < 60°$ does not exceed $2'$.

(d) *Broadening caused by inexact focusing for obliquely diffracted rays*

If diffracted rays in the equator are well focused, the same cannot be true for extra-equatorial cameras because their focal circles lie in planes not at right angles to the film cylinder. The resulting broadening is found by subtracting the values of (8) for the values of γ corresponding to AO and BO in Fig. 1. Now the

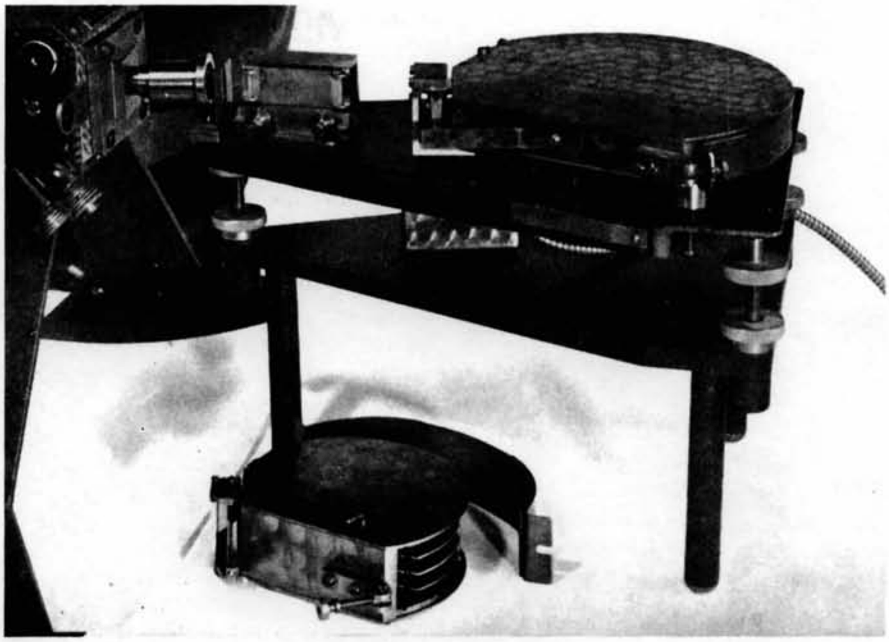

Fig. 7. Twofold and fourfold Guinier cameras, the former mounted in position on a common base with the focusing monochromator. On the fourfold camera (left) the lead rubber band which serves to keep the film in place is loosened so as to show the three septums.

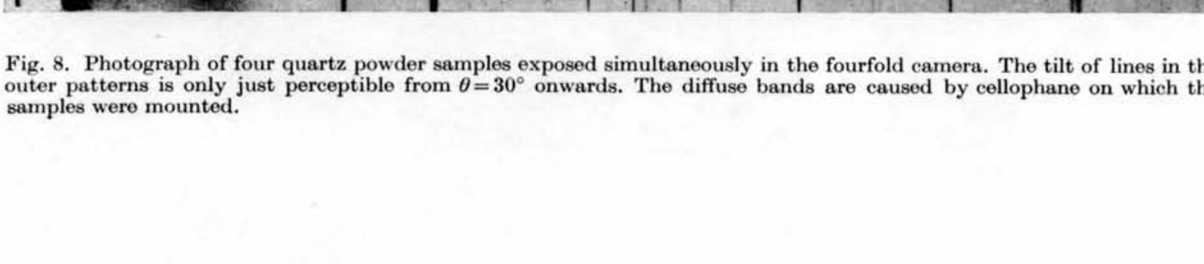

Fig. 8. Photograph of four quartz powder samples exposed simultaneously in the fourfold camera. The tilt of lines in the outer patterns is only just perceptible from $\theta = 30°$ onwards. The diffuse bands are caused by cellophane on which the samples were mounted.

[*To face p.* 211

difference of these values is half the aperture of the beam, say $1\frac{1}{2}°$, so that the broadening is about the tenth part of the difference between the curves for $\gamma=30°$ and $\gamma=45°$ in Fig. 6. Clearly, this amounts to an absolutely negligible effect.

(*e*) *Slope of the diffraction lines*

By differentiating (6) with respect to k' we find the angle with the vertical direction for $k'=k'_m$

$$\frac{\partial}{\partial k'}2\phi d=\frac{k_0}{l}\frac{\sin 2\theta}{\cos(2\theta-\gamma)}. \quad (9)$$

It contains the same function of θ as occurs in Δ_t. Correspondingly, Fig. 2 has been provided with an extra scale so that the slope can be read from the same curves. It is seen to increase almost linearly to a value of about k_0/l for $2\theta=60°$. This will not be a serious inconvenience in photometric measurements, so long as k_0/l does not exceed about $\frac{1}{20}$.

5. Constructional details

In this laboratory a twofold and a fourfold Guinier camera have been constructed. They are illustrated in Fig. 7.

Twofold camera

This instrument was designed as a high-resolving-power camera for quantitative and qualitative analysis of powder mixtures (cf. § 2). It has a film cylinder of diameter 173·2 mm., yielding a dispersion of 6 mm. per degree in θ.

The camera contains a horizontal septum which coincides with the equatorial plane of the monochromator. Moreover, the direct beam is separated from the film by a vertical screen for about two-thirds of its path in the camera in order to suppress air scattering. The film is screened off in such a way that the levels of minimum width lie approximately 2 mm. from the upper and lower edges of the pattern. Thus two patterns on different films are easily compared by letting the edges coincide.

The samples, 6×18 mm.^{2}, are mounted on a small frame provided with V-grooves in the bottom and in the top, corresponding to similar grooves in the camera house. Between these grooves three balls—one at the top and two at the bottom—form a ball race, which allows the specimens to be moved in their own plane by a motor-driven cam in order to obtain smoother diffraction lines if necessary.

Fourfold camera

The diameter of this camera is 115·5 mm. and the dispersion 4 mm. per degree in θ. It is used with the same monochromator as the twofold camera. The available height of the direct beam at S is still larger than in the case of the twofold camera, so that four samples each 4 mm. high with separations of 2 mm. can be placed one above the other.

Of the three septums, only the middle one is plane and coincides with the equatorial plane. The two others are ruled faces containing the point between the centres of the two upper (or lower) samples, and a horizontal circle on the film cylinder. The levels of these circles are so chosen that the locus of minimum width appears approximately as the median level of each pattern. Again the direct beam is separated from the film, but here only for half its path in the camera, in order to obtain as small a minimum value of θ as possible. The value of $2\frac{1}{2}°$ was realized, corresponding to $d=17$ A. for Cu $K\alpha$, with a horizontal aperture of 3°. A removable lead screen permits a short exposure of the film to the direct beam, yielding the focal line as a reference line for θ-measurements. These are made independent of film shrinkage when using fiducial marks.

Fig. 8 is an example of a quadruple photograph of quartz. Exposures of this and similar samples take about 2 hr. using a Philips 800 W. tube (Cu; focus 1×10 mm.^{2}; 25 mA.; 40 kV. peak voltage). In this respect there is no difference between this camera and the twofold one (except for samples yielding diffuse patterns) because the sample heights are proportional to the respective diameters.

References

Guinier, A. (1939). *Ann. Phys., Paris*, **12**, 161.
Guinier, A. (1945). *Radiocristallographie*. Paris: Dunod.
Hanawalt, J. D., Rinn, H. W. & Frevel, L. K. (1938). *Industr. Engng Chem.* (Anal. ed.), **10**, 457.
Menzer, G. (1932). *Fortschr. Min.* **60**, 162.
de Wolff, P. M. (1948). *Appl. Sci. Res.* B, **1**, 119.