DOCUMENTATION SUR LA MINI-CHAMBRE DE DIFFRACTION DES RAYONS X PHILIPS, TYPE DEBYE-SCHERRER

FICHE N° 4036

Période de fabrication : 1925-1949
Fabricant : Philips
Domaines : Chimie, Physique
Sous-domaines : Cristallographie, Cristallographie
Organisme : Université de Rennes
Ville : Rennes
Modèle :
Matériaux : Papier

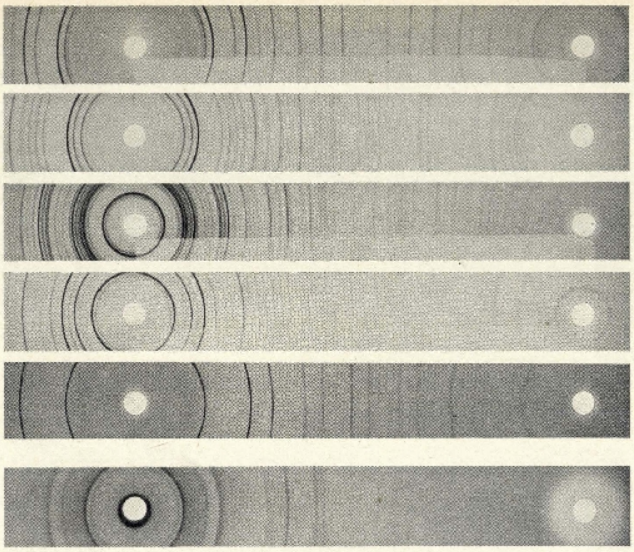
Description

La chambre Debye-Scherrer de diffraction des rayons X (type PW 1026), commercialisée par Philips, est une chambre cylindrique en métal avec un capot amovible. Un article de MM. Parrish et Cisney, paru en 1948, en anglais, dans la revue « Philips Technical Review », détaille la réalisation, les propriétés de cette chambre et présente des clichés photographiques obtenus avec l'appareil.

Utilisation

Elle était utilisée dans les laboratoires de cristallographie et de cristallochimie pour déterminer la structure cristallographique de poudres ou de poly-cristaux. Cette méthode d'analyse, très facile à mettre au point, servait aussi aux étudiants chimistes ou physiciens en travaux pratiques.

La chambre de Debye-Scherrer est un dispositif relativement simple, qui consiste en une chambre de forme cylindrique, un porte échantillon positionné en son centre et une source monochromatique. La source monochromatique produit des rayons incidents qui traversent un collimateur qui sert à limiter le faisceau incident à son entrée dans l'appareil. Les rayons, une fois collimatés, frappent l'échantillon de poudre et sont diffractés sous la forme de cônes. Les cônes formés par les rayons diffractés forment des anneaux elliptiques sur le cliché. Une pellicule de film est placée sur les parois de la chambre et sert à photographier les anneaux de diffraction. Pour faciliter la lecture du cliché, la chambre est par convention, construite de façon que sa circonférence soit égale à 360 millimètres ou à 180 millimètres. De cette façon, la mesure en millimètre des distances entre les anneaux de diffraction et le centre de la pellicule peut facilement être convertie en une valeur d'angle de diffraction.



a Sodium chloride NaCl

b Quartz, SiO_2

c Dickite $Al_2O_3.2SiO_2.2H_2O$

d $(NH_4)H_2PO_4$

e Fluorite, CaF_2

f Montmorillonite, essentially: $Al_4(OH)_{12}Si_8O_{12}(OH)_8$

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Fig. 13. Six diffraction patterns showing performance of new Philips 114.6 mm camera. All taken with copper radiation at 45 kV_{peak}, 25 mA, with exposure times of 1 to 2 hours; *a-e* with general purpose type tube system No. 55 causing small blind areas around film holes, *f* with forward-reflection (only) type causing a large blind area around 180° film hole but no blind area near 0° hole. For films *e* and *f*, a 0.015 mm nickel filter was placed before the window of the X-ray tube, eliminating the undesired copper $K\beta$-radiation so that only the $K\alpha$-diffraction pattern is recorded. For *a*, *c* and *d*, a similar filter sheet covering the lower part of the film was used, so that the major portion of the film represents unfiltered radiation; this technique has the advantage of more rapid exposures combined with easy identification of the undesired $K\beta$-lines. Film *b* was taken with no filter at all. The pattern of fluorite shown in *e* was recorded with black paper being placed over the whole film to prevent the film from being blackened by visible fluorescence caused by the X-rays striking this compound (cf. footnote [4])). In some of the original patterns faint broad diffraction lines are discernible around the 0° film hole; these are caused by a slight devitrification of the Lindemann glass capillary used for mounting the specimen.

(of the 114.6 mm camera) has a width of 0.48 mm at the specimen. Of course intensity is low in this case; it is sacrificed to obtain optimum line shape.

High requirements are set for the precision of the machining in the manufacturing process of the collimator and exit tubes. It may be mentioned, for instance, that the inner diameter of the collimator tube tip must not deviate from the calculated dimensions by more than minus 0 and plus 5 microns. A similar precision is required for the tube fittings in order to insure the necessary exact alignment with the center of the camera. This requirement was made all the more difficult because it had to be combined with an easy interchangeability of the tubes of different types. A practicable solution was found in providing each tube with a precisely machined external surface fitting snugly into a receptacle in the camera wall, while the ultimate positioning on insertion results from matching of very accurately ground faces on the tube collar and the receptacle, these faces being normal to the beam axis.

that of a similar system with 0.75 mm apertures. Compared with the first system, an intensity factor of 3 is gained, when this collimator system is completely filled with radiation.

The value of 0.5 mm was chosen for the aperture widths because it was assumed that in general the specimen would be no thicker than 0.5 mm, and also because this value is well adapted to the focal spot dimensions of the Philips X-ray tubes supplied for use in the Philips diffraction apparatus. A few remarks should be made concerning this latter point.

The collimator system must, on the one hand, insure the beam width and divergence not to exceed the limits set by the desired resolution. On the other hand, it is desired that the radiation of the X-ray tube be used to good efficiency. This evidently will not be the case if the outermost points of the specimen circumference cannot "see" the full projected size of the focal spot because rays coming from the ends of the focal spot are cut off by apertures (cf. fig. 4). Therefore, we might say that the focal spot and the collimator system are well adapted one to the other if the first collimator aperture in fact could be omitted without affecting the beam shape [6]).

With the Philips X-ray tube mentioned above the focal spot is 9 mm long. At an angle of 3° from the face of the anode the projected width of the focal spot is 0.5 mm; in that case, rays from the entire focal spot pass through the apertures of size mentioned above to each point of the specimen cross-section, and the full radiation intensity is utilized. At an angle of 6°, however, which is more commonly used in diffraction apparatus, the projected width of the focal spot will be 0.9 mm, resulting in the ends of the spot not being used.

If the 3° angle is always used the only function of the first collimator aperture is to collimate the beam in case an X-ray tube having a larger focal spot than that of the Philips tubes is to be used.

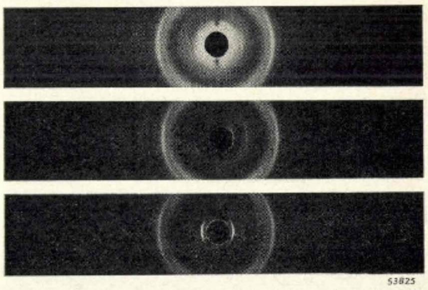
A similar consideration applies to the 2 mm length of the first aperture: the dimensions of the focal spot of Philips X-ray tubes in this direction being on an average only 1.2 mm, the collimating action of the first aperture in this direction likewise becomes apparent only if other tubes, having wider focal spots, are used. With the focus width of 1.2 mm mentioned above, the first aperture is not completely filled by the beam and the intensity gain as compared with two circular 0.5 mm pinholes, therefore, is somewhat smaller than indicated above (gain factor about $2\text{-}2^{1}/_{2}$).

As is well known, incorporating the beam collimating system in a tube inside the camera has, moreover, the important advantage that the focus-to-specimen distance can be made smaller, entailing a considerable increase in intensity.

Anti-air-scatter tubes

The deleterious effect of air scatter on the contrast of diffraction patterns can be eliminated by evacuating the camera. This technique, though applied in some cases, is not convenient in instruments for routine investigations. An alternative and much simpler resource consists in confining the primary beam on its path to and from the specimen within two metal tubes (see fig. 2). The entrance tube also contains the collimator system. Film background is reduced because the air path is now limited to the distance between the ends of the two tubes.

To reduce air scatter to a minimum one would prefer to bring the tubes as close as possible to the specimen. It is obvious, however, that sufficient space must be allowed around the specimen for the emission of the rays diffracted by the specimen. The diffraction lines at angles near 0° and 180° evidently are most liable to be intercepted by the rims of the tubes, and it was quite a common deficiency in cameras previously designed that "blind areas" were caused on the film at these diffraction angles, i.e., around the holes punched in the film at the entrance and exit region for the primary beam. Such a blind area is clearly visible in the pattern of a commercial soap reproduced in *fig. 7b*. On the other hand, fig. 7*a* exhibits the dense background which is produced, particularly near the exit film hole, if no exit tube or one of insufficient length is used.



a

b

c

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Fig. 7. Part of diffraction pattern of soap, containing the range of diffraction angles 2Φ from 0° to about 90°, taken with copper $K\alpha$ radiation and nickel filter.

a) No exit tube used. Considerable background occurs in the range of low diffraction angles, near 0°.

b) Badly designed exit tube. The tube, due to its contour, intercepts the diffraction lines which would otherwise be registered near the film hole (blind area effect).

c) Recorded with new 114.6 mm Philips camera. Background has been reduced to a minimum, without any blind area effect around the film hole, due to proper design of the collimator and exit tubes. Lines at small angles that could not be seen before are now reproduced very clearly.

Closer investigation shows that it is possible to compute specific dimensions of the anti-air-scatter tubes which give best results for different purposes. These computations have been made for our cameras and the tubes now employed have been designed in accordance with the results. For comparison, a pattern of the same specimen as in fig. 7*a* and *b* recorded with one of our improved cameras is

[6]) For a set-up without "first" collimator aperture, cf. A. Guinier, Radiocristallographie, Dunod Paris 1945, p. 80. The same principle is applied also in the Geiger counter spectrometer (cf. footnote[1])).

Camera design considerations relating to quality of pattern and speed of recording

When considering the design factors which influence the abovementioned properties it becomes apparent that in several instances the requirements are conflicting. For the sake of convenience let us start from the sharpness of lines.

Sharp definition of the lines mainly depends on the diameter of the camera, the width and divergence of the primary X-ray beam, and the thickness of the specimen.

Simple geometrical considerations show that the lines become sharper (i.e. narrower in relation to their mutual separation distances) with an increase

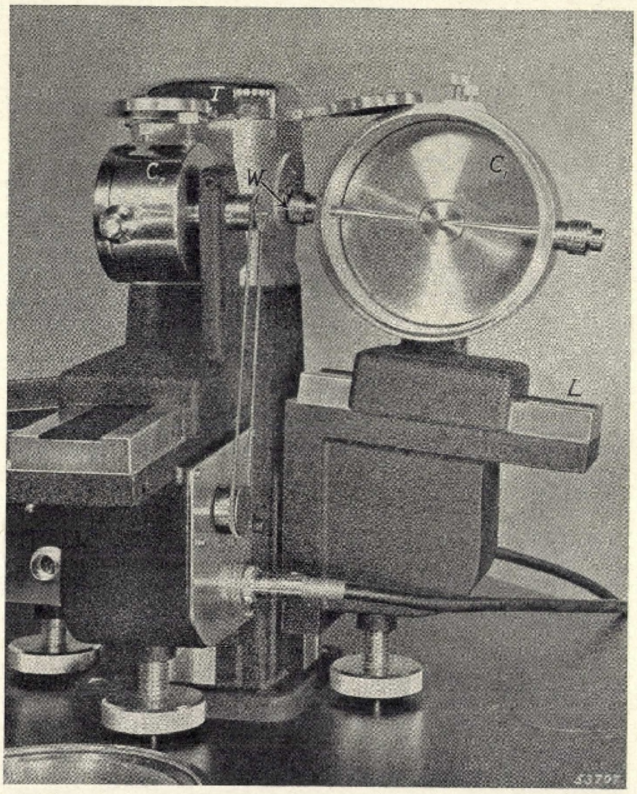

Fig. 3. The two cameras, C_1 and C_2, set up with an X-ray tube T on the desk of a Philips diffraction apparatus (the same tube can, as a rule, be used for from one to four cameras at the same time). Each camera is supported by a bracket and rests on a flat track L. The bracket being fixed, the camera may be rocked around and translated along the specimen axis; the track may be translated along and rocked about a vertical axis (parallel to the X-ray tube housing). This permits an easy aligment of the diffraction camera with the corresponding exit window (W) of the X-ray tube. Once aligned, the camera may be removed for film processing and reloading, and repositioned on the track without need for further alignment. Small and large cameras may be interchanged without altering the position of the track. The X-ray tube, too, is designed to allow changing tubes (e.g., for varying the target material) without affecting camera aligment. The tracks make an angle of 6° with the horizontal plane. Hence, if the camera is rocked around its axis so that the two tubes are parallel to the track, the X-ray beam used makes an angle of 6° with the horizontal face of the X-ray tube target. By slightly rocking the camera and raising the track this angle can be made smaller (e.g., 3°). While the exposure is being made the specimen is rotated continuously around its axis by a pulley attached to a small electric motor covered under the track.

A well designed Debye-Scherrer camera should meet the requirements that, on the one hand, the recording of a pattern be made as easy and quick as possible, while, on the other hand, the highest possible quality of the resulting patterns be secured.

As far as ease of handling is concerned, the cameras produced by North American Philips Co., Inc., have been designed in the main in accordance with the cameras described a few years ago by M. J. Buerger [2]). The principles outlined by Buerger were aimed, among other things, at facilitating the alignment of the camera with the X-ray tube, the recovering of the alignment after temporary removal of the camera from its position, the centering of the specimen in the camera, the rapid mounting of the film, etc. The successful realization of such principles depends mainly on precise mechanical construction. Those are not the subjects which are extensively treated in this article, although some details relating to the aforementioned principles are given in *figs 2* and *3* and explained in the accompanying legends. On the contrary, this article deals much more thoroughly with the speed of recording and the quality of the patterns obtained.

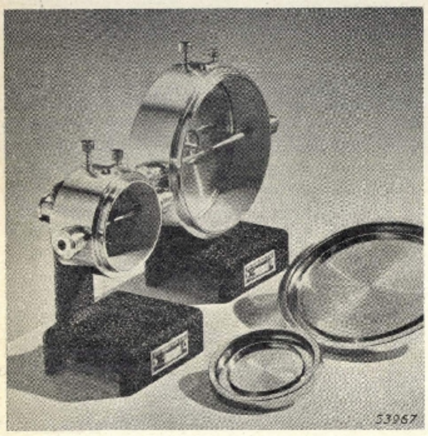

Fig. 2. The Debye-Scherrer cameras with diameters of 57.3 and 114.6 mm, as manufactured by North American Philips Co., Inc. Next to the cameras are the covers, fitting light-tight on the cameras, so that it is not necessary to make exposures in a dark room nor to cover the film with black paper. In each of these cameras the primary X-ray beam passes through two conical tubes between which the very thin rod-shaped specimen is mounted. After placing the specimen roughly on the axis of the camera it is accurately centered by means of a threaded "pusher" perpendicular to the axis. This is facilitated by slipping a small magnifying glass on the end of the exit tube. During the exposure the glass is replaced by a cap containing a small fluorescent screen, on which the primary beam and the shadow of the specimen may be observed. Thus the alignment of the camera and the centering of the specimen are checked. The fluorescent screen is covered at the inside with black paper, making the camera light-tight, and at the outside with lead glass, absorbing the remainder of the primary beam without obstructing the view of the fluorescent screen. The film is placed in the camera according to the Straumanis method: the film takes up nearly 360°, and two holes of normalized width of 9 mm are punched in it where the tubes are to be inserted. Careful design and machining of the tubes make it possible to remove them easily for mounting the film and to replace them in exactly the correct alignment. The film is expanded tightly against the inner wall of the camera by means of a movable finger which pushes one end of the film, the other end being fixed by a stop.

Properties involved in quality of pattern

Information about the nature of the X-rayed specimen can be deduced from the positions (i.e., the diffraction angles) of the diffraction lines, from their relative intensities and from the line shape. High quality patterns, therefore, will exhibit the following properties:

1) Recording of all lines that are of importance. This especially refers to very weak lines, which may often be important in quantitative chemical analysis by X-ray diffraction, and to lines at very small or very large diffraction angles (2Θ near zero or 180°, Θ = Bragg angle).
2) Great sharpness of lines. This will enable the diffraction angles to be determined very accurately and at the same time it will provide a good resolution of adjacent lines.
3) Good contrast of recorded picture, i.e., minimum and relatively uniform background density on the film in comparison to the density of the lines. A strong background would not only affect the observable recording of very weak lines mentioned in (1), but also impair the measurement of the correct relative intensities, for strong as well as for weak lines.
4) Good line shape, i.e., correct contour, uniform density, and constant intensity along the usable length of each line (insofar as the desired data do not actually depend on broadening, spottiness or specific intensity distribution of each line). This property is important for good definition of the position of the lines and for correct intensity measurements.

In order to meet the requirement of quick recording of patterns, especially in view of point (1), we must add to this list of desiderata:

5) High intensity of diffracted rays.

[2]) M. J. Buerger, The design of X-ray powder cameras, J. Appl. Phys. **16**, 501-510, 1945. Cf. also: M. J. Buerger, An X-ray powder camera, Amer. Mineralogist **21**, 11-17, 1936.

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AN IMPROVED X-RAY DIFFRACTION CAMERA

by W. PARRISH*) and E. CISNEY*). 548.73:621.386.1:778.332

For obtaining high quality X-ray diffraction patterns with minimum exposure times, an improved Debye-Scherrer camera has been designed and is produced by North American Philips Co., Inc. Various factors entering the design of the camera and interrelated in their influence on the properties of the patterns are considered in this article. The necessary compromises between such properties as line intensity, line sharpness (resolution), contrast and line shape are favorably affected by several resources. Line intensity is improved without loss of resolution by using a rectangular collimating aperture for the X-ray beam. Contrast is enhanced by surrounding the primary beam on its path to and from the specimen by a collimator and exit tube, thus diminishing the film blackening resulting from radiation scattered in the air. It is shown that these "anti-air-scatter tubes" must have definite dimensions in order to insure the limitation of air scatter to a minimum without causing undesirable blind areas in the diffraction patterns and avoiding any scattering from the tubes themselves. The optimum forms of the tubes for different purposes have been computed, and the cameras can be provided with one of several systems designed in accordance with the results of these computations. The tubes are made easily interchangeable. Handling of the cameras in general is simplified to a considerable extent by the application of certain mechanical design principles outlined by Buerger.

In this article a description is given of an improved camera for the photographic recording of X-ray diffraction patterns of polycrystalline (e.g. powder) specimens according to the Debye-Scherrer method. There is no need to enumerate here the many purposes which these patterns may serve. It is sufficient to state that they are used extensively in research and industrial laboratories for the identification or chemical analysis of materials, for the examination of crystalline structure and grain size, and for the analysis of stresses, texture etc. [1]).

Fig. 1 illustrates the well-known principle of the Debye-Scherrer camera. This camera is a cylindrical enclosure along the axis of which the cylindrical specimen is mounted; the film strip is placed against the inner wall of the camera. The X-ray beam (made as monochromatic as practicable) enters the camera through an aperture in the cylindrical wall. Parts of this beam are diffracted at definite angles by the tiny crystals in the specimen and produce characteristic diffraction lines on the film, while the diffracted part of the (primary) beam passes on to a stop or receiver, or may leave the camera through an aperture in the opposite cylindrical wall.

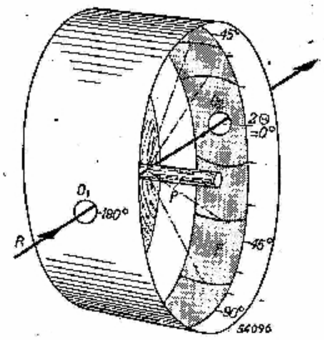

Fig. 1. Principle of the Debye-Scherrer camera. A monochromatic X-ray beam R enters the cylindrical camera through an aperture O_1 and is partly diffracted in the specimen P. The undiffracted part of the beam leaves the camera through the aperture O_2. The diffracted rays cause the lines (ring segments) of the diffraction pattern on the film F.

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[1]) A survey of the applications of the Debye-Scherrer method can be found, for instance, in Philips Techn. Rev. 5, 157-166, 1940. A few months ago an article in this Review was devoted to the "Geiger counter X-ray spectrometer", an apparatus also produced by North American Philips Co., Inc., and enabling the direct measurement of the intensity distribution of X-ray diffraction patterns (Philips Techn Rev. 10, 1-12, 1948 (No.1)). The Geiger counter method and the photographic method are well suited to supplement each other due to their different performance characteristics.