THE HILGER X-RAY CRYSTALLOGRAPH AND THE CUBIC-CRYSTAL ANALYSER

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ABSTRACT. A description is given of an X-ray crystallograph designed on the principle used by Seeman[1] and Bohlin[2] in which the slit, specimen to be analysed and photographic film are disposed along the circumference of a circular camera. Typical crystallograms obtainable are shown.

The cubic-crystal analyser is described and some examples demonstrating its use are given.

§ I. INTRODUCTION

THE basic principle underlying all powder methods of X-ray crystal analysis is essentially that of Bragg[3], but owing to the impracticability of obtaining single crystals of appreciable size, his original method has been modified so as to be adaptable to the various obtainable forms of the material under investigation. This has led to such methods as those used by Debye and Scherrer[4], Hull[5], Weiss[6] and others, which, although differing slightly in their experimental arrangements, owe their success in operation to identical factors. In order to arrive at a correct determination of the atomic structure of any substance by any of the powder methods, it is essential that the substance should consist of a conglomeration of small crystals offering all possible orientations to the incident monochromatic X-ray beam. This condition is ensured by powdering the substance (filings being used in the case of metals and alloys), and spreading them into flat layers or placing them in thin celluloid containers. Rotation or oscillation will further ensure the random orientation necessary, and we would then have all the possible planes present at the required orientation θ to the incident beam so that reflection should result according to the Bragg relationship

$$n\lambda = 2d \sin \theta \qquad \ldots\ldots(\text{I}),$$

d being the spacing between geometrically like planes,

λ the wave-length of the X-rays used, and

n the order of reflection obtained.

Let us now consider the effect of a narrow circular beam of X-rays when incident upon a rod of powdered specimen situated at the centre of a circular camera (Debye and Scherrer method). Wherever it encounters a crystal plane of spacing d at a glancing angle θ such that the Bragg equation is satisfied, then the

ray will be reflected, the total deviation from its original path being 2θ. But owing to the haphazard distribution of the crystals, all orientations of the reflecting plane in question will be possible, and hence the reflected ray will not lie in one single plane but will form a cone of semi-vertical angle 2θ about its incident direction as axis. The intersections of these conical surfaces with the film, which is placed round the circumference of the camera, produce a series of curved lines symmetrically placed about the point of incidence of the direct beam. Measurement of the distances between these lines leads to the evaluation of the glancing angle θ and hence to the solution of the Bragg equation.

For precise measurements it is necessary to take certain precautions and make various vital corrections. Some of the principal ones are enumerated below.

(i) Since the breadth of the spectrum lines recorded is approximately equal to the breadth of the crystalline rod, inaccuracies often occur in the measurement of the inter-lineal distances owing to the difficulty of exactly determining the centre of lines not having sharp edges.

(ii) Approximate measurements only can be made of the crystal-to-film distance. This can be partially remedied by an exposure of some standard substance, such as sodium chloride, placed in a cylindrical container of dimensions identical with those used for the substance under analysis. A high order of accuracy cannot be obtained owing to the variation of the absorption properties of the substances used.

(iii) An important error is that due to absorption, which has the effect of making the calculated value of θ greater than it should be. Corrections have been suggested from theoretical considerations by O. Pauli [7] and by A. J. Bijl and N. H. Kolkmeyer [8]. Practical methods employing comparison of photographs with those of standard substances have been used by W. P. Davey [9] and R. W. G. Wyckoff [10]. If the powder used is pressed into the form of a flat layer, or if flat plates are used in the analysis of metals or alloys as in Weiss's method, the discrepancies due to absorption are modified, but further sources of error are entailed by the new experimental arrangement.

(iv) In Hull's method, where flat sheets of the powder are used either in a compressed condition or between plane glass plates, and are placed normally to the X-ray beam, the errors due to absorption are negligible. However, for accurate measurements precautions must be taken to ensure that the thickness of the sheet is constant and that the surfaces are perfectly plane.

(v) In Weiss's method a plate of the metal or alloy is oscillated in the X-ray beam through any convenient angle. Errors will occur if the surface is not coincident with axis of the cylindrical camera. Corrections as suggested by A. Müller [11] must be applied.

(vi) In the above-mentioned powder methods it is necessary, in order to obtain satisfactory photographs, that the size of the crystal grains be small, that is, about 0·1 mm. to 0·005 mm. If the crystals used are too large, the spectrum lines recorded will appear broken and disjointed, which further hinders the accurate location of the mid point during measurement of the inter-lineal distances.

(vii) Finally a great practical drawback in all of the above methods is the prolonged exposure necessary, unless a powerful and therefore more expensive plant is used.

We thus see that in order to arrive at precise determinations of crystal structures the observer must take special precautions in the preparation of his specimens and in the setting up of his instrument. He must then apply corrections to his calculated results. The following paragraphs, however, describe a method of taking powder photographs without the encumbrance of the aforementioned sources of error.

§ 2. PRINCIPLE OF METHOD

Figure 1 represents diagrammatically the camera of the crystallograph. A monochromatic X-ray beam passes through the slit S and is incident upon the scattering substance placed along BC. Consider a ray striking the powder at the point B. This will be reflected from a lattice plane of spacing d and will record a spectrum line on the photographic film at the point P. The amount of deflection from its incident path, suffered by the ray, is equal to 2θ according to the Bragg equation (1), that is

$$\angle EBP = 2\theta.$$

From the geometry of the figure

$$\angle SBP = \angle SCP,$$

whence $$\angle FCP = 2\theta.$$

Thus if a ray is incident at C upon a lattice plane of the same spacing d as at B, it will be reflected to the point P. Similarly for all points along BC. Hence all the rays which strike lattice planes of identical spacings will be deflected and *focussed* upon the same point P, where a sharp image of the slit should be expected.

Again, from the geometry of the figure

$$\angle SOP = 4\theta.$$

p
r

Hence if p is the distance of spectrum line from slit (arc SP) and r the radius of the camera then

$$p = 4r\theta \qquad \qquad \ldots\ldots(2),$$

Fig. 1.

whence the glancing angle can be calculated. This value of θ substituted in the Bragg equation (1) will then give the spacing of the reflecting lattice plane.
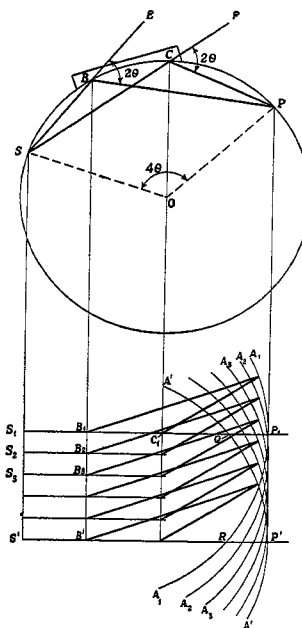
§ 3. FORMATION OF THE SPECTRUM LINES

The actual formation of the spectrum lines can be seen from the vertical projection [2] as shown in the lower half of figure 1. Rays passing through the slit $S_1 S'$ are incident on the scattering substance at $B_1 B_2 \ldots B'$, and will all be deflected at an angle 2θ. (We are considering only lattice planes of spacing d.) The deflected ray will in each case, as in the Debye and Scherrer method, describe a cone of semi-vertical angle 2θ about its incident direction, and will eventually intersect the film, forming curves $A_1 A_2 \ldots A'$. The superimposition of these curves gives rise to the photographic image of shape $P_1 P' R Q$, but with a sharply defined edge $P_1 P'$ which corresponds to the common tangent of the curves and is geometrically defined by equation (2). This image formation is very well illustrated in figure 2 which is an untouched reproduction of an enlargement ($\times 5$ approximately) of a spectrum line that was actually recorded on the crystallograph. The scattering substance in this case was a sheet of annealed metallic aluminium having its crystal grains larger than would be practicable with other powder methods. Even in this case the edge is broken, but its definition is sharp enough for accurate measurement.

This edge does not always lie on the same side. As the glancing angle increases the breadth of the line decreases, as can be seen from the construction of figure 1, till a point is reached where $\theta = 45°$, that is, where the semi-vertical angle 2θ of the intersecting cone $= 90°$. At this position the spectral line formed is a straight-line image of the slit. If the glancing angle is still further increased the breadth of the line will also be increased, but now the sharp edge will be on the opposite side. The turning-point is given by substitution in equations (1) and (2)

$$n\lambda = 2d_0 \sin 45°, \qquad\qquad d_0$$

that is

$$d_0/n = \lambda/\sqrt{2} \qquad \ldots\ldots(3a),$$

and also

$$p_0 = \pi r \qquad \ldots\ldots(3b).$$

§ 4. COMPARISON WITH OTHER POWDER METHODS

In order to facilitate direct comparison with other powder methods, the various factors affecting the accuracy of measurement will be dealt with in approximately the same numerical order as before.

(i) The breadth of line does not affect the accuracy of measurement since readings are taken on one edge only. The breadth is, however, kept within certain limits so as to prevent diffusion of the edge. This is effected by using narrower slits and a narrower width $B_1 B'$ of the scattering material (cf. figure 1).

(ii) No crystal-to-film distance need be measured. The only dimension required is that of the radius of the instrument. This is permanently fixed and can be checked by taking an exposure of some standard substance of known lattice spacings, such as sodium chloride.

(iii) Results are unaffected by absorption, that is, by the varying depth of penetration of the X-ray beam. This is shown in figure 3 where the dotted lines represent the path of the reflected rays from the interior of the scattering medium. The geometric position of the sharp edge P is not influenced by the amount of penetration. This is demonstrated rather well in figure 2, where the images reflected from two layers of crystals can be clearly seen at P and P'.

(iv) Care must be taken to ensure that the whole surface of the reflecting material lies on the circumference of the camera. In the case of metallic sheets this condition is easily fulfilled by bending the metal into an arc of the required radius. Powders, however, may be either compressed into the requisite shape or painted on a specially provided powder holder. The latter is a glass plate which has its face ground to a concave cylindrical curve of radius equal to the focussing radius of the camera.
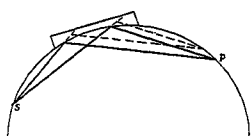
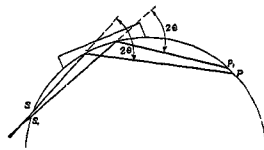

Fig. 3.   Fig. 4.

(v) There is no need to provide for the oscillation or rotation of the specimen, as the whole surface lies in the beam of the incident X-rays.

(vi) The range of crystal-grain size is shifted to a higher limit.

(vii) The exposures are greatly reduced. For example the powder photograph of copper filings was taken in 45 seconds with monochromatic CuK_α radiation generated by a Shearer tube working at peak voltage of 70,000 volts and a slit width of 0·07 mm.

(viii) A very necessary precaution is to ensure that the slit edge S, figure 4, is permanently fixed coincident with the circumference of the camera. The size of slit-width will then not affect the accuracy of readings since the sharp edge corresponds only to the position of S (cf. figure 4).

§ 5. GENERAL CONSTRUCTION OF THE CRYSTALLOGRAPH

A diagrammatic reproduction of the general assembly of the crystallograph camera is shown in figure 5. In figure 6 it is shown in the dismantled condition.

The camera itself is constructed in the form of a shallow cylinder 1 which is 4·4 cm. in height and 4·5 cm. in radius. A portion is cut away to form an angular recess for accommodating the anticathode end of a Hilger-Shearer X-ray tube. The relative position of the tube is fixed by four locating studs 4, 6, 9, 11, one of which a, 4 is adjustable. Once the correct position of the tube is found, its location is permanently secured by seeing that the anticathode end is making proper contact with all four studs. A great advantage which arises in having the crystallograph designed expressly for use with the Shearer X-ray tube is that we thus obtain a
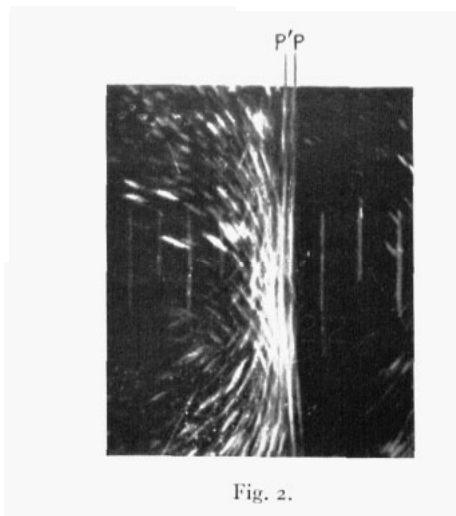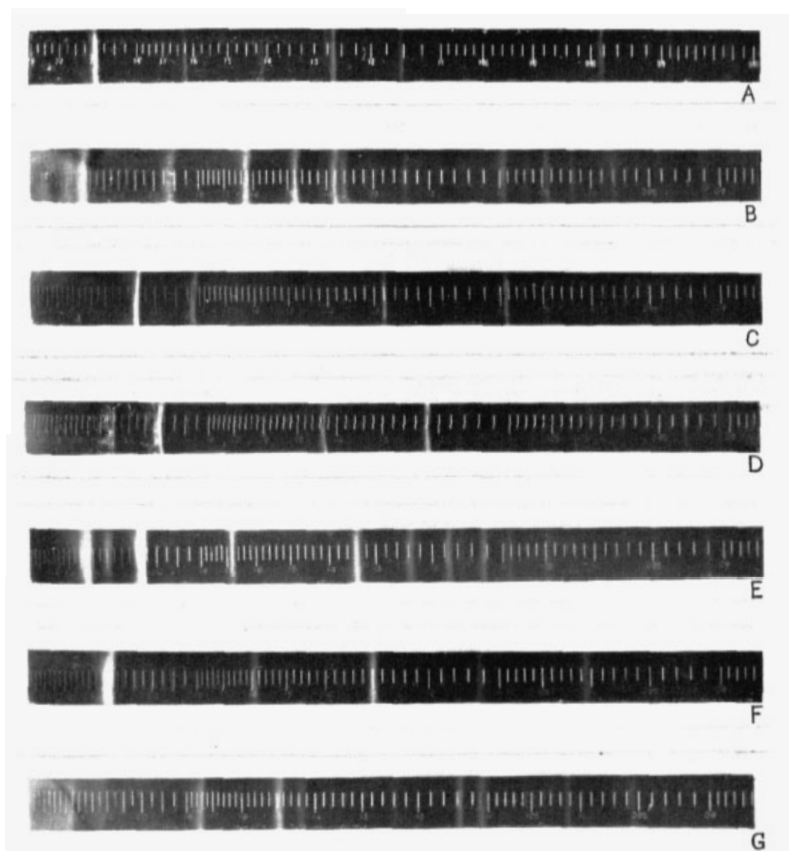
Fig. 2.

Fig. 7. Typical crystallograms. *A*, powdered sodium chloride, exposure 20 min.;
B, powdered zinc oxide, exposure 10 min.; *C*, copper filings, exposure 5 min.;
D, aluminium sheet (annealed), exposure 5 min.; *E*, zinc sheet, exposure 5 min.;
F, tungsten filings, exposure 10 min.; *G*, lead filings, exposure 30 min.

maximum intensity of the incident X-ray beam, since the anticathode of the tube is directly behind its window which is itself almost in contact with the slits, figure 5.

The slit system consists of two brass jaws 5, 8 tipped with a bismuth-lead alloy and cut obliquely at angle of 30° to form knife-edges. The slit jaw S is permanently fixed, whilst slit jaw S_1 is adjustable by hand. A set of slit gauges is used for setting to the required aperture and the slit jaw S_1 is secured in position by two screws. A lead stop b prevents fogging of the film by direct or scattered radiation from the slit system. The glass specimen holder C, 13, 14, previously described, fits into the side of the camera and is secured by a light-tight cover d, 15 and two screws e, 7, 10.
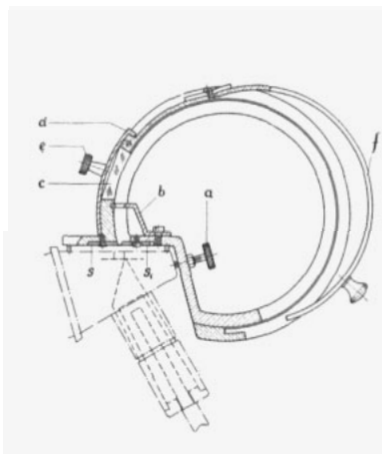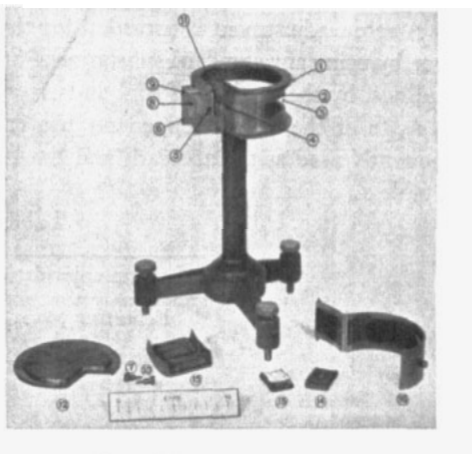

Fig. 5.

Fig. 6. Hilger crystallograph.

The photographic film is 17 cm. long and 2·5 cm. wide; it has one end punched with two accurately gauged holes and is then fitted on the two small pegs which locate it in the camera. It is then wrapped around the circumference of the camera and rests on the cylindrical surfaces 2 on either side of a wide annular slot 3 through which it is exposed to the reflected rays from the scattering medium on the powder-holder. A light-tight brass cover f, 16 clips the film into position and holds it firmly in place.

The camera is provided with a light-tight brass cover plate 12 and is mounted on a firm tripod stand provided with levelling screws, at such a height that the window of the Shearer tube is level with slit of the crystallograph.

§6. THE INTERPLANAR SCALE

Since the constants of the instrument are permanently fixed, it has been possible to devise a method of superimposing an interplanar scale upon the crystallogram. We get by substitution for θ from equation (2) in equation (1)

$$d/n = \lambda/\{2 \sin (\rho/4r)\},$$

that is
$$d_{hkl}/n = \lambda/\{2 \sin (\rho/4r)\} \qquad \ldots\ldots(4),$$

where d_{hkl} is the spacing between like planes whose Miller indices[12] are h, k, l.

d_{hkl}

The scale was calculated from the above relationship between d_{hkl}/n and p and gives value of d_{hkl}/n at every point of the film. It was assumed that filtered Cu-radiation ($\lambda = 1\cdot54$ Å.U.) had been used. This condition is obtained in practice by using a Shearer X-ray tube fitted with a copper anticathode and a nickel-foil window. The interplanar scale is contained in a separate printing-frame provided with two film-locating pins so placed as to correspond approximately to a similar pair fixed in the camera. After exposure in the crystallograph the film is removed in a dark-room and placed in the printing-frame. The interplanar scale is then printed on to the negative by exposure to white light for a fraction of a second, and development brings it up together with the crystallogram.

A screw adjustment is provided for the exact setting of the scale. This can be done by using any standard substance of known spacings and then setting the scale readings, by the method of trial and error, to coincide with the theoretical values of d_{hkl}/n of the lines obtained on the crystallogram. Sodium chloride is most frequently used as the standard and the lines usually chosen for setting are given in table 1.

Table 1.

Sodium chloride ($a_0 = 5\cdot628$ Å.U.)	
Reflecting plane $hkl\ (n)$ *	d_{hkl}/n
110 (2)	1·991
111 (2)	1·625
100 (4)	1·407
120 (2)	1·259
112 (2)	1·149
110 (4)	0·995
100 (6)	0·938

Typical crystallograms are shown in figure 7. These were taken with copper K_a radiation obtained from a Hilger-Shearer X-ray tube having a nickel-foil window and fed with about 5 mA. from a transformer working at a voltage of about 60 kV. r.m.s. A slit-width of 0·1 mm. was used, and the exposures given were in excess of that normally required so as to ensure better printed reproductions.

§7. THE CUBIC-CRYSTAL ANALYSER[13]

The cubic-crystal analyser has been constructed from consideration of the simple cube lattice as shown in figure 8 (1). This cube is taken as the fundamental basis of development of all other cubic structures which are encountered in crystallography, and which are obtained by the addition of lattice points in various symmetrical positions. Thus we get the body-centred cube, figure 8 (2), and the face-centred cube, figure 8 (3); but whatever the cubic structure, the measurement a_0 of the length a_0 offers a *unique specification of the substance undergoing investigation.*

* The values of (n) as given in column 1 have not been corrected to account for the internal structure of the elementary cube. See § 8.

The spacing of geometrically like planes parallel to the plane (*hkl*) is given by

$$d_{hkl} = a_0/(h^2 + k^2 + l^2)^{\frac{1}{2}} \qquad \dots\dots(5).$$

Now in practice with powder photographs it is found that the value of d_{hkl} is derived from a knowledge of the constants in the Bragg equation (1)

$$n\lambda = 2d_{hkl} \sin \theta,$$

provided of course that the order n of the spectrum considered is known. But this is not always determinable at sight, and hence solutions are found primarily for d_{hkl}/n.
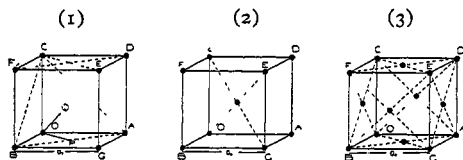

Fig. 8.

Rewriting equation (5) we get

$$d_{hkl}/n = a_0/n\,(h^2 + k^2 + l^2)^{\frac{1}{2}},$$

that is

$$a_0 = n\,(h^2 + k^2 + l^2)^{\frac{1}{2}}\,(d_{hkl}/n) \qquad \dots\dots(6).$$

Integral values being assigned to h, k, l and n, it has been possible to obtain a series of plots showing the linear relationship between a_0 and d_{hkl}/n for all the most probable crystal planes of reflections in various orders, 100 (1), 111 (3) etc. This was the simple process employed in the construction of the analyser, figure 9.

§8. ANALYSIS OF CUBIC CRYSTALLOGRAMS

The method used is applicable to crystal structures having cubic symmetry, and is similar to that employed by Hull and Davey[14] for determining the indices of the reflecting planes in hexagonal and tetragonal structures from graphical charts. A strip of paper is scaled off identically with that of the abscissae of the analyser. Values of d_{hkl}/n for the various powder lines recorded are read directly by means of the interplanar scale and then inscribed along one edge of the paper strip. The latter is then moved parallel to the horizontal axis with the zero mark always on the vertical (a_0) axis until a position is found where there is a full coincidence between the curves on the graphical plot and the markings on the paper strip. (Figure 9 demonstrates coincidence of lead lines.) The indices of the reflecting planes are read off directly, whilst the size of the unit elementary cube is obtained from the point of intersection of the strip edge with the vertical (a_0) axis.

The value of n given by the curves must not be confused with actual order of spectrum line obtained, since the analyser was constructed solely from considerations of the elementary unit cube without allowance for the internal distribution of the
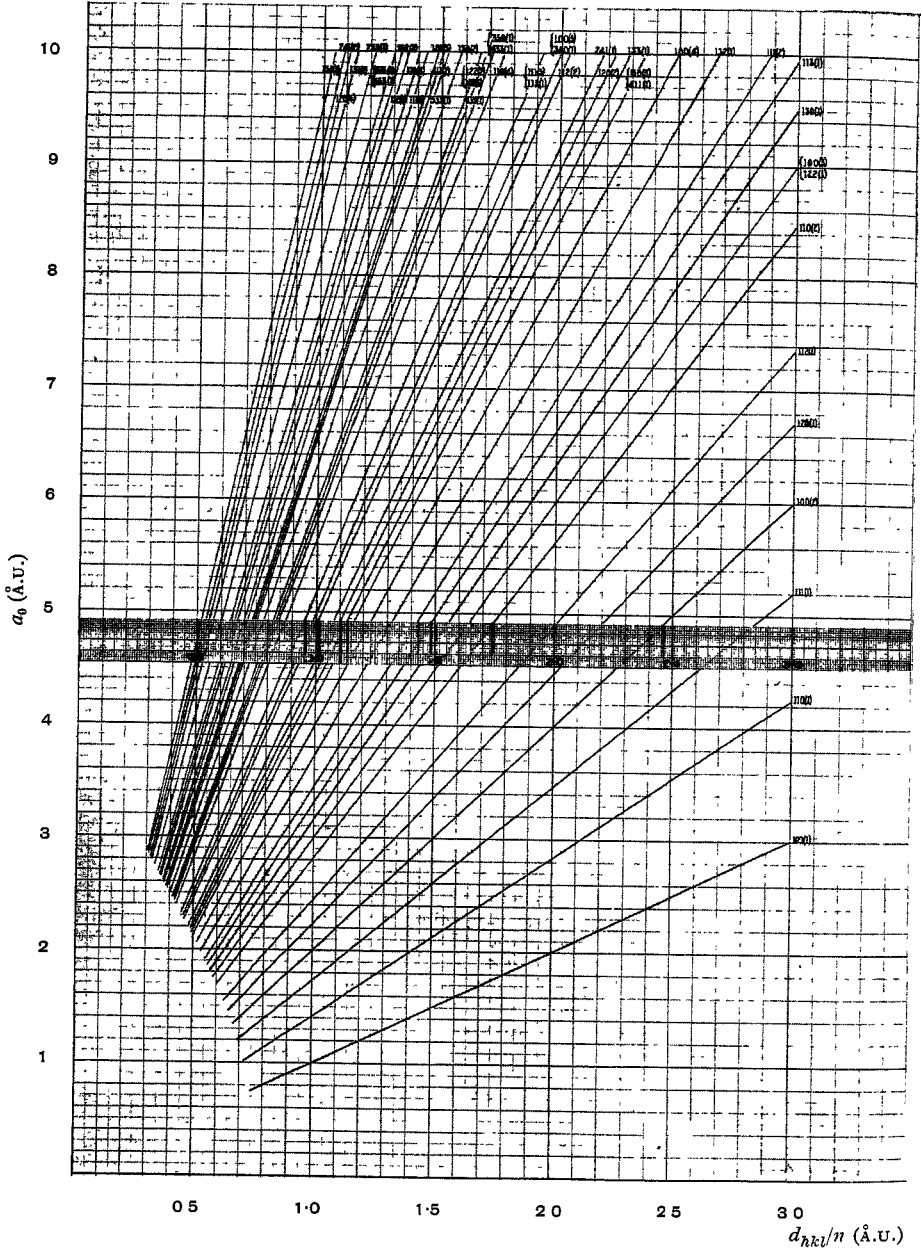
Fig. 9.

lattice points. This is by no means an objection to the use of the analyser, since it provides a method of identifying the various cubic structures by noting the different orders of reflection given by the analyser; for from a comparison of the interplanar distances of types of cubic structures indicated in figure 8, we obtain for the principal reflection planes (100), (110) and (111):

Elementary cube. $\quad d_{100} = a_0; \quad d_{110} = a_0/\sqrt{2}; \quad d_{111} = a_0/\sqrt{3} \quad$ ......(7).

Body-centred cube (B–c). $d_{100} = a_0/2; \quad d_{110} = a_0/\sqrt{2}; \quad d_{111} = a_0/2\sqrt{3}$ ......(8).

Face-centred cube (F–c). $\quad d_{100} = a_0/2; \quad d_{110} = a_0/2\sqrt{2}; \quad d_{111} = a_0/\sqrt{3}$ ......(9).

Thus from the above expression it can be seen that:

(i) d_{100} for the *B–c* and *F–c* structures is half that for the elementary cube. Hence first-order reflection for *B–c* and *F–c* structures from (100) planes will coincide with second-order reflection for an elementary cube; the second-order for *B–c* and *F–c* structures with fourth-order for elementary cube, and so on. Thus the analyser will not show any odd order reflections from (100) planes of *B–c* and *F–c* structures.

(ii) Similarly since d_{110} for *F–c* structures is half that for the elementary cube, no odd order reflections will be shown by the analyser for (110) reflections from *F–c* structures.

(iii) And since d_{111} for *B–c* structures is half that for the elementary cube, no odd-order reflections will be shown by the analyser for (111) reflection from *B–c* structures.

It is thus possible to formulate a double rule for distinguishing between *B–c* and *F–c* structures when the orders of the various reflections are read from the analyser.

Rule 1. If for 100 (*n*) and 110 (*n*) reflections odd values of *n* are missing, the structure is probably *F–c*.

Rule 2. If for 100 (*n*) and 111 (*n*) reflections, odd values of *n* are missing, the structure is probably *B–c*.

Once the structure is known, the correct value of *n* is determinable if required.

§9. PRACTICAL ILLUSTRATIONS

The analysis of crystallograms was quickened by use of a special *T*-square which obviated the necessity for transferring readings of d_{hkl}/n on to a strip of paper. This *T*-square was fitted with a celluloid scale which was an exact replica of and coincident with the d_{hkl}/n scale of the graphical plots. Moving steel pointers were provided for setting to the readings of the powder lines, and the point of coincidence was found by moving the *T*-square along the edge of a drawing-board upon which the analyser was mounted.

Table 2. Lead filings (figure 7 G).

Spacing given by interplanar scale d_{hkl}/n (Å.U.)	Reflection plane given by analyser hkl (n)	
1·74	110	(2)
1·481	113	(1)
1·422	111	(2)
1·23	100	(4)
1·133	133	(1)
1·103	120	(2)
1·015	112	(2)
0·956	111	(3)

Possible planes missing include 100 (3), 110 (3), 100 (5). Full coincidence was obtained at a_o = 4·92 Å.U. Result of analysis: F–c structure, a_o = 4·92 Å.U.

Table 3. Tungsten filings (figure 7 F).

Spacing given by interplanar scale d_{hkl}/n (Å.U.)	Reflection plane given by analyser hkl (n)	
2·22	110	(1)
1·58	100	(2)
1·29	112	(1)
1·12	110	(2)
1·008	130	(1)
0·918	111	(2)

Possible planes missing include 100 (3), 111 (1). Full coincidence was obtained at a_o = 3·16 Å.U. Result of analysis: B–c structure, a_o = 3·16 Å.U.

§ 10. CONCLUSION

The instrument here described simplifies the technique of X-ray crystallography. Owing to the focussing action, the time of exposure can be decreased to such a value that the utility of X-rays for commercial analysis is enhanced. The interplanar scale eliminates hours spent in calculation, and in combination with the cubic-crystal analyser enables a complete analysis of most substances having a cubic structure to be made in less than 10 minutes. The accuracy of the method is greatly dependent upon the accuracy of the machining of the instrument. But if the instrument is calibrated by taking an exposure of some standard substance of known lattice spacings, analysis can be made quite easily with errors less than 1 in 400.

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