GRAPHICAL INDEXING OF POWDER PATTERNS OF CUBIC SUBSTANCES AND THE CHOICE OF RADIATION FOR PRECISION MEASUREMENTS OF LATTICE PARAMETERS

M. E. STRAUMANIS, *University of Missouri, School of Mines and Metallurgy, Department of Metallurgy, Rolla, Missouri*

ABSTRACT

A convenient graphical method is described showing how to find the most suitable x-radiation for precision determination of lattice parameters. At the same time, the method allows one to index the powder patterns. The method is based on the application of three dimensional reciprocal lattice and becomes very simple if used in the case of cubic crystals.

INTRODUCTION

For the precision determination of lattice parameters sharp powder lines (or spots of a single crystal) are necessary in the very back reflection region of the patterns.[1,1a]

It is nearly always possible to find the proper radiation producing lines with a glancing angle ϑ greater than 78°, even in the case of small lattice constants. However, the choice of the wave length[2] takes considerable time and, as far as know by the author, no convenient methods have been described in order to find the best possible radiation.

A simple graphical method, which is easy to apply especially in the case of the cubic powders, is described below. It can be used at the same time for the indexing of powder patterns and is based on the application of the reciprocal lattice constants.

THE THEORY

The section normal to the cylindrical axis of a Debye-Scherrer camera is drawn in Fig. 1 showing the path of the direct and reflected x-ray beams.

It follows directly from the figure that

$$\frac{x}{2r} = \operatorname{Sin}\vartheta \qquad \text{and} \qquad \frac{p}{x} = \operatorname{Sin}\vartheta \qquad (1 \text{ and } 2)$$

[1] Straumanis, M. E., *J. Appl. Phys.*, **20,** 726 (1949).

[1a] Straumanis, M., and Ievins, A., Die Präzisionsbestimmung von Gitterkonstanten nach der asymmetrischen Methode: (Verlag J. Springer, Berlin, Germany, 1940), reprinted by Edwards Brothers, Inc., Ann Arbor, Michigan (1948).

[2] Buerger, M. J., *X*-ray Crystallography: John Wiley and Sons, Inc., New York (**1942**), pp. 171, 393 and 459.

If now the inside wall of the camera, as shown in Fig. 1, is regarded as the sphere of reflection,[3,4] then the chord x represents the reciprocal lattice vector (Fahrstrahl)[5] of the three dimensional reciprocal lattice. This chord connects the origin O of the reciprocal lattice with the reflection (powder line) on the circle of reflection (wall of the camera). Thus,

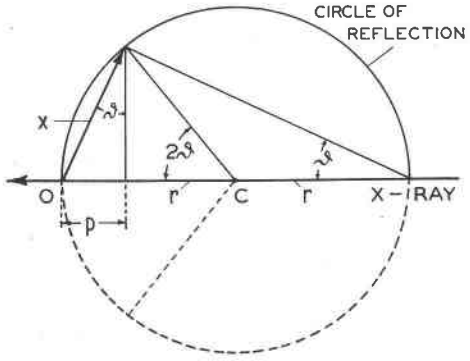

FIG. 1. Path of the x-ray beam in a Debye-Scherrer Camera.
c = the powder sample
x = vector of the reciprocal lattice

p is the projection of the reciprocal lattice vector x on the diameter (marked by the x-ray) of the camera. This p has very interesting properties.

It follows from the combination of Bragg's equation

$$\text{Sin } \vartheta = \frac{n\lambda}{2d} \qquad n = 1$$

with (1 and 2):

$$p = \frac{r\lambda^2}{2d^2}. \tag{3}$$

For the cubic substances d^2 can be replaced by $a^2/\Sigma h^2$, the sum of the squares of the indices h, k, l of the reflecting plane, a, being the lattice parameter of the substance under investigation:

$$p = \frac{r\lambda^2}{2a^2}\Sigma h^2. \tag{4}$$

Working with the same radiation and substance, the part $r\lambda^2/2a^2$ of

[3] Bernal, J. D., *Proc. Roy, Soc. London*, A, **113,** 117 (1926).

[4] Buerger, M. J., *X*-ray Crystallography, J. Wiley and Sons, Inc., New York (1942). pp. 128.

[5] Ewald, P. P., *Z. Krist.*, **56,** 129 (1921); **93,** 396 (1936).

(4) becomes constant and the length of p, resulting from the other lines on the reflection circle, is simply proportional to Σh^2, which represents the integers 1, 2, 3. . . . :

$$p = k\Sigma h^2. \tag{5}$$

This means that all differences of the projections p of two subsequent reciprocal lattice vectors of a cubic substance are equal, including extinct lines and those the Σh^2 of which cannot be split into 3 integers that are squares.

This difference is equal to the smallest p_{min}, resulting if $\Sigma h^2 = 1$; it can also be calculated from (4) if the lattice parameter a is known. Likewise, the lattice parameter a can be calculated if p_{min} is known:[6]

$$a = \lambda\sqrt{\frac{r}{2p_{min}}}. \tag{6}$$

Now, if p is kept constant, the change in radiation from λ_1 to λ_2 will result in a changed radius (r_2) of the reflecting circle. Applying eq. (6) r_2 can be computed using the r_1 adopted previously:

$$r_2 = r_1\left(\frac{\lambda_1}{\lambda_2}\right)^2. \tag{7}$$

Thus, by means of equation (5) a cubic film can easily be indexed and by means of equation (7) the best radiation for precision determination of lattice parameters can be found. How to apply these two formulas is shown in the next section.

Indexing Procedure and Choice of Radiation

The best radiation for the precision determination of the lattice constant of germanium had to be found. The first trial photograph was made with Co-radiation. A very thin germanium powder mount was prepared[1,1a] and the photographs were made in a 64-mm precision camera, using the asymmetric film arrangement.[1] Working with this method standard substances are unnecessary, as well as the knowledge of the camera diameter. Film shrinkage is eliminated and the absorption corrections can be neglected. The exact values of the glancing angles and the lattice constants can be calculated directly from the film, provided the construction of the camera is correct. An example of calculation of the mentioned quantities from an asymmetric film has been given previously.[1]

The measurement of the asymmetric germanium powder film obtained led to the following 2ϑ angles in degrees (only the α or α_1 lines were measured):

[6] Straumanis, M., *Z. Krist.*, **104**, 167 (1942).

31.81; 53.28; 63.42; 87.29; 101.72; 110.65; 126.87; and 138.58°.

Now a reflection circle, corresponding to the inside wall of the camera must be drawn. It is convenient to take the radius of the reflecting circle for copper radiation as being equal to 100 mm. The radii for other radiations, assuming that the projection p_{min} does not change, are calculated by equation (7) and listed in Table 1.

TABLE 1. RADII OF THE REFLECTION CIRCLES IN MM FOR DIFFERENT RADIATIONS, ASSUMING THAT p_{min} IS CONSTANT AND THE RADIUS FOR Cu RADIATION IS EQUAL TO 100 MM

Cu α_1	100 mm	Fe α_1	63.4 mm
Cu β	121.3 mm	Fe β	76.9 mm
Co α_1	74.1 mm	Cr α_1	45.3 mm
Co β	90.4 mm	Cr β	54.6 mm

Further, the following operations must be performed:

(1) The already mentioned 2 ϑ angles of germanium are carried on the reflection circle for Coα_1 radiation as shown in Fig. 2, starting from the origin O on the left side. The figure shows simply the positions of the peaks of the powder lines in a camera with a radius of 74.1 mm. (Table 1).

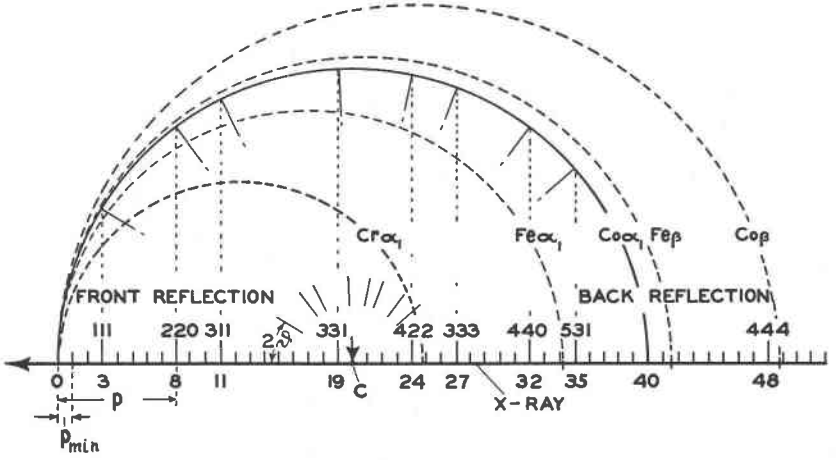

FIG. 2. Graphical indexing of the lines of a germanium film. Choice of best radiation for precision determination of the lattice constant. Crα_1 (and Crα_2) radiation is the best. C = center of the reflecting circle for Coα_1 radiation (place of the powder mount).

(2) The 2 ϑ angles (or more correctly the reciprocal lattice vectors) are projected onto the diameter of the circle as represented by the x-ray beam and the end points are marked as shown on Fig. 1.

(3) Starting from the origin O, the distances between the projection points are divided into the largest possible divisions (equal p_{min}), so that the end point of any one projection from the origin O is an integral multiple of p_{min}. This can be found by trial. Or, since it is known that the first interference of a germanium powder pattern is 111 ($\Sigma h^2 = 3$), the distance between O and 3 should be divided into 3 parts, each part representing p_{min}. Or, if the lattice constant is known p_{min} can be calculated from equation (4), assuming that $\Sigma h^2 = 1$.

(4) The p divisions on the diameter of the circle are numbered successively, starting from the origin as shown in Fig. 2. Each number represents the Σh^2 of the corresponding line and the indices can be easily found.

If all the projections of the points on the reflecting circle coincide with the integers of p_{min} on the diameter (x-axis), the indexing of the cubic crystal is right and there is no other possibility. These are difficulties if the lattice constants are larger; in such cases one must start with a larger radius of the reflecting circle.

The best radiation for the precision measurement of lattice constants is that one which produces lines in the very back reflection region ($\vartheta > 78°$). To find the best radiation, the x-axis with its p-scale is extended if necessary, and reflection circles for the various other radiations (Table 1) are drawn so that the origin O on the x-axis is common to all reflection circles (the centers of the reflection circles are on the x-axis). These reflection circles (broken curves on Fig. 2) intersect the x-axis at different points. Since these intersections correspond to $2\vartheta = 180°$ (back reflection region), that radiation the reflection circle of which intersects closest to a p division is the best one. Of course, the line to which the p belongs must be intense enough. For instance, Fig. 2 shows that Crα_1 and α_2 radiation is the best one in the case of germanium. Coβ radiation would be good also, but the photograph showed that 444β is too weak. In the other cases the very back reflection lines are extinct and the corresponding radiations are unsuitable for precision measurements.

Of course, the whole procedure can also be carried out by calculation using the formulas as given above.

A similar graphical method for the choice of radiation and for indexing of rotation crystal photographs based on the two dimensional reciprocal lattice was described previously.[1a]

Manuscript received July 20, 1951.