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16. Abstract

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A METHOD FOR INDEXING X-RAY POWDER PHOTOGRAPHS

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SUMMARY /1*

A graphical method of indexing X-ray powder photographs without the use of single-crystal data is described.

X-ray examination is a method for the accurate characterization of solids. If sufficiently large unit-crystals of the substance are produced, the determination of the lattice dimensions, the locating of spatial groups and the determination of structure cause no difficulties in theory. However, it is problematical when the substance is available in a fine crystalline form, so that only powder photographs can be taken. In this case, the indexing of X-ray diagrams is very difficult - especially if the substance has a low symmetry - or it is hardly possible at all**.

Several methods for indexing X-ray powder photographs are described in the literature. However, almost all of them are insufficient because the indexing takes such a long time. The determination of the indices and thus of the lattice constants /2 is possible by two methods, in principle: the analytic# [1-3] and the graphic methods##. Graphic methods are often preferred because they lead more quickly to the result. However, they are not as accurate and cannot be applied to all crystal systems, contrary to the analytic method of Ito [2] and De Wolff [2]. Sometimes they require specific conditions of lattice dimensions [3].

The graphic methods are based mostly on the logarithmic formulation of the Bragg law corresponding to the different crystal systems. The quadratic forms of the Bragg equation are also applied to graphic schematics for evaluation of X-ray intereference models.

Footnotes for this page on p. 11.

* Numbers in margin indicate pagination in original foreign text.

As a result of the need of the experimental chemist to be able to evaluate powder photographs, a graphic method is described which permits a potential indexing of powder diagrams of pure substances quickly and without a great deal of effort. The method is theoretically independent of symmetry, and is based on a two-dimensional reproduction of the three-dimensional reciprocal lattice. It is especially useful for cubic, tetragonal, hexagonal, and rhomboid crystalline substances whose powder photographs exhibit a sufficient number of X-ray reflections. The method can also be applied to determine the reciprocal lattice of monocline and tricline substances. The validity of the indexing obtained is naturally no greater than is inherent in the powder photograph.

I. Theoretical Principles of the Indexing Method

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A simple, two-dimensional graphic method for the construction of the three-dimensional lattice of crystalline substances from the data of their powder diagrams is based on the following consideration:

In the reciprocal lattice, the distance from the origin is inversely proportional to the attendant plane in the direct lattice:

$$d^*_{hkl} = K/d_{hkl}. \qquad (1)$$

Here, d^*_{hkl} is the distance from the origin to the point of the reciprocal lattice which corresponds to the family of planes which have the distance d_{hkl}. "K" is an arbitrarily chosen proportionality factor. If we select $K = \lambda$ (= wavelength of the X-rays used), then equation (1), together with the Bragg equation (ϑ_{hkl} = glancing angle) - becomes

$$d^*_{hkl} = \lambda/d_{hkl} = 2 \sin \vartheta_{hkl} \qquad (2)$$

That means that the points h, k, l of the reciprocal lattice lie on spheres of radius $2 \sin \vartheta_{hkl}$, whose center is the origin of the reciprocal lattice.

Moreover, the indices h, k, l of a point in the reciprocal lattice are its coordinates with respect to the reciprocal lattice axes x*, y*, z* (with the corresponding reciprocal lattice con-

stants a*, b*, c* as units). From this it follows that if the lattice constants and the axis angles are known, then any point hkl of the reciprocal lattice can be constructed by addition of its coordinate vectors (h00), (0k0), and (001). If (hkl) is the vector from the origin of the reciprocal lattice to the point hkl, then we have

$$\begin{aligned}(hkl) &= (h00) + (0k0) + (001)\\ &= (hk0) + (001)\\ &= (h01) + (0k0)\\ &= (0kl) + (h00)\end{aligned}$$

Now, imagine the elementary cells of the reciprocal lattice on a two-dimensional intersection of axes (Figure 1) whose interaxial angles α, β, γ, agree with those in the reciprocal lattice, projected so that the origin of the reciprocal lattice coincides /4 with that of the coordinate system and the edges a*, b*, c* of the reciprocal elementary cells lie on the axis (see Figure 1) designated (x), (y), and (z). If b* is plotted also on (y') and if the system of concentric circles of radius $2\sin\vartheta_{hkl}$ is entered around the point of axis intersection, then the reciprocal lattice can be constructed. We only need to enter the parallels to the axes at a distance equal to the reciprocal lattice constants (or whole multiples thereof) in the quadrants determined by the axes (x)(z), (z)(y), and (x)(y'). The points of intersection thus obtained represent points of the reciprocal lattice where they intersect one of the circles.

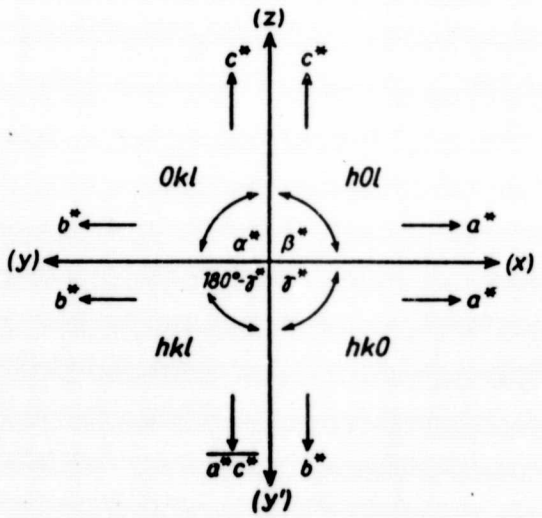


Figure 1: Axes intersection of the Reciprocal lattices

Thus, on the axes[#] a*, b*, c*, we obtain the points with the indices h00, 0k0 and 001; in the a*-c* quadrants, we have the points with the indices h01, in the b*-c* quadrants the points with 0kl and in the a*-b* quadrants, those with hk0.

The points with the indices hkl (h, k, l $\neq$ 0) result by (vector) addition of their coordinate vectors in the quadrants determined from the a*-c* and b* axes. So, in order to construct the point hkl (h, k, l fixed) in the reciprocal lattice, at the point 0k0 we draw the vector (h01) whose length d^*_{hkl} is equal to the distance of the point h01 from the origin and whose direction is given by the angle 180° - γ^* drawn in the origin at b*(##).

Each of these lattice points which lie on a circle, corresponds to a family of reflected crystal-lattice planes in the direct lattice, and all points which do not index with the circle represent crystal-lattice planes whose reflexes were cancelled by spatial group orientations.

II. Indexing Powder Photographs.

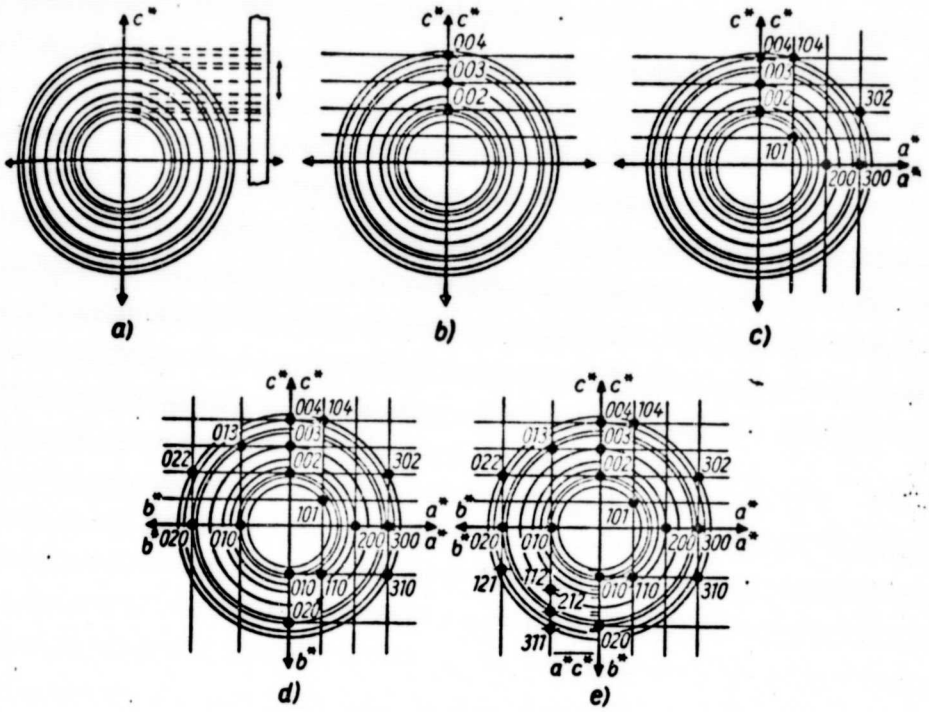
In the evaluation of powder photographs of a uniform substance, one proceeds as follows. (Here, the individual steps of indexing are illustrated by means of an interference model having rhombic symmetry, shown in Figures 2a-2e).

After measuring the glancing angle θ_{hkl} on the x-ray films or diffraction diagrams, by the usual methods, the system of concentric circules of radii $2 \sin \theta_{hkl}$ (###) is drawn in Figure 2a. First, /5

[#]Because of the two-dimensional reproduction of the three-dimensional lattice in one axes intersection and the resultant doubling of axes it was necessary to divide the (y') axis into b* and a*-c*. For this reason, a new designation for the (x), (y), and (z)-axes was introduced: a*, b*, and c* (see Figure 1).

The observations are for a system where a $\neq$ b $\neq$ c. For cubic crystals, the upper half-plane is sufficient for demonstration of the reciprocal lattice; for tetragonal and hexagonal substances, the a*-c*, b*-c*, and a*-b* quadrants are sufficient.

For reasons of space, it is useful to set a d*-unit equal to 1 cm (Figures 3, 4, and 5).



Figures 2a-2e: Stepwise construction of the Reciprocal Lattice.

the c* axis[#] is drawn through the center. Now, the distances $2 \sin \theta_{hkl}$, are marked off on a strip of paper, and by moving this scale along the axis it can be determined which of the marks fell on intersections of the circles with the c*-axis.(Figure 2a). Next, those periodically repeated distances are recorded as lattice constants c* and the lattice grid-lines are drawn in accordingly (perpendicular to the c*-axis). Only after it is certain that circles result which do not contain any of the lattice points so constructed, is the lattice refined[##] by spacing the provisional lattice constants and thus an attempt is made to determine the "true" reciprocal lattice constants (reflections with the indices 001; see Figure 2b). If the c*-constant is

[#]The other axes for cubic, tetragonal, and rhombic systems are perpendicular lines to c* in the origin (see Fig. 3 and 4). For the hexagonal system, the angle between a_1^* and a_2^* must be 60° (Figure 5). For the monocline and tricline system, the axis angle is found by sampling (see Figure 6).

The use of dividers proved useful for this.

established, then the procedure is repeated with the a* and b* units (corresponding to reflections h00 and 0k0) and the perpendicular lines are drawn on the a* and b* axes (Fig. 2c and 2d). The points of intersection of these perpendiculars can only coincide with the circles which have indices hk0 or h0l or 0kl. All /6 circles still not covered with points of intersection have indexing of the type hkl. These are obtained by entering the (h0l)-vectors on the a*-c* axis, and the perpendiculars to this axis (Figure 2e). The points of intersection on the b*-units lie on the remaining circles and correspond to reflections with indices hkl.

The indexing performed on rhombic KNO_3 [4], tetragonal $NH_4Cu_7S_4$ [5], hexagonal Al_2Se_3 [6], and monocline $Bi_6O_4[(OH)_4](OH)(NO_3)_5 \cdot 0.5\ H_2O$ [7] (see page 7), can be seen in Figures 3, 4, 5, and 6; /7 some of the glancing angles are found in the literature.

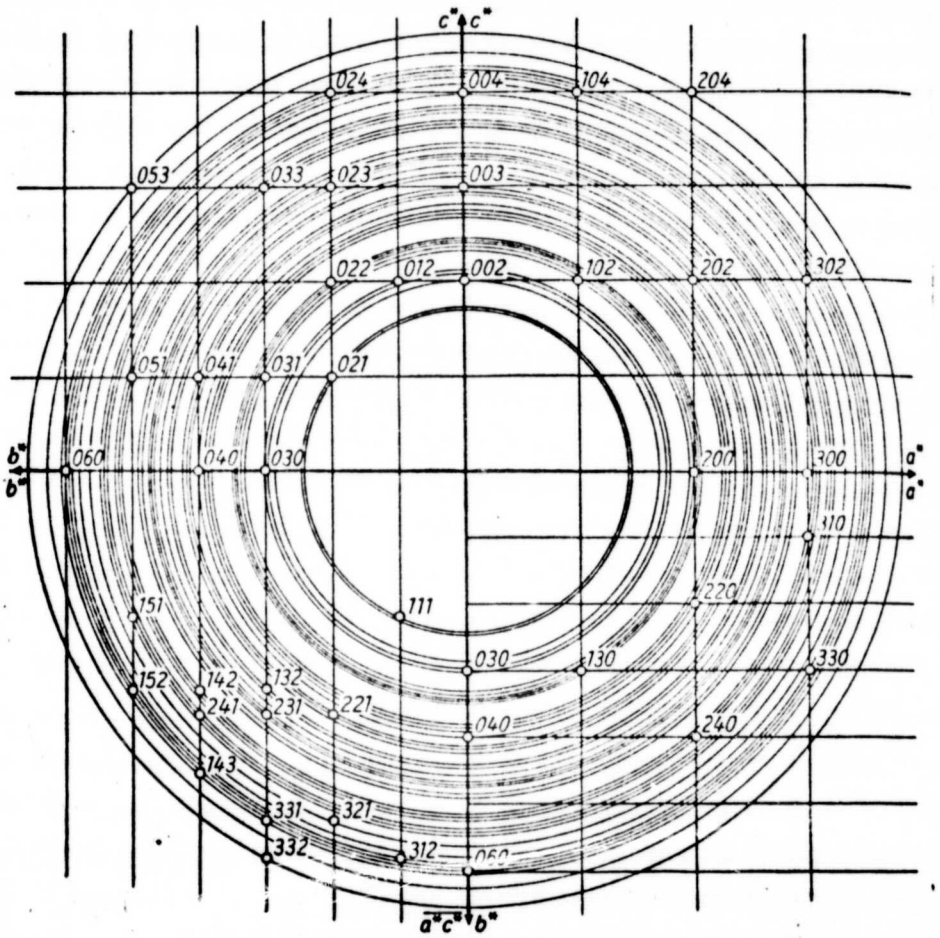


Figure 3: Reciprocal Lattice of the Rhombic Crystal KNO_3 [4].

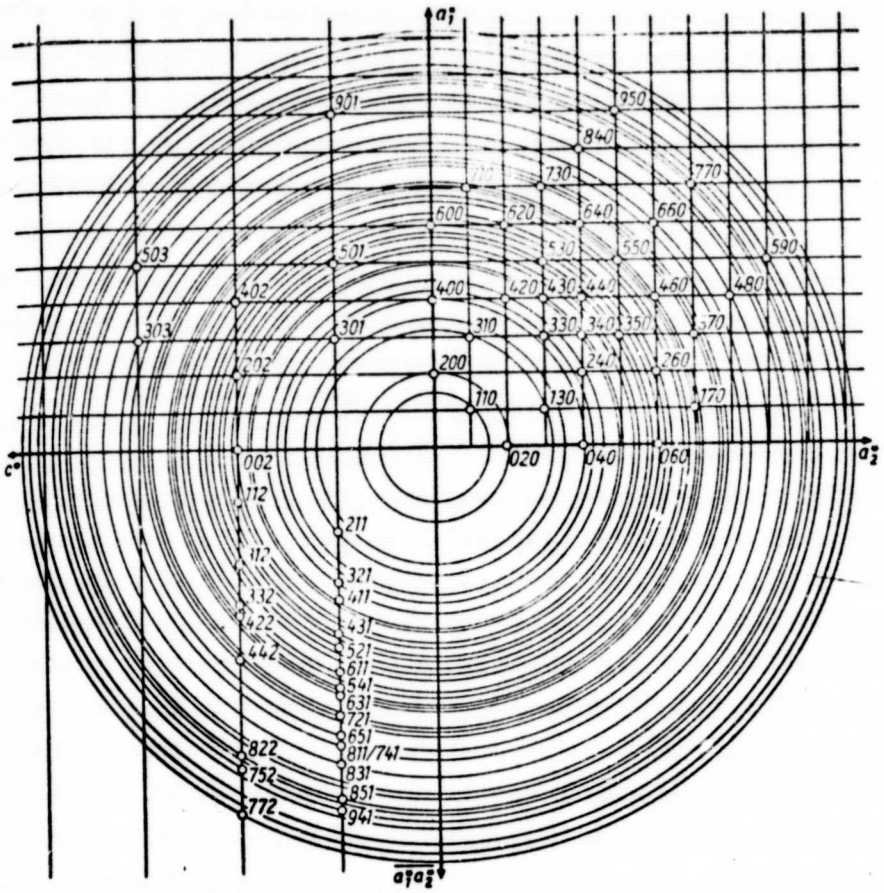


Figure 4: Reciprocal Lattice of Tetragonal $NH_4Cu_7S_4$ [5]

By means of the method described, the possible indices of all interferences on powder photographs can be determined by working backwards. Coincidences are only possible between hkl-reflections, except for special cases of symmetry# for instance, because of geometric reasons. But if such coincidence pairs do occur, they are separated spatially in the reciprocal lattice and can be easily located. Crystalline impurities in the material can also be easily located. /8

#Symmetry can be determined by microscopic examination of the substance in normal and in polarized light in many cases (orthoscopic and conoscopic axis formers) ##

See, for example, E. Kordes, "Optic Data to Determine Inorganic Substances with the Polarization Microscope",Weinheim/Bergstr. 1960.

The determination of the lattice constants can be found directly from the reciprocal lattice from the equation:

$$a = \lambda/a^* \qquad b = \lambda/b^* \qquad c = \lambda/c^*$$

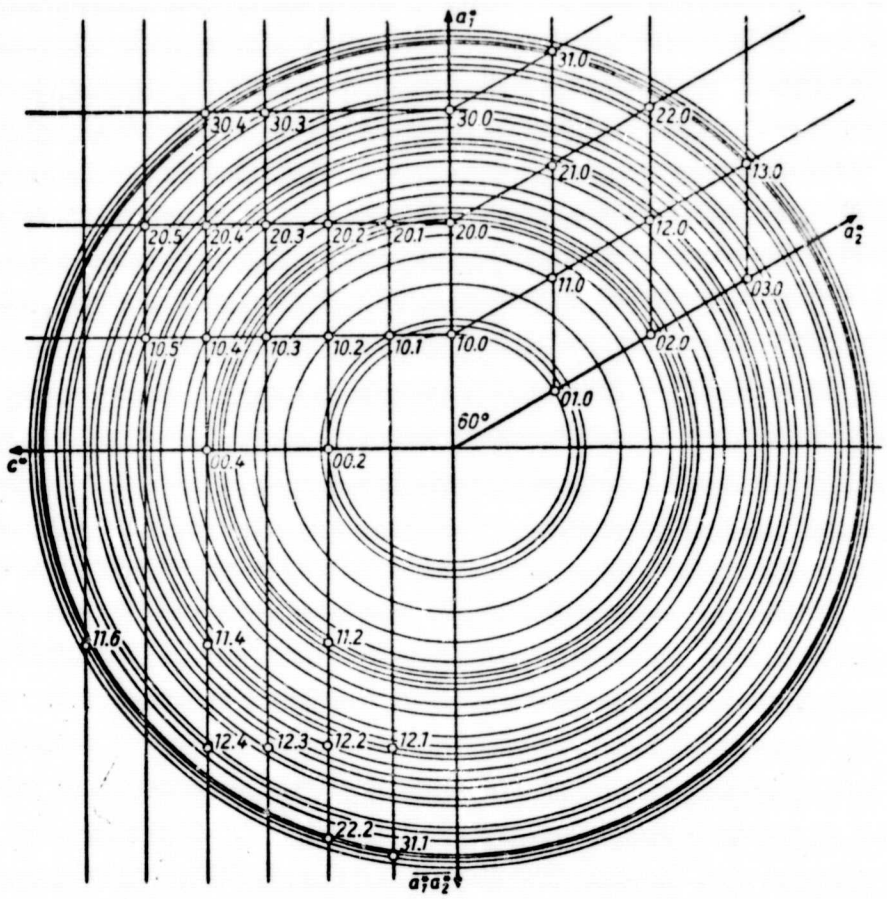


Figure 5: Reciprocal Lattice of Hexagonal Al_2Se_3 [6]

Here: a, b, c = lattice constants in Å; a*, b*, c* = reciprocal lattice constants measured in cm; λ = wavelength of the x-rays used in Å. The accuracy of the lattice dimensions thus determined lies on the same order of magnitude as the accuracy found for single-crystal photographs. If greater accuracy for these constants is desired or required, then the evaluation of the measured glancing angle ϑ_{hkl} must be done according to the usual methods under application of the indices determined by graphic means.

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