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VARIOUS MODES OF ATTACK IN CRYSTALLOGRAPHIC INVESTIGATIONS

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INTRODUCTION

The scope of this paper lies wholly in geometrical and structural crystallography. It is concerned only with the directions of the *crystal planes*, expressing the five known discontinuous vectorial properties of crystals, that is to say: rate of growth, cohesion, twinning, gliding, and *x*-ray diffraction. The corresponding planes, evidence of these properties, are: the faces, cleavage planes, twinning planes, gliding planes, and *x*-ray "reflection" planes.

The investigation may be carried on with different purposes in view and, accordingly, lead to different kinds of crystal descriptions (axial elements) embodying the results obtained. Three of the principal aims of the crystallographer are: (1) the determination of crystals, (2) their morphological characterization, (3) the study of their intimate structure. A descriptive method suitable for one of these aims will not necessarily fit another purpose.

The determinative description of a crystal stands apart from its morphological and structural descriptions. The relation between the last two is incompletely known, and they cannot be unified as yet. Whether it will ever be possible to do so remains an open question. Certainly, in our present state of knowledge, neither of these two descriptions can be discarded in favor of the other under penalty of leaving experimental facts unexpressed that can be expected to contribute to the elucidation of the relationship between form and structure.

I. THE GONIOMETRIC DETERMINATIVE METHOD

The aim of this method is to provide a tool for goniometric determination of crystalline substances by means of simple constants, without transformations of angular values into axial elements.

The principal attempt to devise such a method is that of Fedorov.¹ His work, "Das Krystallreich," contains the determinative criteria of several thousands of substances. They were compiled by Fedorov and his co-workers (D. N. Artemyev, T. V. Barker, B. P. Oryelkin, and V. I. Sokolov) over a period of about twelve years. Although determination is actually possible by means of these tables, the method involved is rather complicated and has not met with great success. This is explained by the fact that Fedorov tried to give a single solution to two distinct problems: that of determination and that of morphological characterization. His ambition was to find the "correct orientation" for each crystal. This correctness of orientation was sought in hypothetical considerations about structure. Determinative tables came out as a by-product of the investigation which was in reality primarily morphological. As a result, the determinative end was largely frustrated by unnecessary complications introduced by the morphological viewpoint and the structural hypotheses.

A student of Fedorov, Boldyrev, tried to obviate the difficulties inherent in the Fedorov system and proposed another determinative scheme,² stripped entirely of structural or morphological concerns. Its principle is to use the available angular values recorded for crystalline substances without transformation of the adopted orientation (or setting). Several entries in the tables are needed for each substance. The bulk of such determinative tables (already completed in manuscript form for tetragonal, trigonal, and hexagonal substances) would be enormous and hinder their practicability in the systems of lower symmetry.

The latest method, the most satisfactory, is due to T. V. Barker.³ Here again, the purpose is solely determinative, and admittedly so. Barker gives rules designed to enable any crystallographer to choose a *standard orientation* for any crystal. Angular values are used as determinative criteria, one of the angles is the main classification angle and the substances are listed (in each crystal system)

¹ Fedorov, E. S., *Das Krystallreich; Tabellen zur krystallochemischen Analyse: Mém. Acad. Sci. Russie* (8), vol. 36, Petrograd, 1920.

² Boldyrev, A. K., *Principe de la nouvelle méthode de diagnose cristallographique de la matière: Mém. Soc. Russe Min.* (2) vol. 53, pp. 251-337, 1924. (Russian text, French summary.)

³ Barker, T. V., *Systematic Crystallography: an essay on crystal description, classification and identification, 1930, London, Thomas Murby and Co., 1 Fleet Lane, E.C. 4.*

according to increasing values of that angle. The rules set for that purpose may appear a little arbitrary but arbitrariness is here entirely justifiable when it leads to an easy determinative scheme.

The first principle advocated by Barker is that of "simplest indices." He calls 0 and 1 "simplest" indices, and all indices higher than 1, "complex" indices. The first step in the determination of a crystal is to plot its stereographic projection from the measured angular values, then to find which orientation of the crystal will permit assignment of "simplest indices" to the largest number of observed forms. On any crystal, twenty-six faces at the most can be given simplest indices; Barker calls them (by analogy with the isometric nomenclature) the six *cubic* faces, the twelve *dodecahedral* faces, and the eight *octahedral* faces. Often, there is only one orientation leading to a maximum of simplest faces among the observed faces. When ambiguity arises, however, Barker proposes *auxiliary rules* to decide between alternative solutions that leave an equal number of faces with complex indices.⁴ When it has been decided which faces are to become "cubic," which "dodecahedral," and which "octahedral," then *ipso facto* the directions of the axes and the axial ratios are fixed, but several possibilities remain as to the naming of the axes and their orientation. As to their names, three cyclic permutations are permissible, which will leave the system of coordinates right-handed (the usual convention of crystallographers at the present time); as to their signs, each one of the eight octants may be selected as "first octant"; hence there is a total of 24 alternatives. Barker first gives rules for naming the axes, then for directing them. Common sense prevails throughout his work; his chief concern is avowedly to make his rules practical and as much in accordance with previous conventions as possible. To illustrate this point, it may be noted that he retains the symmetry axis in the monoclinic system for the *b*-axis, although it would be more logical to make it the *c*-axis; he remarks that "it is 3000 substances too late" to introduce a change in this practice. Similarly, he uses a system of standard letters for form notation, reflecting the common usage outside of French-speaking countries; at the same time

⁴ In several cases, the rules given by Barker in his essay have been found to be insufficient. The rules must be recast to meet such cases. A set of New Auxiliary Rules has been suggested. Terpstra, Donnay, Mélon, van Weerden, Studies on Barker's determinative method of systematic crystallography, *Zeit. f. Krist.*, vol. 87, pp. 281-305, 1934.

he states that the French system of form symbols (so-called Lévy notation) undoubtedly is the most logical.

Barker's classification angles are the six angles:

$$cr, ra, \mathbf{am}, mb, bq, qc$$

between the following faces:

$$a(100), b(010), c(001), r(101), m(110), q(011).$$

Note that the forms may not all be observed forms. Five angles would be sufficient in the most general case (triclinic system), but Barker prefers to list one superfluous angle as a confirmation. In the other crystal systems, he reduces the number of classification angles: four in the monoclinic, three in the orthorhombic, one in the hexagonal, rhombohedral, and tetragonal systems.

The method may be said already to have withstood the test of experience. Barker died without having had time to carry on to completion his highly original work. His determinative tables were only started. Since then, however, Haan⁵ has published tables covering 950 substances, which belong to all crystal systems, and has demonstrated the value and practicability of the Barker determinative method. Other workers are now compiling the complete tables, Professor H. L. Bowman, Miss Mary W. Porter, Mr. R. C. Spiller, and Mr. Powell (Oxford), Mr. Max H. Hey (London), Dr. P. Terpstra and his students (Groningen), and Dr. J. Mélon (Liège). Professor Bowman in Oxford will edit the tables, in which the data given by Haan will be incorporated. The Barker system is simple enough to be mastered by any chemist after a short introduction to geometrical crystallography and crystal measurement. Either one-circle or two-circle goniometry is applicable with nearly equal facility. Calculations are reduced to a minimum, since many computations are replaced by graphic determinations on the stereographic net. The duration of a determination ordinarily ranges from half an hour to four hours. This method will make *crystallochemical analysis* a valuable tool for chemists.

II. THE MORPHOLOGICAL DESCRIPTION OF CRYSTALS

The purpose of a morphological description is to refer the crystal to that set of axial elements which will yield as much information as possible about the presence and respective importance of observed forms, about the habit and, eventually, about the pseudo-symmetry.

⁵ Haan, J. H., *Kristallographische Bestimmungsverfahren*, 1932, J. B. Wolters Ed., Groningen.

The most notable advance towards that goal was made by Bravais. The Bravais Principle states (with certain restrictions) that the faces which occur on a crystal are parallel to the planes with maximum reticular density *in a properly chosen lattice*, and that the denser the net plane, the more important the corresponding face. It is obvious that the lattice in question cannot be known in absolute magnitude since it is determined by reflection goniometry only. Given three axial directions (for instance, by their interaxial angles, α , β , γ) and the axial ratios $a:b:c$, a lattice can be built, in which b is taken as an arbitrary unit of length. Such a lattice is therefore completely determined as soon as the three pinacoids and the unit form (or parametral form) have been selected (*it is not necessary to know which is which*).

Because Bravais arrived at this principle by means of speculations as to the internal structure of the crystal, the truth of his statement was long in question. Only since 1907, when G. Friedel⁶ demonstrated in a convincing way that this principle is purely a law of observation, valid independently of any structural hypothesis, has the principle received general acceptance. It is now known as the Law of Bravais and, although often considered a distinct law, it is nothing else than a more complete and more precise statement of Haüy's law of rationality. In its complete form, the latter might appropriately be called the Law of Haüy-Bravais.

The law of maximum reticular densities leads to the determination of a lattice, the Haüy-Bravais lattice,⁷ which is, for most substances, uniquely determined. In contrast to this, the requirement of *simple indices*, or even Barker's more restrictive principle of *simplest indices*, does not lead to an unambiguous choice of lattice. Hence the lack of agreement prevailing today as to the crystallographic constants of many species.

The various steps of the method will now be briefly outlined.⁸

⁶ His original investigation (*Bull. Soc. franç. Min.*, vol. 30, p. 326, 1907) is summarized in his text-book, G. Friedel, *Leçons de Cristallographie*, 1926.

⁷ Friedel calls it the Bravais lattice. Donnay and Mélon proposed to call it Haüy-Bravais lattice since the term "Bravais lattices" is used with another meaning (the 14 Bravais lattices). The new term stresses the fact that the lattice in question is obtained by giving the law of Haüy-Bravais a proper expression.

⁸ A complete example of the determination of the Haüy-Bravais lattice in the case of a triclinic crystal was recently published in this Journal. To our knowledge, it is the first article in English on the subject. Donnay and Mélon, *Am. Mineral.*, vol. 18, pp. 225-247, 1933.

1. PROVISIONAL LATTICE. A provisional set of axial elements is determined, from the measurements. No special attention need be given to the simplicity of indices or any other consideration at the outset. These axial elements define a space-lattice, that is, the assemblage of all the points at the corners of contiguous parallelepipeds, all identical with the cell built on the three axial directions and the three unit-lengths \bar{a} , \bar{b} , \bar{c} . This lattice is one of the seven primary lattices (of course it is not defined in absolute magnitudes).

2. DETERMINATION OF THE HAÜY-BRAVAIS LATTICE. Observe the order of importance of the forms present on the crystals studied. List these forms according to decreasing importances and number them accordingly: 1, 2, 3, . . . The importance of a form is in proportion to the frequency of occurrence of the form and the size of its faces; the fact that a crystal form coincides with a cleavage form is also an indication of its importance. In terms of *rate of growth*, faces with a slow rate of growth are the most important since they control the outline and general appearance of the crystal; the importance is thus inversely proportional to the rate of growth. The listing of the faces in the order of their importance may present difficulties when the crystals show widely different habits. This investigation is then statistical in scope. Next compute the reticular densities of the denser net planes in the provisional lattice. The reticular density of a net plane is defined as the number of lattice points per unit of area; it is proportional to the *spacing* (or interplanar distance) of parallel net planes; it is inversely proportional to the *reticular area* which is the area of the smallest two-dimensional cell (parallelogram) in the net plane. For the isometric system the reticular area, S , of a plane (hkl) is given by the formula

$$S^2 = a^4(h^2 + k^2 + l^2)$$

where a denotes the length of the edge of the unit-cell (the geometrical crystallographer takes $a = 1$ since he has no way of ascertaining its absolute value). List the net planes in the order of their decreasing reticular densities.

Compare the two lists as to agreement. The known forms should occur at the beginning of the theoretical list and they should appear in the order of their decreasing importances if the lattice is well chosen. Usually this will not be the case.

By trial, modify the first lattice until a correct expression of the Law of Bravais is reached.

These modifications must of course lead to a new lattice isogonal with the first one. That is to say, the angles between lattice planes must always be equal to the corresponding interfacial angles of the crystal. This condition will be fulfilled if the modifications consist of systematic addition or subtraction of lattice points (such as halving or doubling a parameter, for instance). Now since the size of the lattice is immaterial for the present purpose, it is clear that any modification obtained by leaving out points can equally well be reached by adding (other) points (for example, doubling the c parameter leads to the same result as halving both the a and the b parameters). Hence the only modifications to be considered are those brought about by a systematic *addition* of points. The coordinate axes chosen for the provisional lattice may be retained, since the assemblage of points, not the way they are defined, is the important thing. The modifications to be tried are then: to center the provisional cell (body-centering) or to center one, two, or all three of its faces (face-centering). These modifications may be tried in succession, singly or jointly, until the list of lattice planes prepared according to decreasing reticular densities agrees with the list of observed importances of the known crystal faces.

When a lattice has been found to give a satisfactory expression to the Law of Bravais, it is chosen as the morphological lattice. Notice that this Haüy-Bravais lattice is one of the 14 Bravais lattices, that one which best expresses the morphology of the crystal to be described. It should be borne in mind that these morphological lattices (*geometrical pictures* only) are "relative" or "elastic" lattices, in contradistinction to *the* structural lattice (*a physical reality*) determined in absolute magnitudes by x -ray investigation. The primitive translations of the "elastic" lattice are designated by a , b , c ; those of the "absolute" lattice are represented by a_0 , b_0 , c_0 .

Although at the present time the Haüy-Bravais lattice probably affords the best means of accounting for the presence and relative importance of the observed faces of a crystal, it is obvious that, nevertheless, it is an imperfect tool. Let it suffice to recall one of its limitations: faces which are symmetrical (equivalent, or similar) as far as their directions are concerned, may be dissimilar from the physical point of view. Example: the faces of the two comple-

mentary tetrahedra in the tetartoidal class (tetartohedral class of the isometric system), from the viewpoint of their directions only, are all equivalent and constitute an octahedron. In other words, their reticular densities, as computed from the morphological lattice, will be the same. According to the Law of Bravais, they should be equally important (equally developed, equally frequent, and have the same rate of growth), but it is well known that two such physically different complementary forms do not always occur together or have the same development. In all likelihood this is due to the influence of the symmetry of the *motif* (= symmetry of the *crystal*), which in such cases is lower than that of the lattice itself. Friedel has shown, however, that the influence of the *motif* is much smaller than that of the *lattice*: he points out that in many cases complementary forms of high reticular density do occur together and that one of the complementary forms is missing only when the density of the form is sufficiently low.

There is a small chance of finding more than one lattice giving the Law of Bravais a correct expression. In such cases where the Haüy-Bravais lattice is not uniquely determined by the above method, Friedel's "Law of Mean Indices"⁹ provides an additional method of obtaining the desired lattice. The scope of this paper permits only brief mention of this remarkable law.

3. CHOICE OF AXIAL ELEMENTS TO DEFINE THE HAÜY-BRAVAIS LATTICE. The Haüy-Bravais lattice can now be defined (expressed) in a great many different ways. The axes of coordinates may be any three non-coplanar lattice-rows, so that the choice of the axial directions is equivalent to the choice of a *cell* in the lattice. Then, after a certain cell has been chosen, the three axes remain to be directed (given a positive sign). We will consider suggestions as to such choices.

(A) *Choice of the cell used to define the Haüy-Bravais lattice.* Although the lattice is only the assemblage of points in space, it is convenient to consider it as being built up of stacked parallelepipeds or cells. The cell may have an infinite number of shapes. Any four non-coplanar lattice-points may serve to define a cell. When the parallelepiped does not contain any other lattice-point than its eight corner-points, the cell is said to be a *simple cell* (one point per cell). When there is more than one point per cell, the cell is called a *multiple cell*.

⁹ Friedel, G., *Leçons de Cristallographie*, 1926, p. 134.

The choice of the cell may be guided by the following considerations:

(a) Simplicity of indices. A cell leading to simple indices should obviously be given preference for the sake of convenience.

(b) Pseudo-symmetry. If the crystal exhibits a *well-marked* pseudo-symmetry, this fact should be expressed by the choice of the cell, even at some expense of simplicity of indices. A classic example is that of *epidote*, monoclinic, pseudo-orthorhombic ($\beta = 90^\circ 34'$), which was brought out by G. Friedel.¹⁰ There is room for personal divergences of opinion, however, as to what should be considered "well-marked pseudo-symmetry." Some crystals have been called pseudo-symmetrical, which hardly deserve such description. The point should not be stretched and pseudo-symmetries are not to be found at all cost! When pseudo-symmetry is striking enough to be noticed on the crystals, then it seems appropriate to express the fact by the choice of a cell showing this pseudo-symmetry.

(c) Smallest translations. It has been suggested that the cell be chosen with the smallest three primitive translations. This criterion has the advantage of leading to a unique solution. It should always be used unless there are good reasons to adopt another cell (see (a) and (b)).

(B) *Orientation of the axes.* The cell having been chosen, it remains to name and direct the axes. There are 48 alternatives if no restriction be imposed on the type of system of coordinates. Crystallographers have used both the left-handed system (Fedorov, Mallard) and the right-handed system. The latter is almost universally adopted at the present time. With it we still face 24 possibilities. They can be visualized if the origin of coordinates be carried successively to the eight corners of the cell and, in each case, the edges of the cell taken for the positive directions of the axes. At each corner the axes may be called either a, b, c ; or b, c, a ; or c, a, b , since the right-handed character of the system of coordinates is not altered by these three cyclic permutations.

The first suggestion to direct the choice is to express the habit by placing the *main zone* vertically. The main zone is either parallel to the direction of elongation (in prismatic or acicular crystals) or perpendicular to the plane of flattening (tabular habit). The choice of the c -axis at each corner of the cell determines the other two axes

¹⁰ Leçons de Cristallographie, 1926, p. 140.

since the system must be right-handed, so that the number of alternatives is now reduced to eight. This suggestion is apparently the only one that can be made in order to express habit. The others will be mere arbitrary conventions.

Considering the most general case (triclinic system), and using only proposals already made by various crystallographers, we suggest that a be taken smaller than b , that the a -axis slope forward, and that the b -axis slope to the right; this leaves only one alternative.

For monoclinic crystals, the direction of the b -axis is fixed by symmetry. There exists no convention as to the naming of the other two axes. Following the same principle as in the triclinic system, we may place the direction of elongation vertically. A greater elongation along the c -axis than along the a -axis corresponds to a c -parameter smaller than the a -parameter, as the *linear density* must be higher for the c -axis. Finally, the a -axis should slope forward.

In the orthorhombic system the first criterion is the same as in the triclinic system, that is to say, the main zone is placed vertically. The only other necessary condition is the age-old convention: $a < b$.

4. MORPHOLOGICAL SIGNIFICANCE OF THE ADOPTED AXIAL ELEMENTS. To what extent does such a set of axial elements throw light on the morphology of the crystal?

We may distinguish the following points to be considered:

(A) The *crystal forms observed* (all of which need not be found on all the crystals of the same crystalline species).

(B) The *form combinations* observed, irrespective of differential form development. Example: the combination "cube-dodecahedron" in the isometric system.

(C) Unequal development of the forms observed on one combination. Examples: cube dominant modified by dodecahedron; cube-dodecahedron about equally important; dodecahedron with small cubic truncations, etc.

(D) Unequal development of the faces of the same form (malformation, German *Verzerrung*, French *difformité*).

The word *habit* (German *Tracht*, *Habitus*; French *facies*) has been used with different meanings.¹¹ It practically covers the last three points mentioned.

The Haüy-Bravais lattice to which the crystal is referred enables one to forecast what the principal forms will be and their relative

¹¹ Cf. Chudoba, *Centralblatt für Min.*, 1933, Abt. A, p. 99.

importances (they should be among the first in the list of net planes arranged according to decreasing reticular densities). This yields much information on the points, (A), (B), (C).

The cell chosen to define the Haiüy-Bravais lattice brings out pseudo-symmetry if it be present.

The direction of the *c*-axis will also give useful information on the third point. Malformation cannot be expressed by the axial elements.

All the other conventions necessary to determine uniquely the cell orientation have no value insofar as morphological characterization is concerned. They are only useful in standardizing the description of crystals.

5. REMARKS ON THE DETERMINATION OF RETICULAR DENSITIES. The difficulty in determining the proper set of axial elements for accurate morphological description lies in the determination of reticular densities for a fairly large number of planes. A few hints may be given as to how to proceed.

If a calculating machine is available, compute the square of the reticular area (instead of the reticular density), which is given by a formula of analytical geometry.¹² Use of tables of natural values of trigonometric functions¹³ simplifies the procedure. The accuracy of the method is here dependent on the accuracy of the geometric measurements of the crystal.

Graphic methods have been devised for the determination of reticular densities with an accuracy sufficient for the purpose in most cases. A review of these methods is given by Terpstra and van Weerden¹⁴ who generalized the theorem on which these methods are based.

Other methods can be devised to suit particular problems. In all crystal systems except the triclinic a semi-graphical method has been found satisfactory and rapid. The formula giving the value of $S_{(hkl)}^2$, where $S_{(hkl)}$ is the reticular area of the net plane (*hkl*) is of the form:

$$S^2 = h^2b^2c^2 + k^2c^2a^2 + l^2a^2b^2$$

in the orthorhombic system. The values of b^2c^2 , c^2a^2 , a^2b^2 , are computed. Three rulers are then prepared on stiff drawing paper, graduated for the different values of $h^2b^2c^2$, $k^2c^2a^2$, $l^2a^2b^2$, respectively.

¹² This formula may be found in Friedel, *op. cit.*, p. 235.

¹³ Ives, Howard Chapin, Natural trigonometric functions to seven decimal places for every ten seconds of arc. John Wiley & Sons, New York, 1931.

¹⁴ Graphical methods for the determination of reticular densities and lattice parameters (to appear in *Am. Mineral.*).

The first one, for example, shows the divisions $0, b^2c^2, 4b^2c^2, \dots$ numbered $0, 1, 2, \dots$ according to the value of h . A large sheet of millimeter paper is used for plotting the values of S^2 for the various lattice planes. The addition is carried on graphically by means of the three rulers. The result is a sheet covered with points (one for each crystal form). The abscissae of the points are proportional to the square of the reticular area; they are therefore arranged in the order of their decreasing reticular densities.

6. REMARKS ON THE FEDOROV METHOD. As stated in the section on determinative crystallography, Fedorov's main purpose was to find the "correct orientation." His work is little known for the reason that his publication (*Das Krystallreich*), although written in German, is not explicit enough. As a matter of fact, it is so concise that Boldyrev¹⁵ found it necessary to publish explanatory comments on it. Unfortunately, these are in Russian, and are hence, as yet, of little use to most crystallographers outside of Russia.

A few points may be mentioned as to the nature of the Fedorov method. Use is made of the Bravais Principle and it is even attempted to make its application quantitative. The "correctness" of the orientation is measured by a quantity, W , which is, among other things, a function of the ratio R/J , in which R is the sum of the squares of the reticular densities of the n observed forms, and J the sum of the squares of the reticular densities of the n theoretical forms with the highest reticular densities. The closer the quantity W is to one, the better the corresponding orientation. In spite of this apparently quantitative character, the Fedorov method disregards an important criterion—the *order* of importance of the observed forms. It only discriminates between the *presence* or the *absence* of a form, hence the Law of Bravais is not used to full advantage. Moreover, the quantitative "measure" of the correctness of the orientation may be judged somewhat artificial, having, at any rate, less physical reality than the order of importance of the observed forms, qualitative as the latter criterion may be.

III. THE STRUCTURAL DESCRIPTION OF CRYSTALS AND THE RÖNTGENOGRAPHIC DETERMINATIVE METHOD

1. STRUCTURAL ANALYSIS. The use of present-day x-ray diffraction apparatus makes it possible simply and rigorously to determine the *structural space lattice* of a crystal—one of the 14 Bravais lattices—with absolute magnitudes of the lattice di-

¹⁵ Boldyrev, A. K., *Kommentarii k rabote E. S. Fedorova, Das Krystallreich, Acad. Leningrad, 1926.*

mensions. The first determinations of structural space lattices with absolute magnitudes were carried out in 1913 by the Braggs¹⁶ and concerned a series of alkali halides studied with the aid of Laue photographs and ionization spectrometer measurements. Previously neither the absolute wave-lengths of x -rays nor the absolute cell dimensions of any crystal were known. By comparison of the positions and intensities of the x -ray diffraction spectra from successive members of the isomorphous series and with the aid of plausible assumptions W. L. Bragg was able to deduce the atomic arrangements in these compounds and to calculate the absolute spacings of their lattices. Bragg pointed out that it was not possible to prove the conclusions rigorously with the data then available, but he showed that any other interpretation was very improbable. Subsequent determinations of the absolute wave-lengths of x -rays by methods independent of knowledge of crystal structures (such as diffraction by artificially ruled gratings) has confirmed Bragg's conclusions as to the atomic arrangement and lattice dimensions in the alkali halides. The first complete determination of the lattice of a triclinic crystal by purely röntgenographic methods appears to have been accomplished by Schneider¹⁷ with the use of the Weissenberg goniometer, the substance being anhydrous mesotartaric acid.

At present the most convenient way of finding the structural space lattice of a monoclinic or triclinic crystal is by the use of the Weissenberg goniometer¹⁸ and the graphical construction devised by Schneider.¹⁹ This method leads to a unique and rigorous determination of the reciprocal lattice and hence of the structural space lattice, and is very straightforward in its practical application. It has been restated in English in this Journal by one of the present writers²⁰ and need not be reviewed here. With crystals belonging to systems of higher symmetry it is of course readily pos-

¹⁶ *Proc. Roy. Soc. London*, **89A**, pp. 248-277, 1913.

¹⁷ *Zeit. f. Krist.*, vol. **69**, p. 49, 1928.

¹⁸ Weissenberg, K., *Zeit. f. Physik*, vol. **23**, p. 229, 1924.

¹⁹ *Zeit. f. Krist.*, vol. **69**, p. 41, 1928.

²⁰ Tunell, G., *Am. Mineral.*, vol. **18**, p. 276, 1933. (Note. In this paper Tunell did not follow the terminology of Bernal in one particular. Bernal reserves the phrase "circle of reflection" for circular sections of the cone of reflection, whereas Tunell applied this phrase to circular sections of the sphere of reflection, which Bernal refers to simply as "circles of section." Tunell's different usage was unintentional, and we shall adhere to the usage of Bernal hereafter, although Bernal's terminology in this particular is not entirely felicitous.)

sible to work out the structural lattice by means of rotation-oscillation photographs and in some cases from powder or Laue photographs.

When the structural lattice has been determined the choice of a unit cell remains to be made, since the same lattice can be built up by means of different unit cells. In structural analyses the unit cell is conveniently so chosen and so orientated as to permit the direct application of tables of equivalent positions and röntgenographic extinctions such as Wyckoff's "The analytical expression of the results of the theory of space groups,"²¹ Niggli's "Geometrische Kristallographie des Diskontinuums," Astbury and Yardley's "Tabulated data for the examination of the 230 space-groups by homogeneous X-rays,"²² and K. Herrmann's "Röntgenographische Auslöschungstabellen."²³ In these tables particular locations and orientations of the symmetry elements are presupposed and the actual crystal to be compared with the tables must be set up so that its own symmetry elements occupy analogous locations in the unit cell. The choice of the unit cell in structural analysis is thus mainly governed by the röntgenographic extinctions. It is not necessarily the "smallest repeat" or *true period*. The unit cell may be a multiple cell, the smallest multiple cell which possesses the whole symmetry of the lattice.

2. RÖNTGENOGRAPHIC IDENTIFICATION. Although little work has been done as yet along this line, it seems probable that determinative tables based on structural characters as revealed by *x*-rays will be prepared in the future. In the compilation of such determinative tables of absolute unit cell dimensions arbitrary rules must be specified for the selection and naming of the axes. In the triclinic system the unit cell must be chosen from an infinite number of possible cells all having the same volume; we propose that for this purpose the three planes be selected as pinacoids the spacings of which are the largest of any three non-tautozonal planes in the crystal.²⁴ In the monoclinic system the *b*-axis is fixed in direction and unit length; in the zone parallel to the *b*-axis the two planes of greatest and second greatest spacing may be chosen as

²¹ Carnegie Institution of Washington, Publication No. 318, Second Edition, 1930.

²² *Phil. Trans. Roy. Soc. London*, vol. 224A, p. 221, 1924.

²³ *Zeit. f. Krist.*, vol. 68, p. 288, 1928.

²⁴ This suggestion is analogous to the Law of Bravais in that it emphasizes the fundamental character of the planes of greatest spacing or reticular density. The Law of Bravais is, however, a rule concerning the surface form development of the crystal, originally formulated from structural hypotheses, it is true, but now di-

pinacoids. For the determinative tables it is most convenient in the isometric system to take as the unit cell a cube, no matter which of the three cubic lattices is to be built up, notwithstanding the fact that a smaller rhombohedral unit cell could be used for face-centered and body-centered isometric lattices. In the triclinic, monoclinic, and orthorhombic systems arbitrary rules must be adopted for the naming and directing of the three crystallographic axes after the three pinacoidal planes have been selected. With such rules a given compound will always be described in the same way and will not require more than one entry in a table.

When determinative tables of absolute unit cell dimensions have been assembled it will still be true that a determinative investigation can be carried out more quickly with the reflection goniometer than with the *x*-ray goniometer in most cases. However, when dealing with crystals without measurable faces one cannot apply the reflection goniometer at all whereas the *x*-ray goniometer may still be used even if the anedral grain be a twin.

The rules for selecting and orientating the unit cell for determinative purposes will not always lead to the same unit cell and orientation as that utilized in the tables of equivalent positions; the reason for this is that the positions of the symmetry elements are not in general determined by the lengths of the edges of a unit cell or the angles between the edges. It is not necessary, in order to build up and use determinative tables on the principles outlined, to know the positions of all the symmetry elements in the unit cell, and it seems a useless complication of determinative technique to make it depend on such knowledge. In *x*-ray analysis as well as in studies of the external form development we must be prepared in some cases to use different orientations of the same crystal, according as our purpose is the determination of the substance (crystallochemical analysis) or the establishment of its atomic arrangement.

At the present time the construction of determinative tables of absolute unit cell dimensions has not proceeded as far as that of tables of relative dimensions by the method of Barker; nevertheless, extensive tables of absolute unit cell dimensions of isometric chemical elements, compounds, and alloys have been prepared by Knaggs, Karlik, and Elam,²⁵ and will serve a useful purpose just

vorced from them. It is obvious that in some cases the Haüy-Bravais lattice may not be geometrically similar to the absolute unit cell determined by the rule suggested for use in compilation and application of determinative tables.

²⁵ Knaggs, I. E., Karlik, B., and Elam, C. F., *Tables of Cubic Crystal Structure of Elements and Compounds with a Section on Alloys*, London, 1932.

where the tables of relative dimensions are of no avail (isometric system).²⁶

A few words may be added concerning the relative precision of the x -ray and reflection goniometer measurements in present practice. In the x -ray method the instrumental error varies greatly with different arrangements of apparatus. The measurements may be made with extreme precision (to seconds of arc) by means of the double crystal spectrometer; on the other hand a rough estimation of the dimensions of the unit cell can be obtained from Laue photographs, although, as Wyckoff states, it is much more satisfactory to secure them from single-face spectra. Measurements with the Weissenberg goniometer are of intermediate accuracy with an error of $\pm \frac{1}{2}^\circ$ down to as little as $\pm \frac{1}{4}^\circ$ in favorable cases. In reflection goniometry the precision depends chiefly on the perfection of the crystal faces and with good crystals it is usually a matter of a few minutes, in exceptional cases as little as $1'$ or even $\frac{1}{2}'$.

IV. RELATION BETWEEN THE MORPHOLOGICAL AND THE STRUCTURAL SPACE-LATTICES

Inasmuch as the rules leading to the choice of determinative crystal constants (Barker or röntgenographic) are arbitrary conventions, it is not surprising that the "determinative lattices" arrived at by such methods should be at variance with the other two kinds of space-lattice, morphological and structural. But since the latter are the expression of *observed facts* concerning the crystal constitution they might *a priori* be expected to be one and the same thing. It is a baffling fact that the *Hairy-Bravais lattice*, as determined by the morphology of the crystal, may or may not be the same as the *Bravais lattice* resulting from the structural investigation. Two examples will illustrate this observation.

1. EXAMPLE OF AGREEMENT: Pseudobrookite. The axial elements of pseudobrookite have recently been determined by Charles Palache,²⁷ who gives the following values as the mean of his own and other reliable determinations:

$$a:b:c = 0.9777:1:0.3727.$$

²⁶ A powder photograph is characteristic of a substance. Hence a complete collection of powder pictures might serve for determinative purposes. It is recognized that this procedure is very serviceable as a means of checking an identification, but it is rather obvious that the comparison of powder photographs is inherently inconvenient as a method of determining an unknown substance that may be any one of thousands.

²⁷ *Am. Mineral.*, vol. 19, pp. 14-20, 1934.

Pseudobrookite, being orthorhombic, can be referred to four different types of lattice:

- 1—Simple orthorhombic lattice or rectangular hexahedral mode;
- 2—Body-centered orthorhombic lattice or rectangular octahedral mode;
- 3—All-face-centered orthorhombic lattice or rhombic octahedral mode;
- 4—One-face-centered lattice or rhombic hexahedral mode. Some authors always place the centered face horizontal, hence the other name of the mode: base-centered orthorhombic lattice.

In the simple orthorhombic lattice, the square of the reticular area, S , for any plane (hkl) is given by the formula:

$$S_{(hkl)}^2 = a^2b^2c^2 \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right),$$

which may be written in the more convenient form:

$$S_{(hkl)}^2 = a^2b^2(h^2m' + k^2m'' + l^2) \tag{A}$$

where $m' = c^2a^2$, $m'' = c^2b^2$.

The following values are found for pseudobrookite:

$$m' = 0.1453, \quad m'' = 0.1389.$$

The formula (A) can easily be computed graphically or semi-graphically.

A list of planes is obtained (for the simple lattice) arranged according to decreasing reticular densities or, what is equivalent, increasing S^2 , since S is inversely proportional to the reticular density. Similar lists can be obtained for the other modes of the orthorhombic lattice by applying the following rules:

1. For the body-centered lattice, multiply by 4 the S^2 of all planes (hkl) for which the sum of the indices $(h+k+l)$ is odd.
2. For the all-face-centered lattice, multiply the S^2 by 4 for all planes (hkl) whose indices are *not all odd*.
3. For the one-face-centered lattice, multiply the S^2 by 4,
 - (a) if the cell is centered on $\{100\}$, for all planes (hkl) when the sum $(k+l)$ is odd;
 - (b) if the cell is centered on $\{010\}$, for all planes (hkl) when the sum $(l+h)$ is odd;
 - (c) if the cell is centered on $\{001\}$, for all planes (hkl) when the sum $(h+k)$ is odd.

These rules yield lists of planes in the proper order of decreasing reticular densities, although they only give values of S^2 which are proportional to the true values.

The results of our semi-graphic determinations are shown in Table I.

TABLE I

LIST OF PLANES ACCORDING TO DECREASING RETICULAR DENSITIES IN VARIOUS MODES OF LATTICE FOR PSEUDOBROOKITE

Simple	Body-centered	{100}-centered	{010}-centered
<i>b</i> 010*	<i>m</i> 110*	<i>a</i> 100*	<i>b</i> 010*
<i>a</i> 100*	<i>b</i> 010*	<i>b</i> 010*	<i>a</i> 100*
<i>m</i> 110*	<i>a</i> 100*	<i>n</i> 120*	μ 210*
<i>n</i> 120*	011	{ <i>m</i> 110*	{ <i>m</i> 110*
μ 210*	<i>e</i> 101*		
001	130	<i>q</i> 111*	<i>q</i> 111*
011	310	211	<i>s</i> 121*
<i>e</i> 101*	<i>s</i> 121*	320	230
<i>q</i> 111*	211	<i>y</i> 031*	<i>l</i> 301*
130	<i>y</i> 031*	140	<i>p</i> 131*
310	<i>l</i> 301*	<i>p</i> 131*	410
021	310	231	<i>n</i> 120*
201	<i>n</i> 120*	μ 210*	321
<i>s</i> 121*	231	411	141
211	μ 210*	<i>h</i> 340*	331
230	141	331	430
320	411	001	001
...
The above forms are followed, but not consecutively, by:			
<i>y</i> 031*	<i>q</i> 111*	<i>e</i> 101*	<i>y</i> 031*
<i>l</i> 301*	<i>p</i> 131*	<i>s</i> 121*	<i>h</i> 340*
<i>p</i> 131*	<i>h</i> 340*	<i>l</i> 301*	
<i>h</i> 340*			

N.B. For every observed form, marked by an asterisk, the letter preceding the Miller symbol is that used by Palache (op. cit.).

A scrutiny of the various descriptions of pseudobrookite from 8 different localities and of artificially prepared crystals leads to the following conclusions as to the observed importance of forms: 1—*b*{010}, the only cleavage, a very frequent form although not always present.

2—*a*{100} and 3— μ {210}, both universally present, the two largest forms, *a* being larger than μ , tabular on *a*.

4—5—*m*{110}, *e*{101}, listed as equally important: *e* is universally present whereas *m* is only fairly frequent; on the other hand, *m* belongs to the main zone thus making up in length

- what it lacks in width so that it can compare in size with the more equant e .
- 6— $q\{111\}$, it is still possible to recognize q as the next important form: rather frequent and probably larger than any of the other subordinate forms.
- 7 to 11— $s\{121\}$, $l\{301\}$, $p\{131\}$, $n\{120\}$, $y\{031\}$, all uncommon, minor forms, hard to differentiate.
- 12— $h\{340\}$, undoubtedly the least important, found in one locality only.

Comparison of the list of observed form importances with the theoretical lists in Table I clearly shows that the only mode which fits the facts is the lattice centered on $\{010\}$. The first plane in that list is the only cleavage of the mineral, $b\{010\}$, the next four are the four most important forms: $a\{100\}$, $\mu\{210\}$, $m\{110\}$, $e\{101\}$ in their correct order;²⁸ the first four planes belong to the vertical zone, highly dominant since the crystals are prismatic to acicular in that direction; the last observed plane, $h\{340\}$, is the least important. Out of 12 forms observed, 10 appear among the first in the list: they are the first ten except for two gaps: one after the 7th form, and one after the 9th. No lattice mode except the lattice centered on $\{010\}$ shows as many as 10 observed forms among the first 12 in the list. The other modes have only 7. Gaps occur in the other modes, much more frequently and earlier in the list than in the $\{010\}$ -centered lattice. The other possible lattice modes are not given here. It can be seen at a glance that the modifications in the order of forms brought about by centering all the faces of the cell will make the theoretical list depart even more from the experimental list. The same is true of the other alternatives.

The translation group determined by L. Pauling²⁹ is Γ_0' , the same as the one found here by morphological methods. In this case, the structural lattice and the morphological lattice are identical, with the restriction of course that the morphological lattice is not determined with absolute values of the parameters but only ratios thereof. In this sense, the morphological lattice of pseudobrookite is strictly proportional to its structural lattice. This is not true

²⁸ Prof. Charles Palache pointed out to us that the form $e\{101\}$ comes rather far down in the theoretical list. We found that the reticular densities of $m\{110\}$ and $e\{101\}$ are proportional to 0.938 and 0.936 respectively, and it is obvious that a difference of the order of two-tenths of one per cent is here meaningless. The theory thus brings out the observed "nearly equal importance" of m and e .

²⁹ *Zeit. f. Krist.*, vol. 73, p. 97, 1930.

of all substances, however. In numerous cases the two lattices are not the same.

2. EXAMPLE OF DISAGREEMENT: Calcite. The most spectacular example of divergence between the two lattices is found in calcite, which was studied by G. Friedel (see *Leçons de Cristallographie*, pp. 142 et seq.). He has shown that the true morphological lattice is rhombohedral with the cleavage rhombohedron as a unit cell

TABLE II

<i>Structural lattice of calcite</i> Unit cell is $e^3 \{11\bar{3}\} \{04\bar{4}1\}$, the true period	<i>Morphological lattice of calcite</i> Unit cell is $p \{100\} \{10\bar{1}1\}$, the cleavage rhombohedron
$a^1 \{111\} \{0001\}^{**}$	$p \{100\} \{10\bar{1}1\}^{**}$
$e^3 \{11\bar{3}\} \{04\bar{4}1\}^*$	$d^1 \{10\bar{1}\} \{1120\}^*$
$e^1 \{11\bar{1}\} \{02\bar{2}1\}^{**}$	$e^1 \{11\bar{1}\} \{02\bar{2}1\}^{**}$
$p \{100\} \{10\bar{1}1\}^{**}$	$b^1 \{110\} \{01\bar{1}2\}^{**}$
$e^{1/3} \{3\bar{3}1\} \{04\bar{4}5\}^*$	$e^2 \{11\bar{2}\} \{0110\}^{**}$
$d^1 \{10\bar{1}\} \{1120\}^*$	$d^2 \{20\bar{1}\} \{21\bar{3}1\}^{**}$
$\alpha \{51\bar{3}\} \{44\bar{8}3\}^*$	$a^1 \{111\} \{0001\}^{**}$
$e^{5/3} \{33\bar{5}\} \{08\bar{8}1\}^*$	$e_2 \{21\bar{1}\} \{1232\}^*$
$a^5 \{511\} \{40\bar{4}7\}^*$	$b^2 \{210\} \{11\bar{2}3\}^*$
$b^1 \{110\} \{01\bar{1}2\}^{**}$	$e_{1/2} \{21\bar{2}\} \{1341\}^*$
$e_3 \{31\bar{1}\} \{22\bar{4}3\}^*$	$e^3 \{11\bar{3}\} \{04\bar{4}1\}^*$
$e^7 \{117\} \{0885\}^*$	$d^3 \{30\bar{1}\} \{3143\}^*$
$y \{517\} \{4.8.12.1\}^*$	$a^2 \{211\} \{10\bar{1}4\}^*$
$e^{3/5} \{55\bar{3}\} \{0887\}^*$	$e^{1/2} \{22\bar{1}\} \{01\bar{1}1\}^*$
$e_{1/3} \{31\bar{3}\} \{24\bar{6}1\}^*$	$d^{3/2} \{30\bar{2}\} \{3251\}^*$
$a^3 \{311\} \{20\bar{2}5\}^*$	$\{21\bar{3}\} \{1450\}^*$
$d^2 \{20\bar{1}\} \{21\bar{3}1\}^{**}$	$e_3 \{31\bar{1}\} \{2243\}^*$
$\{73\bar{1}\} \{4489\}^*$	$\{31\bar{2}\} \{2352\}^*$
$a^{1/5} \{551\} \{0.4.\bar{4}.11\}^*$	$b^3 \{310\} \{2134\}^*$
$e^2 \{11\bar{2}\} \{0110\}^{**}$	$e^{3/2} \{22\bar{3}\} \{0551\}^*$

N.B. Every observed form is given in the Lévy form-notation as well as by its Miller indices.

$p\{100\}\{10\bar{1}1\}$. The structural period, however, is a much more elongated rhombohedron: $e^3\{11\bar{3}\}\{04\bar{4}1\}$. Friedel refers calcite to a set of three coordinate axes (left-handed system), the lower terminal edges of the cleavage rhombohedron. We reproduce here two of his lists of planes according to decreasing densities with the Bravais-Miller four-index symbols next to Friedel's symbols. We

do this only in order to facilitate the reading of these lists by American crystallographers, since the four-index symbols are still widely used in this country for the five classes of the rhombohedral subsystem, even when the lattice is known to be rhombohedral. We believe that, in these five classes, it would be better to use the 3-index notation when the lattice is rhombohedral, reserving the 4-index symbols for crystals with hexagonal lattices.

Friedel's lists are given in Table II.

In these lists, the forms observed on calcite crystals are marked by asterisks; the six most important known forms are indicated by two asterisks, the remainder by one. A glance at the two lists will convince the reader that the second lattice accounts for the relative importance of the known forms much better than the first one. With one exception³⁰ (for, as Friedel himself points out, "reticular densities do not explain everything"!), the six main forms are at the top of the list; moreover, the cleavage forms p , and b^1 and e^1 are certainly more important than the next three in the list, and a^1 is the least important morphologically among the six dominant forms. Friedel also considers another lattice, based on the unit cell $e^1\{11\bar{1}\}\{02\bar{2}1\}$. Incidentally this is the true structural lattice of the high-temperature form of NaNO_3 , which has the calcite structure, but whose structural period along the c -axis nevertheless is only half that of calcite (due to a rotation of the NO_3 -ions with consequent structural equality of all the NO_3 -ions). This lattice would account for the morphological observations on calcite better than that based on $e^3\{11\bar{3}\}\{0441\}$ but it is far from being as satisfactory as the lattice based on the cleavage rhombohedron as unit cell. Friedel remarks that the latter cell would be the period if no distinction were made between the Ca-ions and the CO_3 -ions (Fig. 1).

He also makes a similar observation in the case of halite (sodium chloride). The morphological lattice is here simple cubic whereas the structural lattice is face-centered. If the difference between the Na- and the Cl-ions be disregarded, however, all ions being then

³⁰ This apparent exception can be explained by an observation due to Friedel, G. (*Bull. Soc. fr. Min.*, vol. 25, pp. 113-115, 1902), who showed that calcite actually has three cleavages: $p\{100\}$, $d^1\{10\bar{1}\}$, $d^1\{10\bar{1}\}$, $d^1\{11\bar{2}0\}$, and $b^1\{110\}$, $b^1\{01\bar{1}2\}$, the latter often wrongly considered as parting. According to the facility with which these cleavages can be produced, they can be listed as follows: p , d^1 , b^1 . The high density of the form d^1 is thus accounted for.

considered equivalent, the structural lattice becomes simple cubic (with the parameters halved).

For chemical elements (in which all atoms are alike) one may expect the morphological and the structural lattices to coincide. From preliminary results obtained by one of us in an investigation now in progress, it appears that this is actually the case in most instances. Examples: Cu, Ag, Au, Al, Ge, Th, C (diamond), Si, Pb, Rh, Pd, Ir, Pt, all have the octahedron as their dominant form, hence their Haüy-Bravais lattice is face-centered; so is also their structural lattice.

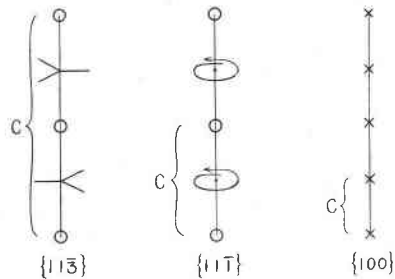


FIG. 1.

Schematic illustration of the relation between the three different lattices considered in the discussion of calcite.

The first figure represents the structure of calcite. Between the Ca-atoms (open circles) are indicated the positions of the CO_3 -groups; they form equilateral triangles with the O-atoms in the corners: the two triangles are not structurally identical, but are turned 60° in relation to each other. The true identity period is therefore twice as great as the distance between two Ca-atoms. This corresponds to the lattice based on the form $\{11\bar{3}\}$ of calcite.

The second figure shows that if the CO_3 -groups were rotating (as for example the NO_3 -groups do rotate in the high temperature modification of NaNO_3) the period of identity would be only half as great as in the first case, corresponding to a lattice based on the form $\{11\bar{1}\}$ of calcite.

The third figure shows that if the Ca-atoms and the CO_3 -groups be regarded as geometrical points the identity period would be only one-quarter as great as in the first case, corresponding to a lattice based on the form $\{100\}$ of calcite.

Aside from such meagre information, little is known about this challenging question of the relation between the external morphology and the intimate structure of crystals, which remains one of the principal problems of crystallography at the present time.