CHAPTER 3

Crystallography

3.1. Descriptive Crystallography

Quantitative crystallography began with Carangeot's invention of the contact goniometer (1780), an instrument with which the angles between the faces of a crystal could be crudely measured. The accuracy of this angular measurement was greatly increased, and extended to smaller crystals, by W. H. Wollaston's construction of an optical goniometer (1809). In this instrument light made parallel after passing through a slit in the focal plane of a collimating telescope is reflected by a crystal face, and focussed by a second telescope, so that the observer sees an image of the slit. The crystal is mounted in soft wax on an axis at right angles to the plane of the light path so that a 'zone axis,' i.e. the edge direction which is common to two or more crystal faces, coincides with the axis of rotation. If the crystal is rotated until a second face reflects into the telescope, then the angle of rotation, which can be read accurately on a graduated circle, is the angle formed by the normals of the two planes. With one setting of the crystal, only the normals of one 'zone,' which all lie in the plane at right angles to the zone axis, can be obtained. In order to measure the other angles the crystal has either to be re-set with a different zone axis coinciding with the axis of rotation, or a two-circle goniometer has to be used where this adjustment can be made without resetting.

The goniometer led to the discovery of the three fundamental laws of descriptive or morphological crystallography:

(i) Crystals grow naturally with plane faces.

(ii) Whereas the size of the crystal, the relative sizes of its faces, and thence the overall shape or 'habit' of a particular kind of crystal may vary widely according to the circumstances of its formation, the angles between the faces are characteristic for the chemical composition. It is true that the same angles occur in all crystals

Contents

belonging to the so-called cubic system (see below), but apart from these crystals, angular measurements may be used to identify each kind of crystal. If the same chemical compound occurs in several crystalline forms (as in the case of SiO_2 which forms α– and β–Quartz, Cristobalite, Tridymite) these are distinct thermodynamical phases and the substance is called polymorphic.

(iii) Taking as axes any three edges of a crystal which do not lie in one plane, suitable unit lengths may be determined on these so that all observed faces of the crystal have rational positions. By this is meant that their intercepts on the three edges, measured each in the appropriate unit of length, stand in the ratio of three small integral numbers (Law of Rational Positions). The directions of the edges together with their unit lengths are called the crystal axes and are given the symbols a, b, c, or a_1, a_2, a_3. A change of scale common to the three unit lengths would clearly shift all planes parallel to themselves and leave the angles between them unaffected. It follows that in descriptive crystallography only the *ratio* of the axial lengths can be determined. It is only in X-ray crystallography that the absolute value of these lengths (in cm or in Å) makes sense. It also follows from the law of rationality that if axes are chosen along three other edges occurring on the same crystal then, by a suitable transformation of the unit lengths, the rational planes of the old axial system are again rational in the new system. The axial system is thus not uniquely determined; usually that axial system is adopted in which the principal observed faces can be described by the lowest integers—but there may be reasons for deviating from this.

Bravais (1850) introduced a dual expression of the Law of Rational Positions which can be shown to be mathematically equivalent to the previous one and which has the advantage of dealing directly with the directions of the face normals as obtained on the goniometer. The law is then stated as follows: Take any three non-coplanar directions of face normals; to each of these a unit length may be ascribed such that the direction of any other observed face normal is obtained by geometrical composition (vector addition) of small integer lengths along these directions. The axial system in the directions of the three chosen normals together with the unit length in each direction forms what Bravais called the Polar Axes; we denote them by a^*, b^*, c^* or by b_1, b_2, b_3. Again, since we are dealing only with directions, the absolute scale of the units on the polar axes remains arbitrary. Only in X-ray crystallography will the scale obtain a meaning, and, including this, the axes are usually called the Reciprocal Axes to those of the crystal.

3.2. Symmetry

Potters and architects used symmetry and periodicity for creating artistic values even in prehistoric times. All the great civilizations of the past offer examples of the intricate beauty and the refined complexity of their application. But essentially these examples are limited to two dimensions. Crystallographers extended the notion to three dimensions, and it took them the greater part of a century to formulate a correct and complete geometrical theory of symmetry in space.

By Symmetry of an object we understand the equivalence of directions within the object. To a chosen direction there exist one or more different ones which show the same geometrical relations to all other directions defined in relations to the geometry of the object. It is therefore not possible to define in general a direction uniquely within the geometry of the object. A vase produced on a potter's wheel has 'cylindrical' or 'axial' symmetry. Except for the axis of rotation itself, it is not possible to define a direction uniquely by the geometry of the vase; for to any direction making an angle α with the axis there exists an infinite number of equivalent directions, forming a cone of opening α around the rotation axis; these are indistinguishable from one another by their properties with respect to the object. The axis of rotation is called a symmetry axis of infinite order.

Take the centre line of the lead in a six-sided pencil. This is a symmetry (or rotation) axis of the sixth order because to every direction (except along the axis) there are five equivalent ones, which, neglecting the imprint on the pencil, are indistinguishable.

Or take a match-box (again neglecting the print). The normal directions to its faces, taken at the centres of the faces, are two-fold axes because after one half full rotation about these directions the object is in a 'covering position'. Besides, there are 'mirror planes' each of which passes through the mid-points of one of the three sets of four parallel edges of the box. Reflection on a mirror plane brings the box to a covering position, and reflecting twice across the same mirror plane restores the original position. For this reason a mirror plane is called a symmetry element of the second order.

Finally, as an example, consider a cube and an octahedron; the latter is the figure obtained by cutting away the eight corners of the cube until the former cube faces are reduced to their mid-points which form the corners of the octahedron. Both figures have the same symmetry, comprising the following symmetry elements:

3 fourfold axes (through opposite corners of the octahedron)
6 twofold axes (through the mid-points of opposite edges of the cube)
4 threefold axes (through opposite corners of the cube, or normal to the faces of the octahedron)
9 mirror planes (three midway between parallel faces of the cube and six through opposite parallel edges of the cube).

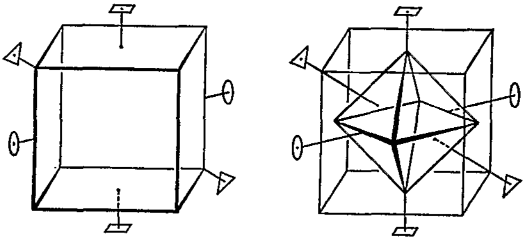

Fig. 3–2(1). Cube and octahedron with some of their symmetry elements.

Besides, we may distinguish a centre of inversion at the centre of the figure, that is, a symmetry element of order two which transforms any direction into the opposite one without change of length.

Not all symmetry elements are independent of one another. A fourfold axis always contains a twofold parallel one which results from the twofold application of the quarter-rotation. Two mirror planes intersecting at right angles always produce a twofold axis along their intersection. On the other hand symmetry elements may be incompatible with one another, such as a four-fold and a three-fold axis intersecting at right angles. For if this were the case, repeated application of the symmetry operations would show that *every* direction of space contains axes of both kinds—which is true for isotropy, but not compatible with crystallinity.

* * *

In the first half of the 19th Century the paramount symmetry problem was that of *Point Symmetry*: to enumerate all possible combinations of crystallographic symmetry elements which pass through a common point, the origin, and therefore leave this point single. The crystallographic symmetry elements were observed to be exclusively 2, 3, 4 and

6-fold axes, mirror planes, and centres of inversion. Fivefold axes, common in botany (flower petals) and zoology (starfish) do not occur in crystals; nor are there axes of 7th or higher order.

It was finally shown by Hessel in 1830 that geometrically there exist only 32 combinations of crystallographic symmetry elements, called the *symmetry classes,* and examples of substances were found for nearly all classes. For assigning a crystal to a class not only the geometrical symmetry of its faces is indicative but also the physical symmetry of the bulk crystal, namely of its dielectric and optical behaviour, its conductivity for electricity and heat, its elastic properties etc. The lowest common symmetry of the geometrical and physical behaviour is that proper to the crystal, namely that part of the symmetry of the physical observations which can not be accounted for by the inherent symmetry of the physical process itself. As an illustration take the optical property, the refractive index. Since the velocity of light is always the same in a direction and its opposite, the optical behavior always adds a centre of symmetry, whether the crystal possesses it or not. Therefore optical refraction alone does not allow distinction between those classes which differ only by the presence or absence of a centre of symmetry.

A cruder, and more easily effected assignment of a crystal than to one of the 32 symmetry classes is to one of the 7 *crystal systems* into which the classes can be divided according to the axial systems suitable for expressing their symmetry. There are, for instance, five classes which are all referred to a cubic (Cartesian) system of axes, i.e. three mutually orthogonal axes of equal length. Similarly, there are three classes referred to orthogonal axes of three different lengths, and these form the orthorhombic system. The seven systems are the cubic, tetragonal, orthorhombic, hexagonal, trigonal, monoclinic and triclinic. The face development and the optical properties are usually sufficient for assigning a crystal to one of the systems.

The establishment of the 32 classes provided an infallible framework by which the ever increasing data of observations on minerals and on other chemical compounds could be classified. Before the end of the nineteenth century, crystallography was mainly the domain of the mineralogists, but in the last two decades chemists took an increasing interest in the crystalline properties of the many new substances they isolated or synthesized, both organic and inorganic.

3.3. *Theories of Crystal Structure*

a. *General physical considerations.* Even before the laws of descriptive crystallography were fully explored, speculations were rife as to the peculiar nature of the crystalline state. They were prompted by the cleavage properties which were first noted about 1720 by metallurgists on the brittle fractures of metals, and then studied on rock salt and calcite (Iceland spar) by others. The father of crystallography, the Abbé René Just Haüy (1743–1826) concluded that a shape similar to the one that could be obtained by splitting must be preformed in the inner structure of the crystal. The cleavage planes, be they prominent in the usual development of the habit of the crystal or not, must exist in the crystal like the mortar joints in a brick wall. The crystal then is built up of ultimate crystal molecules or particles of the shape obtained by cleavage, and in cleaving, the surface common to such block-shaped elements of crystal structure is laid bare. If faces other than the cleavage faces occur on a naturally grown crystal, Haüy explained them as resulting from a stepwise growth on a sub-microscopic scale similar to the average inclination of stairs being formed by the off-setting of equal bricks. If this off-setting is by whole bricks only, in the ratio of step width to height of 1 : 1 or 2 : 1 or 3 : 2, etc., it accounts for the rational positions of the observable planes. Haüy did not hesitate to generalize this 'Theory of Decrescence' also to crystals which show no splitting because it offers such an easy explanation of the law of rational plane positions.

According to this view, then, the distinctive property of the crystalline state is its ultimate internal periodicity. Haüy could not decide what was the nature of the ultimate particles forming the repeat unit. This unit could clearly not be smaller than a molecule, but it could well consist of a whole cluster of molecules, that is, a multiple of the chemical formula. Haüy chose therefore for the repeat unit the name 'molécule intégrante'. This matter was settled by the first actual crystal structure determination, but that was not until 1913.

Meanwhile the assumption of a periodic internal structure of crystals came up in a long discussion between the founders of the Theory of Elasticity, notably Navier, Cauchy and Poisson, from 1821 onwards. In this year, Navier presented to the Paris Academy a paper (published in 1827) in which one of the pressing problems of the time received an answer, namely the establishment of equations governing the motion of an elastic deformation in a solid body, for instance the deformation of a struck plate or bell. In order to derive these equations, Navier assumed the body to consist of randomly arranged molecules which exert central forces on one another. If the body is deformed, the distances and forces between the molecules are changed, and the change of the latter constitute the stress associated with the deformation. Objections were voiced against Navier's method of replacing sums of forces from individual molecules in random positions by integrals. Cauchy, who belonged to the referees of the paper, took up the matter in an independent and more formal way by replacing the use of a physical model of the solid by the mathematical assumption that deformations (strains) and forces (stresses) were proportional to one another—a generalization of Hooke's Law. For an isotropic medium Cauchy arrived at equations similar to Navier's, except for the fact that they contained two elastic constants (i.e. proportionality factors), whereas Navier's equations contained only one.

Was this discrepancy a consequence of the different physical assumptions, or was it introduced only by the approximations that had been made, in particular Navier's replacement of the sum by an integral? In order to decide this point, Cauchy adopted Navier's model of molecular force centres and made the model a fully determined one by assuming the molecules to lie at the nodal points of a lattice. This also enabled him to deal with the case of an anisotropic medium by assuming the lattice to be of low symmetry. The result of this second paper of Cauchy's was a system of equations of motion for the components of the deformation in which, for the general triclinic case, 15 elastic constants appear expressing the relations between the six components of strain and stress, respectively. The most general proportionality-assumption between two sets of six quantities requires 6 × 6 coefficients; in the case of central forces (or, more generally because of conservation of energy) this number is reduced from 36 to 21 in the triclinic, and to 2 in the isotropic medium. Cauchy obtained further 6 relations in the triclinic, and one in the isotropic case, by expressing the condition that the undeformed state of the medium is without stress. The equations for the isotropic medium are then the same as Navier's.

The assumption underlying the Cauchy relations seemed incontestible from the physical point of view,—but the reduction in the number of independent elastic coeffcients was not borne out by the measurements. The application of the experimental results of Wertheim (1848) was not immediate because of the two substances he used, brass is polycrystalline, and glass, with its strong elastic aftereffects is not a representative of a body fulfilling Hooke's Law. Not until 1887 was the non-validity of Cauchy's relations convincingly demonstrated by Woldemar Voigt's measurement of elastic deformations of anisotropic crystals. Yet, long before the convincing proof, it seemed probable that the Cauchy relations did not hold, and this opinion discredited the model from which the relations sprang, namely that in the natural state of a crystal its molecules are arrayed in a three-dimensional lattice.

Thus it came about that the concept of internal regularity and periodicity as a characteristic for crystalline matter, after having emerged in a very promising way, lay dormant for more than seventy years as a brilliant, but unfortunately not acceptable speculation which neither physicists nor crystallographers dared to use seriously.

Once Laue's discovery of 1912 had brought the irrefutable proof of the crystal's inner periodicity, it became the most urgent task to find where Cauchy's argument failed that had misled not only him, but all the other great mathematicians who had tried to escape his conclusion. It was Max Born's great achievement in 1913 to detect the flaw. Cauchy had assumed the molecules, that is, the force centres, to form a simple lattice. In this, each molecule is at a centre of symmetry of the entire (unlimited) system, and remains so in the case of a homogeneous deformation of the body. The forces exerted on a particular molecule by all others therefore balance, whatever the deformation may be. Born considered, instead, the more general case where each cell contains more than one molecule. A homogeneous deformation then consists of a change in the shape of the cell—which leads to the observable macroscopic strain—and a rearrangement of the molecules inside the cell, an 'inner displacement', which is not observable, except in some cases such as piezoelectric crystals where it leads to a change of the electric moment of each cell. The greater freedom gained by the crystal capable of inner displacements eliminates the interdependence of the elastic constants which is expressed in the Cauchy relations.—Only after having thus shown that Cauchy's results should not be applied to crystals of a sufficiently general structure was the way open for Born to develop his *Dynamik der Kristallgitter* (1914), the fundamental book on classical crystal dynamics.

b. *Space Group Theory.* The gist of Haüy's view was that a crystal is a periodic arrangement of equal particles, the 'molécules intégrantes', whatever these may be physically. The observation of symmetry puts certain restrictions on the arrangement and leads to the general, purely geometrical problem of finding all the types of symmetry that can be obtained by suitably arranging equal particles in space. In any such arrangement the particles have to remain equal, i.e. indistinguishable one from the other by any internal geometrical criterion. A medium of this kind has been called by P. Niggli (1919) a Homogeneous Discontinuum; it must, of course, be continued indefinitely filling all space, because otherwise the particles on or near to a boundary would be differently surrounded from those deep in the medium. The concept of a homogeneous discontinuum implies the periodicity of the internal structure, and therefore applies only to the crystalline state. If the demand of indistinguishability of the particles is restricted to average values, periodicity ceases to be required, and the resulting 'statistically homogeneous discontinuum' covers liquids and gases which are quite unordered, and fibres, high-polymers, and mesomorphic phases* which are partially ordered.

The problem of finding all symmetry types of homogeneous discontinua was solved in three steps, attached to the names of A. Bravais (1848), L. Sohncke (1867), and A. Schoenflies and E. von Fedorov (both 1891). Common to all of them are the following features:

(1) Symmetry axes of order 5,7 or higher are geometrically not compatible with a periodic structure; this is in accordance with the laws deduced from the morphology of crystals.

(2) Any periodic arrangement of particles is based on the repetition of a '*cell*', i.e. a parallelopipedon containing one or more particles; its shape and volume v_a is determined by three edges a_1, a_2, a_3 meeting in a corner point. The edges are called the *translations*, because by shifting the cell and its contents parallel to itself by integer multiples of the edges the entire structure is obtained from an original cell. The edges or translations may also be taken as the axial system of vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ by which to describe the whole array of particles. If the cell contain n particles at positions given by vectors $\mathbf{x}^k$ ($k = 1 \ldots n$), these form the '*base*' within the cell. If then $\mathbf{x}_l = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3$ (l_i integers) denotes the position of the origin of the l^{th} cell (l standing for the three integers l_i), then the position of the k^{th} particle of the l^{th} cell is

$$\mathbf{x}_l^k = \mathbf{x}_l + \mathbf{x}^k,$$

i.e. the particle is reached from the origin by first finding the vector leading to the origin of the l^{th} cell and then adding to it the base vector of the k^{th} kind of particle.

(3) The description of a homogeneous discontinum by means of a

---

* These are also known under the name of liquid crystals.

particular cell, and its corresponding base and axes, is largely arbitrary and therefore void of physical consequence. For instance one of the axes, say a_1, might be doubled; then the cell volume and the number of base particles and base vectors would be doubled, but this is merely a different description of the same array of particles as before. Usually that cell is preferred which offers an easy visualization of the symmetry and is the smallest and therefore contains the least number of base particles.

(i) *Bravais*' fundamental contribution to structure theory is the proof that equal particles can be arranged in 14 types of 'lattices' differing by symmetry and geometry, such that each particle is translationally equivalent to any other. This last condition means that the system of particles can be brought to a covering position by a mere translation from one particle to any other particle. Or, to put it other-

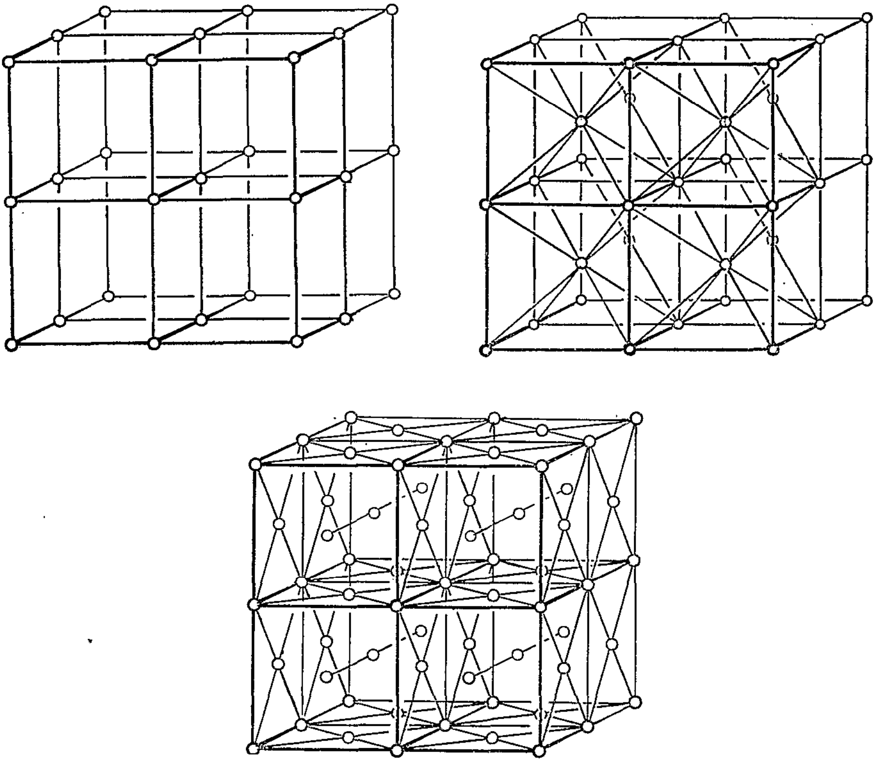

Fig. 3–3(1) a, b, c. The simple, body-centered and face-centered cubic Bravais lattices.

wise, if you were suddenly transported from one particle to any other, you would find the same view of the surroundings as before without turning your head. Fig. 3–3(1) illustrates a few cells of each of the three cubic Bravais lattices on which the correctness of the statement can be checked, while also showing that the arrangements are fundamentally different. (Compare the number of nearest neighbours in the three lattices, which are 6, 8, and 12, respectively.)

(ii) *Sohncke* saw the geometrical problem in greater generality. The condition of translational equivalence presents an unjustified restriction. It implies an external means of orientation, such as a compass or an external panorama in order to judge whether, while being transported from one particle to another, you have changed your direction of view. This extraneous orientation is alien to the definition of symmetry as given on pg. 19. Demanding then that the view of the system be the same from every particle, but not necessarily a parallel one, Sohncke found 65 different spatial arrangements. This answer of the problem included the introduction of novel symmetry elements in which a rotation about an axis, or the reflection on a mirror plane is coupled with a translation of the system along the axis, or in the plane of reflection. The first combination gives a '*screw axis*', the second a '*glide mirror plane*'. The translation contained in such glide symmetry elements is unnoticeable in an unbounded system of particles. As an example consider Fig. 3–3(2) where fourfold screw axes are arranged in a quadratic array. It is seen that a quarter full rotation of the system about one of the axes together with a translation along the axis of one quarter the pitch of the screw produces a covering motion of the un-

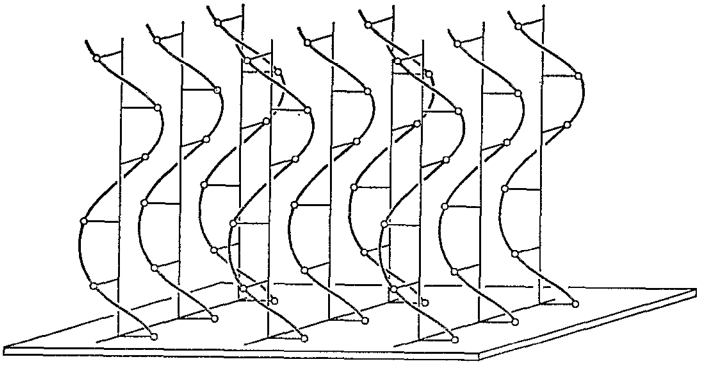

Fig. 3–3(2). A tetragonal Sohncke 'point system' with left-hand screw axes.

bounded system. It is also seen that no particle can be distinguished from any other by geometrical means, provided the aspects of the system may be compared after a suitable change of orientation. It is also easily seen that a similar arrangement might be shown using right-handed screws instead of the left-handed ones of the drawing. This second arrangement is the mirror image of the one shown, but it differs from it, since the two systems cannot be brought to coincidence —no more than a right-hand glove and a left-hand glove.

(iii) *Schoenflies,* then a lecturer in mathematics in Göttingen, worked out *230 Space Groups,* that is, different periodic arrangements of symmetry elements in space, and showed that they formed within the conditions given, a *complete* system. He considered the problem as one of geometrical group theory, a counterpart of the algebraic and the abstract Theories of Groups which began to be, in 1880–90, a very topical part of mathematics. Given the space pervading frame work of rotation and screw axes and of ordinary and glide mirror planes, a particle of any shape inserted anywhere will be reproduced by the symmetry elements, like the beads in a kaleidoscope, until the system of equivalent particles extends throughout space. Any one of the 230 arrangements, described either by the distribution of symmetry elements or by the coordinates of equivalent points, is called a Space Group. Sohncke's arrangements are Space Groups, but they formed only part of the complete system. The greater number obtained by Schoenflies is the result of abolishing yet another restriction, implicitly introduced in Sohncke's derivation, which contains an extraneous criterion not expressible by the geometry of the system itself.

It comes as quite a shock even to many scientifically trained minds to realize for the first time that the distinction between right and left and thence between a right-hand and a left-hand screw, is not expressible by purely geometrical relations. This follows from the fact that the change from right to left is produced by reflection on a mirror plane, which leaves all distances and angles unchanged. It is entirely a matter of convention to define the right-hand side, and every child has to be taught by long practise to distinguish it from the left-hand side. If we desired to convey to an intelligent being living on Mars which side we call right, we would have to appeal to a common observation for demonstrating the meaning of 'right', for instance by stating that for a man standing on the planet so that he can observe Ursa minor the sun will rise to his right. Every attempt at a purely geometrical definition would sooner or later beg the issue.

For this reason Schoenflies, in defining the equivalence of the particles, admitted that the view from one particle could change to its mirror image on transition to another particle. Of course the number of particles having a 'right' environment is equal to the number of those with a 'left' environment—otherwise there would be a distinctive feature between them.

Fedorov, the great Russian crystallographer, obtained independently and at the same time as Schoenflies the same system of 230 space groups.

⁂

In spite of the elaborately worked out theory the physical significance of these geometrical constructions remained obscure. What was the nature of the 'particle' inserted in, and multiplied by, the framework of symmetry elements? It could be any type of 'molécule intégrante' of Haüy's. Only conjectures were possible. Following the suggestion expressed by Sohncke in 1888, the eminent mineralogist and chemist P. Groth stressed the possibility of placing *atoms* in equivalent positions of a space group,—the various kinds of atoms of the crystal occupying not necessarily points of the same space group, but the interpenetrating space groups to be based on the same cell. Groth points out as a consequence of this that the molecular concept, while having a definite meaning in an amorphous body, loses this in the crystal since arbitrary atoms could be combined equally well to a 'molecule'.

With all this, the ideas about the size and contents of the cell remained rather vague. Also it was not possible to correlate an actual crystal with any space group, beyond choosing one of those which have the same point-symmetry (or class) as the crystal. Since there are 32 classes as against 230 space groups, this left many alternatives open.

The author's experience in 1911 may illustrate this statement. After having carried through in general terms a theory of double refraction caused by a simple orthorhombic arrangement of resonators he wanted to check it by a numerical calculation based on the axial ratio of some actual orthorhombic crystal. So he went to Professor Groth asking him what would be the most likely crystal to have its molecules arranged according to a simple orthorhombic Bravais lattice. Groth thought for a minute or two; then his face brightened and he said: 'there is only *one* crystal I can think of where this is nearly certain to be the case. This is Anhydrite. And I will give you the reason:

anhydrite shows excellent, good and fairly good cleavage on the three basic planes. I know of no other orthorhombic crystal having this property, and it means that it cannot be built according to any of the other three orthorhombic Bravais lattices.' The structure of anhydrite, determined in 1925, was found to be built according to a Bravais lattice in which one face is centered; there are four molecular units in the cell instead of one.

⁂

c. *Packing Theory of Crystal Structure.* A fundamentally different and much less systematic approach to crystal structure was made by the metallurgists, like Tammann in Göttingen and the chemists Barlow and Pope in Cambridge in the case of very simple compounds. They visualized atoms as spheres of a characteristic diameter which are closely packed so as to touch one another. The packing of equal spheres might be considered in the case of elements, while spheres of two sizes are required for the arrangement of the atoms in binary compounds such as the alkali halides NaF, NaCl, KCl etc. This theory, while offering by no means a complete geometrical-logical system of crystal structure, had certain features of physical reality which the other theory lacked. It was known to W. L. Bragg in 1912 when he discussed the photographs obtained with zincblende, and it gave him the clue for explaining why certain spots were missing which one would have expected to see on the diagrams. Pope, like others, had predicted a simple structure for alkali halides, consisting in the case of rock salt, NaCl, of an alternating arrangement of Na and Cl along the three cubis axes. On Pope's suggestion, W. L. Bragg took Laue photographs of these crystals and soon confirmed Pope's conjecture. This was the first full structure determination (published in *Proc. Roy. Soc.* June 1913). Since the wave-length of X-rays was at that time not yet known, the result could not have been obtained except by an inspired guess; by producing this, Pope's theory proved more fertile than the rival structure theories.

Next Section