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THE
INTERNATIONAL
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INTERNATIONAL SCIENTIFIC SERIES

VOLUME XCVIII.

DIRECT REPRODUCTIONS OF AUTOCHROME PHOTOGRAPHS OF SCREEN PICTURES IN POLARISED LIGHT.

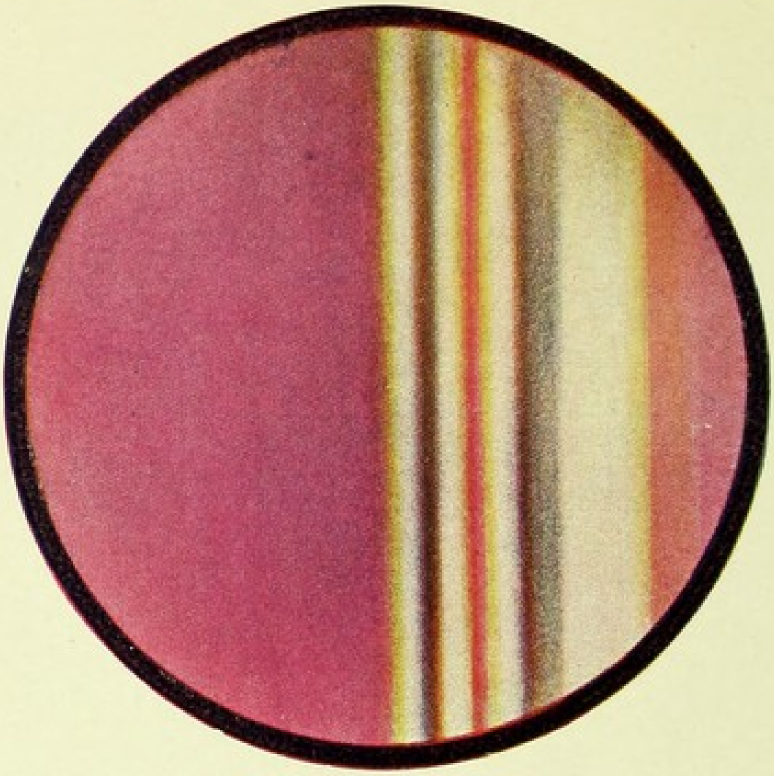

Fig. 90

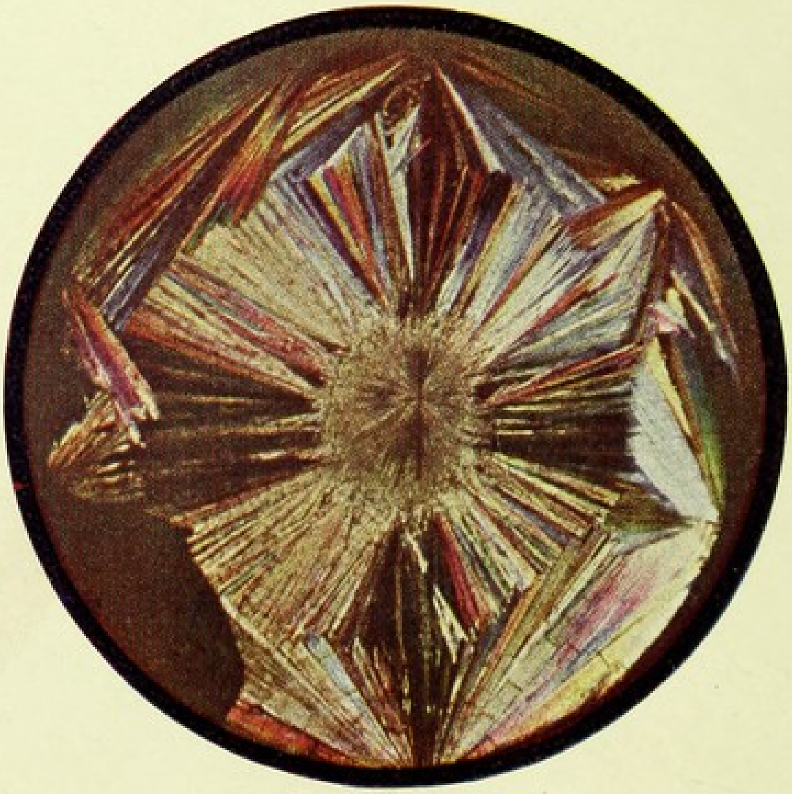

Fig. 97

Fig. 90.—Screen Picture in Polarised Light, with Nicols crossed, of a thick Plate perpendicular to the Axis of a naturally twinned Crystal of Quartz, the left half being of right-handed Quartz and the right half of alternately left and right-handed Quartz, the Planes of Demarcation being oblique to the Plate.

Fig. 97.—Crystals of Benzoic Acid in the Act of Growth, as seen on the Screen in Polarised Light with crossed Nicols.

THE INTERNATIONAL SCIENTIFIC SERIES

CRYSTALS

BY

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ADVANCEMENT OF SCIENCE

WITH 120 ILLUSTRATIONS

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1911

PREFACE

The idea underlying this book has been to present the phenomena of crystallography to the general reading public in a manner which can be comprehended by all. In the main the sequence is that of the author's evening discourse to the British Association at their meeting at Winnipeg in the summer of 1909. It is hoped, however, that the book combines the advantages of sufficient amplification of the story there told to make it an adequately detailed account of the development of the subject, and of the immense progress which has been made in it during recent years, with a full description of the numerous experimental illustrations given in the lecture, involving some of the most beautiful phenomena displayed by crystals in polarised light. Such an account has not been otherwise published, the brief abstract appearing in the Report of the British Association for 1909 giving no account of the experiments, which were a feature of the lecture, owing to the employment of a fine projection polariscope of more or less novel construction, and including two magnificent large Nicol prisms, a pair of the original ones made by Ahrens. The author has been frequently requested to publish a fuller account of this discourse, and as the general plan of it so fully embodies the present aspect of this fascinating science, it was determined, when invited by the publishers to write a generally readable book on " Crystals," to comply with these requests.

There is also included an account of the remarkable work of Lehmann and his fellow workers on " Liquid Crystals," and the bearing of these discoveries on the nature of crystal structure is discussed in so far as the experimental evidence has gone. Similarly, the theory of Pope and Barlow, connecting crystalline structure with the chemical property of valency, is referred to and explained, as this theory has called forth deep and widespread interest. In both cases, however, the author has been careful to avoid any expression of opinion on purely theoretical questions for which there is as yet no definite experimental evidence, and has confined himself strictly to indicating how far such interesting theories are supported by actual experimental facts.

No forbidding mathematical formulæ and no unessential technical terms will be found in the book, the aim of the author being to make any ordinarily cultured reader feel at the conclusion that the story has been readily comprehensible, and that crystallography is not the abstruse and excessively difficult subject which it has so generally been supposed to be, but that, on the contrary, it is both simple and straightforward, and full of the most enthralling interest, as well for the exquisite phenomena with which it deals, as for the exceedingly important bearing which it has on the nature, both chemical and physical, of solid matter.

If any of its readers should be so impressed with the value of work in this domain of science as to be desirous of joining the very thin ranks of the few who are engaged in it, they will find a guide to practical goniometry and to the experimental investigation of crystals in all its branches and details, as well as the necessary theoretical help, in the author's book on " Crystallography and Practical Crystal Measurement " (Macmillan & Co., 1911), and also an account of the author's own contributions to the subject in a monograph entitled " Crystalline Structure and Chemical Constitution " (Macmillan & Co., 1910).

A. E. H. TUTTON.

January 1911.

CONTENTS

CRYSTALS
(INCLUDING LIQUID CRYSTALS)

CHAPTER I

INTRODUCTION.

It is a remarkable fact that no definition of life has yet been advanced which will not apply to a crystal with as much veracity as to those obviously animate objects of the animal and vegetable world which we are accustomed to regard in the ordinary sense as "living." A crystal *grows* when surrounded by a suitable environment, capable of supporting it with its natural food, namely, its own chemical substance in the liquid or vaporous state or dissolved in a solvent. Moreover, when a crystal is broken, and then surrounded with this proper environment, it grows much more rapidly at the broken part than elsewhere, repairing the damage done in a very short space of time and soon presenting the appearance of a perfect crystal once more. In this respect it is quite comparable with animal tissue, the wonderful recuperative power of which after injury, exhibited by special growth at the injured spot, is often a source of such marvel to us. Indeed, a crystal may be broken in half, and yet each half in a relatively very brief interval will grow into a crystal as large as the original one again. The longevity and virility of the spores and seeds of the vegetable kingdom have been the themes of frequent amazement, although many of the stories told of them have been unable to stand the test of strict investigation. The virility of a crystal, however, is unchanged and permanent.

A crystal of quartz, rock-crystal, for instance—detached, during the course of the disintegration of the granitic rock of which it had originally formed an individual crystal, by the denuding influences at work in nature thousands of years ago, subsequently knocked about the world as a rounded sand grain, blown over deserts by the wind, its corners rounded off by rude contact with its fellows, and subjected to every variety of rough treatment—may eventually in our own day find itself in water containing in solution a small amount of the material of which quartz is composed, silicon dioxide SiO_2. No sooner is this favourable environment for continuing its crystallisation presented to it, than, however old it may be, it begins to sprout and grow again. It becomes surrounded in all probability by a beautiful coating of transparent quartz, with exterior faces inclined at the exact angles of quartz, although no sign of exterior faces had hitherto persisted through all the stages of its varied adventures. Or it may grow chiefly at two or three especially favourable places, and in the course of a few weeks, under suitable conditions, at each place a perfect little quartz crystal will radiate out from the sand grain, composed of a miniature hexagonal prism terminated by the well-known pyramid, really consisting of a pair of trigonal (rhombohedral) pyramids more or less equally developed, and together producing an apparently hexagonal one. Four such grains of sand, from which quartz crystals are growing, are shown in Fig. 1, as they appear under a microscope magnifying about fifty diameters. One of them shows a perfectly developed doubly terminated crystal of quartz growing from the tip of a singly terminated one, attached to and growing directly out of the grain.

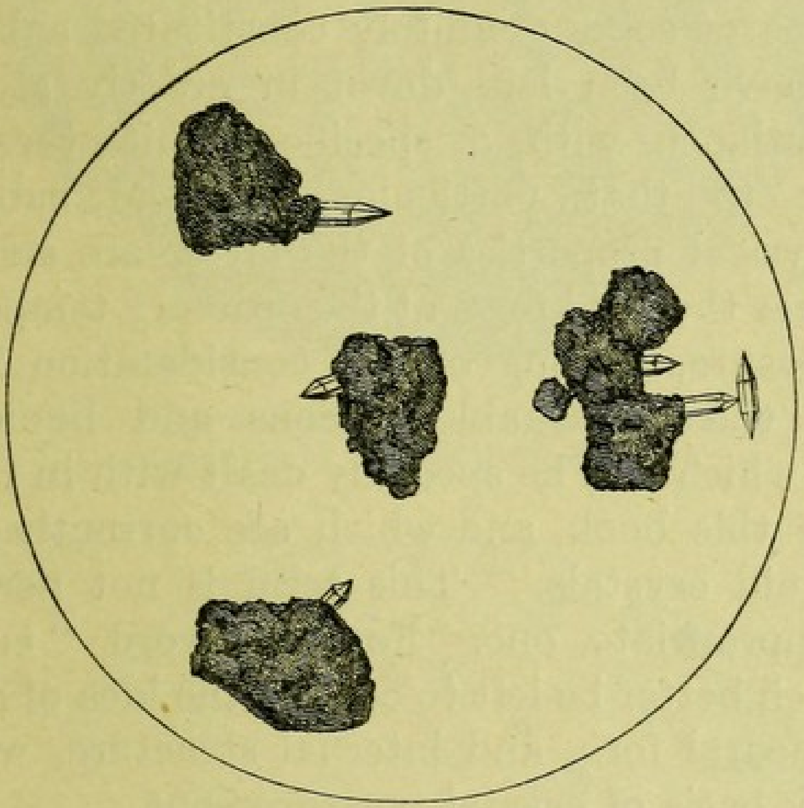

FIG. 1.—Sand Grains with Quartz Crystals growing from them.

This marvellously everlasting power possessed by a crystal, of silent imperceptible growth, that is, of adding to its own regular structure further accretions of infinitesimal particles, the chemical molecules, of its own substance, is one of the strangest functions of solid matter, and one of the fundamental facts of science which is rarely realised, compared with many of the more obvious phenomena of nature.

A crystal in the ordinary sense of the word is solid matter in its most perfectly developed and organised form. It is composed of the chemical molecules of some definitely constituted substance, which have been laid down in orderly sequence, in accordance with a specific architectural plan peculiar to that particular chemical substance. The physical properties of the latter are such that it assumes the solid form at the ordinary temperature and pressure, leaving out of consideration for the present the remarkable viscous and liquid substances which will be specially dealt with in Chapter XVI. of this book, and which are currently known as "liquid crystals." This term is not perhaps a very appropriate one. For the word "crystal" had much better be left to convey the idea of rigidity of polyhedral form and internal structure, which is the very basis of crystal measurement.

The solid crystal may have been produced during the simple act of congealment from the liquid state, on the cooling of the heated liquefied substance to the ordinary temperature. Sulphur, for instance, is well known to crystallise in acicular crystals belonging to the monoclinic system under such conditions, a characteristic crop being shown in Fig. 2 (Plate I.); they were formed within an earthenware crucible in which the fusion had occurred, and became revealed on pouring out the remainder of the liquid sulphur when the crystallisation had

Fig. 2.—Monoclinic Acicular Crystals of Sulphur produced by Solidification of Liquid.

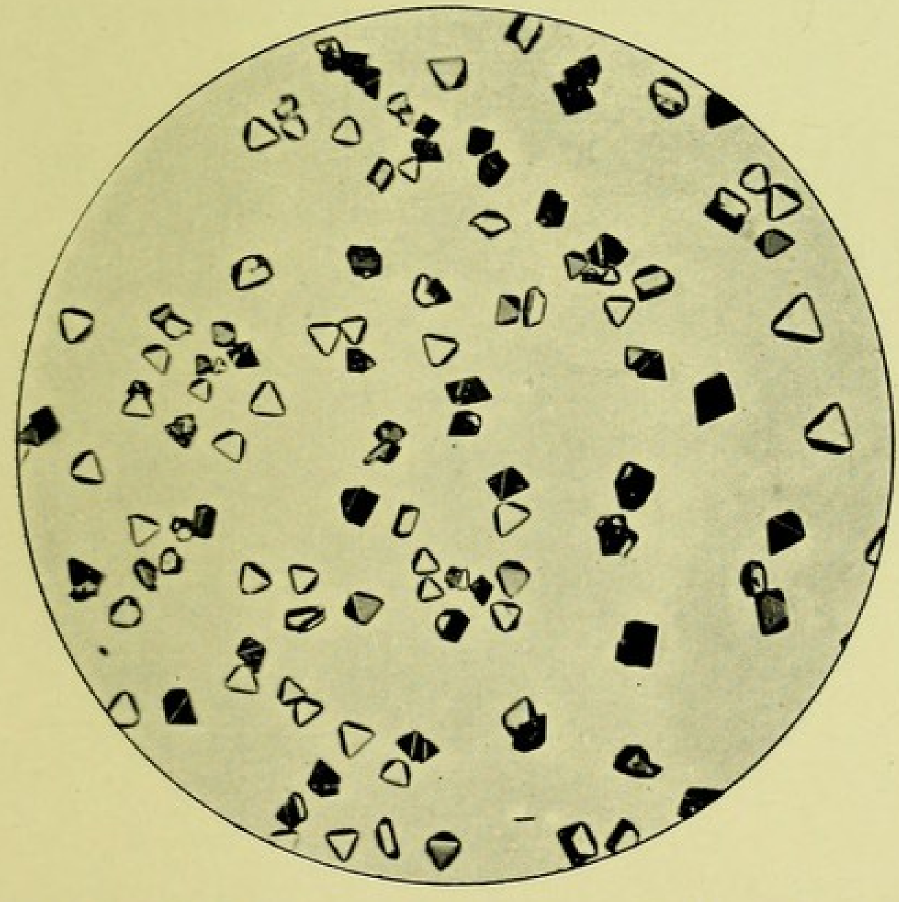

Fig. 3.—Octahedral Crystals of Arsenious Oxide produced by Condensation of Vapour.

Crystals formed by Different Processes.

To face p. 4.

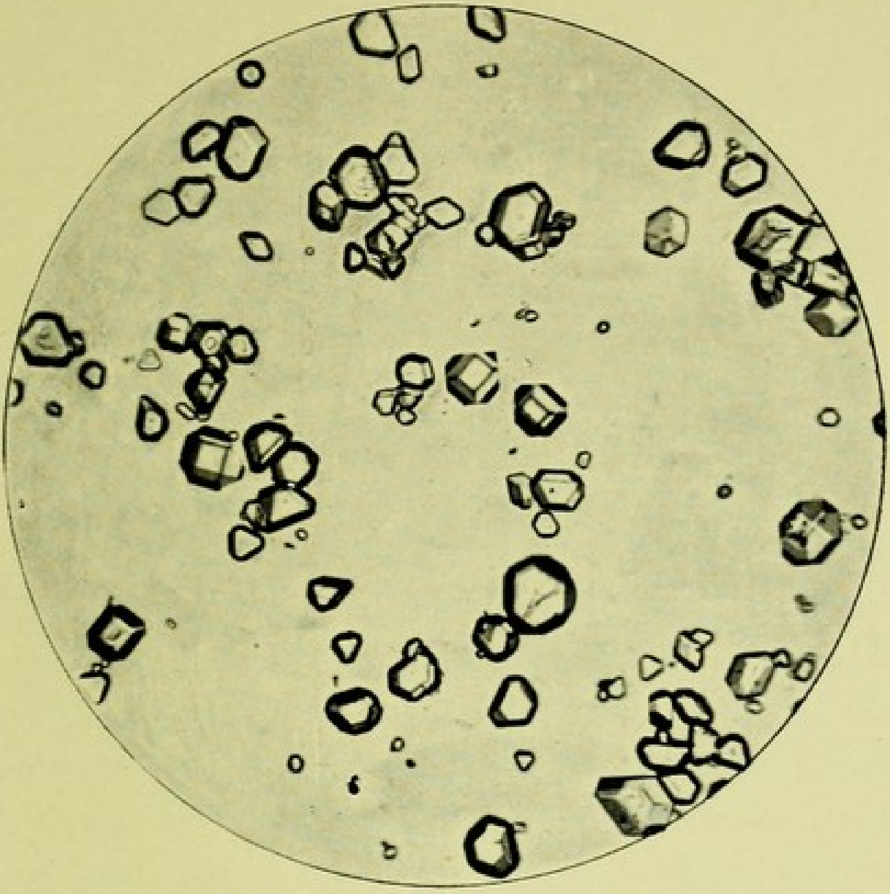

FIG. 4.—Cubic Octahedral Crystals of Potash Alum growing from Solution.

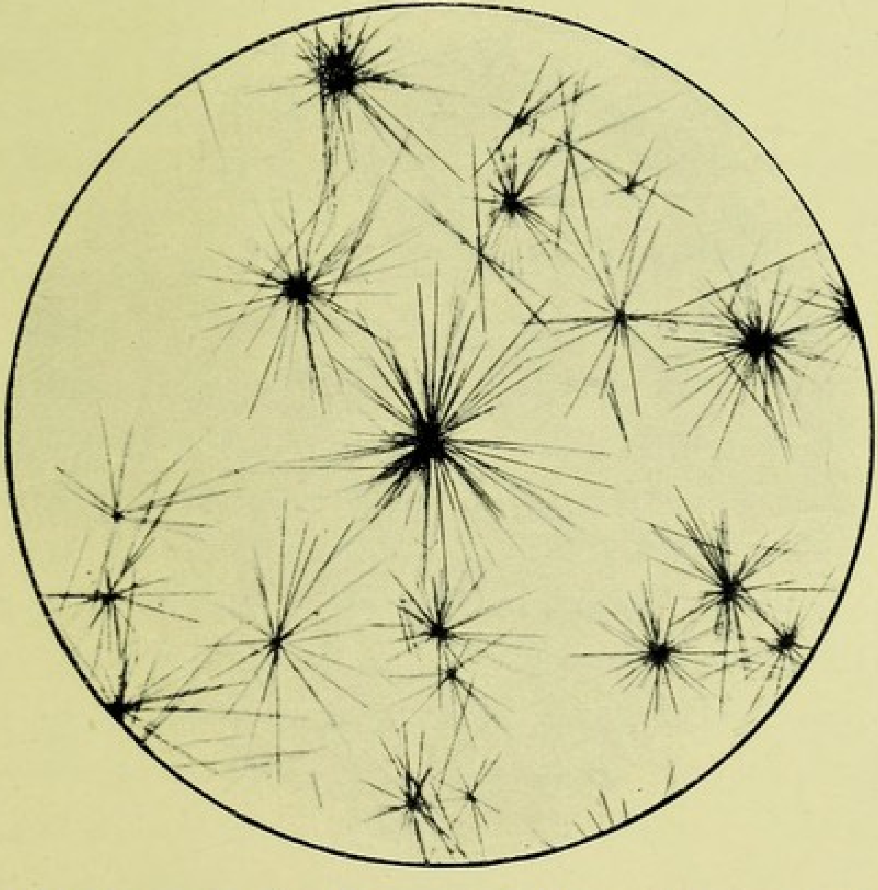

FIG. 10.—Micro-Chemical Crystals of Gypsum (Calcium Sulphate) produced by Slow Precipitation (see p. 14).

CRYSTALS FORMED BY DIFFERENT PROCESSES.

To follow Pl I.

proceeded through about one-half of the original amount of the "melt."

Or the substance may be one which passes directly from the gaseous to the solid condition, on the cooling of the vapour from a temperature higher than the ordinary down to the latter, under atmospheric pressure. Oxide of arsenic, As_2O_3, is a substance exhibiting this property characteristically, and Fig. 3 (Plate I.) is a reproduction of a photograph of crystals of this substance thus produced. The white solid oxide was heated in a short test tube over a Bunsen flame, and the vapour produced was allowed to condense on a microscope glass slip, and the result examined under the microscope, using a $1\frac{1}{2}$ inch objective. Fig. 3 represents a characteristic field of the transparent octahedral crystals.

Or again, the crystal may have been deposited from the state of solution in a solvent, in which case it is a question of the passage of the substance from the liquid to the solid condition, complicated by the presence of the molecules of the solvent, from which the molecules of the crystallising solid have to effect their escape. Fig. 4 (Plate II.) represents crystals of potash alum, for instance, growing from a drop of saturated solution on a glass slip placed on the stage of the miscroscope, the drop being spread within a hard ring of gold-size and under a cover glass, in order to prevent rapid evaporation and avoid apparent distortion by the curvature of an uncovered drop. The crystals are of octahedral habit like those of oxide of arsenic, but many of them also exhibit the faces of the cube.

In any case, however it may be erected, the crystal edifice is produced by the regular accretion of molecule on molecule, like the bricks or stone blocks of the builder, and in accordance with an architectural plan more elaborate and exact than that of any human architect. This plan is that of one of the thirty-two classes into which crystals can be naturally divided with respect to their symmetry. Which specific one is developed, and its angular dimensions, are traits characteristic of the substance. The thirty-two classes of crystals may be grouped in seven distinctive systems, the seven styles of crystal architecture, each distinguished by its own elements of symmetry.

A crystal possesses two further fundamental properties besides its style of architecture. The first is that it is bounded externally by plane faces, arranged on the definite geometrical plan just alluded to and mutually inclined at angles which are peculiar to the substance, and which are, therefore, absolutely constant for the same temperature and pressure. The second is that a crystal is essentially a homogeneous solid, its internal structure being similar throughout, in such wise that the arrangement about any one molecule is the same as about every other. This structure is, in fact, that of one of the 230 homogeneous structures ascertained by geometricians to be possible to crystals with plane faces. The first property, that of the planeness of the crystal faces, and their arrangement with geometrical symmetry, is actually determined by the second, that of specific homogeneity. For, as with human nature developed to its highest type, the external appearance is but the expression of the internal character.

When nature has been permitted to have fair play, and the crystal has been deposited under ideal conditions, the planeness of its faces is astonishingly absolute. It is fully equal to that attained by the most skilled opticians after weeks of patient labour, in the production of surfaces on glass or other materials suitable for such delicate optical experiments as interference-band production, in which a distortion equal to one wave-length of light would be fatal. In all such cases of ideal deposition, those interfacial angles on the crystal which the particular symmetry developed requires to be equal actually are so, to this same high degree of refinement. This fact renders possible exceedingly accurate crystal measurement, that is, the determination of the angles of inclination of the faces to each other, provided refined measuring instruments (goniometers), pure chemical substances, and the means of avoiding disturbance, either material or thermal, during the deposition of the crystal, are available.

The study of crystals naturally divides itself into two more or less distinct but mutually very helpful branches, and equally intimately connected with the internal structure of crystals, namely, one which concerns their exterior configuration and the structural morphology of which it is the eloquent visible expression, and another which relates to their optical characters. For the latter are so definitely different for the different systems of crystal symmetry that they afford the greatest possible help in determining the former, and give the casting vote in all cases of doubt left after the morphological investigation with the goniometer. It is, of course, their brilliant reflection and refraction of light, with production of numerous scintillations of reflected white light and of refracted coloured spectra, which endows the hard and transparent mineral crystals, known from time immemorial as gem-stones, with their attractive beauty. Indeed, their outer natural faces are frequently, and unfortunately usually, cut away most sacrilegiously by the lapidary, in order that by grinding and polishing on them still more numerous and evenly distributed facets he may increase to the maximum the magnificent play of coloured light with which they sparkle.

An interesting and very beautiful lecture experiment was performed by the author in a lecture a few years ago at the Royal Institution, which illustrated in a striking manner this fact that the light reaching the eye from a crystal is of two kinds, namely, white light reflected from the exterior faces and coloured light which has penetrated the crystal subtance and emerges refracted and dispersed as spectra. Two powerful beams of light from a pair of widely separated electric lanterns were concentrated on a cluster of magnificent large diamonds, kindly lent for the purpose by Mr Edwin Streeter, and arranged in the shape of a crown, it being about the time of the Coronation of His late Majesty King Edward VII. The effect was not only to produce a blaze of colour about the diamonds themselves, but also to project upon the ceiling of the lecture theatre numerous images in white light of the poles of the electric arc, derived by reflection from the facets, interspersed with equally numerous coloured spectra derived from rays which had penetrated the substance of the diamonds, and had suffered both refraction and internal reflection.

CHAPTER II

THE MASKING OF SIMILARITY OF SYMMETRY AND CONSTANCY OF ANGLE BY DIFFERENCE OF HABIT, AND ITS INFLUENCE ON EARLY STUDIES OF CRYSTALS.

NOTHING is more remarkable than the great variety of geometrical shapes which the crystals of the same substance, derived from different localities or produced under different conditions, are observed to display. One of the commonest of minerals, calcite, carbonate of lime, shows this feature admirably; the beautiful large rhombohedra from Iceland, illustrated in Fig. 5, or the hexagonal prisms capped by low rhombohedra from the Bigrigg mine at Egremont in Cumberland, shown in Fig. 6, appear totally different from the "dog-tooth spar" so plentifully found all over the world, a specimen of which from the same mine is illustrated in Fig. 7. No mineral specimens could well appear more dissimilar than these represented on Plate III. in Figs. 6 and 7, when seen side by side in the mineral gallery of the British Museum (Natural History) at South Ken-

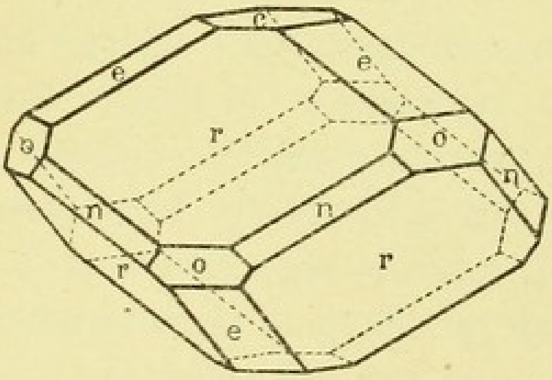

FIG. 5.—Natural Rhombohedron of Iceland Spar with Subsidiary Faces.

PLATE III.

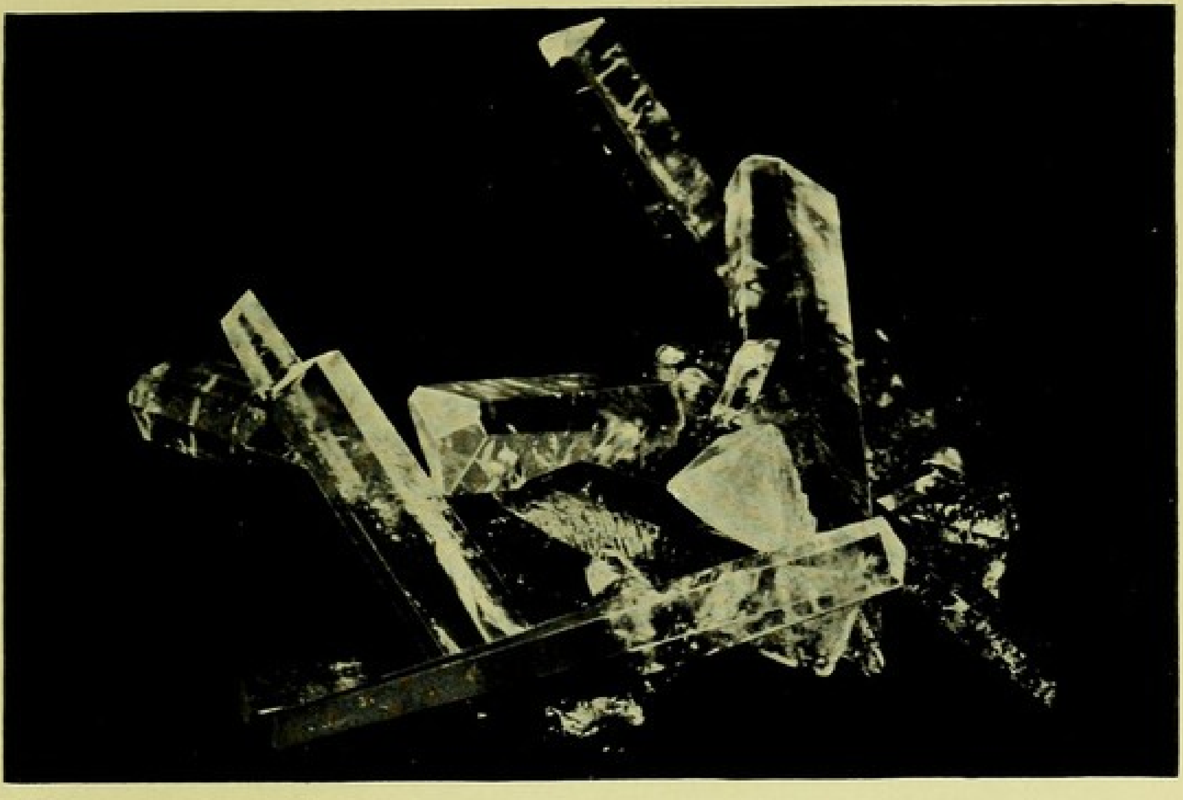

FIG. 6.—Hexagonal Prisms of Calcite terminated by Rhombohedra.

FIG. 7.—Scalenohedral Crystals of Calcite, "Dog-tooth Spar."

CRYSTALS OF CALCITE FROM THE SAME MINE, ILLUSTRATING DIVERSITY OF HABIT.

(Photographed from Specimens in the Natural History Department of the British Museum, by kind permission.)

To face p. 10.

sington. But all are composed of similar chemical molecules of calcium carbonate, $CaCO_3$; and when the three kinds of crystals are investigated they are found to be identical in their crystalline system, the trigonal, and indeed further as to the subdivision or class of that system, which has come to be called the calcite class from the importance of this mineral.

Moreover, many of the same faces, that is, faces having the same relation to the symmetry, are present on all three varieties, the "forms" to which they equally belong being the common heritage of calcite wherever found. A "form" is the technical term for a set of faces having an equal value with respect to the symmetry. Thus the prismatic form in Fig. 6 is the hexagonal prism, a form which is common to the hexagonal and trigonal systems of symmetry, and the form "indices" (numbers[1] inversely proportional to the intercepts cut off from the crystal axes by the face typifying the form) of which are $\{2\bar{1}\bar{1}\}$; the large development of this form confers the elongated prismatic habit on the crystal. The terminations are faces of the flat rhombohedron $\{110\}$. The pyramidal form of the dog-tooth spar shown in Fig. 7 is the scalenohedron $\{20\bar{1}\}$, and it is this form which confers the tooth-like habit, so different from the hexagonal prism, upon this variety of calcite. But many specimens of dog-tooth spar, notably those from Derbyshire, consist of scalenohedra the middle portion of which is replaced by faces of the hexagonal prism $\{2\bar{1}\bar{1}\}$, and the terminations of which are replaced by

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[1] See page 57 for explanation of indices.

the characteristic rhombohedron {100} of Iceland spar; indeed, it is quite common to find crystals of calcite exhibiting on the same individual all the forms which have been mentioned, that is, those dominating the three very differently appearing types. The author has quite recently measured such a crystal, which, besides showing all these four forms well developed, also exhibited the faces of two others of the well-known forms of calcite, $\{3\bar{1}\bar{1}\}$ and {310}, and a reproduction of a drawing of it to scale is given in Fig. 8. Instead of indices the faces of each form bear a distinctive letter; $m=\{2\bar{1}\bar{1}\}$, $r=\{100\}$, $e=\{110\}$, $v=\{20\bar{1}\}$ (the faces of the scalenohedron are of somewhat small dimensions on this crystal), $n=\{3\bar{1}\bar{1}\}$, and $t=\{310\}$.

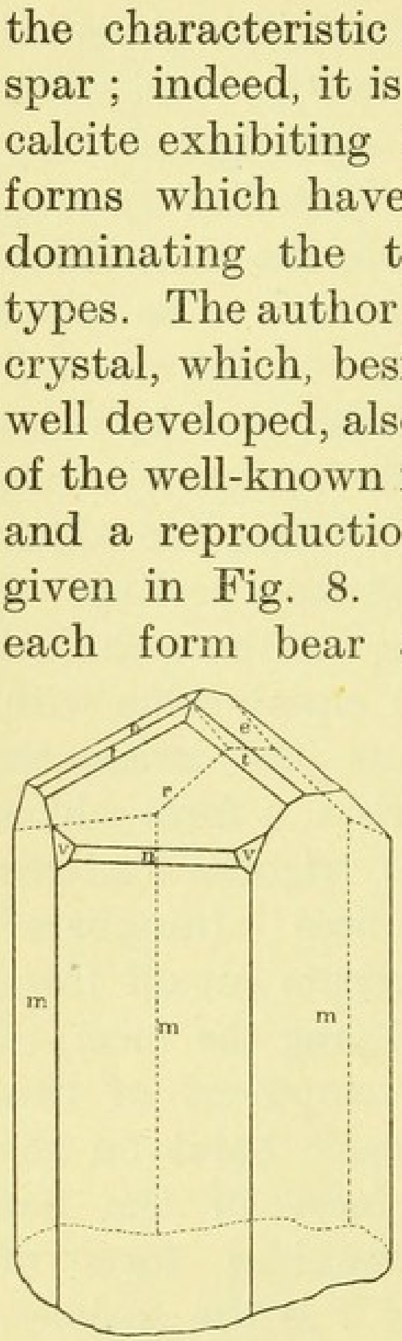

Fig. 8.—Measured Crystal of Calcite.

It is obviously then the "habit" which is different in the three types of calcite—Iceland spar, prismatic calc-spar, and dog-tooth spar—doubtless owing to the different local circumstances of growth of the mineral. Habit is simply the expression of the fact that a specific "form," or possibly two particular forms, is or are much more prominently developed in one variety than in another. Thus the principal rhombohedron $r = \{100\}$, parallel to the faces of which calcite cleaves so readily, is the predominating form in Iceland spar, while the scalenohedron $v=\{20\bar{1}\}$ is the habit-conferring form in dog-tooth spar. Yet on the latter the rhombohedral faces are frequently developed, blunting the sharp terminations of the scalenohedra, especially in dog-tooth spar from Derbyshire or the Hartz mountains; and on the former minute faces of the scalenohedron are often found, provided the rhombohedron consists of the natural exterior faces of the crystal and not of cleavage faces. In the same manner the prismatic crystals from Egremont are characterised by two forms, the hexagonal prism $m=\{2\bar{1}\bar{1}\}$ and the secondary rhombohedron $e=\{110\}$, but both of these forms, as we have seen on the actual crystal represented in Fig. 8, are also found developed on other crystals of mixed habit.

This illustration from the naturally occurring minerals might readily be supplemented by almost any common artificial chemical preparation, sulphate of potash for instance, K_2SO_4, the orthorhombic crystals of which take the form of elongated prisms, even needles, on the one hand, or of tabular plate-like crystals on the other hand, according as the salt crystallises by the cooling of a supersaturated solution, or by the slow evaporation of a solution which at first is not quite saturated. In both cases, and in all such cases, whether of minerals or chemical preparations, the same planes are present on the crystals of the same substance, although all may not be developed on the same individual except in a few cases of crystals particularly rich in faces; and these same planes are inclined at the same angles. But their relative development may be so very unlike on different crystals as to confer habits so very dissimilar that the fact of the identity of the substance is entirely concealed.

A further example may perhaps be given, that of a substance, hydrated sulphate of lime, $CaSO_4.2H_2O$, which occurs in nature as the beautiful transparent mineral gypsum or selenite—illustrated in Fig. 9, and which is found in monoclinic crystals often of very large size—and which may also be chemically prepared by adding a dilute solution of sulphuric acid to a very dilute solution of calcium chloride. The radiating groups of needles shown in Fig. 10 (Plate II.) slowly crystallise out when a drop of the mixed solution is placed on a microscope slip and examined under the microscope, using the one-inch objective. These needles, so absolutely different in appearance from a crystal of selenite, are yet similar monoclinic prisms, but in which the prismatic form is enormously elongated compared with the other (terminating) form.

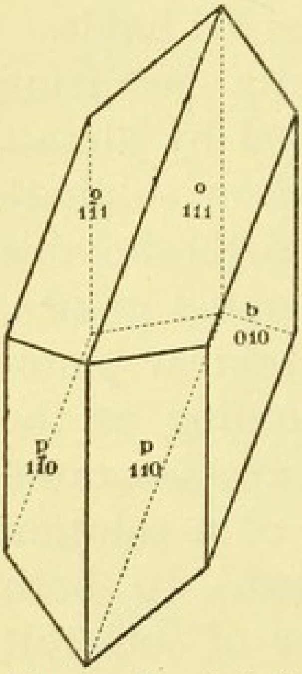

Fig. 9.—Crystal of Gypsum.

This difference of facial development, rendering the crystals of one and the same substance from different sources so very unlike each other, was apparently responsible for the very tardy discovery of the fundamental law of crystallography, the constancy of the crystal angles of the same substance. Gessner, sometime between the years 1560 and 1568, went so far as to assert that not only are different crystals of the same substance of different sizes, but that also the mutual inclinations of their faces and their whole external form are dissimilar.

What was much more obvious to the early students of crystals, and which is, in fact, the most striking thing about a crystal after its regular geometric exterior shape, was the obviously homogeneous character of its internal structure. So many crystals are transparent, and so clear and limpid, that it was evident to the earliest observers that they were at least as homogeneous throughout as glass, and yet that at the same time they must be endowed with an internal structure the nature of which is the cause of both the exterior geometric regularity of form, so different from the irregular shape of a lump of glass, and of the peculiar effect on the rays of light which are transmitted through them. From the earliest ages of former civilisations the behaviour of crystals with regard to light has been known to be different for the different varieties of gem-stones.

About the year 1600 Cæsalpinus observed that sugar, saltpetre, and alum, and also the sulphates of copper, zinc and iron, known then as blue, white and green vitriol respectively, separate from their solutions in characteristic forms. Had he not attributed this to the operation of an organic force, in conformity with the curious opinion of the times concerning crystals, he might have had the credit of being the pioneer of crystallographers. The first two real steps in crystallography, however, with which in our own historic times we are acquainted, were taken in the seventeenth century within four years of each other, one from the interior structural and the other from the exterior geometrical point of view. For in 1665 Robert Hooke in this country made a study of alum, which he appears to have obtained in good crystals, although he was unacquainted with its true chemical composition. He describes in his "Micrographia" how he was able to imitate the varying habits of the octahedral forms of alum crystals by building piles of spherical musket bullets, and states that all the various figures which he observed in the many crystals which he examined could be produced from two or three arrangements of globular particles. It is clear that the homogeneous partitioning of space in a crystal structure by similar particles building up the crystal substance was in Hooke's mind, affording another testimony to the remarkably prescient insight of our great countryman.

Four years later, in 1669, Nicolaus Steno carried out in Florence some remarkable measurements, considering the absence of proper instruments, of the angles between the corresponding faces of different specimens of rock-crystal (quartz, the naturally occurring dioxide of silicon, concerning which there will be much to say later in this book), obtained from different localities, and published a dissertation announcing that he found these analogous angles all precisely the same.

In the year 1688 the subject was taken up systematically by Guglielmini, and in two memoirs of this date and 1705 he extended Steno's conclusions as to the constancy of crystal angles in the case of rock-crystal into a general law of nature. Moreover, he began to speculate about the interior structure of crystals, and, like Hooke, he took alum as his text, and suggested that the ultimate particles possessed plane faces, and were, in short, miniature crystals. He further announced the constancy of the cleavage directions, so that to Guglielmini must be awarded the credit for having, at a time when experimental methods of crystallographic investigation were practically *nil*, discovered the fundamental principles of crystallography.

The fact that a perfect cleavage is exhibited by calcite had already been observed by Erasmus Bartolinus in 1670, and in his "Experimenta Crystalli Islandici" he gives a most interesting account of the great discovery of immense clear crystals of calcite which had just been made at Eskifjördhr in Iceland, minutely describing both their cleavage and their strong double refraction. Huyghens in 1690 followed this up by investigating some of these crystals of calcite still more closely, and elaborated his laws of double refraction as the result of his studies.

There now followed a century which was scarcely productive of any further advance at all in our real knowledge of crystals. It is true that Boyle in 1691 showed that the rapidity with which a solution cools influences the habit of the crystals which are deposited from it. But neither Boyle, with all his well known ability, so strikingly displayed in his work on the connection between the volume of a gas and the pressure to which it is subjected, nor his lesser contemporaries Lemery and Homberg, who produced and studied the crystals of several series of salts of the same base with different acids, appreciated the truth of the great fact discovered by Guglielmini, that the same substance always possesses the same crystalline form the angles of which are constant. Even with the growth of chemistry in the eighteenth century, the opinion remained quite general that the crystals of the same substance differ in the magnitude of their angles as well as in the size of their faces.

We begin to perceive signs of progress again in the year 1767, when Westfeld made the interesting suggestion that calcite is built up of rhombohedral particles, the miniature faces of which correspond to the cleavage directions. This was followed in 1780 by a treatise " De formis crystallorum " by Bergmann and Gahn of Upsala, in which Guglielmini's law of the constancy of the cleavage directions was reasserted as a general one, and intimately connected with the crystal structure. It was in this year 1780 that the contact goniometer was invented by Carangeot, assistant to Romé de l'Isle in Paris, and it at once placed at the disposal of his master a weapon of research far superior to any possessed by previous observers.

In his " Crystallographie," published in Paris in 1783, Romé de l'Isle described a very large number of naturally occurring mineral crystals, and after measuring their angles with Carangeot's goniometer he constructed models of no less than 500 different forms. Here we have work based upon sound measurement, and consequently of an altogether different and higher value than that which had gone before. It was the knowledge that his master desired to faithfully reproduce the small natural crystals which he was investigating, on the larger scale of a model, that led Carangeot to invent the contact goniometer, and thus to make the first start in the great subject of goniometry. The principle of the contact goniometer remains to-day practically as Carangeot left it, and although replaced for refined work by the reflecting goniometer, it is still useful when large mineral crystals have to be dealt with. An illustration of a duplicate of the original instrument is shown in Fig. 11, by the kindness of Dr H. A. Miers. This duplicate was

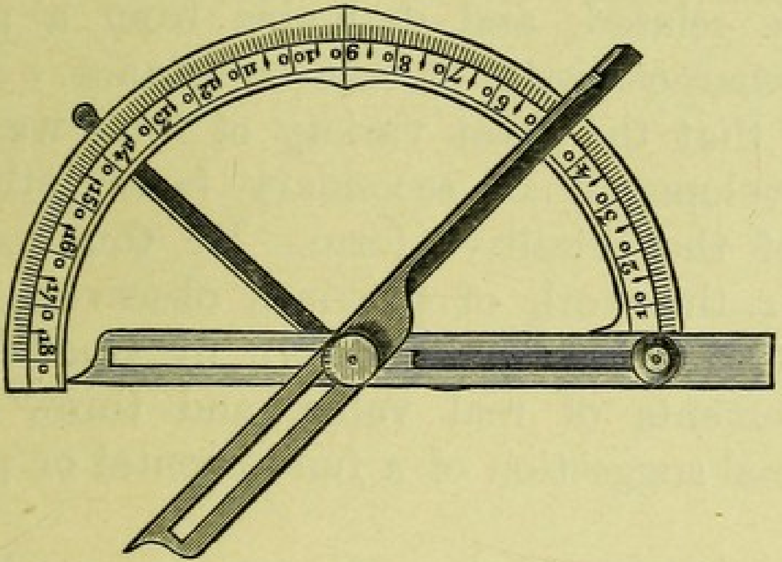

FIG. 11.—Contact Goniometer as used by Romé de l'Isle.

presented to Prof. Buckland by the Duke of Buckingham in the year 1824, and is now in the Oxford Museum.

From the time that measurement of an accurate description was possible by means of the contact goniometer, progress in crystallography became rapid. Romé de l'Isle laid down the sound principle, as the result of the angular measurements and the comparison of his accurate models with one another, that the various crystal shapes developed by the same substance, artificial or natural, were all intimately related, and derivable from a primitive form, characteristic of the substance. He considered that the great variety of form was due to the development of secondary faces, other than those of the primitive form. He thus connected together the work of previous observers, consolidated the principles laid down by Guglielmini by measurements of real value, and threw out the additional suggestion of a fundamental or primitive form.

About the same time Werner was studying the principal forms of different crystals of the same substance. The idea of a fundamental form appears to have struck him also, and he showed how such a fundamental form may be modified by truncating, bevelling, and replacing its faces by other derived forms. His work, however, cannot possess the value of that of Romé de l'Isle, as it was not based on exact measurement, and most of all because Werner appears to have again admitted the fallacy that the same substance could, in the ordinary way, and not in the sense now termed polymorphism, exhibit several different fundamental forms.

But a master mind was at hand destined definitely to remove these doubts and to place the new science on a firm basis. An account of how this was achieved is well worthy of a separate chapter.

CHAPTER III

THE PRESCIENT WORK OF THE ABBÉ HAÜY.

THE important work of Romé de l'Isle had paved the way for a further and still greater advance which we owe to the University of Paris, for its Professor of the Humanities, the Abbé Réné Just Haüy, a name ever to be regarded with veneration by crystallographers, took up the subject shortly after Romé de l'Isle, and in 1782 laid most important results before the French Academy, which were subsequently, in 1784, published in a book, under the auspices of the Academy, entitled "Essai d'une Théorie sur la Structure des Crystaux." The author happens to possess, as the gift of a kind friend, a copy of the original issue of this highly interesting and now very rare work. It contains a brief preface, dated the 26th November 1783, signed by the Marquis de Condorcet, perpetual secretary to the Academy (who, in 1794, fell a victim to the French revolution), to the effect that the Academy had expressed its approval and authorised the publication "under its privilege."

The volume contains six excellent plates of a large number of most careful drawings of crystals, illustrating the derivation from the simple forms, such as the cube, octahedron, dodecahedron, rhombohedron, and hexagonal prism, of the more complicated forms by the symmetrical replacement of edges and corners, together with the drawings of many structural lattices. In the text, Haüy shows clearly how all the varieties of crystal forms are constructed according to a few simple types of symmetry; for instance, that the cube, octahedron, and dodecahedron all have the same high degree of symmetry, and that the apparently very diverse forms shown by one and the same substance are all referable to one of these simple fundamental or systematic forms. Moreover, Haüy clearly states the laws which govern crystal symmetry, and practically gives us the main lines of symmetry of five of the seven systems as we now classify them, the finishing touch having been supplied in our own time by Victor von Lang.

Haüy further showed that difference of chemical composition was accompanied by real difference of crystalline form, and he entered deeply into chemistry, so far as it was then understood, in order to extend the scope of his observations. It must be remembered that it was only nine years before, in 1774, that Priestley had discovered oxygen, and that Lavoisier had only just (in the same year as Haüy's paper was read to the Academy, 1782) published his celebrated "Elements de Chimie"; and further, that Lavoisier's memoir "Reflexions sur le Phlogistique" was actually published by the Academy in the same year, 1783, as that in which this book was written by Haüy. Moreover, it was also in this same year, 1783, that Cavendish discovered the compound nature of water.

Considering, therefore, all these facts, it is truly surprising that Haüy should have been able to have laid so accurately the foundations of the science of crystallography. That he undoubtedly did so, thus securing to himself for all time the term which is currently applied to him of "father of crystallography," is clearly apparent from a perusal of his book and of his subsequent memoirs.

The above only represents a small portion of Haüy's achievements. For he discovered, besides, the law of rational indices, the generalisation which is at the root of crystallographic science, limiting, as it does, the otherwise infinite number of possible crystal forms to comparatively few, which alone are found to be capable of existence as actual crystals. The essence of this law, which will be fully explained in Chapter V., is that the relative lengths intercepted along the three principal axes of the crystal, by the various faces other than those of the fundamental form, the faces of which are parallel to the axes, are expressed by the simplest unit integers, 1, 2, 3, or 4, the latter being rarely exceeded and then only corresponding to very small and altogether secondary faces.

This discovery impressed Haüy with the immense influence which the structure of the crystal substance exerts on the external form, and how, in fact, it determines that form. For the observations were only to be explained on the supposition that the crystal was built up of structural units, which he imagined to be miniature crystals shaped like the fundamental form, and that the faces were dependent on the step-like arrangement possible to the exterior of such an assemblage. This brought him inevitably to the intimate relation which cleavage must bear to such a structure, that it really determined the shape of, and was the expression of the nature of, the structural units. Thus, before the conception of the atomic theory by Dalton, whose first paper (read 23rd October 1803), was published in the year 1803 in the Proceedings of the Manchester Literary and Philosophical Society, two years after the publication of Haüy's last work (his "Traité de Minéralogie," Paris, 1801), Haüy came to the conclusion that crystals were composed of units which he termed "*Molécules Intégrantes,*" each of which comprised the whole chemical compound, a sort of gross chemical molecule. Moreover, he went still further in his truly original insight, for he actually suggested that the *molécules intégrantes* were in turn composed of "*Molécules Elémentaires,*" representing the simple matter of the elementary substances composing the compound, and hinted further that these elementary portions had properly orientated positions within the *molécules intégrantes*.

He thus not only nearly forestalled Dalton's atomic theory, but also our recent work on the stereometric orientation of the atoms in the molecule in a crystal structure. Dalton's full theory was not published until the year 1811, in his epoch-making book entitled "A New System of Chemical Philosophy," although his first table of atomic weights was given as an appendix to the memoir of 1803. Thus in the days when chemistry was in the making at the hands of Priestley, Lavoisier, Considering, therefore, all these facts, it is truly surprising that Haüy should have been able to have laid so accurately the foundations of the science of crystallography. That he undoubtedly did so, thus securing to himself for all time the term which is currently applied to him of "father of crystallography," is clearly apparent from a perusal of his book and of his subsequent memoirs.

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The basis of Haüy's conceptions was undoubtedly cleavage. He describes most graphically on page 10 of his "Essai" of 1784 how he was led to make the striking observation that a hexagonal prism of calcite, terminated by a pair of hexagons normal to the prism axis, similar to the prisms shown in Fig. 6 (Plate III.) except that the ends were flat, showed oblique internal cleavage cracks, by enhancing which with the aid of a few judicious blows he was able to separate from the middle of the prism a kernel in the shape of a rhombohedron, the now well-known cleavage rhombohedron of calcite. He then tried what kinds of kernels he could get from dog-tooth spar (illustrated in Fig. 7) and other different forms of calcite, and he was surprised to find that they all yielded the same rhombohedral kernel. He subsequently investigated the cleavage kernels of other minerals, particularly of gypsum, fluorspar, topaz, and garnet, and found that each mineral yielded its own particular kernel. He next imagined the kernels to become smaller and smaller, until the particles thus obtained by cleaving the mineral along its cleavage directions *ad infinitum* were the smallest possible. These miniature kernels having the full composition of the mineral he terms "*Molécules Constituantes*" in the 1784 "Essai," but in the 1801 "Traité" he calls them "*Molécules Intégrantes*" as above mentioned. He soon found that there were three distinct types of *molécules intégrantes,* tetrahedra, triangular prisms, and parallelepipeda, and these he considered to be the crystallographic structural units.

Having thus settled what were the units of the crystal structure, Haüy adopted Romé de l'Isle's idea of a primitive form, not necessarily identical with the *molécule intégrante*, but in general a parallelepipedon formed by an association of a few *molécules intégrantes*, the parallelepipedal group being termed a "*Molécule Soustractive.*" The primary faces of the crystal he then supposed to be produced by the simple regular growth or piling on of *molécules intégrantes* or *soustractives* on the primitive form. The secondary faces not parallel to the cleavage planes next attracted his attention, and these, after prolonged study, he explained by supposing that the growth upon the primitive form eventually ceased to be complete at the edges of the primary faces, and that such cessation occurred in a regular step by step manner, by the suppression of either one, two, or sometimes three *molécules intégrantes* or *soustractives* along the edge of each layer, like a stepped pyramid, the inclination of which depends on how many bricks or stone blocks are intermitted in each layer of brickwork or masonry. Fig. 12 will render this quite clear, the face AB being formed by single block-steps, and the face CD by two blocks being intermitted to form each step. The plane AB or CD containing the outcropping edges of the steps would thus be the secondary plane face of the crystal, and the *molécules intégrantes* or *soustractives* (the steps can only be formed by parallelepipedal units) being infinitesimally small, the re-entrant angles of the steps would be invisible and the really furrowed surface appear as a plane one. Haüy is careful to point out, however, that the crystallising force which causes this stepped development (or lack of development) is operative from the first, for the minutest crystals show secondary faces, and often better than the larger crystals.

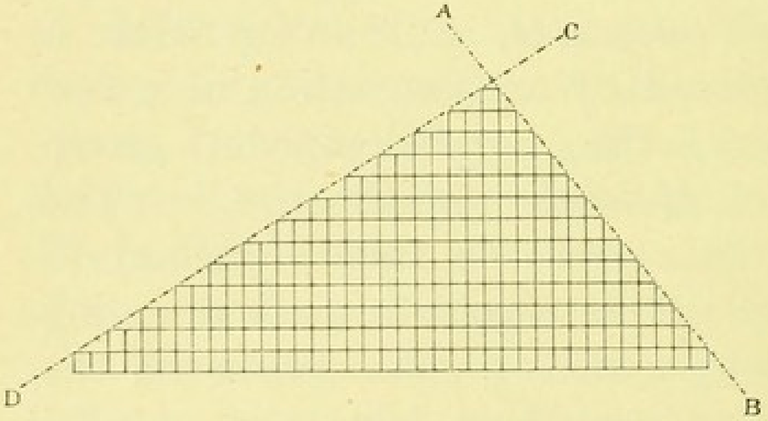

Fig. 12.

An instance of a mineral with tetrahedral *molécules intégrantes* Haüy gives in tourmaline, and the primitive form of tourmaline he considered to be a rhombohedron, conformably to the well-known rhombohedral cleavage of the mineral, made up of six tetrahedra. Again, hexagonal structures formed by three prismatic cleavage planes inclined at 60° are considered by him as being composed of *molécules intégrantes* of the form of 60° triangular prisms, or *molécules soustractives* of the shape of 120° rhombic prisms, each of the latter being formed by two *molécules intégrantes* situated base to base. This will be clear from Figs. 13 and 14, the former representing the structure as made up of equilateral prismatic structural units, and the latter portraying the same structure but composed of 120°-parallelepipeda by elimination of one cleavage direction; each unit in the latter case possesses double the volume of the triangular one, and being of parallelepipedal section is capable of producing secondary faces when arranged step-wise, whereas the triangular structure is not. The points at the intersections in these diagrams should for the present be disregarded; they will shortly be referred to for another purpose.

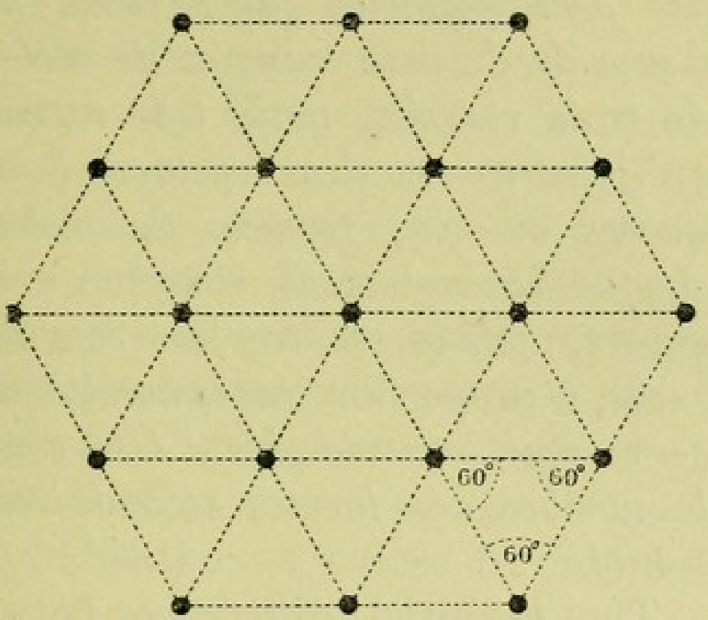

Fig. 13.

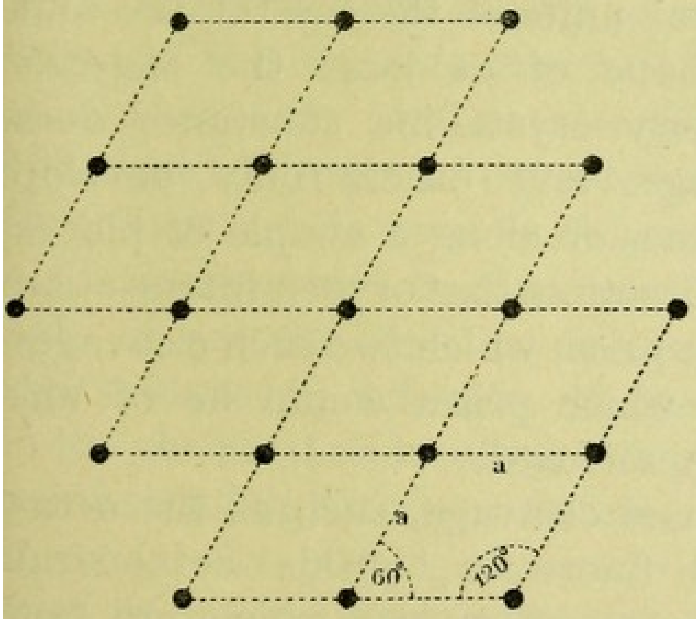

Fig. 14.

Probably the most permanent and important of Haüy's achievements was the discovery of the law of rational indices. At first this only took the form of the observation of the very limited number of rows of *molécules intégrantes* or *soustractives* suppressed.

In introducing it on page 74 of his 1784 " Essai " he says : " *Quoique je n'aie observé jusqu'ici que des décroissemens qui se sont par des soutractions d'une ou de deux rangées de molécules, et quelquefois de trois rangées, mais très rarement, il est possible qu'il se trouve des crystaux dans lesquels il y ait quatre ou cinq rangées de molécules supprimées à chaque décroissement, et même un plus grand nombre encore. Mais ces cas me semblent devoir être plus rares, à proportion que le nombre des rangées soutraites sera plus considérable. On conçoit donc comment le nombre des formes secondaires est nécessairement limité.*"

The essential difference between Haüy's views and our present ones, which will be explained in Chapter IX., is that Haüy takes cleavage absolutely as his guide, and considers the particles, into which the ultimate operation of cleavage divides a crystal, as the solid structural units of the crystal, the unit thus having the shape of at least the *molécule intégrante.* Now every crystalline substance does not develop cleavage, and others only develop it along a single plane, or along a couple of planes parallel to the same direction, that of their intersection and of the axis of the prism which two such cleavages would produce, and which prism would be of unlimited length, being unclosed.

Again, in other cases cleavage, such as the octahedral cleavage of fluor-spar, yields octahedral or tetrahedral *molécules intégrantes* which are not congruent, that is to say, do not fit closely together to fill space, as is the essence of Haüy's theory. Hence, speaking generally, partitioning by means of cleavage directions does not essentially and invariably yield identical plane-faced molecules which fit together in contact to completely fill space, although in the particular instances chosen from familiar substances by Haüy it often happens to do so. Haüy's theory is thus not adequately general, and the advance of our knowledge of crystal forms has rendered it more and more apparent that Haüy's theory was quite insufficient, and his *molécules intégrantes* and *soustractives* mere geometrical abstractions, having no actual basis in material fact ; but that at the same time it gave us a most valuable indication of where to look for the true conception.

This will be developed further into our present theory of the homogeneous partitioning of space, in Chapter IX. But it may be stated here, in concluding our review of the pioneer work of Haüy, that in the modern theory all consideration of the shape of the ultimate structural units is abandoned as unnecessary and misleading, and that each chemical molecule is considered to be represented by a point, which may be either its centre of gravity, a particular atom in the molecule (for we are now able in certain cases to locate the orientation of the spheres of influence of the elementary atoms in the chemical molecules), or a purely representative point standing for the molecule. The only condition is, that the points chosen within the molecules shall be strictly analogous, and similarly orientated. The dots at the intersections of the lines in Figs. 13 and 14 are the representative points in question. We then deal with the distances between the points, the latter being regarded as molecular centres, rather than with the dimensions of the cells themselves regarded as solid entities. We thus avoid the as yet unsolved question of how much is matter and how much is interspace in the room between the molecular centres. In this form the theory is in conformity with all the advances of modern physics, as well as of chemistry. And with this reservation, and after modifying his theory to this extent, one cannot but be struck with the wonderful perspicacity of Haüy, for he appears to have observed and considered almost every problem with which the crystallographer is confronted, and his laws of symmetry and of rational indices are perfectly applicable to the theory as thus modernised.

CHAPTER IV

THE SEVEN STYLES OF CRYSTAL ARCHITECTURE.

It is truly curious how frequently the perfect number, seven, is endowed with exceptional importance with regard to natural phenomena. The seven orders of spectra, the seven notes of the musical octave, and the seven chemical elements, together with the seven vertical groups to which by their periodic repetition they give rise, of the "period" of Mendeléeff's classification of the elements, will at once come to mind as cases in point. This proverbial importance of the number seven is once again illustrated in regard to the systems of symmetry or styles of architecture displayed by crystals. For there are seven such systems of crystal symmetry, each distinguished by its own specific elements of symmetry.

It is only within recent years that we have come to appreciate what are the real elements of symmetry. For although there are but seven systems, there are no less than thirty-two classes of crystals, and these were formerly grouped under six systems, on lines which have since proved to be purely arbitrary and not founded on any truly scientific basis. It was supposed that those classes in any system which did not exhibit all the faces possible to the system owed this lack of development to the suppression of one-half or three-quarters of the possible number, and such classes were consequently called "hemihedral" and "tetartohedral" respectively. As in the higher systems of symmetry there were usually two or more ways in which a particular proportionate suppression of faces could occur, it happened that several classes, and not merely three—holohedral (possessing the full number of faces), hemihedral, and tetartohedral—constituted each of these systems.

Thanks largely to the genius of Victor von Lang, who was formerly with us in England at the Mineral Department of the British Museum, and to his successor there, Nevil Story Maskelyne, we have at last a much more scientific basis for our classification of crystals, and one which is in complete harmony with the now perfected theory of possible homogeneous structures. Victor von Lang showed that the true elements of symmetry are planes of symmetry and axes of symmetry. A crystal possessing a plane of symmetry is symmetrical on both sides of that plane, both as regards the number of the faces and their precise angular disposition with respect to one another.

It is quite possible, and even the usual case, that the relative development of the faces, that is their actual sizes, may prevent the symmetry from being at first apparent; but when we come to measure the angles between the faces, by use of the reflecting goniometer, and to plot their positions out on the surface of a sphere, or on a plane representation of the latter on paper, the exceedingly useful "stereographic projection," we at once perceive the symmetry perfectly plainly.

Thus in Fig. 15 is represented a crystal of the salt potassium nickel sulphate, $K_2Ni(SO_4)_2.6H_2O$, belonging to the monoclinic system of symmetry, and which, therefore, possesses only one plane of symmetry. In Fig. 16 its stereographic projection is shown, in which each face in one of the symmetrical halves is represented by a dot, the plane of symmetry, parallel to the face *b*, being the plane of the paper, so that each dot not on the circumference really represents two symmetrical faces, one above and one below the paper, while the circumferential dots represent faces perpendicular to the symmetry plane and paper. The mode of arriving at such a useful projection, or plan of the faces, will be discussed more fully later in Chapter VI. But for the present purpose it will be sufficient to note that the right and left halves of the crystal shown in Fig. 15 are obviously symmetrical to each other, and that the plan of either half, projected on the dividing plane of symmetry itself, may be taken as given in Fig. 16; that is, we may imagine the crystal shown in

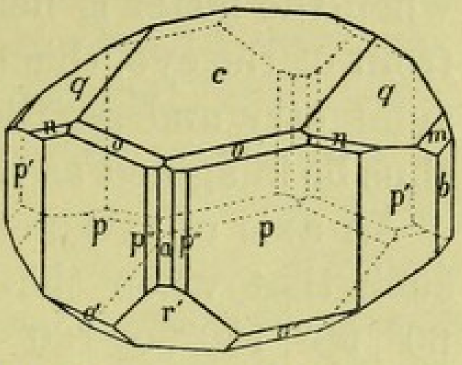

FIG. 15.—Crystal of Potassium Nickel Sulphate.

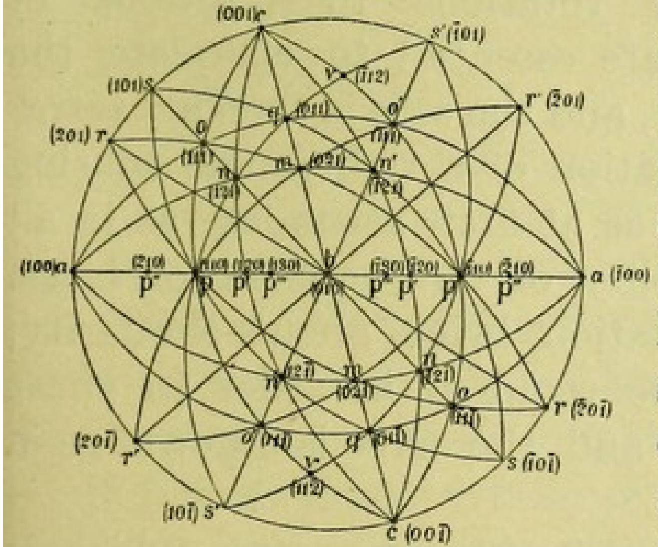

FIG. 16.—Stereographic Projection of Potassium Nickel Sulphate and its Isomorphous Analogues.

Fig. 15 to be equally divided by a section plane which is vertical and perpendicular to the paper when the latter is held up behind the crystal and in front of the eye, this section plane being the plane of symmetry and parallel to the face $b=(010)$. It may thus be imagined as the plane of projection of Fig. 16.

An axis of symmetry is a direction in the crystal such that when the latter is rotated for an angle of 60°, 90°, 120°, or 180° around it, the crystal is brought to look exactly as it did before such rotation. When a rotation for 180° is necessary in order to reproduce the original appearance, the axis is called a "digonal" axis of symmetry, for two such rotations then complete the circle and bring the crystal back to identity, not merely to similarity. When the rotation into a position of similarity is for 120°, three such rotations are required to restore identity, and the axis is then termed a "trigonal" one. Similarly, four rotations to positions of similarity 90° apart are essential to complete the restoration to identity, and the axis is then a "tetragonal" one, each rotation of a right angle causing the crystal to appear as at first, assuming, as in all cases, the ideal equality of development of faces. Lastly, if 60° of rotation bring about similarity, six such rotations are required in order to effect identity of position, and the axis is known as a "hexagonal" one.

Now, there is one system of symmetry which is characterised by the presence of a single hexagonal axis of symmetry, and this is the *hexagonal system.* A crystal of this system, one of the naturally occurring mineral apatite, which has been actually measured by the author, is shown in Fig. 17. There is another system, the chief property of which is to possess a tetragonal axis of symmetry, and which is therefore termed the *tetragonal system*. A tetragonal crystal of anatase, titanium dioxide, TiO_2, which has likewise been measured on the goniometer by the author, is shown in Fig. 18. And there is yet another system, the trigonal, the chief attribute of which is the possession of a single trigonal axis

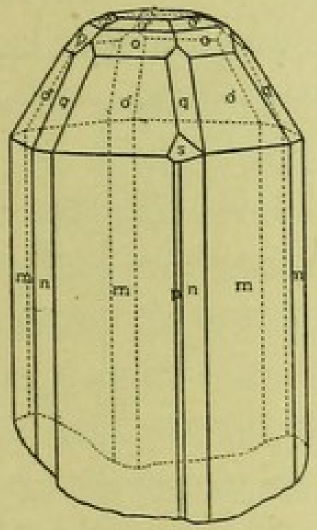

FIG. 17.—Measured Crystal of Apatite.

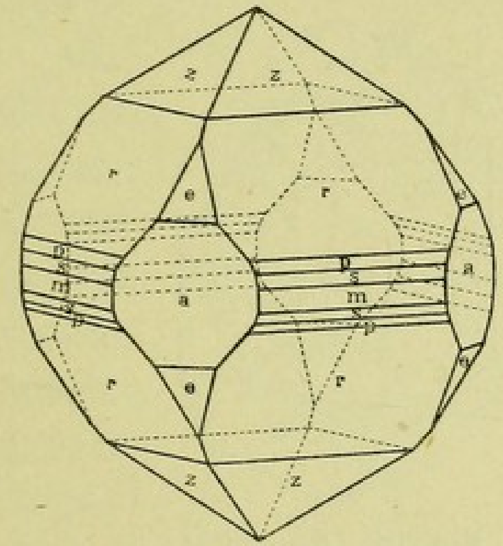

FIG. 18.—Measured Crystal of Anatase.

of symmetry, and which is consequently named the *trigonal system*. In Fig. 19 is shown a crystal of calcite, within which the directions of the three rhombohedral crystallographic axes of the trigonal system, and that of the vertical trigonal axis of symmetry, are indicated in broken-and-dotted lines.

But there is one system of symmetry, the highest possible, and which has already been referred to as the *cubic system*, which combines in itself all but one (the hexagonal axis) of the elements of symmetry. Indeed, not only does it possess a tetragonal, a trigonal, and a digonal axis of symmetry, but also ten other symmetry axes ; for these three automatically involve altogether the presence of no less than three tetragonal, four trigonal, and six digonal axes of symmetry, together with nine planes of symmetry, twenty-two elements of symmetry being thus present in all.

The perfections of the cube, the simple lines of which are illustrated in Fig. 20, as the expression of the highest kind of symmetry, with angles all right angles and sides and edges all equal, were so fully

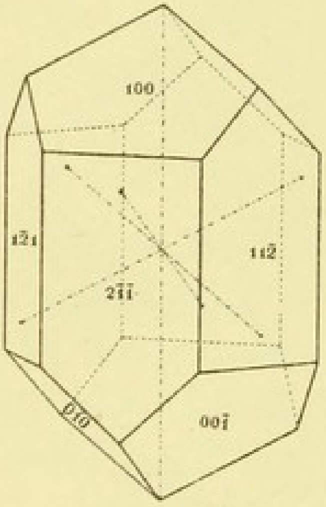

Fig. 19.—Crystal of Calcite.

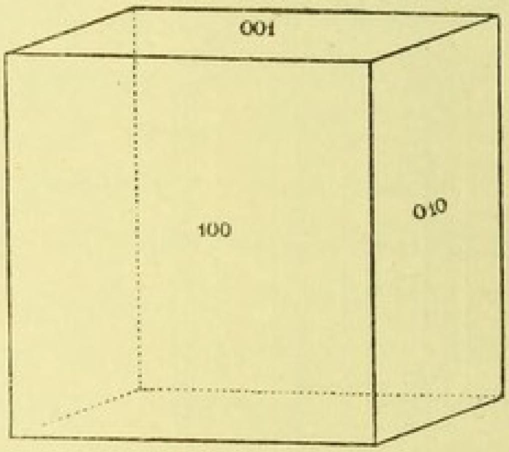

Fig. 20.—The Cube.

appreciated by the geometrical minds of the ancient Greek philosophers, imbued with the innate love of symmetry characteristic of their nation, that to them the cube became the emblem of perfection. We are reminded of this interesting fact in the Book of Revelation, which, in describing in its inimitable language the wonders of the Holy City, speaks of it as "lying foursquare," and attributes to it the properties of the cube, that "The length and the breadth and the height of it are equal."

The full symmetry of the cubic system is not realised, however, by a study of the cube alone ;

we only appreciate it when we come to examine the general form of the cubic system, that which is produced by starting with a face oblique to all three axes, and with different amounts of obliquity to each, and seeing how many repetitions of the face the symmetry demands. The presence of such a face involves as a matter of fact, when all the elements of symmetry are satisfied, the presence also of no less than forty-seven others, symmetrically situated, the forty-eight-sided figure produced being the hexakis octahedron shown in Fig. 21, and which is occasionally actually found developed in nature as the diamond. All diamonds do not by any means exhibit this form so wonderfully rich in faces, but diamonds are from time to time found which do show all the forty-eight faces well developed.

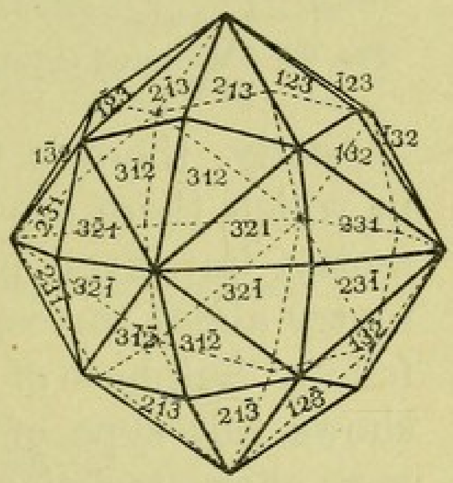

Fig. 21.—The Hexakis Octahedron.

Besides these four more highly symmetrical systems or styles of crystal architecture, a fifth, the *monoclinic system*, characterised by a single plane of symmetry and one axis of digonal symmetry perpendicular thereto, has already been alluded to, and a typical crystal illustrated in Fig. 15. A sixth, the *rhombic system*, perhaps in some ways the most interesting of all, and certainly so optically, possesses three rectangular axes of symmetry, identical in direction with the crystallographic axes, and three mutually rectangular planes of symmetry, coincident with the axial planes and intersecting each other in the axes. The lengths of the three crystal axes are unequal, however, and herein lies the essential difference from the cube. A very typical rhombic substance is topaz, a crystal of which, about three millimetres in diameter, is shown very much enlarged in Fig. 22. Every face on this crystal has been actually investigated on the goniometer, and the interfacial angles measured.

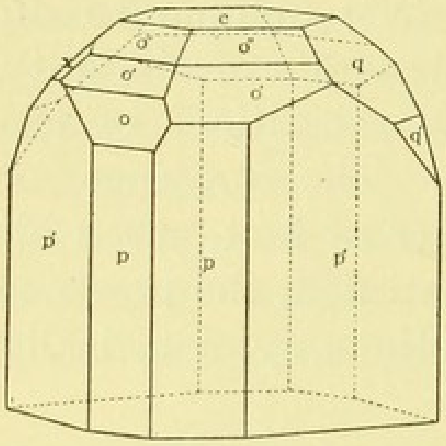

Fig. 22.—Measured Crystal of Topaz.

Lastly, there is the seventh, the *triclinic system*, in which there are neither planes nor axes of symmetry, but, even in its holohedral class, only symmetry about the centre, each face having a parallel fellow. Sulphate of copper, blue vitriol, $CuSO_4.5H_2O$, shows this type of symmetry, or rather lack of it, very characteristically, and a crystal of this beautiful deep blue salt, measured by the author, is represented in Fig. 23.

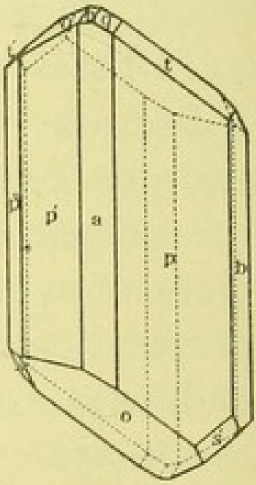

Fig. 23.—Measured Crystal of Copper Sulphate.

Hence, we have arrived logically at seven systems of symmetry or styles of crystal architecture, distinguished by the nature of their essential axes of symmetry, and the planes of symmetry which may accompany them. Now the full degree of symmetry of each system may be reduced to a certain minimum without lowering the system, and in all the systems but the triclinic there are several definite stages of reduction before the minimum is reached, each stage corresponding to

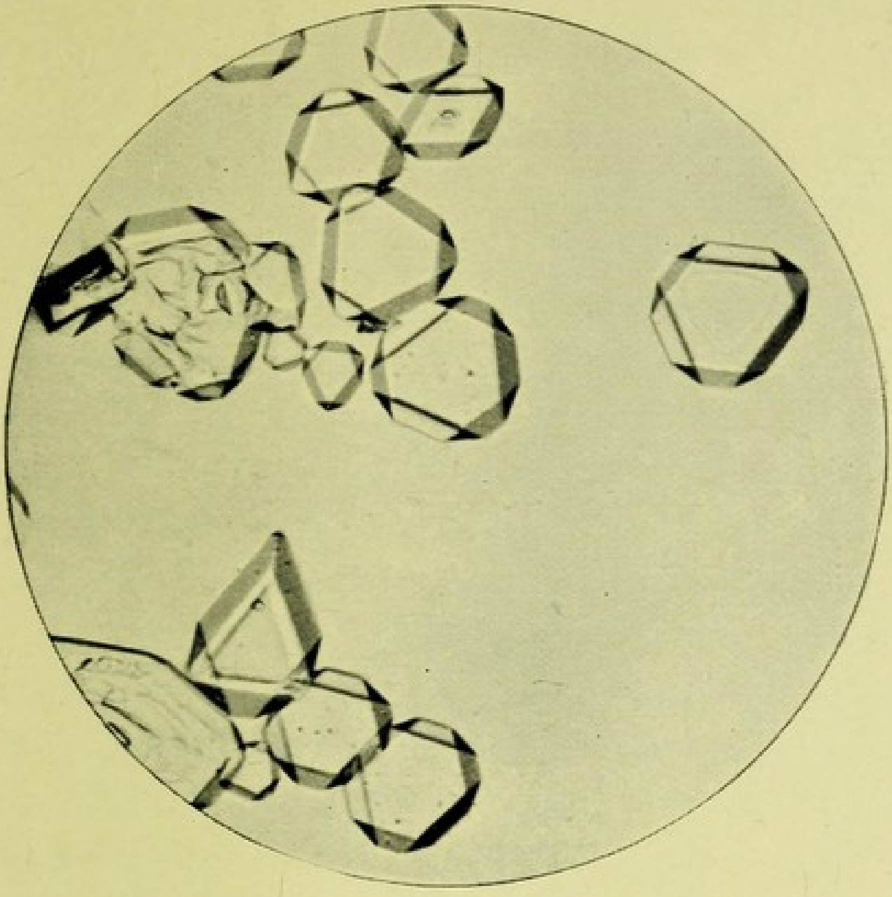

FIG. 24.—Octahedra of Potassium Cadmium Cyanide.

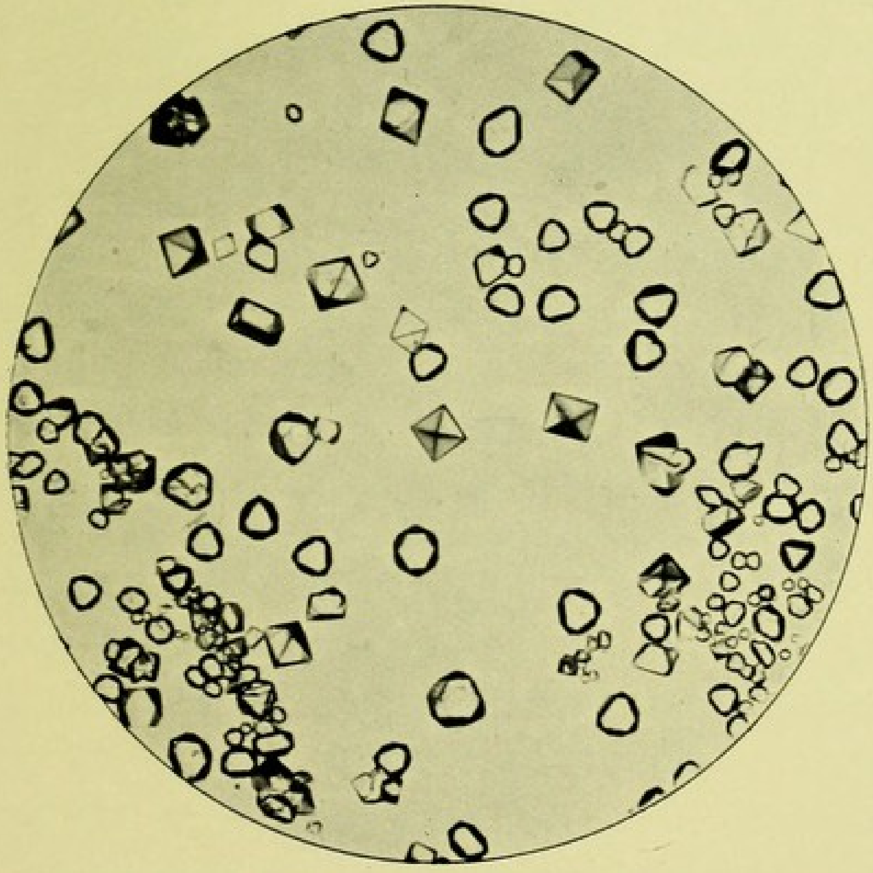

FIG. 25.—Octahedra of Cæsium Alum.

CUBIC CRYSTALS GROWING FROM SOLUTION.

one of the thirty-two classes of crystals. Thus in the cubic system there are four classes besides the holohedral, in the tetragonal six, in the hexagonal four, in the trigonal six, in the rhombic and monoclinic two each, and in the triclinic one.

We have thus attained at length to a truly scientific classification of crystal forms, by using axes and planes of symmetry as *criteria.* There is no occasion whatever to imagine suppression of faces in the classes of lower than the holohedral or highest symmetry of any system. In these classes it is simply the fact that less than the full number of elements of symmetry possible to the system are present and characterise the class, which still conforms, however, to the minimum symmetry absolutely essential to the system.

The drawings of crystals of the seven systems in the foregoing illustrations will have given a correct idea of the nature of the symmetry in each case. But now it may be much more interesting to present a series of reproductions of photographs of some actual crystals of the different systems. Such a series is given in Figs. 24 to 33, Plates IV. to VIII. They were taken with the aid of the microscope, the substances being crystallised from a slightly supersaturated solution in each case, on a microscope-slip. A ring of gold size was first laid on the slip, and allowed to dry for several days. The drop of solution, in the metastable supersaturated condition (corresponding to the region of solubility which lies between the solubility and supersolubility curves, Fig. 98, page 240), was placed in the middle of the ring, and crystallisation just allowed to start, either owing to evaporation and consequent production of the labile condition for spontaneous crystallisation, or by access of a germ crystal from the air. It was then covered with a cover-glass, which had the desired effect of enclosing the solution in a parallel-sided cell, a film of the thickness of thick paper, suitable for undistorted microscopic observation and photomicrography, and also the effect of arresting evaporation and therefore the rapidity of the growth of the crystals, so that a photomicrograph taken with the minimum necessary exposure was quite sharp.

The crystals shown in the accompanying photographic reproductions, Figs. 24 to 33 (Plates IV. to VIII.), as well as Fig. 4 (Plate II.), already described, were thus photographed in the very act of slow growth, employing a one-inch objective very much stopped down. Such photographs are infinitely sharper and more beautifully and delicately shaded than those taken of dry crystals.

Fig. 24, Plate IV., represents cubic octahedra of the double cyanide of potassium and cadmium, $2KCN.Cd(CN)_2$, a salt which crystallises out in relatively large and wonderfully transparent and well-formed single octahedra on a micro-slip, and is particularly suitable for demonstrating the character of this highest system, the cubic, of crystal symmetry. Special development of the pair of faces of the octahedron parallel to the glass surfaces has occurred, owing to greater freedom of growth at the boundaries of these faces, as is usual in such circumstances of deposition, but the other pairs of faces are quite large enough to show their nature clearly.

Fig. 25, on the same Plate IV., shows a slide of cæsium alum, $Cs_2SO_4.Al_2(SO_4)_3.24H_2O$, in which the

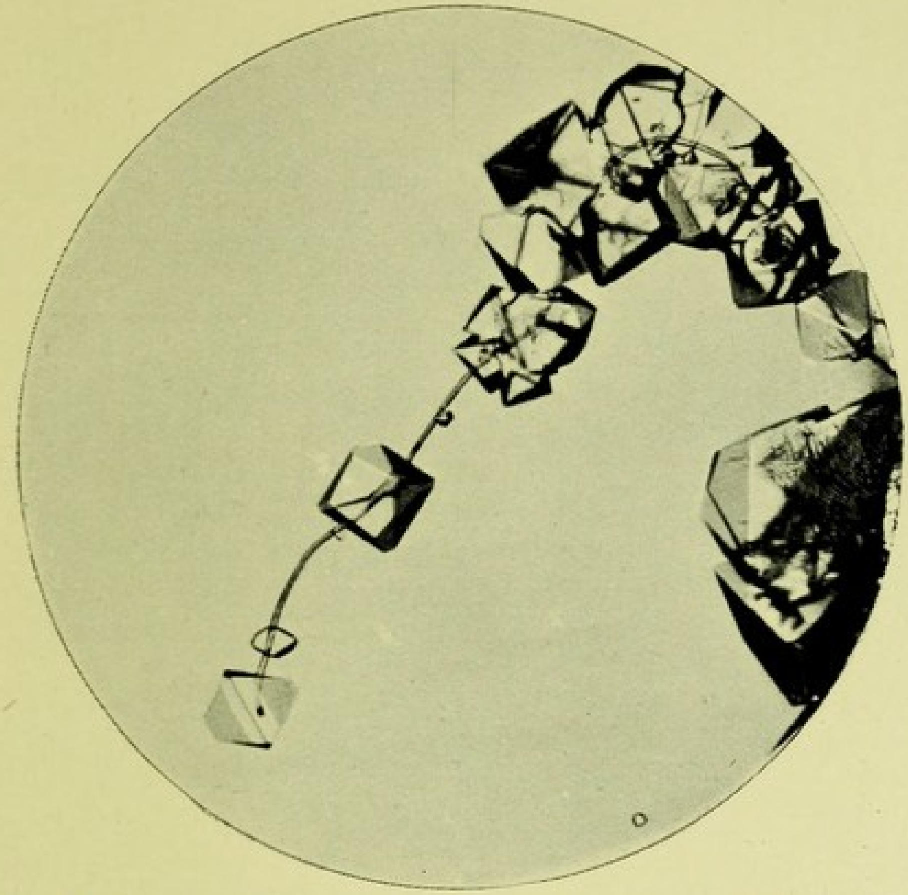

FIG. 26.—Octahedra of Ammonium Iron Alum crystallising on a Hair.

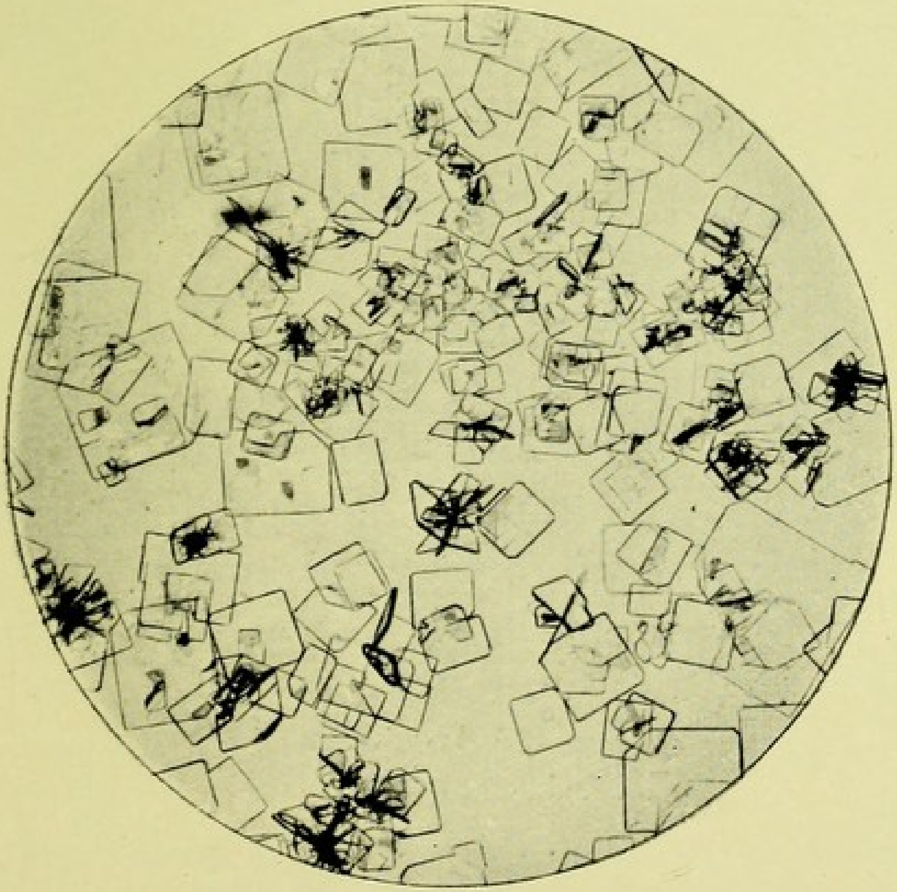

FIG. 27.—Tetragonal Crystals of Potassium Ferrocyanide.

CRYSTALS GROWING FROM SOLUTION.

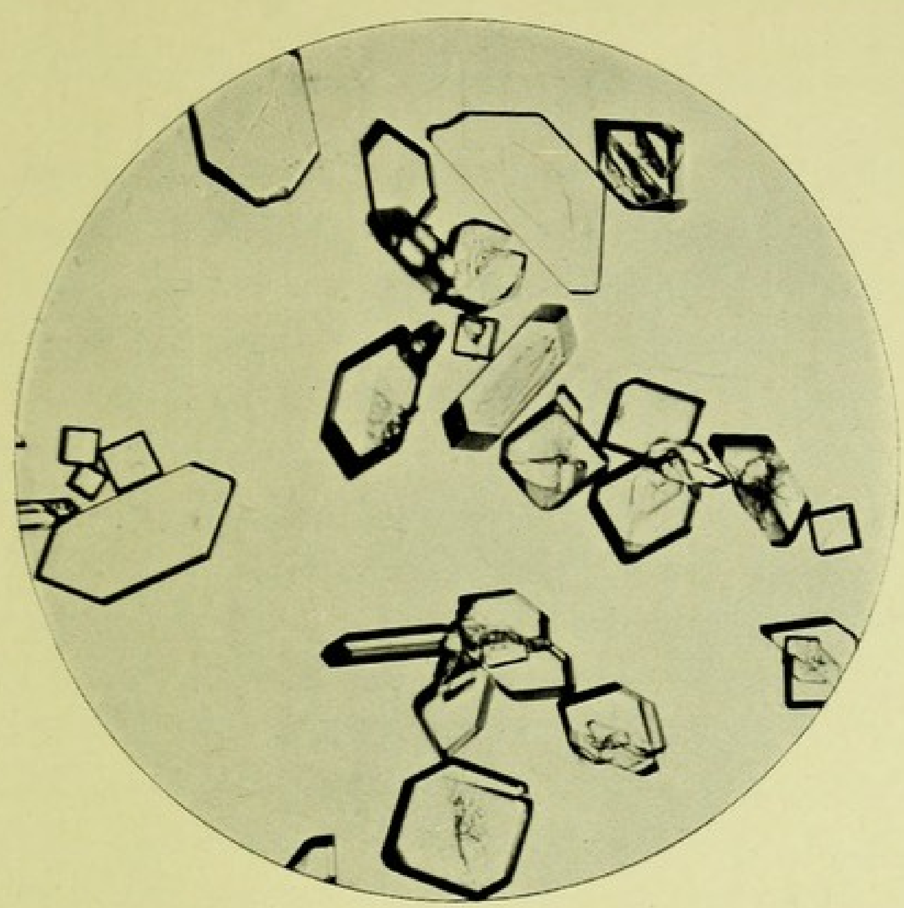

Fig. 28.—Rhombic Crystals of Potassium Hydrogen Tartrate.

Fig. 29.—Rhombic Crystals of Ammonium Magnesium Phosphate, showing Special Growth along Line of Scratch.

Rhombic Crystals growing by Slow Precipitation.

To follow Pl. V.

octahedra are smaller, and some of them, notably one in the centre of the field, are perfectly proportioned.

Fig. 26, Plate V., represents octahedra of ammonium iron alum (formula like that of cæsium alum, but with NH_4 replacing Cs and Fe replacing Al) crystallising on a hair. It illustrates the interesting manner in which crystallisation will sometimes occur, under conditions of quietude, when some object or other on which the crystals can readily deposit themselves is present or introduced, such as a silk or cotton thread, or a hair as in this case.

Fig. 27, on the same Plate V., represents tetragonal crystals of potassium ferrocyanide, $K_4Fe(CN)_6$, composed of tabular crystals parallel to the basal pinakoid, bounded by faces of one order, first or second, of tetragonal prism, the corners being modified at 45° by smaller faces of the other order of tetragonal prism.

Fig. 28, Plate VI., is a photograph of large rhombic crystals of hydrogen potassium tartrate, $HKC_4H_4O_6$, obtained by addition of tartaric acid to a dilute solution of potassium chloride. They are rectangular rhombic prisms capped by pyramidal forms, and also modified by other prismatic and domal forms.

Fig. 29, also on Plate VI., represents another rhombic substance, ammonium magnesium phosphate, $NH_4MgPO_4.6H_2O$, obtained by very slow precipitation of a dilute solution of magnesium sulphate containing ammonium chloride and ammonia with hydrogen disodium phosphate. It illustrates in an interesting manner how, when a saturated solution is kept quiet, and then the surface of the vessel containing it is scratched by a needle point, a line of small crystals at once starts forming along the line of scratch, even although the latter has made no actual impression on the glass itself. Such a line of crystals will be observed running across the middle of the slide.

Fig. 30, Plate VII., shows a monoclinic substance, ammonium magnesium sulphate $(NH_4)_2Mg(SO_4)_2.6H_2O$, which crystallises out splendidly on a micro-slip. The field includes several very well-formed typical crystals of the salt, which is one of the same exceedingly important isomorphous series to which potassium nickel sulphate, Fig. 15, belongs; it is obtained by mixing solutions containing molecularly equivalent quantities of ammonium and magnesium sulphates. The primary monoclinic prism is the chief form, terminated by clinodome faces and smaller strip-faces of the basal plane, the latter, however, being occasionally the chief end form. Small pyramid faces are also seen here and there modifying the solid angles.

Another beautifully crystallising monoclinic substance is shown in the next slide, Fig. 31, on the same Plate VII., namely, potassium sodium carbonate, $KNaCO_3.6H_2O$, obtained from a solution of molecular proportions of potassium and sodium carbonates. Numerous forms of the monoclinic system are developed, on relatively large and perfectly transparent and delicately shaded individuals.

A triclinic substance is represented in Fig. 32, Plate VIII., potassium ferricyanide, $K_6F_2(CN)_{12}$. The triply oblique nature of the symmetry is clearly exhibited by this salt, the absence of any right angles being very marked.

Fig. 33, also on Plate VIII., illustrates more particularly a class of one of the systems, the cubic, which is of lower than holohedral (full) systematic symmetry. This is the case also with hydrogen potassium tartrate and ammonium magnesium phosphate,

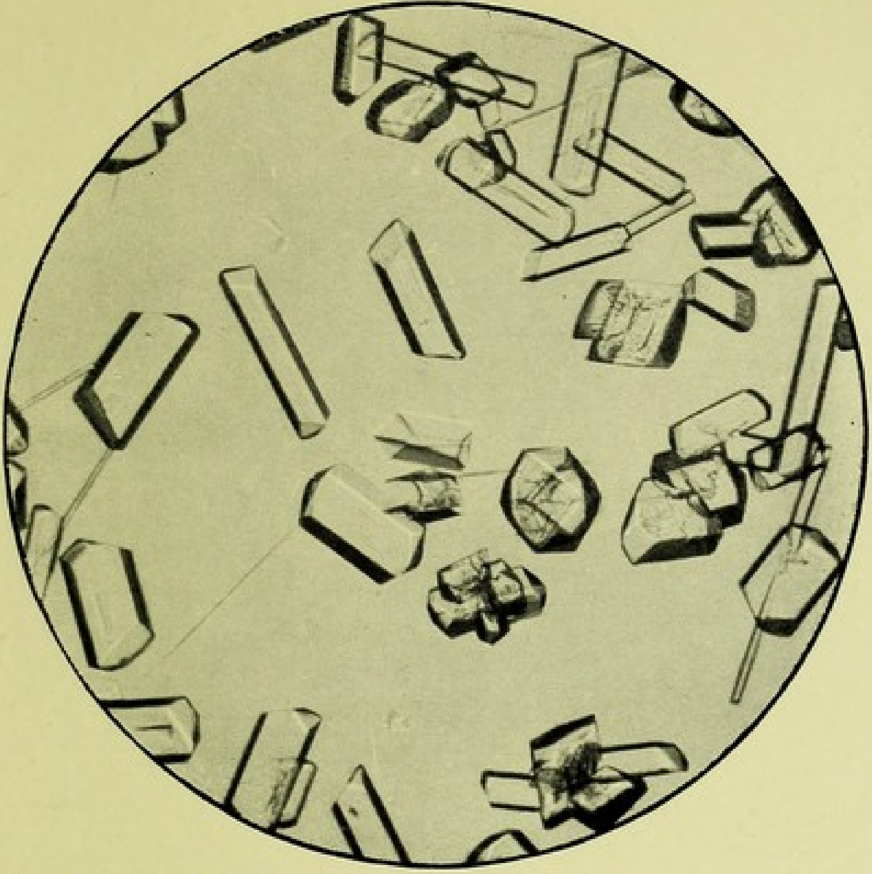

FIG. 30.—Monoclinic Crystals of Ammonium Magnesium Sulphate.

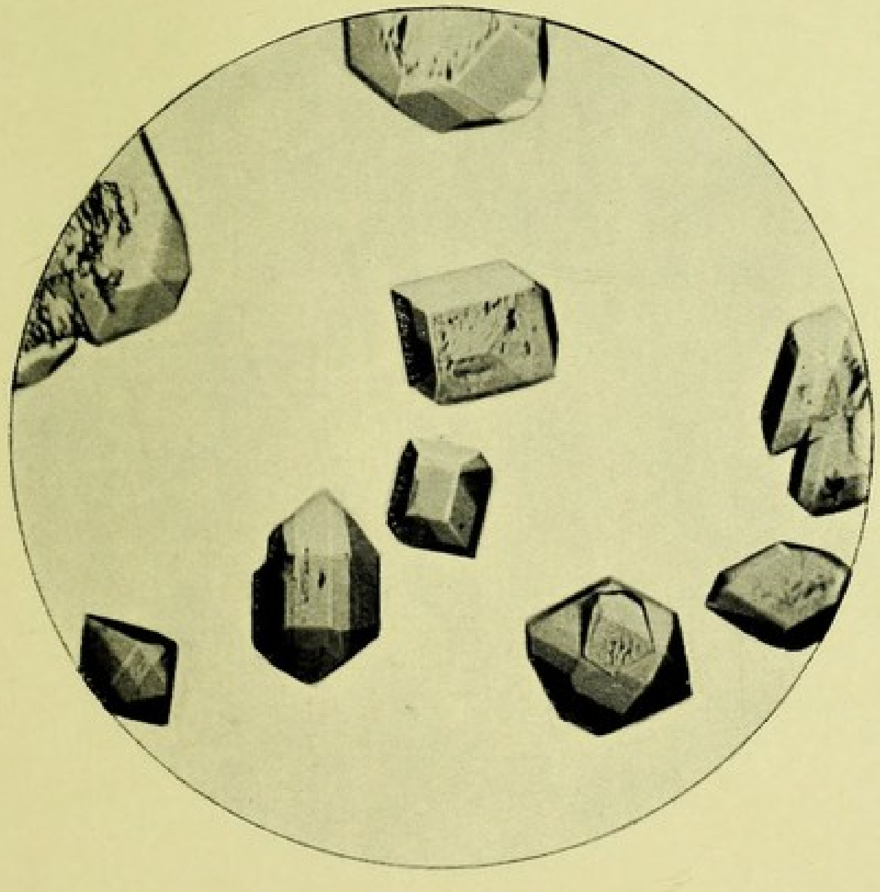

FIG. 31.—Monoclinic Crystals of Sodium Potassium Carbonate.

MONOCLINIC CRYSTALS GROWING FROM SOLUTION.

[*To face p.* 44.

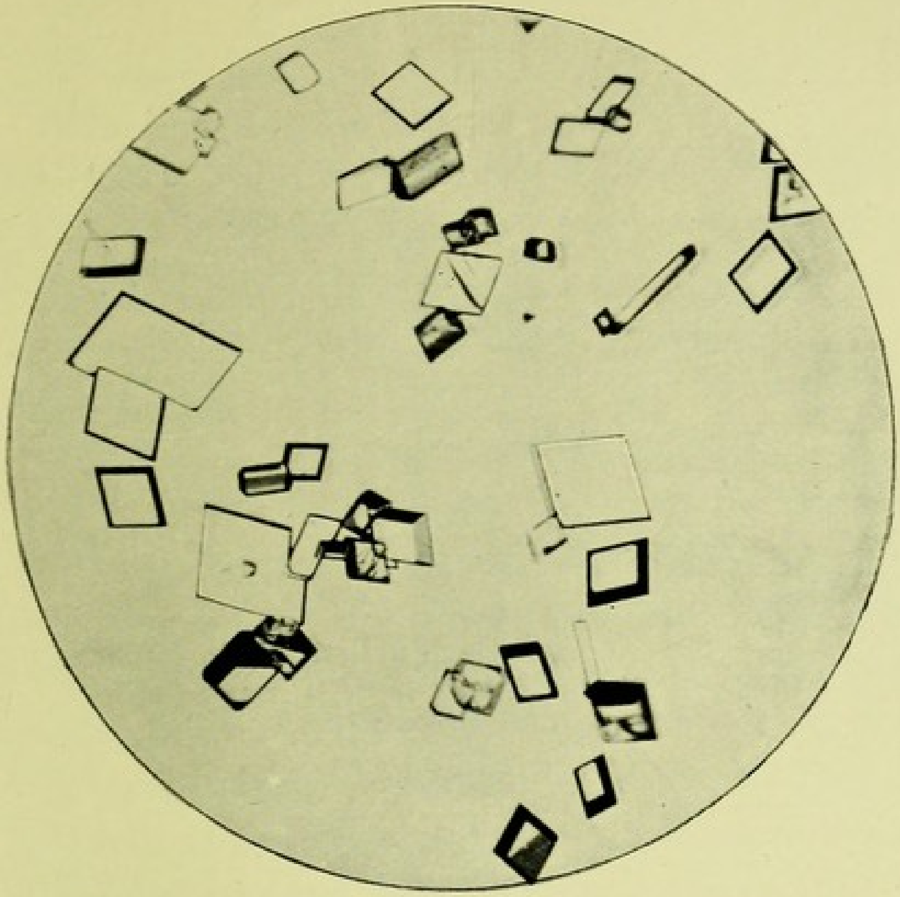

FIG. 32.—Triclinic Crystals of Potassium Ferricyanide.

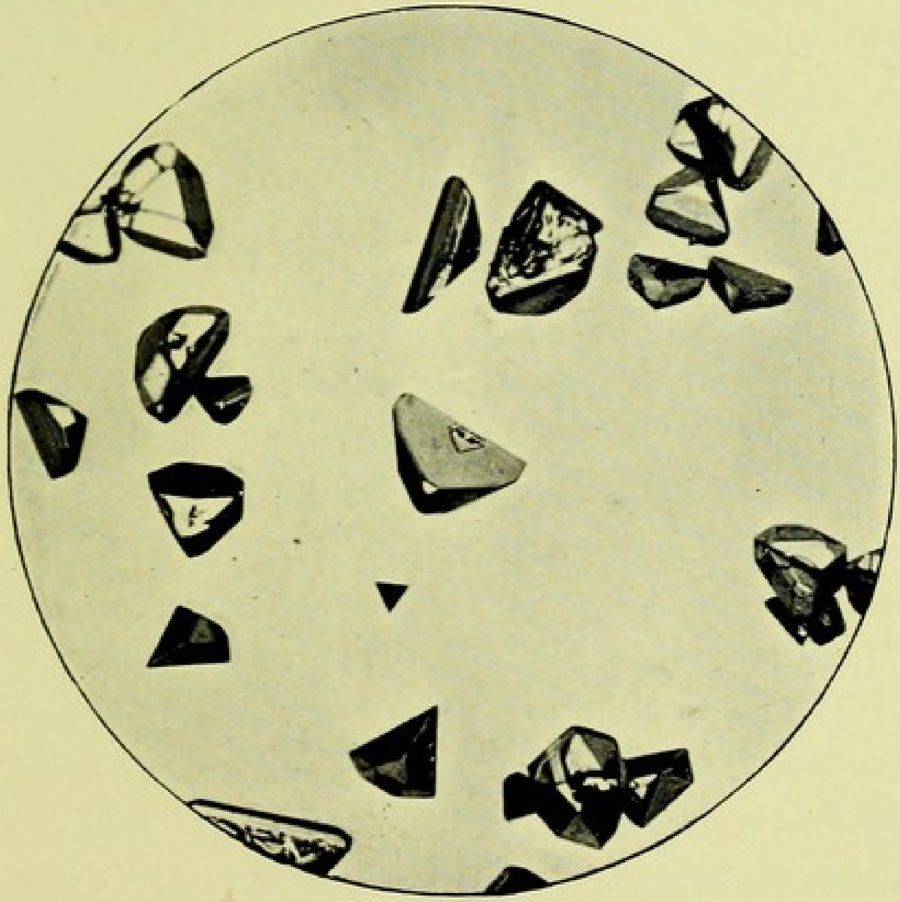

FIG. 33.—Tetrahedral Crystals of Sodium Sulphantimoniate, Cubic Class 28.

CRYSTALS GROWING FROM SOLUTION.

To follow Pl VII.

but the forms shown of those salts on the slides represented in Figs. 28 and 29 are chiefly those which are also common to the holohedral classes of their respective systems, and the lower class symmetry is not emphasised. But here in Fig. 33, representing Schlippe's salt, sodium sulphantimoniate, $Na_3SbS_4 . 9H_2O$, we have very clear development of the tetrahedron, belonging to the lowest of the five classes (class 28) of the cubic system. The crystals are almost all combinations of two complementary tetrahedra, one of which is developed so very much more than the other that the faces of the latter only appear as minute replacements at the corners of the predominating tetrahedron.

This is the last for the present of these fascinating growths of crystals under the microscope, but three more will be given subsequently, in Figs. 99 and 100, on Plate XXI., and Fig. 101, Plate XI., to illustrate crystallisation from metastable and labile solutions.

Fig. 34, Plate IX., represents another kind of phenomenon, equally instructive. It shows a field in a crystal of quartz, as seen under the same power of the microscope, a one-inch objective with small stop and an ordinary low power eyepiece. Just above and to the left of the centre of the field is a cavity, the shape of which is remarkable, for it is that of a quartz crystal, a hexagonal prism terminated by rhombohedral faces. The cavity is filled with a saturated solution of salt, except for a bubble of water vapour, and a beautiful little cube of sodium chloride which has crystallised out from the solution. This slide, therefore, gives us an example of a natural cubic crystal, and also an indication of the shape of quartz crystals, the cavity itself being a kind of negative quartz crystal. The crystal in which it occurs must have been formed very deep down in a reservoir of molten material beneath a volcano, under the great pressure of superincumbent rock masses. It was probably one of the quartz crystals of a granite rock which had crystallised under these conditions. Almost every crystal of quartz found in such granite rocks displays thousands of small cavities filled with liquid and a bubble, although it is very rare to find one with so good a cube of salt and having the configuration of a quartz crystal for the shape of the cavity. Many such cavities, however, contain as the liquid compressed carbonic acid, the very fact of the carbonic acid being in the liquefied state affording ample evidence of the pressure under which the crystal was formed. The proof that the liquid is carbonic acid in these cases is afforded by the fact that when the crystal is warmed to 32°C., the critical temperature of carbon dioxide, under which it can no longer remain liquid, but must become a gas, the bubble disappears and the cavity becomes filled with gas. Carbonic acid cavities are readily recognised, inasmuch as the bubble is extremely mobile, and is normally in a state of movement on the very slightest provocation.

The liquid cavity in the remarkable quartz crystal illustrated in Fig. 34, and the bubble of vapour formed on cooling, and consequent contraction of the liquid more than the solid quartz (the thermal dilatation of liquids being usually greater than that of solids) when it was no longer able to fill the cavity, remind one of the beautiful water flowers formed for the contrary

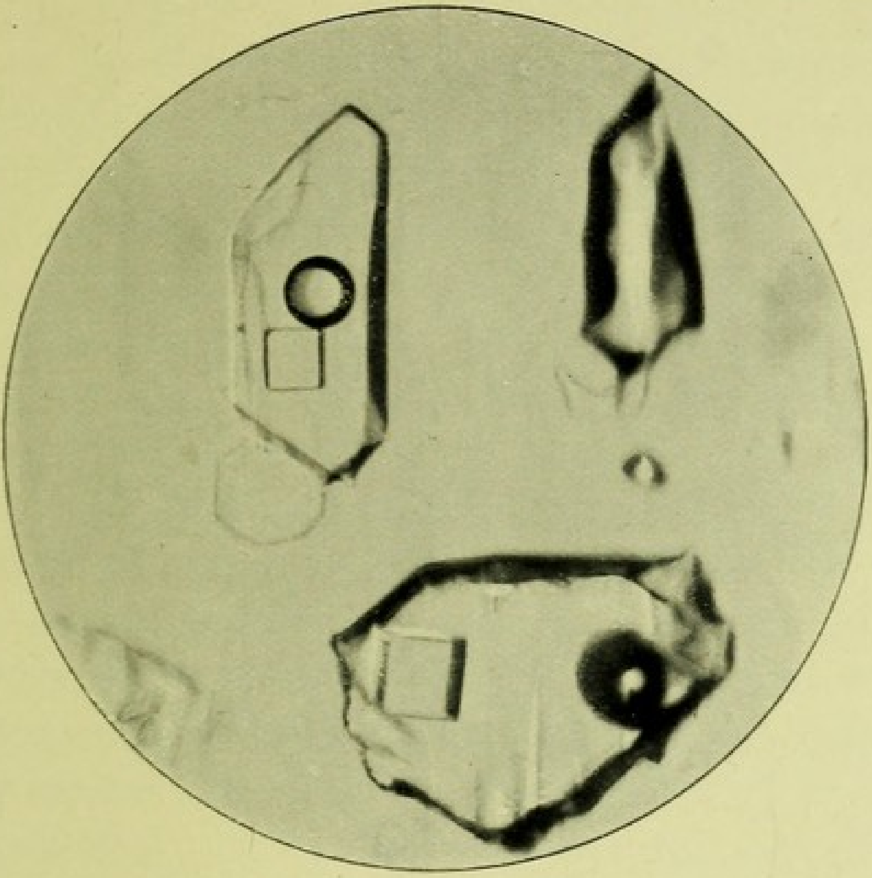

FIG. 34.—Liquid Cavities in Quartz Crystal (Trigonal) containing Saturated Solution and Cubic Crystals of Sodium Chloride.

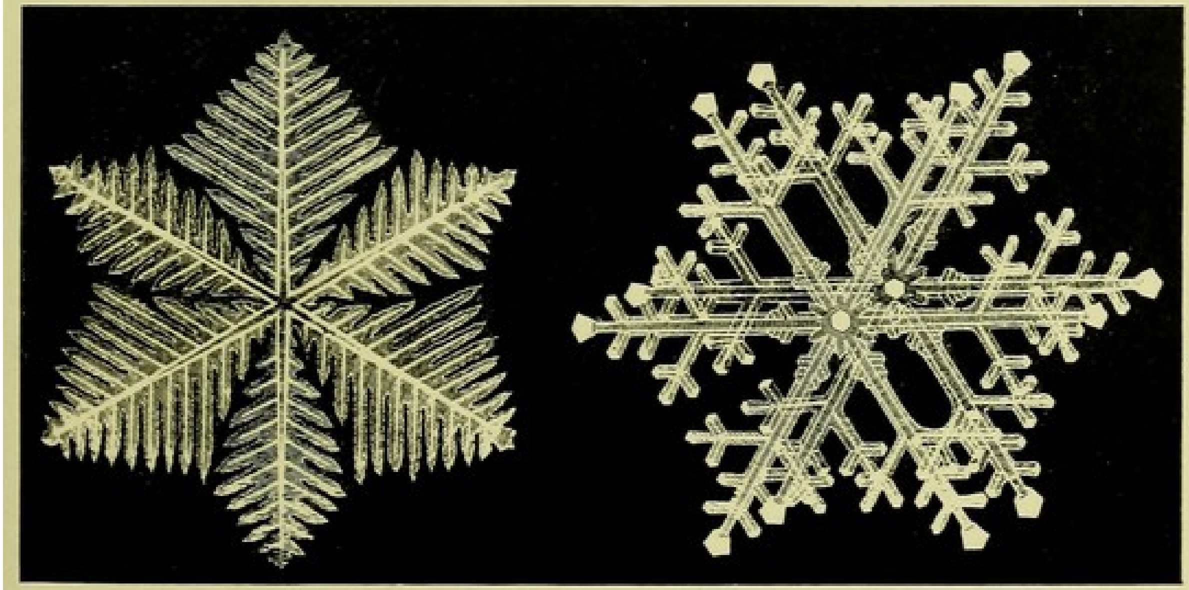

FIG. 36.—Two characteristic Forms of Snow Crystals (Trigonal).

To face p. **46.**

reason in ice on passing a beam of light through a slab, owing to the warming effect of the accompanying heat rays. Water crystallises like quartz, in the trigonal system, its normal forms being the hexagonal prism and the rhombohedron. A slab of lake ice is generally a huge crystal plate perpendicular to the trigonal axis, or in the case of disturbed growth an interlacing mass of such crystals, all perpendicular to the optic axis, the axis of the hexagonal prism and of trigonal symmetry. When the heat rays from the lantern pass through such a slab of ice, the surface of which is focussed on the screen by a projecting lens, they cause the ice to begin to melt in numerous spots in the interior of the slab simultaneously; and the structure of the crystal is revealed by the operation occurring with production of cavities taking the shape of hexagonal stars, which when focussed appear on the screen as shown in Fig. 35. They are filled with water except for a bubble (vacuole), which contains only water vapour. For the liquid water occupies less room than did the ice from which it was produced, owing to the well-known fact that water expands on freezing. This abnormal expansion with cooling begins at the temperature of the maximum density of water,

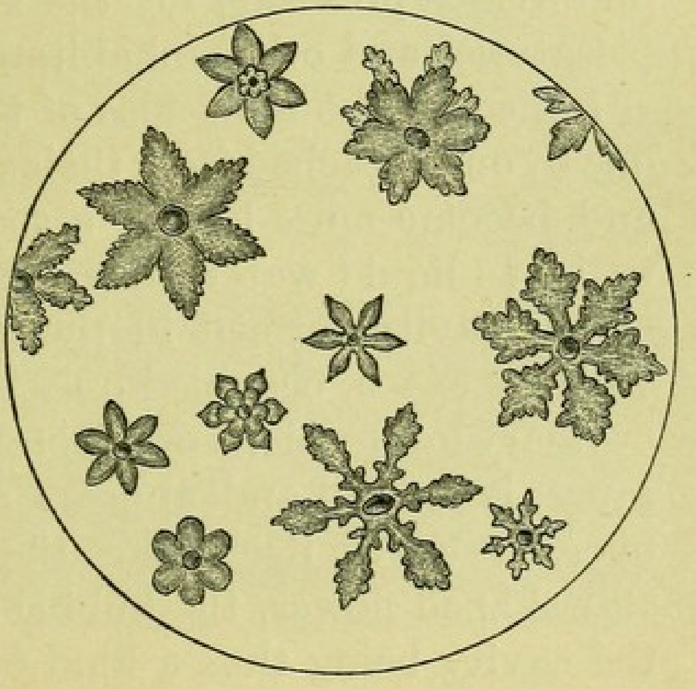

Fig. 35.—Negative Ice Crystals, or "Water Flowers," in Ice.

4° C., and proceeds steadily until the freezing point 0° is reached, when, at the moment of crystallisation, the mass suddenly increases in volume by as much as 10 per cent. This expansive leap when the molecules of water marshal themselves into the organised order of the homogeneous structure, that of the space-lattice of the trigonal (rhombohedral) system, is one of the most remarkable phenomena in nature, and its exceptional character, so contrary to the usual contraction on solidification of a liquid, is of vital moment to aquatic life. For the layer of ice formed, being lighter than water, floats on the surface of the latter, and thus forms a protective layer and prevents to a large extent further freezing, except as a slow thickening of the layer, the total freezing of the water of a lake or river being rendered practically impossible, an obvious provision for the security of life of the piscatorial and other inhabitants of the waters.

Hence, as the molecules of the substance H_2O are one by one detached from their solid assemblage as ice, and become more loosely associated as the less voluminous liquid water, they cannot occupy the whole of the cavity formed in the solid ice, and a small vacuous space, occupied only by water vapour at its ordinary low tension corresponding to the low temperature, is formed and appears as the bubble. Moreover, the cavity itself takes the shape of a hexagonal star-shaped flower, the bubble showing at its centre, the cavity being thus a kind of negative ice crystal, like the negative quartz crystal shown in Fig. 34. Apparently in the production of these cavities, just as in the production of the well-known etched

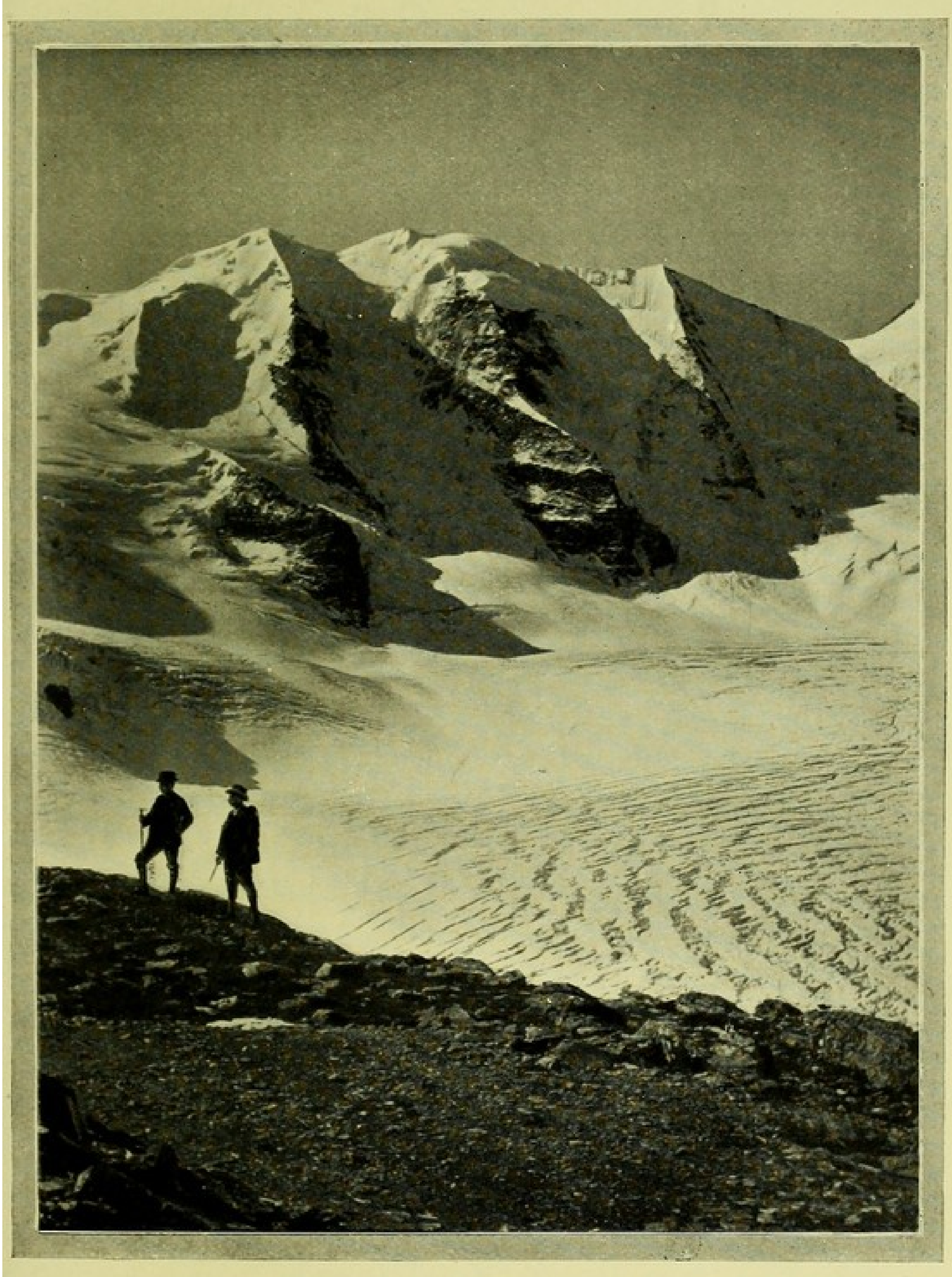

FIG. 37.—Piz Palü and Snow-field of the Pers Glacier, from the Diavolezza Pass, Upper Engadine.

(From a Photograph by the author.)

To face p 48.

figures on crystal faces by the application of a minute quantity of a solvent for the crystal substance, the crystal edifice is taken down, molecule by molecule, in a regular manner, resulting in the formation of a cavity showing the symmetry of the space-lattice which is present in the crystal structure.

The water flowers of Fig. 35 remind one very much of snow crystals, two of which, re-engraved from the wonderfully careful drawings of the late Mr Glaisher, are represented in Fig. 36, Plate IX. They all exhibit the symmetry of the hexagonal prism, which is equally a form of the trigonal system as it is of the hexagonal system. The snow crystals, being formed from water vapour condensed in the cold upper layers of the atmosphere, appear more or less as skeleton crystals, owing to the rarity of the semi-gaseous material condensed, compared with the extent of the space in which the crystallisation occurs. Indeed the exquisite tracery of these snow crystals appears to afford a visual proof of the existence of the trigonal-hexagonal space-lattice as the framework of the crystal structure of ice. When one considers the countless numbers of such beautiful gems of nature's handiwork massed together on an extensive snow-field of the higher Alps—such as that of the Piz Palü in the Upper Engadine, shown in Fig. 37, Plate X., as seen from the Diavolezza Pass—produced in the pure air of the higher regions of the atmosphere, and frequently seen by the early morning climber lying uninjured in all their beauty on the surface of the snow-field, one is lost in amazement at the prodigality displayed in the broadcast distribution of such peerless gems.

CHAPTER V

HOW CRYSTALS ARE DESCRIBED. THE SIMPLE LAW LIMITING THE NUMBER OF POSSIBLE FORMS.

THE most wonderful of all the laws relating to crystals is the one already briefly referred to which limits and regulates the possible positions of faces, within the lines of symmetry which have been indicated in the last chapter. Having laid down the rules of symmetry, it might be thought that any planes which obey these laws, as regards their mode of repetition about the planes and axes of symmetry, would be possible. But as a matter of fact this is not so, only a very few planes inclined at certain definite angles, repeated in accordance with the symmetry, being ever found actually developed. The reason for this is of far-reaching importance, for it reveals to us the certainty that a crystal is a homogeneous structure composed of definite structural units of tangible size, probably the chemical molecules, built up on the plan of one of the fourteen space-lattices made known to us by Bravais, and to be referred to more fully in Chapter VIII. In order to render this fundamental law comprehensible, it will be essential to explain in a few simple words how the crystallographer identifies and labels the numerous faces on a crystal, in short, how he describes a crystal, in a manner which shall be understood immediately by everybody who has studied the very simple rules of the convention.

It is a matter of common knowledge that the mathematical geometrician defines the position of any point in space with reference to three planes, which in the simplest case are all mutually at right angles to each other like the faces of a cube, and which intersect in three rectangular axes *a*, *b*, *c*, the third *c* being the vertical axis, *b* the lateral one, and *a* the front-and-back axis. The distances of the point from the three reference planes, as measured by the lengths of the three lines drawn from the point to the planes parallel to the three axes of intersection, at once gives him what he calls the "co-ordinates" of the point, which absolutely define its position. In the same way we can imagine three axes drawn within the crystal, by which not only the position of any point on any face of the crystal may be located, but which may be used more simply still to fix the position of the face itself. The directions chosen as those of the three axes are the edges of intersection of three of the best developed faces.

If there are three such faces inclined at right angles they would be chosen in preference to all others, as they would certainly prove to be faces of prime significance as regards the symmetry of the crystal. If there are no such rectangularly inclined faces developed on the crystal, then the three best developed faces nearest to 90° to each other are chosen, the two factors of nearness to rectangularity and excellence of development being simultaneously borne in mind in making the choice of axial planes, and discretion used.

If the crystal belong to the cubic, tetragonal, or rhombic systems, for instance, three faces meeting each other rectangularly are possible planes on the crystal, and will very frequently be found actually developed; such would obviously be chosen as the axial planes. The edges of the cube, or of the tetragonal or rectangular rhombic prism, will be the directions of the crystallographic axes in this case, and we can imagine them moved parallel to themselves until the common centre of intersection, the "origin" of the analytical geometrician, will occupy the centre of the crystal, and the faces of the latter be built up symmetrically about it. When the crystal is cubic, the three axes will be of equal length, as shown in Fig. 38; if tetragonal, the two horizontal axes will be equal, but will differ in length from the vertical axis, as represented in Fig. 39. If the crystal be rhombic, all three axes will be of different lengths, as indicated in Fig. 40, which represents the axes and axial planes

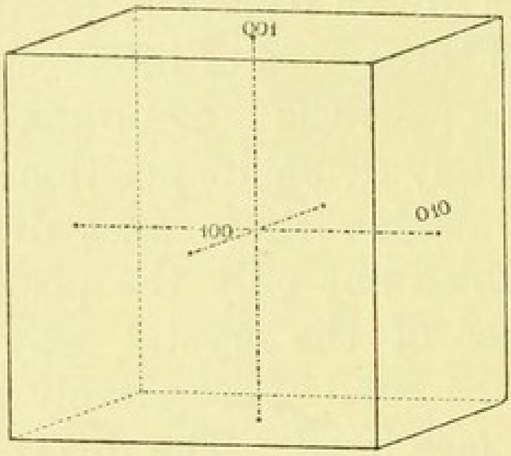

Fig. 38.—The Cube and its Three Equal Rectangular Axes.

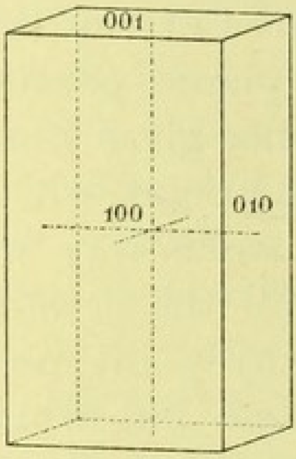

Fig. 39.—Tetragonal Prism and its three Rectangular Axes.

of an actual rhombic substance, topaz, for which the lateral axis *b* and vertical axis *c* are nearly but not quite equal, while the front-and-back axis *a* is very different.

When the crystal is of monoclinic symmetry, as in Fig. 41, three axes will similarly be found as the intersection of three principal parallel pairs of faces, but two of them will be inclined at an angle other than 90° to each other, while the third, the lateral one in Fig. 41, will be at right angles to those first two and to the plane containing them ; moreover, all three are unequal in length. In the case of a triclinic crystal, shown in Fig. 42, however, there can be no right angles, and the intersections of three important faces meeting each other at angles as near 90° as possible are chosen as the axes, regard being had to both factors of approximation to rectangularity and importance of development. These triclinic axes are the most general type of crystal axes, for not only are the angles not right angles, but the lengths of the axes are also unequal.

The cases of the hexagonal and trigonal systems are somewhat special. The hexagonal has four such axes, as represented in Fig. 43, the lines of intersection of the faces of the hexagonal prism closed by a pair of perpendicular terminal planes, namely, one vertical axis parallel to the vertical edges, and three horizontal axes inclined at 120° to each other, and parallel to the pair of basal plane faces, equal to each other in length, but different from the length of the vertical axis. The hexagonal axial-plane prism shown in Fig. 43 is known as one of the first order. The hexagonal prism corresponding to the tetragonal one of Fig. 39, in which the

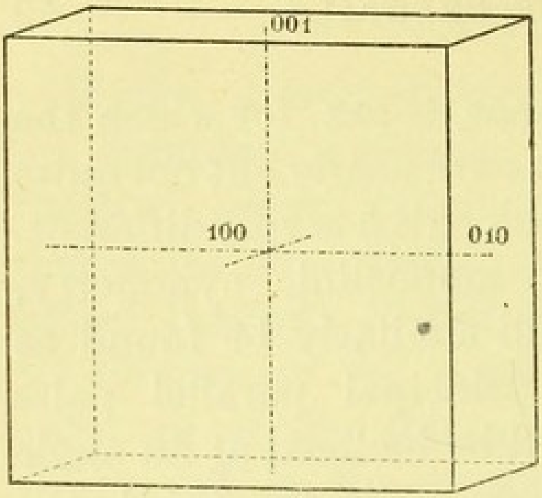

FIG. 40.—Axial Planes of a Rhombic Crystal.

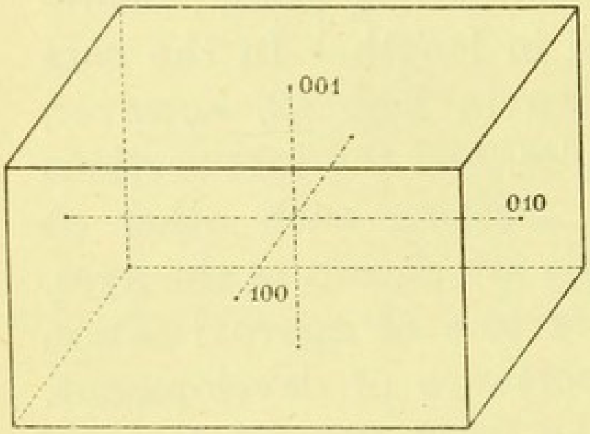

FIG. 41.—Axial Planes of a Monoclinic Crystal.

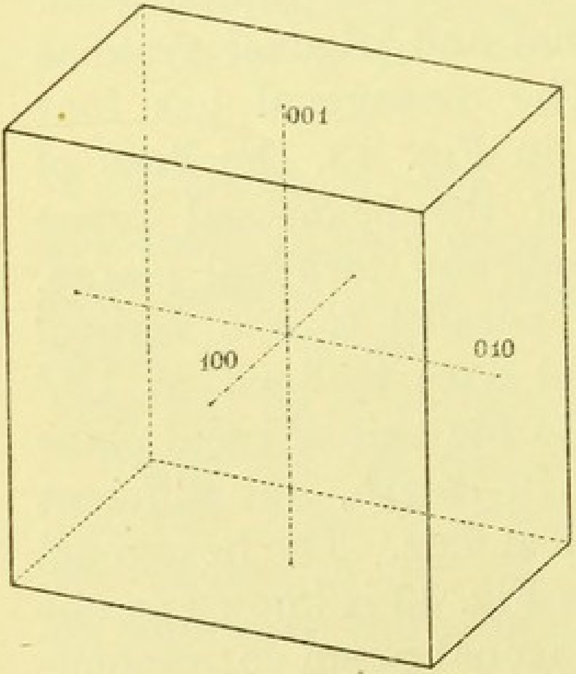

FIG. 42.—Axial Planes of a Triclinic Crystal.

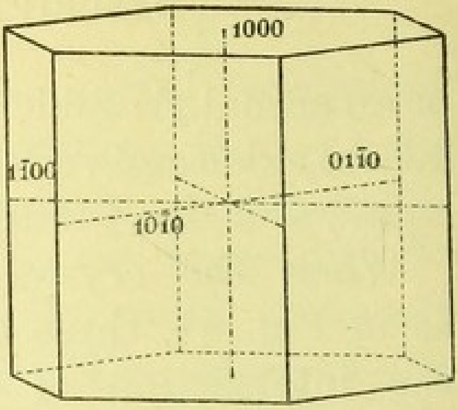

FIG. 43.—Hexagonal Prism of the First Order and its Four Axes.

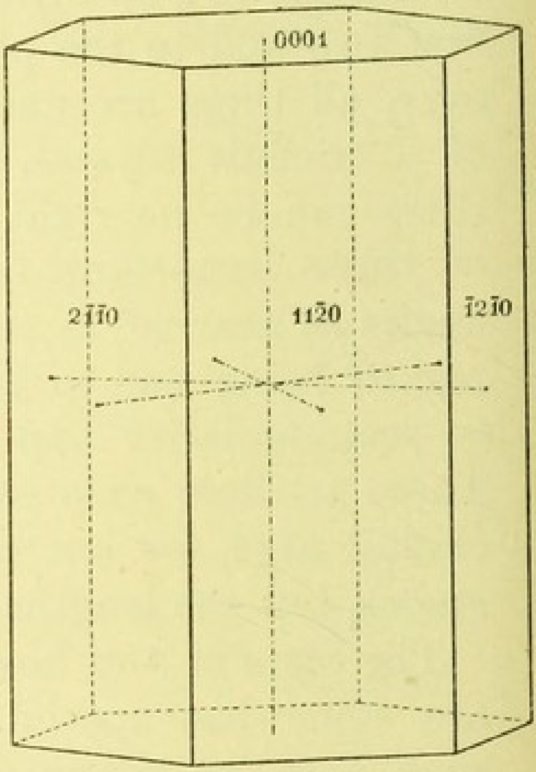

FIG. 44.—Hexagonal Prism of the Second Order.

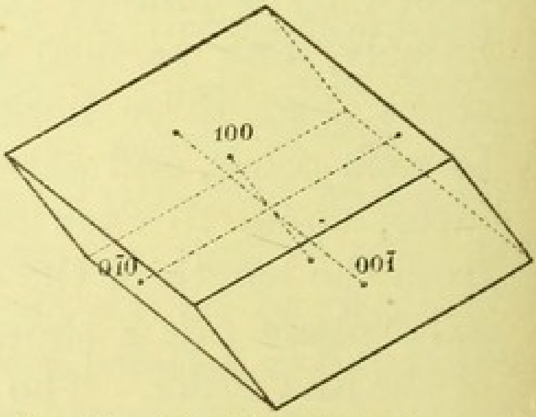

FIG. 45.—The Rhombohedron and its Three Equal Axes.

axes emerge in the centres of the faces, is said to be of the second order, and is shown in Fig. 44. The trigonal system of crystals is best described with reference to three equal but not rectangular axes, parallel to the faces of the rhombohedron, one of the principal forms of the system, so well seen in Iceland spar, and illustrated in Fig. 45. The rhombohedron may be regarded as a cube resting on one of its corners (solid angles), with the diagonal line joining this to the opposite corner vertical, and the cube then deformed by flattening or elongating it along the direction of this diagonal. The edges meeting at the ends of this vertical diagonal are then the directions of the three trigonal crystallographic axes.

In this last illustration the vertical direction of the altered diagonal is that of the trigonal axis of symmetry, for the rhombohedron is brought into apparent coincidence with itself again if rotated for 120° round this direction. But although a symmetry axis, this is not a crystallographic axis of reference. It is not shown in Fig. 45, therefore, but is given in Fig. 19. On the other hand, the singular vertical axis of reference of the tetragonal and hexagonal systems is identical with the tetragonal or hexagonal axis of symmetry of these systems, and the three crystallographic axes of reference of the cube are identical with the three tetragonal axes of symmetry of the cubic system. In the rhombic system also, the three rectangular axes of reference are identical with the three digonal axes of symmetry, and in the monoclinic system the one axis of reference which is normal to the plane of the two inclined axes is the unique digonal axis of symmetry of that system.

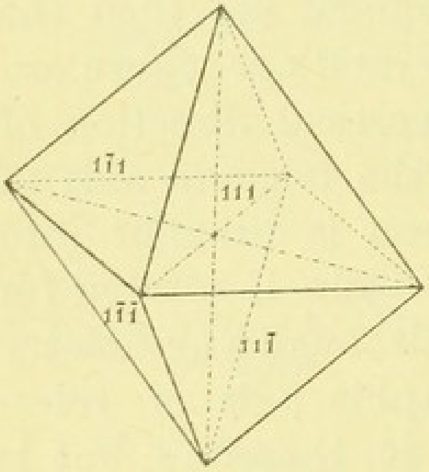

FIG. 46.—Triclinic Equivalent of the Octahedron.

Having thus evolved a scientific scheme of reference axes for the faces of a crystal, it is necessary in all the systems other than the cubic and trigonal, in which the axes are of equal lengths, to devise a mode of arriving at the relative lengths of the axes ; for on this depends the mode of determining the positions of the various faces, other than the three parallel pairs (or four in the case of the hexagonal system) chosen as the axial planes. This is very simply done by choosing a fourth important face inclined to all three axes, when one of this character is developed, as very frequently happens, as the determinative face or plane fixing the unit lengths of the axes. When no such face is present on the crystal, two others can usually be found, each of which is inclined to two different axes, so that between them all three axial lengths are determined. The faces of the octahedron, of the primary tetragonal pyramid and the primary rhombic pyramid, and of the corresponding forms of the other systems, are such determinative planes, fixing the lengths of the axes. This fact will be clear from the typical illustration of the most general of these primary or "parametral" forms, the triclinic equivalent of the octahedron, given in Fig. 46, the faces being obviously obtained by joining the points marking unit lengths of the three axes.

Having thus settled the directions of the crystallographic axes and their lengths, it is the next step which reveals the remarkable law to which reference was made at the opening of this chapter. For we find that all other faces on the crystal, however complicated and rich in faces it may be, cut off lengths from the axes which are represented by low whole numbers, that is, either 2, 3, 4, or possibly 5, and very rarely more than 6 unit lengths. By far the greater number of faces do not cut off more than three unit-lengths from any axis. Prof. Miller of Cambridge, in the year 1839, gave us a most valuable mode of labelling and distinguishing the various faces by a symbol involving these three values, employed, however, not directly but in an indirect yet very simple manner. If m, n, r be the three numbers expressing the intercepts cut off by a face on the three axes, a, b, c respectively, and if the Millerian index numbers be represented by h, k, l, then—

$$m=\frac{a}{h}, \qquad n=\frac{b}{k}, \qquad r=\frac{c}{l},$$

or,

$$h=\frac{a}{m}, \qquad k=\frac{b}{n}, \qquad l=\frac{c}{r}.$$

Each figure or "index" of the Millerian symbol is thus inversely proportional to the length of the intercept on the axis concerned. The intercepts themselves are used as symbols in another mode of labelling crystal faces, suggested by Weiss, but this method proves too cumbersome in practice.

The Millerian symbol of a face is always placed within ordinary curved brackets ( ), but if the symbol is to stand for the whole set of faces composing the form, the brackets are of the type { }.

Thus the Millerian symbol of the fourth face (that in the top-right front octant), determinative of the unit axial lengths, is (111), as shown in Fig. 46, the face in question being marked with this symbol; while the symbol {111} indicates the set of faces of the whole or such part of the double pyramid as composes the unit form. In the triclinic system this form only consists of the face (111) and the parallel one $(\bar{1}\bar{1}\bar{1})$, but in the case of the regular octahedron of the cubic system it embraces all the eight faces. The triclinic octahedron, Fig. 46, is thus made up of four forms of two faces each. A negative sign over an index indicates interception on the axis a behind the centre, on the axis b to the left of the centre, or on the vertical axis c below the centre.

To take an actual example, suppose a face other than the primary one to make the intercepts on the axes 4, 2, 1; in this case $h=a/4$, $k=b/2$, and $l=c/1$, that is, when referred to the fundamental primary form for which a, b, c are each unity, $h=\frac{1}{4}$, $k=\frac{1}{2}$, $l=1$, or, bringing them to whole numbers by multiplying by 4, $h=1$, $k=2$, $c=4$, and the symbol in Millerian notation is (124). Again, suppose we wish to find the intercepts on the three cubic axes made by the face (321) of the hexakis octahedron shown in Fig. 21. To get each intercept we multiply together the two other Millerian indices, and if necessary afterwards reduce the three figures obtained to their simplest relative values. For the face (321) we obtain 2, 3, 6. This means that the face (321) in the top-right-front octant of the hexakis octahedron cuts off two unit lengths of axis a, three unit lengths of axis b, and six unit lengths of axis *c*. No fractional parts thus ever enter into the relations of the axial lengths intercepted by any face on a crystal, and the whole numbers representing these relations are always small, the number 6 being the usual limit.

This important law is known as the "Law of Rational Indices," and is the corner-stone of crystallography. A forecast of it was given in Chapter III., in describing how it was first discovered by Haüy, and it was shown how impressed Haüy was with its obvious significance as an indication of the brick-like nature of the crystal structure. What the "bricks" were, Haüy was not in a position to ascertain with certainty, as chemistry was in its infancy, and Dalton's atomic theory had not then been proposed.

That Haüy had a shrewd idea, however, that the structural units were the chemical molecules, and that while the main lines of symmetry were determined by the arrangement of the molecules its details were settled by the arrangement of the atoms in the molecules, is clear to any one who reads his 1784 "Essai" and 1801 "Traité," and interprets his *molécules intégrantes* and *élémentaires* in the light of our knowledge of to-day.

Before we pass on, however, to consider the modern development of the real meaning of the law of rational indices, as revealed by recent work on the internal structure of crystals, it will be well to consider first, in the next chapter, a few more essential facts as to crystal symmetry, and the current mode of constructing a comprehensive, yet simple, plan of the faces present on a crystal.

CHAPTER VI

THE DISTRIBUTION OF CRYSTAL FACES IN ZONES, AND THE MODE OF CONSTRUCTING A PLAN OF THE FACES.

It will have been clear from the facts related in the previous chapters that the salient property possessed by all crystals, when ideal development is permitted by the circumstances of their growth, and the substance is not one of unusual softness or liable to ready distortion, is that the exterior form consists of and is defined by truly plane faces inclined to each other at angles which are specific and characteristic for each definite chemical substance; and that these angles are in accordance with the symmetry of some particular one of the thirty-two classes of crystals, and are such as cause the indices of the faces concerned to be rational small numbers.

It will also be clear that, given the presence of any face other than the three axial planes, the symmetry of the class--supposing the crystal to exhibit some development of symmetry and not to belong to class 32, the general case possessing no symmetry—will require the repetition of this face a definite number of times on other parts of the crystal. Such a set of faces possessing the same symmetry value we have already learnt to call a " Form," and the faces composing it will have the same Millerian index numbers in their symbols, but differently arranged and with negative signs over those which relate to the interception of the back part of the *a* axis, the left part of the *b* axis, or the lower part of the vertical *c* axis; that is, parts to the front and right, and above, the centre of intersection of the three crystal axes are considered as the positive parts of those axes.

A form, if of general character, that is, if composed of faces each of which is inclined to all three axes, will comprise more faces the higher the symmetry. Thus, in the cubic system, the form shown in Fig. 21, the hexakis octahedron, comprises as many as forty-eight faces, all covered by the form symbol {321}; while in the rhombic system the highest number of faces in a form is eight, in the monoclinic only four, and in the triclinic system two. It will also have become clear that the law of rational indices limits the number of forms possible of any one type. For instance, very few hexakis octahedra are known, the most frequently occurring ones besides {321} being {421}, {531}, and {543}. Forms, of any class, possessing higher indices than these are very rare, especially in the systems of lower symmetry.

We next come to a further very interesting fact about crystals. Let us imagine a crystal, on which the faces are fairly evenly developed, to be placed in the middle of a sphere of jelly, as indicated in Fig. 47 (reproduced from a Memoir by the late Prof. Penfield), so that the centre or origin of the axial system of the crystal and the centre of the sphere coincide. Let us now further imagine that long needles are stuck through the jelly and the crystal, one perpendicular to each crystal face, and so as to reach the centre. The crystal represented in Fig. 47 is a combination of the cube *a*, octahedron *o*, and rhombic dodecahedron *d*. If such a thing as we have imagined were possible, we should find that the needles would emerge at the surface of the sphere in points which would lie on great circles, that is, on circles which represent the intersection of the sphere by planes passing through the centre. Moreover, the points would be distributed along these circles at regularly recurring angular positions, corresponding to the symmetry of the crystal. If the crystal belonged to one of the higher systems of symmetry, it would happen that four of the points on at least one of these great circles, and possibly on three of them, would be 90° apart, that is, would be at the ends of rectangular diameters, which would most likely be the axes of reference. The other points would be distributed symmetrically on each side of these four points.

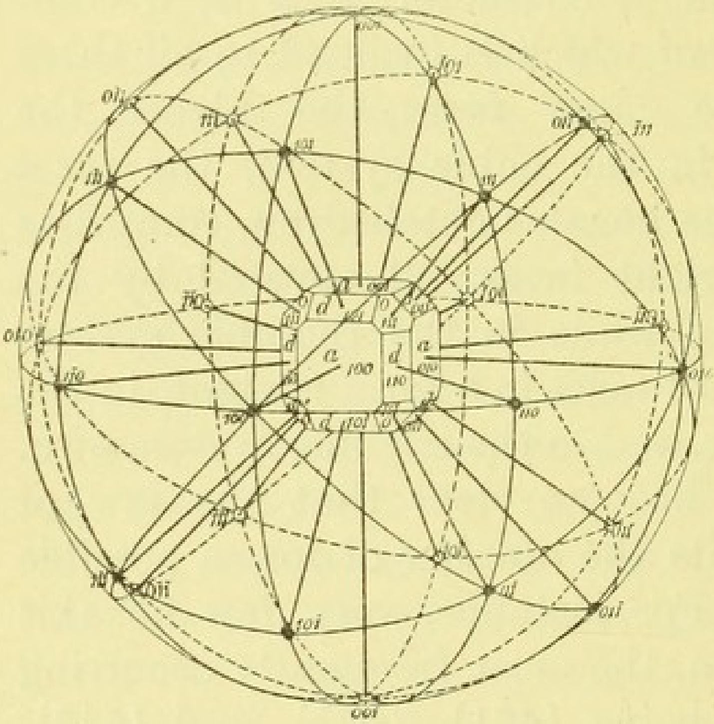

Fig. 47.—The Spherical Projection.

The great circles on which the points are thus symmetrically distributed—and they may legitimately be taken to represent the faces, for tangent planes to the sphere at these points would be parallel to the faces—are known as "zone circles," and the faces represented by the points on any one of them form a "zone." Now a zone of faces has this practical property, that when the crystal is supported so as to be rotatable about the zone axis—which is parallel to the edges of intersection of all the faces composing the zone, and is the normal to the plane of the great circle representing the zone—and a telescope is directed towards the crystal perpendicularly to the zone axis, while a bright object such as an illuminated slit is arranged conveniently so as to be reflected from any face of the crystal into the telescope, an image of it being thus visible in the latter, then it will be found that on rotating the crystal a similar image will be seen reflected in the telescope from every face of the zone in turn. Moreover, when the crystal is mounted on a graduated circle, the angle of rotation between the positions of adjustment to the cross-wires of the telescope of any two successive images, reflected from adjacent faces of the crystal, is actually the angle between the two points representing the faces concerned on the zone circle, and is the supplement of the internal dihedral angle between the two crystal faces themselves. It is, in fact, the angle between the normals (perpendiculars) to the two faces, the angle which is measured on the goniometer.

This is, indeed, the very simple principle of the reflecting goniometer, invented by Wollaston in the year 1809, and which in its modern improved form is the all-important principal instrument of the crystallographer's laboratory. The work with it consists largely in the measurement of the angles between the faces in all the principal zones developed on the crystal. The very fact, however, that crystal faces occur so absolutely accurately in zones immeasurably lightens the labours of the crystallographer, and is one of prime importance.

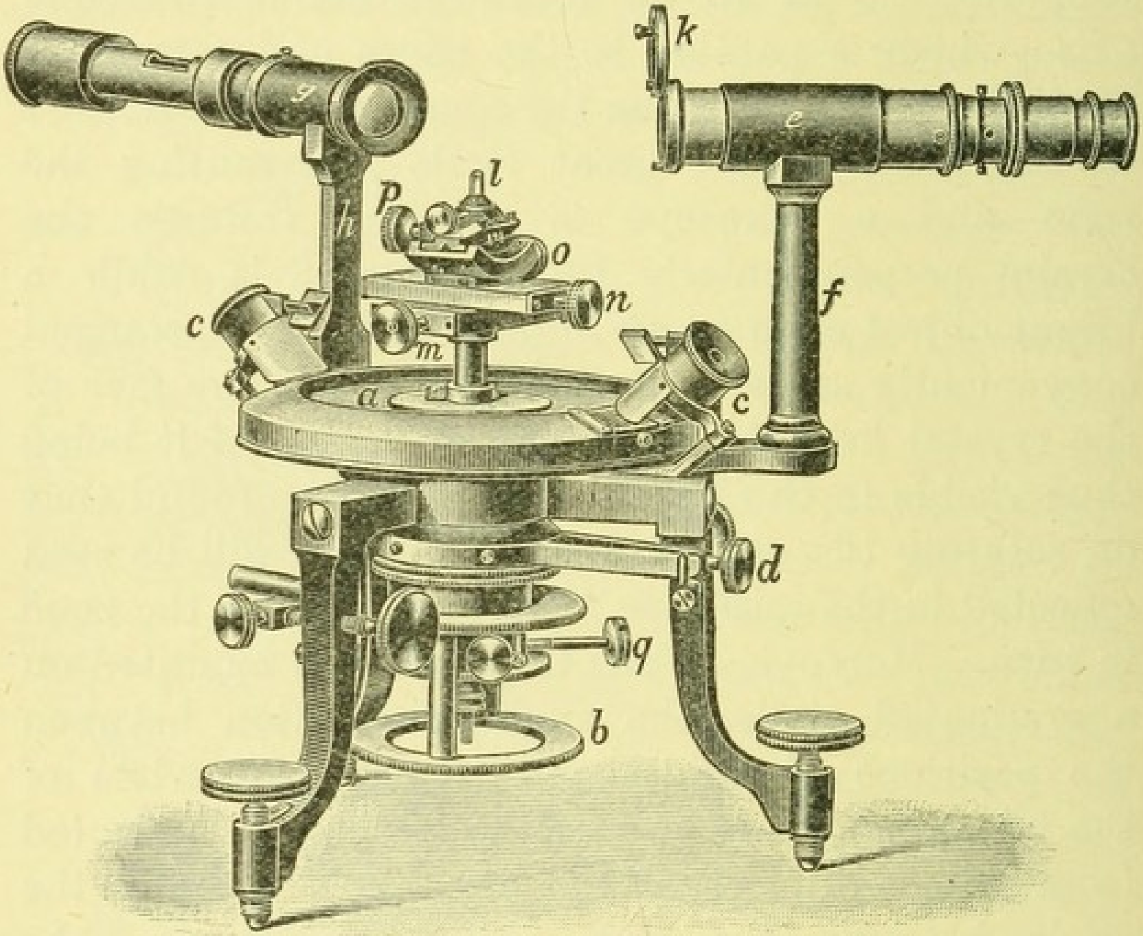

Fig. 48.—The Reflecting Goniometer.

The most accurate and convenient modern form of reflecting goniometer, reading to half-minutes of arc, and provided with a delicate adjusting apparatus for the crystal, is shown in Fig. 48. It is constructed by Fuess of Berlin.

The graduated circle *a* is horizontal and is divided directly to 15′, the verniers enabling the readings to be carried further either to single minutes, which is all that is usually necessary, or to half-minutes in the cases of very perfect crystals. The divided circle is rotated by means of the ring *b* situated below, and the reading of the verniers is accomplished with the aid of the microscopes *c*. The circle which carries the verniers is not fixed, except when this is done deliberately by means of the clamping screw *d*, but rotates with the telescope *e* to which it is rigidly attached by means of an arm and a column *f*. A fine adjustment is provided with the clamping arrangement, so that the telescope can be adjusted delicately with respect to the divided circle. Both telescope and collimator are rigidly fixed at about 120° from each other during the actual measurements. The collimator *g* is carried on a column *h* definitely fixed to one of the legs (the back one in Fig. 48) of the main basal tripod of the instrument. The signal slit of the collimator is carried at the focus of the objective about the middle of the tube *g*, the outer half of the latter being an illumination tube carrying a condensing lens to concentrate the rays of light from the goniometer lamp on the slit. The latter is not of the usual rectilinear character, but composed of two circular-arc jaws, so that, while narrow in the middle part like an ordinary spectroscope slit, it is much broader at the two ends in order to be much more readily visible; the central part is narrow in order to enable fine adjustment to the vertical cross-wire of the telescope to be readily and accurately carried out. The shape of this signal-slit will be gathered from the images of the slit shown in Fig. 61 (page 126) in Chapter X. The telescope carries an additional lens *k* at its inner, objective, end, in order that when this lens is rotated into position the telescope may be converted into a low-power microscope for viewing the crystal and thus enabling its adjustment to be readily carried out.

The crystal *l* is mounted on a little cone of goniometer wax (a mixture of pitch and beeswax) carried by the crystal holder. The latter fits in the top of the adjusting movements, which consist of a pair of rectangularly arranged centring motions, and a pair of cylindrical adjusting movements; the milled-headed manipulating centring screws of the former are indicated by the letters *m* and *n* in Fig. 48, and those which move the adjusting segments are marked *o* and *p*. The top screw fixes the crystal holder.

The crystal on its adjusting apparatus can be raised or lowered to the proper height, level with the axes of the telescope and collimator, by means of a milled head at the base of the instrument, there being an inner crystal axis moving (vertically only) independently of the circle. Moreover, a second axis outside this enables the crystal to be rotated independently of the circle, the conical axis of which is outside this again. The two can be locked together when desired, however, by a clamping screw provided with a fine adjustment *q*. Freedom of movement of the crystal axis, unimpeded by the weight of the circle, is thus permitted for all adjusting purposes, the circle being only brought into play when measurement is actually to occur. With this instrument the most accurate work can be readily carried out, and for ease of manipulation and general convenience it is the best goniometer yet constructed.

The idea of regarding the centre of the crystal as the centre of a sphere, within which the crystal is placed (Fig. 47, page 62), gives crystallographers a very convenient method of graphically representing a crystal on paper, by projecting the sphere on to the flat surface of the paper, the eye being supposed to be placed at either the north or south pole of the sphere, and the plane of projection to be that of the equatorial great circle. The faces in the upper hemisphere are represented by dots which are technically known as the "poles" of the faces, corresponding to the points where the needles normal to the faces emerge from the imaginary globe, and all these points or poles lie on a few arcs of great circles, which appear in the projection either also as circular arcs terminating at diametrically opposite points on the circumference of the equatorial circle, which forms the outer boundary of the figure and is termed the "primitive circle," or else, when the planes of the great circles are at right angles to the equatorial primitive circle, they appear as diametral straight lines passing through the centre of the primitive circle.

Such a stereographic projection offers a comprehensive plan of the whole of the crystal faces, which at once informs us of the symmetry in all cases other than very complicated ones. A typical one, that of the rhombic crystal of topaz shown in Fig. 22 (page 40), is given in Fig. 49.

It will happen in all cases of higher symmetry, as in that of topaz, for instance, that the poles in the lower hemisphere will project into the same points as those representing the faces in the upper hemisphere; but in cases of lower symmetry, where they are differently situated, they are usually represented by miniature rings instead of dots. From the interfacial angles measured on the goniometer the relative lengths and angular inclinations (if other than 90°) of the crystal axes can readily be calculated, by means of the simple formulæ of spherical trigonometry; and the stereographic projection constructed from the measurements as just described proves an inestimable aid to these calculations, by affording a comprehensive diagram of all the spherical triangles required in making the calculations.

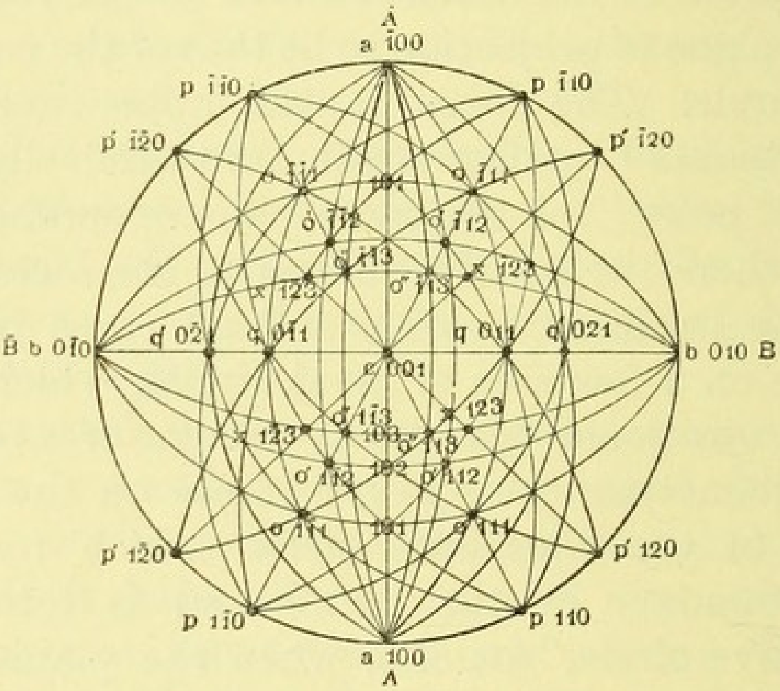

Fig. 49.—Stereographic Projection of Topaz.

The relative axial lengths $a : b : c$ (in which b is always arranged to be $= 1$), and the axial angles α (between b and c), β (between a and c), and γ (between *a* and *b*), form the "elements" of a crystal. These, together with a list of the "forms" observed, and a table of the interfacial angles, define the morphology of the crystal, and are included in every satisfactory description of a crystallographic investigation. They are preceded by a statement of the name and chemical composition and formula of the substance, the system and the class of symmetry, and the habit or various habits developed by crystals form a considerable number of crops. An example of the mode of setting out such a description will be found on pages 157 to 160.

Having thus made ourselves acquainted with the real nature of the distribution of faces on a crystal, and learnt how the crystallographer measures the angles between the faces by means of the reflecting goniometer, plots them out graphically on a stereographic projection, and calculates therefrom the "elements" of the crystal, it will be convenient again to take up the historical development of the subject so far as it relates to crystal forms and angles, and their bearing on the chemical composition of the substance composing the crystal, by introducing the reader to the great work of Mitscherlich, whose influence in the domain of chemical crystallography was as profound as that of Haüy proved to be as regards structural crystallography.

CHAPTER VII

THE WORK OF EILHARDT MITSCHERLICH AND HIS DISCOVERY OF ISOMORPHISM.

DURING the height of the French Revolution, which caused the work of the Abbe Haüy to be suspended for a time, although he was fortunately not one of the many scientific victims of that terrible period, there was born, on the 7th of January 1794, in the village of Neuende, near Jever, in Oldenburg, the man who was destined to continue that work on its chemical side. Eilhardt Mitscherlich was the son of the village pastor, and nephew of the celebrated philologer, Prof. Mitscherlich of Göttingen. His uncle's influence appears to have given young Mitscherlich a leaning towards philological studies, for during his later terms at the Gymnasium at Jever, where he received his early education, he devoted himself with great energy to the study of history and languages, for which he had a marked talent, under the able direction and kind solicitude of the head of the Gymnasium at that time, the historian Schlosser. He eventually specialised on the Persian language, and when Schlosser was promoted to Frankfort young Mitscherlich accompanied him, and there prosecuted these favourite studies until the year 1811, when he went to the university of Heidelberg.

For some time now he had cherished the hope of proceeding to Persia and conducting philological investigations on the spot, and in 1813, an opportunity presenting itself in the prospect of an embassy being despatched to Persia by Napoleon, he transferred himself to the university of Paris, with the object of obtaining permission from Napoleon to accompany the embassy. This visit to Paris must have been one of Mitscherlich's most exciting and interesting experiences. For Napoleon had just returned from the disastrous Russian campaign of 1812, and was feverishly engaged in raising a new army wherewith to stem the great rise of the people which was now re-awakening patriotic spirit throughout the whole of Germany, and which threatened to sweep away, as it eventually did, the huge fabric of his central European Empire.

Indeed Mitscherlich appears to have been detained in Paris during the exciting years 1813 and 1814, and with the abdication of Napoleon on April 4th of that year, he was obliged to give up all idea of proceeding to Persia. He decided that the only way of accomplishing his purpose was to attempt to travel thither as a doctor of medicine. He therefore returned to his native Germany during the summer of 1814, and proceeded to Göttingen, which was then famous for its medical school. Here he worked hard at the preliminary science subjects necessary for the medical degree, while still continuing his philology to such serious purpose as to enable him to publish, in 1815, the first volume of a history of the Ghurides and Kara-Chitayens, entitled "Mirchondi historia Thaheridarum." It is obvious from the sequel, however, that he very soon began to take much more than a merely passing interest in his scientific studies, and he eventually became so fascinated by them, and particularly chemistry, as to abandon altogether his cherished idea of a visit to Persia. Europe was now settling down after the stormy period of the hundred days which succeeded Napoleon's escape from Elba, terminating in his final overthrow on June 18th, 1815, at Waterloo, and Mitscherlich was able to devote himself to the uninterrupted prosecution of the scientific work now opening before him. He had the inestimable advantage of bringing to it a culture and a literary mind of quite an unusually broad and original character; and if the fall of Napoleon brought with it the loss to the world of an accomplished philologist, it brought also an ample compensation in conferring upon it one of the most erudite and broad-minded of scientists.

In 1818 Mitscherlich went to Berlin, and worked hard at chemistry in the university laboratory under Link. It was about the close of this year or the beginning of 1819 that he commenced his first research, and it proved to be one which will ever be memorable in the annals both of chemistry and of crystallography. He had undertaken the investigation of the phosphates and arsenates, and his results confirmed the conclusions which had just been published by Berzelius, then the greatest chemist of the day, namely, that the anhydrides of phosphoric and arsenic acids each contain five equivalents of oxygen, while those of the lower phosphorous and arsenious acids contain only three. But while making preparations of the salts of these acids, which they form when combined with potash and ammonia, he observed a fact which had escaped Berzelius, namely, that the phosphates and arsenates of potassium and ammonium *crystallise in similar forms*, the crystals being so like each other, in fact, as to be indistinguishable on a merely cursory inspection.

Being unacquainted with crystallography, and perceiving the importance of the subject to the chemist, he acted in a very practical and sensible manner, which it is more than singular has not been universally imitated by all chemists since his time. He at once commenced the study of crystallography, seeing the impossibility of further real progress without a working knowledge of that subject. He was fortunate in finding in Gustav Rose, the Professor of Geology and Mineralogy at Berlin, not merely a teacher close at hand, but also eventually a life-long intimate friend. Mitscherlich worked so hard under Rose that he was very soon able to carry out the necessary crystal measurements with his newly prepared phosphates and arsenates. He first established the complete morphological similarity of the acid phosphates and arsenates of ammonium, those which have the composition $NH_4H_2PO_4$ and $NH_4H_2AsO_4$ and crystallise in primary tetragonal prisms terminated by the primary pyramid faces; and then he endeavoured to produce other salts of ammonia with other acids which should likewise give crystals of similar form. But he found this to be impossible, and that only the phosphates and arsenates of ammonia exhibited the same crystalline forms, composed of faces inclined at similar angles, which to Mitscherlich at this time appeared to be identical. He next tried the effect of combining phosphoric and arsenic acids with other bases, and he found that potassium gave salts which crystallised apparently exactly like the ammonium salts.

He then discovered that not only do the acid phosphates and arsenates of potassium and ammonium, H_2KPO_4, $H_2(NH_4)PO_4$, H_2KAsO_4, and $H_2(NH_4)AsO_4$ crystallise in similar tetragonal forms, but also that the four neutral di-metallic salts of the type HK_2PO_4 crystallise similarly to each other.

He came, therefore, to the conclusion that there do exist bodies of dissimilar chemical composition having the same crystalline form, but that these substances are of similar constitution, in which one element, or group of elements, may be exchanged for another which appears to act analogously, such as arsenic for phosphorus and the ammonium group (although its true nature was not then determined) for potassium. He observed that certain minerals also appeared to conform to this rule, such as the rhombohedral carbonates of the alkaline earths, calcite $CaCO_3$, dolomite $CaMg(CO_3)_2$, chalybite $FeCO_3$, and dialogite $MnCO_3$; and the orthorhombic sulphates of barium (barytes, $BaSO_4$), strontium (celestite, $SrSO_4$), and lead (anglesite, $PbSO_4$). Wollaston, who, in the year 1809, had invented the reflecting goniometer, and thereby placed a much more powerful weapon of research in the hands of crystallographers, had already, in 1812, shown this to be a fact as regards the orthorhombic carbonates (witherite, strontianite, and cerussite) and sulphates (barytes, celestite, and anglesite) of barium, strontium, and lead, as the result of the first exact angular measurements made with his new instrument; but his observations had been almost ignored until Mitscherlich reinstated them by his confirmatory results.

While working under the direction of Rose, Mitscherlich had become acquainted with the work of Haüy, whose ideas were being very much discussed about this time, Haüy himself taking a very strong part in the discussion, being particularly firm on the principle that every substance of definite chemical composition is characterised by its own specific crystalline form. Such a principle appeared to be flatly contradicted by these first surprising results of Mitscherlich, and it naturally appeared desirable to the latter largely to extend his observations to other salts of different groups. It was for this reason that he had examined the orthorhombic sulphates of barium, strontium, and lead, and the rhombohedral carbonates of calcium, magnesium, iron, and manganese, with the result already stated that the members of each of these groups of salts were found to exhibit the same crystalline form, a fact as regards the former group of sulphates which had already been pointed out not only by Wollaston but by von Fuchs (who appears to have ignored the work of Wollaston) in 1815, but had been explained by him in a totally unsatisfactory manner. Moreover, about the same time the vitriols, the sulphates of zinc, iron, and copper, had been investigated by Beudant, who had shown that under certain conditions mixed crystals of these salts could be obtained; but Beudant omitted to analyse his salts, and thus missed discovering the all-important fact that the vitriols contain water of crystallisation, and in different amounts under normal conditions. Green vitriol, the sulphate of ferrous iron, crystallises usually with seven molecules of water of crystallisation, as does also white vitriol, zinc sulphate; but blue vitriol, copper sulphate, crystallises with only five molecules of water under ordinary atmospheric conditions of temperature and pressure. Moreover, copper sulphate forms crystals which belong to the triclinic system, while the sulphates of zinc and iron are dimorphous, the common form of zinc sulphate, $ZnSO_4.7H_2O$, being rhombic, like Epsom salts, the sulphate of magnesia which also crystallises with seven molecules of water, $MgSO_4.7H_2O$, while that of ferrous sulphate, $FeSO_4.7H_2O$, is monoclinic, facts which still further complicate the crystallography of this group and which were quite unknown to Beudant and were unobserved by him. But Beudant showed that the addition of fifteen per cent. of ferrous sulphate to zinc sulphate, or nine per cent. to copper sulphate, caused either zinc or copper sulphate to crystallise in the same monoclinic form as ferrous sulphate. He also showed that all three vitriols will crystallise in mixed crystals with magnesium or nickel sulphates, the ordinary form of the latter salt, $NiSO_4.7H_2O$, being rhombic like that of Epsom salts.

The idea that two chemically distinct substances not crystallising in the cubic system, where the high symmetry determines identity of form, can occur in crystals of the same form, was most determinedly combated by Haüy, and the lack of chemical analyses in Beudant's work, and the altogether incorrect "vicarious" explanation given by von Fuchs, gave Haüy very grave cause for suspicion of the new ideas. The previous observations of Rome de l'Isle in 1772, Le Blanc in 1784, Vauquelin in 1797, and of Gay-Lussac in 1816, that the various alums, potash alum, ammonia alum, and iron alum, will grow together in mixed crystals or in overgrowths of one crystal on another, when a crystal of any one of them is hung up in the solution of any other, does not affect the question, as the alums crystallise in the cubic system, the angles of the highly symmetric forms of which are absolutely identical by virtue of the symmetry itself.

It was while this interesting discussion was proceeding that Mitscherlich was at work in Berlin, extending his first researches on the phosphates and arsenates to the mineral sulphates and carbonates. But he recognised, even thus early, what has since become very clear, namely, that owing to the possibility of the enclosure of impurities and of admixture with isomorphous analogues, minerals are not so suitable for investigation in this regard as the crystals of artificially prepared chemical salts. For the latter can be prepared in the laboratory in a state of definitely ascertained purity, and there is no chance of that happening which Haüy was inclined to think was the explanation of Mitscherlich's results, namely, that certain salts have such an immense power of crystallisation that a small proportion of them in a solution of another salt may coerce the latter into crystallisation in the form of that more powerfully crystallising salt. Mitscherlich made a special study, therefore, of the work of Beudant, and repeated the latter observer's experiments, bringing to the research both his crystallographic experience and that of a skilful analyst. He prepared the pure sulphates of ferrous iron, copper, zinc, magnesium, nickel and cobalt, all of which form excellent crystals. He soon cleared up the mystery in which Beudant's work had left the subject, by showing that the crystals contained water of crystallisation, and in different amounts. He found what has since been abundantly verified, that the sulphates of copper and manganese crystallise in the triclinic system with five molecules of water, $CuSO_4.5H_2O$ and $MnSO_4.5H_2O$; in the case of manganese sulphate, however, this is only true when the temperature is between 7° and 20°, for if lower than 7° rhombic crystals of $MnSO_4.7H_2O$ similar to those of the magnesium sulphate group are deposited, and if higher than 20° the crystals are tetragonal and possess the composition $MnSO_4.4H_2O$. The Epsom salts group crystallising in the rhombic system with seven molecules of water consists of magnesium sulphate itself, $MgSO_4.7H_2O$, zinc sulphate $ZnSO_4.7H_2O$, and nickel sulphate $NiSO_4.7H_2O$. The third group of Mitscherlich consists of sulphate of ferrous iron $FeSO_4.7H_2O$ and cobalt sulphate $CoSO_4.7H_2O$, and both crystallise at ordinary temperatures with seven molecules of water as indicated by the formulæ, but in the monoclinic system. Thus two of the groups contain the same number of molecules of water, yet crystallise differently. But Mitscherlich next noticed a very singular fact, namely, that if a crystal of a member of either of these two groups be dropped into a saturated solution of a salt of the other group, this latter salt will crystallise out in the form of the group to which the stranger crystal belongs. Hence he concluded that both groups are capable of crystallising in two different systems, rhombic and monoclinic, and that under the ordinary circumstances of temperature and pressure three of the salts form most readily the rhombic crystals, while the other two take up most easily the monoclinic form. Mitscherlich then mixed the solutions of the different salts, and found that the mixed crystals obtained presented the form of some one of the salts employed. Thus even so early in his work Mitscherlich indicated the possibility of dimorphism. Moreover, before the close of the year 1819 he had satisfied himself that aragonite is a second distinct form of carbonate of lime, crystallising in the rhombic system and quite different from the ordinary rhombohedral form calcite. Hence this was another undoubted case of dimorphism.

During this same investigation in 1819, Mitscherlich studied the effect produced by mixing the solution of each one of the above-mentioned seven sulphates of dyad-acting metals with the solution of sulphate of potash, and made the very important discovery that a double salt of definite composition was produced, containing one equivalent of potassium sulphate, one equivalent of the dyad sulphate (that of magnesium, zinc, iron, manganese, nickel, cobalt, or copper), and six equivalents of water of crystallisation, and that they all crystallised well in similar forms belonging to the monoclinic system. Some typical crystals of one of these salts, ammonium magnesium sulphate, are illustrated in Fig. 30 (Plate VII., facing page 44). This is probably the most important series of double salts known to us, and is the series which has formed the subject of prolonged investigation on the part of the author, no less than thirty-four different members of the series having been studied crystallographically and physically since the year 1893, and many other members still remain to be studied. An account of this work is given in a Monograph published in the year 1910 by Messrs Macmillan & Co., and entitled, "Crystalline Structure and Chemical Constitution."

This remarkable record for a first research was presented by Mitscherlich to the Berlin Academy on the 9th December 1819. During the summer of the same year Berzelius visited Berlin, and was so struck with the abilities of Mitscherlich, then twenty-five years old, that he persuaded him to accompany him on his return to Stockholm, and Mitscherlich continued his investigations there under the eye of the great chemist. His first work at Stockholm consisted of a more complete study of the acid and neutral phosphates and arsenates of potash, soda, ammonia, and lead. He showed that in every case an arsenate crystallises in the same form as the corresponding phosphate. Moreover, in 1821 he demonstrated that sodium dihydrogen phosphate, NaH_2PO_4, crystallises with a molecule of water of crystallisation in two different forms, both belonging to the rhombic system but with quite different axial ratios; this was consequently a similar occurrence to that which he had observed with the sulphates of the iron and zinc groups.

It was while Mitscherlich was in Stockholm that Berzelius suggested to him that a name should be given to the new discovery that analogous elements can replace each other in their crystallised compounds without any apparent change of crystalline form. Mitscherlich, therefore, termed the phenomenon "isomorphism," from *ἰσός*, equal to, and *μορφή*, shape. The term "isomorphous" thus strictly means "equal shaped," implying not only similarity in the faces displayed, but also absolute equality of the crystal angles. The fact that the crystals of isomorphous substances are not absolutely identical in form, but only very similar, was not likely to be appreciated by Mitscherlich at this time. For the reflecting goniometer had only been invented by Wollaston in 1809, and accurate instruments reading to minutes of arc were mechanical rarities. It will be shown in the sequel, as the result of the author's investigations, that there *are* angular differences, none the less real because relatively very small, between the members of such series. But Mitscherlich was not in the position to observe them. It must be remembered, moreover, that he was primarily a chemist, and that he had only acquired sufficient crystallographic knowledge to enable him to detect the system of symmetry, and the principal forms (groups of faces having equal value as regards the symmetry) developed on the crystals which he prepared. His doctrine of isomorphism, accepted in this broad sense, proved of immediate and important use in chemistry. For there were uncertainties as to the equivalents of some of the chemical elements, as tabulated by Berzelius, then the greatest authority on the subject, and these were at once cleared up by the application of the principle of isomorphism.

The essence of Mitscherlich's discovery was, that the chemical nature of the elements present in a compound influences the crystalline form by determining the number and the arrangement of the atoms in the molecule of the compound; so that elements having similar properties, such for instance as barium, strontium, and calcium, or phosphorus and arsenic, combine with other elements to form similarly constituted compounds, both as regards number of atoms and their arrangement in the molecule. Number of atoms alone, however, is no criterion, for the five atoms of the ammonium group NH_4 replace the one atom of potassium without change of form.

This case of the base ammonia had been one of Mitscherlich's greatest difficulties during the earlier part of his work, and remained a complete puzzle until about this time, when its true chemical character was revealed. For until the year 1820 Berzelius believed that it contained oxygen. Seebeck and Berzelius had independently discovered ammonium amalgam in 1808, and Davy found, on repeating the experiment, that a piece of sal-ammoniac moistened with water produced the amalgam with mercury just as well as strong aqueous ammonia.

Both Berzelius and Davy came to the conclusion that ammonia contains oxygen, like potash and soda, and that a metallic kind of substance resembling the alkali metals, potassium and sodium, was isolated from this oxide or hydrate by the action of the electric current, which Seebeck had shown facilitated the formation of the so-called ammonium amalgam. Davy, however, accepted in part the views of Gay-Lussac and Thénard, who, in 1809, concluded from their experiments that ammonium consisted of ammonia gas NH_3 with an additional atom of hydrogen, the group NH_4 then acting like an alkali metal, views which time has substantiated. But their further erroneous conclusion that sodium and potassium also contained hydrogen was rejected by him. Berzelius, however, set his face both against this latter fallacy and the really correct NH_4 theory, and it was not until four years after Ampère, in 1816, had shown that sal-ammoniac was, in fact, the compound of the group NH_4 with chlorine, that Berzelius, about the year 1820, after thoroughly sifting the work of Ampère, accepted the view of the latter that in the ammonium salts it is the group NH_4, acting as a radicle capable of replacing the alkali metals, which is present.

The fact that this occurred at this precise moment, four years after the publication of Ampère's results, leads to the conclusion that the observation of Mitscherlich, that the ammonium compounds are isomorphous with the potassium compounds, was the compelling argument which caused Berzelius finally to admit what has since proved to be the truth.

While still at Stockholm Mitscherlich showed that the chromates and manganates are isomorphous with the sulphates, and also that the perchlorates and permanganates are isomorphous with each other. Although these facts could not be properly explained at the time, owing to the inadequate progress of the chemistry of manganese, it was seen that potassium chromate, K_2CrO_4, contained the same number of atoms as potassium sulphate, K_2SO_4, and that potassium permanganate $KMnO_4$ and perchlorate $KClO_4$ likewise resembled each other in regard to the number of atoms contained in the molecule.

As a good instance of the use of the principle of isomorphism, we may recall that when Marignac, in 1864, found himself in great difficulty about the atomic weights of the little known metals tantalum and niobium which he was investigating, he discovered that their compounds are isomorphous; the pentoxides of the two metals occur together in isomorphous mixture in several minerals, and the double fluorides with potassium fluoride, K_2TaF_7 and K_2NbF_7 are readily obtained in crystals of the same form. The specific heat of tantalum was then unknown, so that the law of Dulong and Petit connecting specific heat with atomic weight could not be applied, and the vapour density of tantalum chloride, as first determined by Deville and Troost with impure material, did not indicate an atomic weight for tantalum which would give it the position among the elements that the chemical reactions of the metal indicated. Yet Marignac was able definitely to decide, some time before the final vapour density determinations of Deville and Troost with pure salts, from the fact of the isomorphism of their compounds, that the only possible positions for tantalum and niobium were such as corresponded with the atomic weights 180 and 93 respectively. Time has only confirmed this decision, and we now know that niobium and tantalum belong to the same family group of elements as that to which vanadium belongs, and the only difference which modern research has introduced has been to correct the decimal places of the atomic weights, that of niobium (now also called columbium, the name given to it by its discoverer, Hatchett, in 1801) being now accepted as 92.8 and that of tantalum 179.6, when that of hydrogen=1.

Applying the law of isomorphism in a similar manner, Berzelius was enabled to fix the atomic weights of copper, cadmium, zinc, nickel, cobalt, iron, manganese, chromium, sulphur, selenium, and chlorine, the numbers accepted to-day differing only in the decimal places, in accordance with the more accurate results acquired by the advance of experimental and quantitative analytical methods. But with regard to several other elements, owing to inadequate data, Berzelius made serious mistakes, showing how very great is the necessity for care and for ample experimental data and accurate measurements, before the principle of isomorphism can be applied with safety. Given these, and we have one of the most valuable of all the aids known to us in choosing the correct atomic weight of an element from among two or three possible alternatives. We are only on absolutely sure ground when we are dealing not only with a series of compounds consisting of the same number of atoms, but when also the interchangeable elements are the intimately related members of a family group, such as we have since become familiar with in the vertical groups of elements in the periodic table of Mendeléeff.

Before leaving Stockholm Mitscherlich showed, from experiments on the crystallisation of mixtures of the different sulphates with which he had been working, that isomorphous substances intermix in crystals in all proportions, and that they also replace one another in minerals in indefinite proportions, a fact which has of recent years been wonderfully exemplified in the cases of the hornblende (amphibole) and augite (pyroxene) groups.

In November 1821 Mitscherlich closed these memorable labours at Stockholm and returned to Berlin, where he acted as extraordinary professor of the university until 1825, when he was elected professor in ordinary. His investigations for a time were largely connected with minerals, but on July 6th, 1826, he presented a further most important crystallographic paper to the Berlin Academy, in which he announced his discovery of the fact that one of the best known chemical elements, sulphur, is capable of crystallising in two distinct forms. The ordinary crystals found about Etna and Vesuvius and in other volcanic regions agree with those deposited from solution in carbon bisulphide in exhibiting rhombic symmetry. But Mitscherlich found that when sulphur is fused and allowed to cool until partially solidified, and the still liquid portion is then poured out of the crucible, the walls of the latter are found to be lined with long monoclinic prisms. These have already been illustrated in Fig. 2, Plate I., in Chapter I.

Here was a perfectly clear case of an element—not liable to any charge of difference of chemical composition such as might have applied to the cases of sodium dihydrogen phosphate, carbonate of lime, and iron vitriol and its analogues, which he had previously described as cases of the same substance crystallising in two different forms—which could be made to crystallise in two different systems of symmetry at will, by merely changing the circumstances under which the crystallisation occurred. His explanation being thus proved absolutely, he no longer hesitated, but at once applied the term "dimorphous" to these substances exhibiting two different forms, and referred to the phenomenon itself as "dimorphism." The case of carbonate of lime had given rise to prolonged discussion, for the second variety, the rhombic aragonite, had been erroneously explained by Stromeyer, after Mitscherlich's first announcement in 1819, as being due to its containing strontia as well as lime, and the controversy raged until Buchholz discovered a specimen of aragonite which was absolutely pure calcium carbonate, so that Mitscherlich's dimorphous explanation was fully substantiated.

Dimorphism is very beautifully illustrated by the case of the trioxide of antimony, Sb_2O_3, a slide of which, obtained by sublimation of the oxide from a heated tube on to the cool surface of a glass microscope-slip, is seen reproduced in Fig. 50, Plate XI. The two forms are respectively rhombic and cubic. The rhombic variety usually takes the form of long needle-shaped crystals, which are shown in Fig. 50 radiating across the field and interlacing with one another; the cubic variety crystallises in octahedra, of which several are shown in the illustration, perched on the needles, one interesting individual being poised on the end of one of the needles. The two forms occur also in nature as the rhombic mineral valentinite and the cubic mineral senarmontite, which latter crystallises in excellent regular octahedra. Antimonious oxide, moreover, is not only isomorphous, but isodimorphous with arsenious oxide, a slide of octahedra of which has already been reproduced in Fig. 3, Plate I., in Chapter I. For besides this common octahedral form of As_2O_3 artificial crystals of arsenious oxide have been prepared of rhombic symmetry, resembling valentinite. Hence the two lower oxides of arsenic and antimony afford us a striking case of the simultaneous display of Mitscherlich's two principles of isomorphism and dimorphism.

Thus the position in 1826 was that Mitscherlich had discovered the principle of isomorphism, and had also shown the occurrence of dimorphism in several well-proved specific cases, and that he regarded at this time isomorphism as being a literal reality, absolute identity of form.

These striking results appeared at once to demolish the theory that any one substance of definite chemical composition is characterised by a specific crystalline form, which was Haüy's most impor-

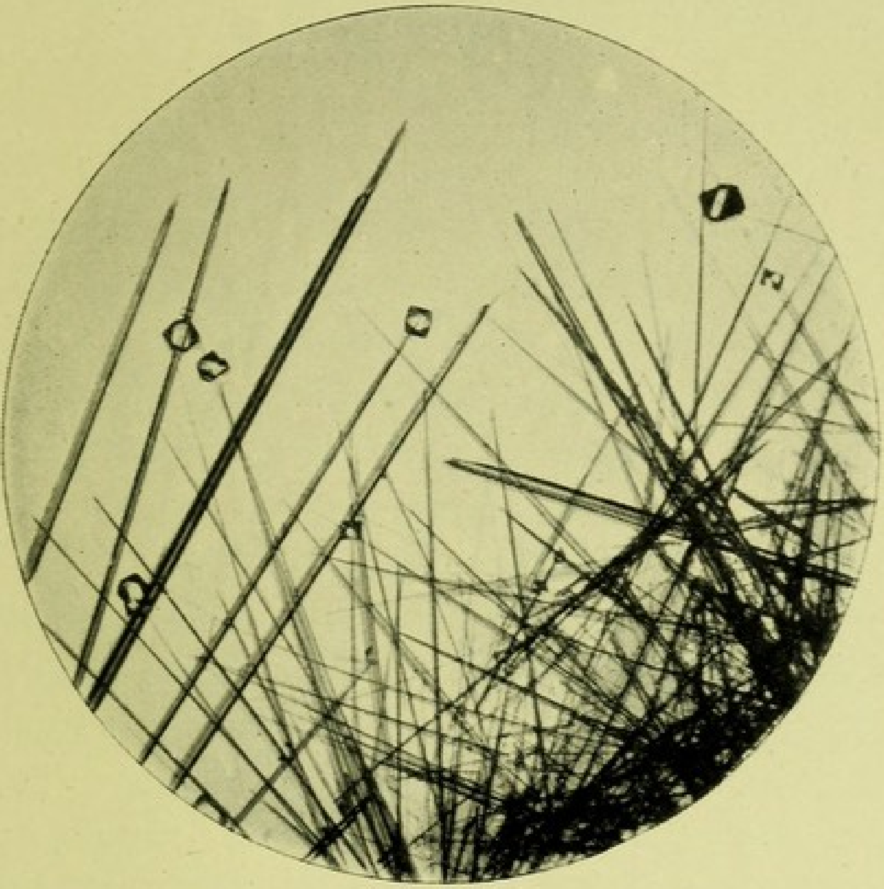

FIG. 50.—Rhombic Needles and Cubic Octahedra of Antimony Trioxide obtained by Sublimation. An interesting Example of Dimorphism.

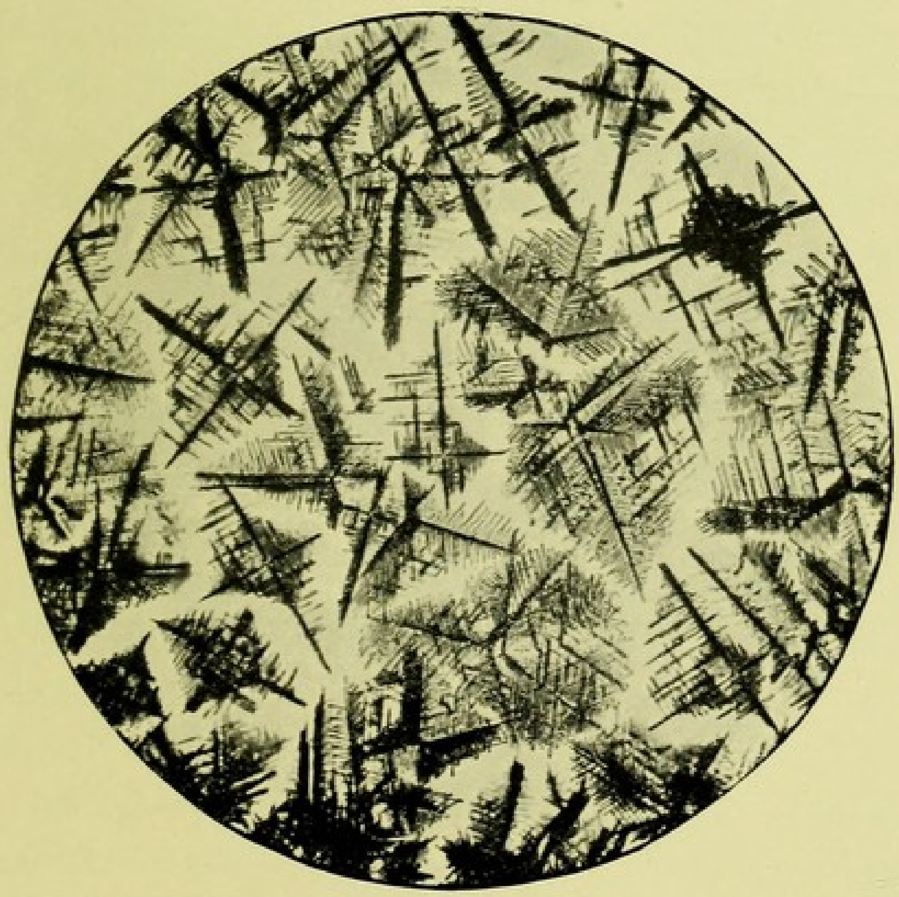

FIG. 101.—Ammonium Chloride crystallising from a Labile Supersaturated Solution (see p. 248).

REPRODUCTIONS OF PHOTOMICROGRAPHS.

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tant generalisation. Mitscherlich, however, soon expressed doubts as to the absolute identity of form of his isomorphous crystals, and saw that it was quite possible that in the systems other than the cubic (in which latter system the highly perfect symmetry itself determines the form, and that the angles shall be identically constant), there might be slight distinctive differences in the crystal angles. For he caused to be constructed, by the celebrated optician and mechanician, Pistor, the most accurate goniometer which had up till then been seen, provided with four verniers, each reading to ten seconds of arc, and with a telescope magnifying twenty times, for viewing the reflections of a signal, carried by a collimator, from the crystal faces. Unfortunately in one respect, he was almost at once diverted, by the very excess of refinement of this instrument, to the question of the alteration of the crystal angles by change of temperature, and lost the opportunity, never to recur, of doing that which would at once have reconciled his views with those of Haüy in regard to this important matter, namely, the determination of these small but real differences in the crystal angles of the different members of isomorphous series, and the discovery of the interesting law which governs them, a task which in these later days has fallen to the lot of the author.

Another remarkable piece of crystallographic work, this time in the optical domain, which has rendered the name of Mitscherlich familiar, was his discovery of the phenomenon of crossed-axial-plane dispersion of the optic axes in gypsum. (The nature and meaning of "optic axes" will be explained in Chapter XIII., page 185.) During the course of a lecture to the Berlin Academy in the year 1826 Mitscherlich, always a brilliant lecturer and experimenter at the lecture table, exhibited an experiment with a crystal of gypsum (selenite) which has ever since been referred to as the "Mitscherlich experiment." He had been investigating the double refraction of a number of crystalline substances at different temperatures, and had observed that gypsum, hydrated calcium sulphate, $CaSO_4.2H_2O$, was highly sensitive in this respect, especially as regards the position of its optic axes. At the ordinary temperature it is biaxial, with an optic axial angle of about 60°, but on heating the crystal the angle diminishes, until just above the temperature of boiling water the axes become identical, as if the crystal were uniaxial, and then they again separate as the temperature rises further, but in the plane at right angles to that which formerly contained them; hence the phenomenon is spoken of as "crossed-axial-plane dispersion." Mitscherlich employed a plate of the crystal cut perpendicularly to the bisectrix of the optic axial angle, and showed to the Academy the interference figures (see Plate XII.) which it afforded in convergent polarised light with rising temperature. At first, for the ordinary temperature, the usual rings and lemniscates surrounding the two optic axes were apparent at the right and left margins of the field; as the crystal was gently heated (its supporting metallic frame being heated with a spirit lamp) the axes approached each other, with ever changing play of colour and alteration of shape of the rings and lemniscates, until eventually the dark hyperbolic brushes, marking by their well defined vertices the positions of the two optic axes within the innermost rings, united in the centre of the field to produce the uniaxial dark rectangular cross; the rings around the centre had now become circles, the lemniscates having first become ellipses which more and more approximated, as the temperature rose, to circles. Then the dark cross opened out again, and the axial brushes separated once more, but in the vertical direction, and the circles became again first ellipses and then lemniscates, eventually developing inner rings around the optic axes; if the source of heat were not removed at this stage the crystal would suddenly decompose, becoming dehydrated, and the field on the screen would become dark. If, however, the spirit lamp were removed before this occurred, the phenomena were repeated in the reverse order as the crystal cooled.

This beautiful experiment is now frequently performed, as gypsum is perhaps the best example yet known which exhibits the phenomenon of crossed-axial-plane dispersion by change of temperature alone. A considerable number of other cases are known, such as brookite, the rhombic form of titanium dioxide TiO_2, and the triple tartrate of potassium, sodium, and ammonium, but these are more sensitive to change of wave-length in the illuminating light than to change of temperature.

The author has recently exhibited the "Mitscherlich experiment" to the Royal Society,[1] and

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[1] *Proc. Roy. Soc.*, 1908, A, 81, 40.

also in his Evening Discourse to the British Association at their 1909 meeting in Winnipeg, in a new and more elegant manner, employing the large Nicol-prism projection polariscope shown in Fig. 51, and a special arrangement of lenses for the convergence of the light, which is so effective that no extraneous heating of the crystal is required. The convergence of the rays is so true on a single spot in the centre of the crystal plate about two millimetres diameter, that a crystal plate not exceeding 6 mm. is of adequate size, mounted in a miniature holder-frame of platinum or brass with an aperture not more than 3 mm ; the thickness of the crystal should remain about 2 mm., in order that the rings round the axes may not be too large and diffuse, the crystal being endowed with very feeble

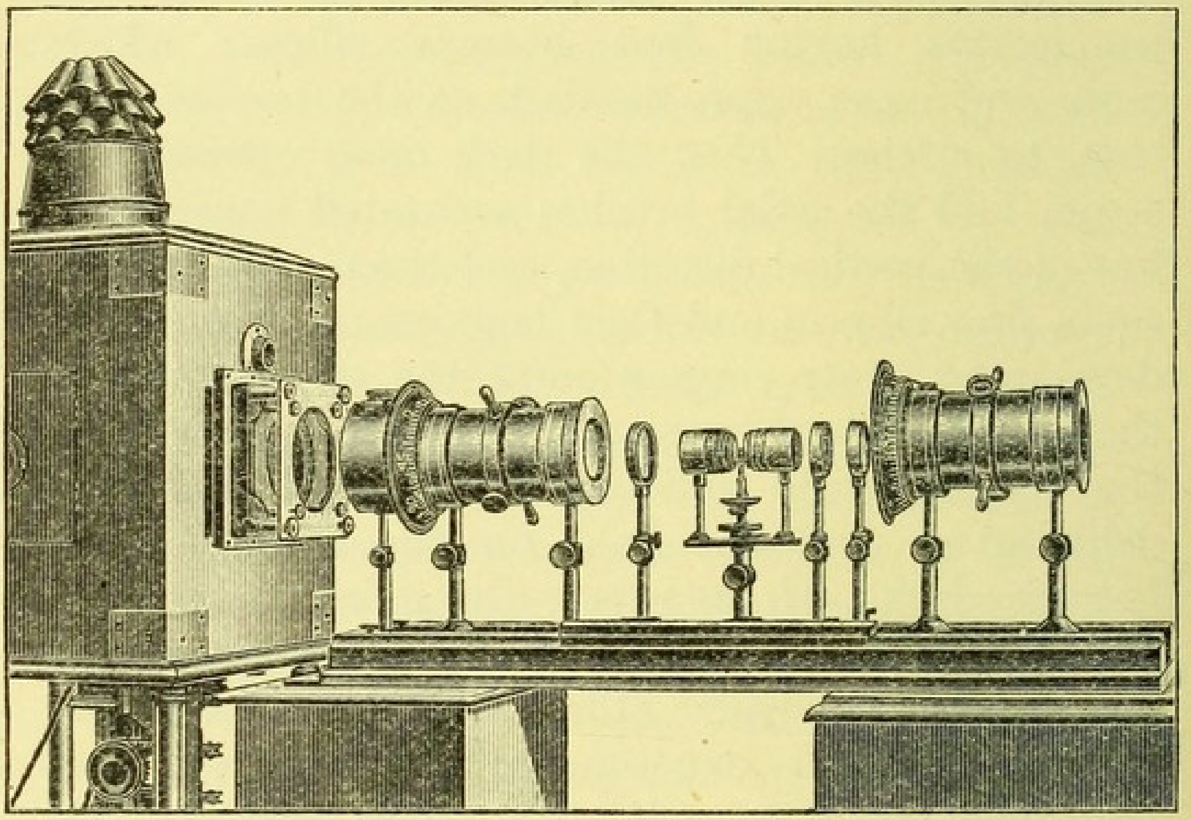

FIG. 51.—The Mitscherlich Experiment with Gypsum.

PLATE XII.

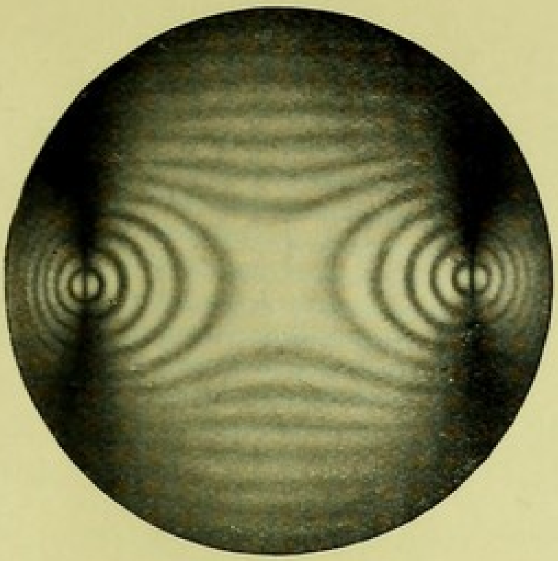

Fig. 52.—Appearance of the Interference Figure half a Minute after commencing the Experiment. Temperature of Crystal about 40° C.

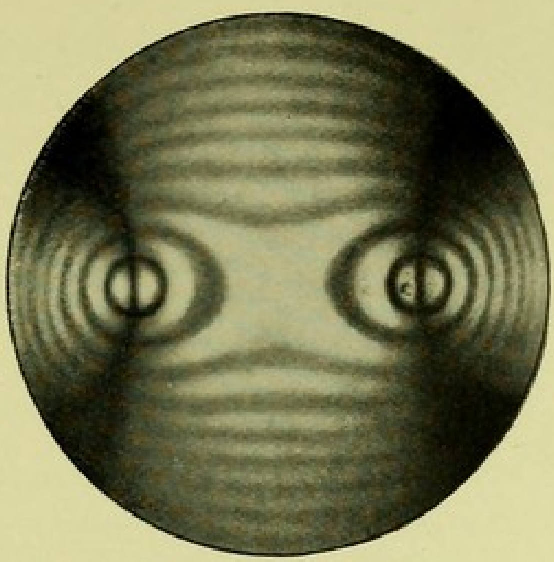

Fig. 53.—Appearance a Minute or so later, the Axes approaching the Centre. Temperature of Crystal about 85° C.

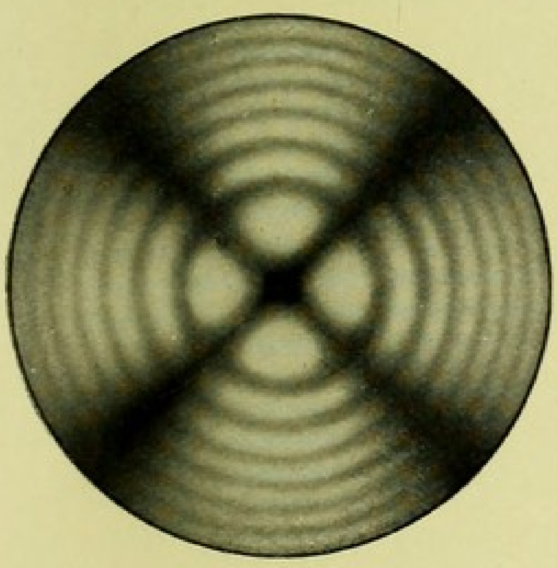

Fig. 54.—The Two Optic Axes coincident in the Centre of the Figure, two or three Minutes from the commencement. Temperature of Crystal 106° C.

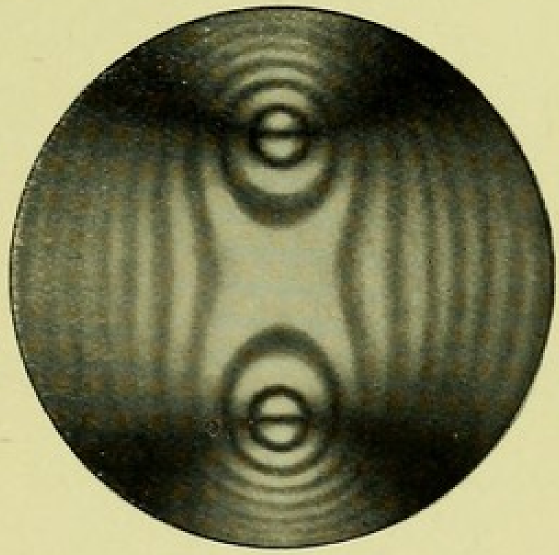

Fig. 55.—The Axes re-separated in the Vertical Plane a Minute or two later. Temperature of Crystal about 125° C.

The Mitscherlich Experiment with Gypsum.

Four Stages in the Transformation of the Interference Figure in Convergent Polarised Light, from Horizontally Biaxial through Uniaxial to Vertically Biaxial, on Raising the Temperature to 125° C.

(From Photographs by the author.)

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double refraction, which is one of the causes of the phenomenon. Such a small crystal heats up so rapidly in the heat rays accompanying the converging light rays—even with the essential cold water cell two inches thick between the lantern condenser and the polarising Nicol, for the protection of the balsam of the latter—that any extraneous heating by a spirit or other lamp is entirely unnecessary. The moment the electric arc of the lantern is switched on, the optic axial rings appear at the right and left margins of the screen, when the crystal is properly adjusted and the arc correctly centred, and they march rapidly to the crossing point in the centre, where the dark hyperbolæ unite to produce the rectangular St Andrew's cross, the rings, figure-eight curves, and other lemniscates passing through the most exquisite evolutions and colour changes all the time until they form the circular Newton's rings, around the centre of the cross; after this the cross and circles again open out, but along the vertical diameter of the screen, into hyperbolæ and rings and loop-like lemniscates surrounding two axes once more. It is wise as soon as the separation in this plane is complete and the first or second separate rings have appeared round the axes, to arrest the heating by merely interposing intermittently a hand screen between the lantern and polariser, or by blowing a current of cool air past the crystal, which will cause the axes to recede again, and the phenomena to be reversed, the crossing point being repassed, and the axes brought into the original horizontal plane again. By manipulation of the screen, or air-current, the axes can thus be caused to approach or to recede from the centre at will, along either the horizontal or vertical diameter. Four characteristic stages of the experiment are shown in Figs. 52 to 55, Plate XII. Fig. 52 exhibits the appearance just after commencing the experiment, the optic axes being well in the field of view. Fig. 53 shows the axes horizontally approaching the centre. Fig. 54 shows the actual crossing, which occurs for different crystals at temperatures varying from 105°.5 to 111°.5 C.; and Fig. 55 represents the axes again separated, but vertically.

The experiment as thus performed is one of the most beautiful imaginable, and it can readily be understood how delighted were Mitscherlich's audience on the occasion of its first performance by him. The author has since discovered no less than six other cases of substances which exhibit crossed-axial-plane dispersion of the optic axes, in the course of his investigations, one of which is illustrated in Plate XIII., facing page 108; and, moreover, has arrived at a general explanation of the whole phenomenon, the main points of which are that such substances, besides showing very feeble double refraction (the two extreme of the three refractive indices being very close together), also exhibit very close approximation of the intermediate refractive index β to either the minimum index α or the maximum index γ. Also, change of temperature, or of wave-length, or most usually both, must so operate as to bring the two indices closest together into actual identity and then to pass beyond each other, these two indices thus exchanging positions, the extreme one becoming the intermediate index. In other words, the uniaxial cross and circular rings are produced owing to two of the three refractive indices (corresponding to the directions of the three rectangular axes of the ellipsoid which, in general, expresses the optical properties of a crystal) becoming equal at the particular temperature at which the phenomenon is observed to occur, and for light of the specific wave-length in question. The ellipsoid of general form which represents the optical properties of a biaxial crystal thus becomes converted into a rotation ellipsoid corresponding to a uniaxial crystal. Brookite and the triple tartrate are excellent examples of the predominance of the effect of change of wave-length, for the optic axes are separated in both cases widely in one plane for red light and almost equally widely in the perpendicular plane for blue light. The new cases observed by the author are sensitive both to change of wave-length and to change of temperature, and so fall midway between the cases just quoted and the case of gypsum. The cause of it, in four of these new instances, is a very interesting one, connected with the regular change of the refractive indices in accordance with the law of progression in an isomorphous series according to the atomic weight of the alkali metal present, which will be discussed in Chapter X.

A further most important discovery was made by Mitscherlich in the year 1827, which also profoundly concerns the work of the author, namely, that of selenic acid, H_2SeO_4, analogous to sulphuric acid, and of the large group of salts derived from it, the selenates, analogous to the sulphates. He showed first that potassium selenate, K_2SeO_4, is isomorphous with potassium sulphate, K_2SO_4, and subsequently that the selenates in general are isomorphous with the corresponding sulphates; consequently it followed that selenium is a member of the sulphur family of elements. This element selenium had only been discovered ten years previously by his friend Berzelius, and doubtless Mitscherlich had seen a great deal of the work in connection with it during the two years which he spent in the laboratory of Berzelius at Stockholm, and was deeply interested in it.

The discovery has proved a most fruitful one, for the selenates are beautifully crystalline salts, particularly suitable for crystallographic researches, and their detailed investigation has afforded a most valuable independent confirmation of the important results obtained for the sulphates.

Again in 1830 Mitscherlich, following up the preliminary work already referred to, definitely established another fact bearing on the same series, namely, the isomorphism of potassium manganate K_2MnO_4 with the sulphate and selenate of potash; moreover, on continuing his study of the manganese salts he further substantiated the isomorphism of the permanganates with the perchlorates, and isolated permanganic acid. This also proved a most important step forward, as these salts likewise afford admirable material for crystallographic investigation, and such an examination, carried out by Muthmann and Barker, has yielded most valuable results.

Much later in his career Mitscherlich also described the dimorphous iodide of mercury, HgI_2, one of the most remarkable and interesting salts known to us, the unstable yellow rhombic modification being converted into the more stable red tetragonal form by merely touching with a hard substance. Also we are indebted to him at the same later period for our knowledge of the crystalline forms of the elements phosphorus, iodine, and selenium, when crystallised from solution in bisulphide of carbon.

From the record of achievements which has now been given in this chapter it will be obvious how much chemical crystallography owes to Mitscherlich. The description of his work has taken us into almost every branch of the subject, morphological, optical, and thermal, and although it has consequently been necessary to refer to phenomena which have not yet been explained in this book, it has doubtless proved on the whole most advantageous thus to present the life work of this great master as a complete connected story.

CHAPTER VIII

MORPHOTROPY AS DISTINCT FROM ISOMORPHISM.

It has been shown in the last chapter how Mitscherlich discovered the principle of isomorphism, as applying to the cases of substances so closely related that their interchangeable chemical elements are members of the same family group; and also how the principle enabled him to determine the chemical constitution of two hitherto unknown acids which he isolated, selenic H_2SeO_4 and permanganic $HMnO_4$. For he observed that the selenates were isomorphous with the sulphates, and the permanganates with the perchlorates. It was further made clear that the principle as bequeathed to us by Mitscherlich was only defined in very general terms, and its details have only recently been precisely decided.

Before proceeding further (in Chapter X.) with the elucidation of the true nature of isomorphism, however, some important crystallographic relationships between substances less closely related than family analogues must be referred to, as the outcome of a series of investigations by von Groth, chiefly between the derivatives of the hydrocarbon benzene. Also, some suggestive results obtained by the author from an investigation of an organic homologous series, that is, one the members of which differ by the regular addition of a CH_3 group, may be briefly referred to.

The interval between the work of Mitscherlich and that of von Groth was one of doubt, discouragement, and somewhat of discredit for chemical crystallography. The chemists Laurent[1] and Nicklès[2] carried out during the years from 1842 to 1849 measurements of numerous organic substances and of some inorganic compounds, the former chiefly halogen or other derivatives of particular hydrocarbons or salts of homologous fatty acids. Laurent, for instance, found that naphthalene tetrachloride, $C_{10}H_8.Cl_4$, and chlornapthalene tetrachloride, $C_{10}H_7Cl.Cl_4$, crystallise in different systems, the former in the monoclinic and the latter in the rhombic system. Yet the primary prism angles of the two are less than a degree different, namely, 109° 0′ and 109° 45′. Laurent named this kind of similarity "hemimorphism," a most unfortunate term as it was already employed in crystallography in its other well-known geometrical significance, that is, to denote a crystal differently terminated at the two ends of an axis. Many other like similarities were discovered by Laurent, and he again coined an objectionable term, now discarded, to represent the cases of similarity extending over more than the same system, namely, "isomeromorphism."

Nicklès observed similar facts in connection with the barium salts of the fatty acids, which crystallise in different systems with different

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[1] *Comptes Rendus*, 1842, **15**, 350, and 1845, **20**, 357.

[2] *Comptes Rendus*, 1848, **27**, 611, and 1849, **29**, 339.

amounts of water of crystallisation. But their prism angles are all within a couple of degrees of each other, varying from 98° to 100°. Thus the phenomenon of " isogonism," a term much less objectionable than those invented by Laurent, appears to be a common observance not only for different kinds of derivatives of the same original hydrocarbon or other organic nucleus, but also for the case of homologous series. But Nicklès missed the real point by including salts with different amounts of water, which, it will be shown later, entirely upset the crystalline structure. When this is eliminated the resemblance between true similarly constituted homologues, differing by regular increments of CH_3, is very much closer than would appear from Nicklès' results.

Unfortunately, some of the work of Laurent and Nicklès was not carried out with the care and accuracy which is indispensable for researches which are to retain permanent value, and critics were not slow to arise. Kopp,[1] in 1849, unmercifully exposed these failings, so that the real kernel of the work, which was of considerable value, came into discredit.

Pasteur,[2] however, in 1848, besides the important observations regarding enantiomorphism, to be described in Chapter XI., had noticed similar zonal likenesses between related tartrates, amounting only therefore to isogonism and not to isomorphism ; for here again the system often differed, particularly when the members of a series compared

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[1] *Jahresbericht*, 1849, 19.

[2] *Comptes Rendus*, 1848, **26**, 535.

differed in their water of crystallisation. Thus there was ample evidence of a really significant series of facts in the work of these authors, but they were not properly arranged and explained.

So high was the feeling against the whole subject carried, however, after Kopp's memoir, that had it not been for the steadying influence of Rammelsberg and Marignac, who themselves carried out many crystallographic measurements as new substances continued to be discovered with great rapidity, the science would have suffered a serious set-back. Moreover, even Rammelsberg was led astray in the direction of the views of the chemists of the time, that isomorphism could be extended over the crystal system. Frankenheim, whose discovery of the space-lattice, to be referred to in the next chapter, will ever render his name famous, strongly opposed this view. Delafosse, on the other hand, recognised some truth in both views, and assumed that there were two kinds of isomorphism, that of Mitscherlich on the one hand, and the broader one of Laurent on the other hand, and that in the case of the latter kind the overstepping of the system is no bar.

Hjortdahl,[1] in the year 1865, supported the views of Delafosse more or less, at any rate so far as to assume the possibility of the existence of partial isomorphism, that is, of isogonism. He was very definite, however, against accepting the proposition that any general law could be applied. He himself discovered a partial similarity of angles in several homologous series of organic compounds.

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[1] *Journ. für Prakt. Chemie.*, 1865, **94**, 286.

About this time Sella[1] uttered a warning which is one worthy of being prominently posted in every research laboratory, namely, that *It is unwise to make hasty generalisations from the results of a small number of observations.* Were this principle more generally followed, much greater progress would in the end be achieved, and without the discouragement and discredit which inevitably follows the detection of errors due to lack of broad experimental foundation. It is certainly an incontrovertible fact that only such generalisations as find themselves in accordance with all new but well-verified experimental facts as they are revealed can stand the test of time and become accepted universally as true laws of nature. And it is unreasonable to expect any generalisation to be of such a character unless it is already based on so large a number of facts that there is little fear of other new ones upsetting them.

Some order was, however, introduced into this chaotic state of chemical crystallography in the year 1870 by P. von Groth.[2] He investigated systematically the derivatives of the hydrocarbon benzene, C_6H_6, many of which are excellently crystallising solids suitable for goniometrical measurement. He showed that although the crystal system may be and often is altered, yet there is a striking similarity in the angles between the faces of certain zones, which for the purposes of comparison he arranged to be parallel to each other in his descriptions of the crystals, so that the relationship

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[1] *Mem. R. Accad. di Torino*, 2A, **17**, 337, and **20**, 355.

[2] *Pogg. Ann.*, **141**, 31.

would then consist in an elongation or a shortening of this particular zone axis, which was usually a crystallographic axis. He recognised that this was a totally different phenomenon from isomorphism, and called it "morphotropy." Although it may possibly be permissible from one point of view to regard isomorphism as a particular case of complete morphotropy along all zones, such a course is not advisable, as morphotropic similarities are frequently of a comparatively loose and often indeed of a somewhat vague character, while isomorphous relationships are governed by very precise laws.

Thus von Groth showed first that benzene, C_6H_6, crystallises in the rhombic system with axial ratios $a:b:c=0.891:1:0.977$. Next, that when one or two of the hydrogen atoms are replaced by hydroxyl OH groups the substances produced, phenol $C_6H_5.OH$ and resorcinol $C_6H_4(OH)_2$, are found also to crystallise in the rhombic system, and in the second case, for which alone the axial ratios could be determined, the ratio $a:b$ proved to be very similar, but the ratio $c:b$ was different, the actual values being $a:b:c=0.910:1:0.540$. Pyrocatechol, the isomer of resorcinol, also crystallises in the rhombic system, but the crystals have not been obtained sufficiently well formed to enable any deductions to be made from any measurements carried out with them.

Similarly, the nitro-derivatives of phenol, orthonitrophenol $C_6H_4.OH.NO_2$, dinitrophenol $C_6H_3.OH.(NO_2)_2$, and trinitrophenol $C_6H_2.OH.(NO_2)_3$, also crystallise in the rhombic sytem, and with the following respective axial ratios: 0.873 : 1 : 0.60;

0.933 : 1 : 0.753 ; 0.937 : 1 : 0.974. Again, the value for the ratio *a* : *b* is not very different from that of benzene itself, while the ratio *c* : *b* differs considerably in the first two cases. Similar relations were also found to hold good in the cases of meta-dinitrobenzene, $C_6H_4(NO_2)_2$, axial ratios 0.943 : 1 : 0.538, and trinitrobenzene, $C_6H_3(NO_2)_3$, which possesses the axial ratios 0.954 : 1 : 0.733.

The introduction of a chlorine or bromine atom or a CH_3 group in place of hydrogen was found by von Groth to produce more than the above effect, the symmetry being often lowered to monoclinic, a fact which had also been observed to occur in the cases of certain isomers of the substances quoted above, ortho-dinitrobenzene for instance. But it was nevertheless observed that the angles between the faces in the prism zone remained very similar, the angles between the faces of the primary prism (110) and ($1\bar{1}0$), for instance, only varying in eight such derivatives of all three types, whether rhombic or monoclinic, from 93° 45′ to 98° 51′.

The crystallographic relationships of organic substances, however, are very much complicated by the possibilities of isomerism, the ortho, meta, and para compounds—corresponding to the replacement of the two hydrogen atoms attached to two adjacent, alternate, or opposite carbon atoms respectively, of the six forming the benzene ring—generally differing extensively and sometimes completely in crystalline form. Consequently, the phenomenon of morphotropy is best considered quite independently of isomorphism.

An interesting intermediate case between morphotropy and true isomorphism was investigated by the author in the year 1890, namely, a series of homologous organic compounds differing by regular increments of the organic radicle CH_3. They were prepared by Prof. Japp and Dr Klingemann, and consisted of the methyl, CH_3, ethyl, C_2H_5, and propyl, C_3H_7, derivatives of the substance triphenyl pyrrholone, all of them being solids crystallising well. The problem was somewhat complicated by the development of polymorphism, the methyl, ethyl, and propyl compounds having each been found to be dimorphous, and not improbably trimorphous, but only two varieties of each salt were obtained in crystals adequately perfect for measurement. That the production of these different forms was due to polymorphism and not to chemical isomerism (different arrangement of the chemical atoms in the molecule) was shown by the fact that one variety could be obtained from the other by simply altering the conditions of crystallisation from the same solvent. Their identical chemical composition was established by direct analysis.

The methyl (CH_3) compound crystallised in rhombohedra and in triclinic prisms. The ethyl (C_2H_5) derivative was deposited in triclinic prisms exactly resembling those of the methyl compound in habit and disposition of faces. A crystal of the triclinic methyl derivative which would represent equally well the ethyl compound is shown in Fig. 56. The angles also of the crystals of the two substances are so similar that one might infer the existence of true and complete isomorphism. The actual angular differences rarely exceeded three degrees.

Besides the triclinic form the ethyl derivative was also obtained in monoclinic crystals, one of which is represented in Fig. 57. This illustration might serve equally well, however, for a corresponding monoclinic form of the propyl (C_3H_7) derivative, and the angles of these two monoclinic ethyl and propyl compounds are even closer than those of the triclinic methyl and ethyl derivatives, the closeness increasing with the advent of symmetry.

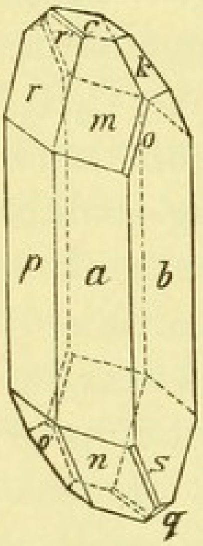

FIG. 56.—Crystal of Methyl Triphenyl Pyrrholone.

This similarity of angles in the cases of the two pairs of triclinic and monoclinic compounds is not only true about particular zones, but about all the zones, so that it is a case of isomorphism rather than of isogonism (morphotropy). The similarity of optical properties is also very close, and so much so in the cases of the monoclinic crystals of ethyl and propyl triphenyl pyrrholone that both exhibit very high dispersion of the optic axes. In the case of the propyl derivative the difference between the apparent angle of the optic axes for red lithium light and for green thallium light amounts to 11°. In the case of the ethyl compound this difference is enhanced so considerably that the crystals afford a remarkable instance of dispersion of the optic axes in crossed axial planes, resembling the case of gypsum discovered by Mitscherlich and described in the

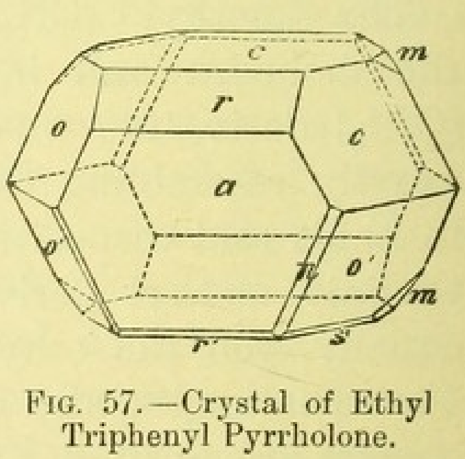

FIG. 57.—Crystal of Ethyl Triphenyl Pyrrholone.

last chapter, except that the sensitiveness is to change of wave-length in the illuminating light rather than to change of temperature. The optic axial plane is perpendicular to the symmetry plane for lithium and sodium light, as it is also in the case of the propyl compound ; but in the ethyl derivative it crosses over for thallium light and rays beyond that towards the violet, into a plane at right angles to the former plane, namely, the symmetry plane itself. The total dispersion between the two axes as separated in the one plane for red light, and as separated in the other perpendicular plane for blue light, is more than 70°. Fig. 58, Plate XIII., shows the nature of the interference figures afforded in convergent polarised light of different wave-lengths by a section-plate perpendicular to the first median line. The figure at *f* represents what is observed in white light, as far as is possible by a drawing in black and white. It consists of a series of concave coloured curves, falling in between the arms of the cross, and looping round the axes, a figure very much like that afforded by brookite and triple tartrate of ammonium, potassium, and sodium, the substances already mentioned in Chapter VII. as being similarly very sensitive to change of wave-length. The figure in red monochromatic lithium light is shown at *a* in Fig. 58, and that for yellow sodium light at *b*, the axes being now much closer together. On changing to green thallium light the line joining the optic axes becomes vertical instead of horizontal, as shown at *d*.

When, instead of employing monochromatic flames, the spectroscopic monochromatic illuminator (Fig. 75, page 193), described by the author some years ago to the Royal Society, is employed to illuminate the polariscope, the source of light being the electric arc, the change of the figure from that given by the extreme red of the spectrum to that afforded by the violet may be beautifully followed, and the exact wave-length in the greenish yellow determined for which the crossing occurs and an apparently uniaxial figure of circular rings and rectangular cross is produced. For it is possible with the aid of this illuminator directly to observe the production of the uniaxial figure. The wave-length is either directly afforded by the graduation of the fine-adjustment micrometric drum or is obtained from a curve of wave-lengths, constructed to correspond to the circle readings of the illuminator. The appearance of the interference figure for this critical wave-length is shown at *c* in Fig. 58. The remaining figure at *e* represents the appearance when a mixture of sodium and thallium light is employed, which clearly indicates the four extreme axial positions, and assists in elucidating the nature of the figure *f* exhibited in white light.

The second form of the propyl derivative belongs to the rhombic system, and a similar rhombic form of the ethyl compound was once obtained, but lost again on attempting to recrystallise.

These interesting relationships of the homologous methyl, ethyl, and propyl derivatives of triphenyl pyrrholone thus appear to form a connecting link between cases of isogonism or morphotropy and of true isomorphism.

We are now, therefore, in a position to approach the question of true isomorphism, and as leading up to the fuller treatment of the subject in Chapter X.

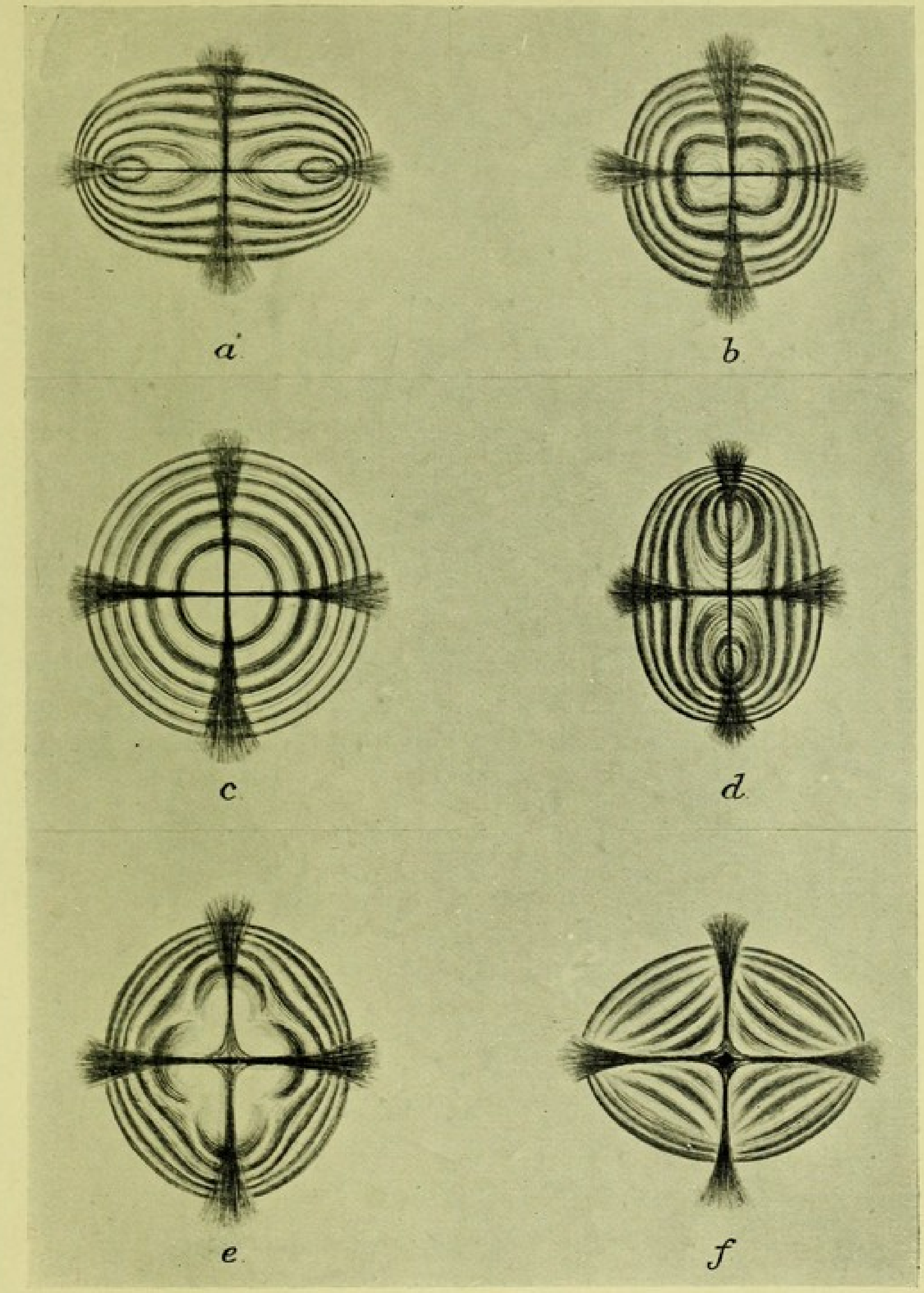

FIG. 58.—Interference Figures in Convergent Polarised Light of different Wave-lengths afforded by the Monoclinic Variety of Ethyl Triphenyl Pyrrholone; *a*, in Red Lithium Light; *b*, in Yellow Sodium Light; *c*, in Greenish-Yellow Light of the Critical Wave-length for Production of the Uniaxial Figure; *d*, in Green Thallium Light; *e*, in mixed Sodium and Thallium Light; and *f*, in White Light.

(Reproductions of Drawings by the author.)

we may conclude this chapter by referring first to one important investigation in which the necessity for extreme accuracy of measurement and perfection of material was fully appreciated. This was an admirable research carried out in the years 1887 and 1888 by H. A. Miers[1] on the red silver minerals, proustite, sulpharsenite of silver, Ag_3AsS_3, and pyrargyrite, the analogous sulphantimonite of silver, Ag_3SbS_3, which afforded a further indication of the existence of real small differences of angle between the members of truly isomorphous series. These two minerals form exceptionally beautiful crystals belonging to the trigonal system, the hexagonal prism being always a prominent form, terminated by the primary and other rhombohedra, scalenohedra and various pyramidal forms, many of the crystals being exceedingly rich in faces. When the crystals are freshly obtained from the dark recesses of the silver mine they are very lustrous and transparent, but they are gradually affected by light, like many silver compounds, and require to be stored in the dark in order to preserve their transparency. A magnificent crystal of proustite from Chili is one of the finest objects in the British Museum at South Kensington, but is rarely seen on account of the necessity for preservation from light. Pyrargyrite is generally dark grey in appearance, and affords a reddish-purple " streak " (colour of the powder on scratching or pulverising). Proustite, however, possesses a beautiful scarlet-vermilion colour, and affords a very bright red streak.

Now these two beautiful minerals are obviously

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[1] *Mineralogical Magazine*, 1888, 8, 37.

analogous compounds of the same metal, silver, with the sulpho-acid of two elements, arsenic and antimony, belonging strictly to the same family group, the nitrogen-phosphorus group, of the periodic classification of the elements according to Mendeleéff. Consequently, they should be perfectly isomorphous. Miers has shown in a most complete manner that they are so, that they occur in very perfect crystals of similar habit belonging to the same class of the trigonal system, the ditrigonal polar class, both minerals being hemimorphic, that is, showing different forms at the two terminations, in accordance with the symmetry of the polar class of the trigonal system. But the angles of the two substances were not found to be identical, although constant for each compound within one minute of arc, there being slight but very real differences, which are very well typified by the principal angle in each case, that of the primary rhombohedron. In the case of proustite it is 72° 12′, while the rhombohedron angle of pyrargyrite is 71° 22′.

This interesting and beautiful investigation of Miers thus gave us an inkling of the truth, that small angular differences do exist between the members of isomorphous compounds. It paved the way for, and indeed partly suggested, the author's systematic investigation of the sulphates, selenates, and double salts of the alkali series of metals, a brief account of the main results of which will be given in Chapter X.

CHAPTER IX

THE CRYSTAL SPACE-LATTICE AND ITS MOLECULAR UNIT CELL. THE 230 POINT-SYSTEMS OF HOMOGENEOUS CRYSTAL STRUCTURE.

THE interval between the morphotropic work described in the last chapter and the present time has been remarkable for the completion of the geometrical and mathematical investigation, and the successful identification, of all the possible types of homogeneous structures possessing the essential attributes of crystals. It has now been definitely established that there are 230 such types of homogeneous structures possible, and the whole of them conform to the conditions of symmetry of one or other of the thirty-two classes of crystals. This fact is now thoroughly agreed upon by all the authorities who have made the subject their special study, and may truly be considered as fundamental.

There has long been a concensus of opinion that the crystal edifice is built up of structural units which can be likened to the bricks or stone blocks of the builder, but which in the case of the crystal are so small as to be invisible even under the highest power of the microscope. The conceptions of their nature, however, have been almost as numerous as the investigators themselves, everyone who has thought over the subject forming his own particular ideas concerning them. We have had the "Molécules intégrantes" of Haüy, the "Polyhédres" of Bravais, the "Fundamentalbereich" of Schönflies, the "Parallelohedra" of von Fedorow, and the fourteen-walled cell, the "Tetrakaidecahedron" of Lord Kelvin, and again the "Polyhedra" of Pope and Barlow. Ideas have thus been extremely fertile, and indeed almost every variety of speculation has been indulged in as to the shape and nature of the unit of the structure which can exhibit such remarkable evidences of organisation and such extraordinary optical and other physical properties as those of a crystal.

There is one inherent difficulty, however, which renders all such speculations more or less chimerical, until we know very much more as to the structure of the chemical atom, and the organisation of the corpuscles composing it. Such speculations, however, are deeply interesting, and the difficulty alluded to accounts largely for the great variety of conception possible. It is this, that the matter of the molecules, and again that of the atoms composing them, is not necessarily, nor even probably, continuous and in contact throughout, but that on the contrary the space which may legitimately be assigned to the unit of the structure is partly void. How much of this unit space is matter and how much is unoccupied, and how the one is related to the other as regards its position or distribution in space, we have yet no means of knowing, although there are signs that the day is not far distant when we shall know at least something concerning it. The recent brilliant work of Sir J. J. Thomson and his school of physicists has rendered it clear that the chemical atom is composed of cycles of electronic corpuscles, the orbital motions of which determine its boundaries.

In this condition of our knowledge obviously the only safe course is to consider each atom of the chemical molecule as occupying a "sphere of influence," within the limits of which the material parts of the atom, the corpuscles in organised motion, are confined. The "Fundamentalbereich" of Schönflies and the "Sphere of Influence" of Barlow, are the conceptions which in all probability have the greatest value in the present state of our knowledge, and if we adopt the latter we shall not be committing ourselves to anything more than the experimental facts fully warrant.

It may be quite definitely stated, however, that there is a considerable amount of experimental evidence that the unit of the space-lattice of the crystal structure is certainly not more complex than the chemical molecule, the idea of an aggregation of chemical molecules to form a "physical molecule" acting as a structural unit having proved to be a misleading myth.

Fortunately, however, there is no necessity whatever to introduce the subject of the actual shape of the unit, and the greatest progress has been effected by disregarding it altogether, and agreeing to the representation of the unit by a point. This leads us at once to perceive the importance of the brilliant work of the geometricians, who have now completed their theory of the homogeneous partitioning of space into point-systems possible to crystals, the structural units of the latter being regarded as points. The investigations extend from those of Frankenheim in the year 1830 to the finishing touches given by Barlow in 1894, and prominently standing forth as those of the greatest contributors to the subject, besides the two investigators just mentioned, are the names of Bravais, Sohncke, Schönflies and von Fedorow.

Bravais, perfecting the work of his predecessor Frankenheim, made us acquainted with the fourteen fundamentally important space-lattices, or same-ways orientated arrangements of points. If we regard each chemical molecule as represented by a point, disregarding the separate atoms of which it is composed, then these fourteen space-lattices represent the possible arrangements of the molecules in the crystal in all the simpler cases; three of these lattices have cubic symmetry; the tetragonal, hexagonal, trigonal, rhombic and monoclinic systems claim two space-lattices each; while one space-lattice conforms to the lack of symmetry of the triclinic system.

The fourteen space-lattices of Bravais thus represent the arrangement of the chemical molecules in the crystal, and determine the systematic symmetry. The points being taken absolutely analogously in all the molecules, and the whole assemblage being homogeneous, that is, such that the environment about any one spot is the same as about every other, the arrangement is obviously a same-ways orientated one, the molecules being all arranged parallel-wise to each other.

But the fact that the structure is that of a space-lattice also causes the crystal to obey the law of rational indices. To enable us to see how this comes about it is only necessary to regard a space-lattice. In Fig. 59 is represented the general form of space-lattice, that which corresponds to triclinic symmetry. It is obviously built up of parallelepipeda, the edges of which are proportional to the lengths of the three triclinic axes, and their mutual inclinations are those of the latter. As we may take our representative point anywhere in the molecule, so long as the position chosen is the same for all the molecules of the assemblage, we may imagine the points occupying the centres of the parallelepipeda instead of the corners if we choose, for that would only be equivalent to moving the whole space-lattice slightly parallel to itself. Hence, each cell may be regarded as the habitat of the chemical molecule.

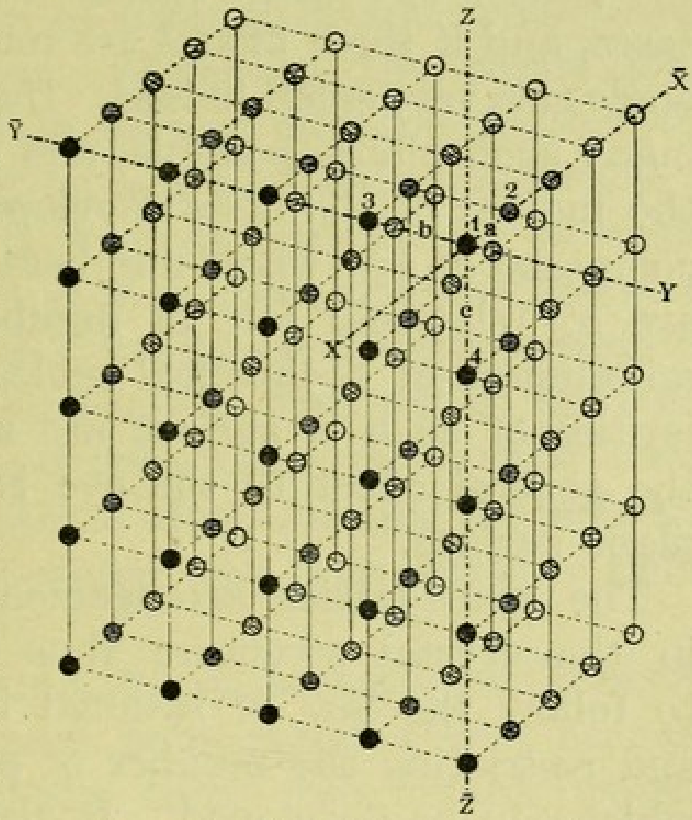

FIG. 59.—Triclinic Space-Lattice.

Now the faces of the crystal parallel to each two of the three sets of parallel lines forming the space-lattice will be the three pairs of axial-plane faces, and any fourth face inclined to them must be got by removing parallelepipedal blocks in stepwise fashion, precisely like bricks, as already shown in

Fig. 12 (page 28) in Chapter III., in order to illustrate the step by step removal of Haüy's unit blocks. It will readily be seen that if one more cell be removed from each row than from the row below it, the line of contact touching the projecting corner of the last block of each row will be inclined more steeply than if two more cells were removed from each row. Moreover, the angle varies considerably between the two cases, and if three blocks are removed at a time the angle gets very small indeed. Hence, there cannot be many such planes possible, and we see at once why the indices of the faces developed on a crystal are composed of low whole numbers and why the forms are so relatively few in number. Owing to the minuteness of a chemical molecule, all the irregularities of such a surface are submicroscopic, and the general effect to the eye is that of a smooth plane surface.

The space-lattice arrangement of the molecules in the crystal structure thus causes the crystal to follow the law of rational indices, by limiting and restricting the number of possible facial forms which can be developed. It also determines which one of the seven systems of symmetry or styles of crystal architecture the crystal shall adopt. It does not determine the details of the architecture, however, that is, to which of the thirty-two classes it shall conform, this not being the function of the molecular arrangement but of the atomic arrangement, that is, of the arrangement of the cluster of atoms which form the molecule, and this leads us to the next step in the unravelling of the internal structure of crystals.

The credit of this next stage of further progress is due to Sohncke, whose long labours resulted in the discrimination and description of sixty-five "Regular Point-Systems," homogeneous assemblages of points symmetrically and identically arranged about axes of symmetry, which are sometimes screw axes, that is, axes about which the points are spirally distributed. Sohncke's point-systems express the number of ways in which symmetrical repetition can occur. Moreover, the points may always be grouped in sets or clusters, the centres of gravity of which form a Bravais space-lattice.

This latter fact is of great interest, for it means that Sohncke's points may represent the chemical atoms, and that the stereometric arrangement of the atoms in the molecule is that which produces the point-system and determines the crystal class, while the whole cluster of atoms forming the molecule furnishes, as above stated, the representative point of the space-lattice.

This, however, is not the whole story, for the sixty-five Sohnckian regular point-systems only account for twenty-one of the thirty-two crystal classes, the remaining eleven being those of lower than full holohedral systematic symmetry, and which are characterised by showing complementary right and left-handed forms. In other words, they exhibit two varieties, on one of which faces of low symmetry are developed on the right, while on the other symmetrically complementary faces are developed on the left; that is, these little faces modify on the right and left respectively the solid angles formed by those faces of the crystal which are common to both the holohedral class of the system and to the lower symmetry class in question. In some cases, moreover, these two complementary forms are known to exist alone, without the presence of faces common to both the holohedral class and the class of lower symmetry. The two varieties of the crystals are the mirror images of each other, being related as a right-hand glove is to a left-hand one.

Further, the crystals of these eleven classes very frequently exhibit the power of rotating the plane of polarised light to the right or to the left, and complementarily in the cases of the two varieties of any one substance, corresponding to the complementariness of the two crystal forms. The converse is even more absolute, for no optically active crystal has yet been discovered which does not belong to one or other of these eleven classes of lower than holohedral symmetry.

The final step of accounting for the structure of these highly interesting eleven classes of crystals was taken simultaneously by a German, Schönflies, a Russian, von Fedorow, and an Englishman, Barlow, who quite independently and by totally different lines of reasoning and of geometrical illustration showed that they were entirely accounted for by the introduction of a new element of symmetry, that of mirror-image repetition, or " enantiomorphous similarity " as distinguished from " identical similarity." These three investigators all united in finally concluding that when the definition of symmetrical repetition is thus broadened to include enantiomorphous similarity, 165 further point-systems are admitted, and the whole 230 point-systems then account for the whole of the thirty-two classes of crystals.

Schönflies' simple definition of the nature of the structure is that every molecule is surrounded by the rest collectively in like manner, when likeness may be either identity or mirror-image resemblance. Von Fedorow finds the extra 165 types to be comprised in "double systems," consisting of two "analogous systems" which are the mirror images of each other. Barlow proceeds to find in how many ways the two mirror-image forms can be combined together, there being in general three distinct modes of duplication, including the insertion of one inside the other. He also shows that all homologous points in a structure of the type of one of these additional 165 point-systems together form one of the 65 Sohnckian point-systems, the structure being capable of the same rotations or translations, technically known as "coincidence movements" (movements which bring the structure to exhibit the same appearance as at first), as those which are characteristic of that point-system.

This fascinating subject of mirror-image symmetry, and the optical activity connected with it, will be reverted to and the latter explained in Chapter XI.

We have thus seen how satisfactorily the geometrical theory of the homogeneous partitioning of space has been worked out, and how admirably it agrees with our preliminary supposition that a crystal is a homogeneous structure. The fact that the 230 homogeneous point-systems all fall into and distribute themselves among the thirty-two classes of crystals, the symmetry of which has also now been fully established, affords undeniable proof that as regards this branch of the subject something like finality and clearness of vision has now been arrived at.

CHAPTER X

LAW OF VARIATION OF ANGLES IN ISOMORPHOUS SERIES. RELATIVE DIMENSIONS OF UNIT CELLS. FIXITY OF ATOMS IN CRYSTAL.

We are now in a position to approach the conclusion of the long controversy as to the constancy or otherwise of crystal angles in the cases of greatest similarity, those of isomorphous substances, and to appreciate how the conflicting views of Haüy and Mitscherlich and their schools of thought have at length been reconciled. As the result of a comprehensive study, on the part of the author, of the sulphates and selenates of the rhombic series $R_2\genfrac{}{}{0pt}{}{S}{Se}O_4$, and of the double sulphates and selenates of the monoclinic series $R_2M(\genfrac{}{}{0pt}{}{S}{Se}O_4)_2.6H_2O$, in which R represents the alkali metals, potassium, rubidium and cæsium, and in which M may be magnesium, zinc, iron, nickel, cobalt, manganese, copper or cadmium, four facts of prime significance have been definitely established.

(1) The crystals of the different members of an isomorphous series exhibit slight but real differences in their interfacial angles, the magnitude of the angle changing regularly with the alteration of the atomic weight of the interchangeable metals or negative elements of the same family group which give rise to

the series, as one metal or acid-forming element is replaced by another. The amount of the difference increases as the symmetry of the system diminishes. Thus the maximum difference for the more symmetrical rhombic series of sulphates and selenates is 56′, which occurs in the case of one angle between potassium and cæsium selenates, and it is usually much less than this; in the case of the less symmetrical monoclinic series of double salts the maximum angular difference observed was 2° 21′, between potassium and cæsium magnesium sulphates.

(2) The physical properties of the crystals, such as their optical and thermal constants, are also functions of the atomic weights of the elements of the same family group which by their interchange produce the series.

(3) The dimensions of the elementary parallelepipedon of the space-lattice, or in other words, the separation of the molecular centres of gravity, the points or nodes of the space-lattice, along the three directions of the crystal axes, also vary with the atomic weight of the interchangeable elements.

(4) Specific chemical replacements are accompanied by clearly defined changes in the crystal structure along equally specific directions. Thus, when the metal, say potassium, in an alkali sulphate or selenate is replaced by another of the same alkali-family group, rubidium or cæsium, there is a marked alteration in the crystal angles and in the dimensions of the space-lattice, corresponding to elongation of the vertical axis; and when the acid-forming element sulphur is replaced by selenium, its family analogue, a similar very definite change occurs, but the expan-

sion in this case takes place in the horizontal plane of the crystals.

Confirmatory results have also been obtained as regards the morphological constants, the investigations not extending to the optical or thermal properties, by Muthmann for the permanganates, and by Barker for the perchlorates, of the alkali metals. Hence, there can be no doubt whatever that, as regards the various series investigated, which are such as would be expected to afford the most definite results owing to the electro-positive nature of metals being at its maximum strength in the alkali group, the above rules are definite laws of nature.

Thus it is clear that in the cases of isomorphous substances, which were the only possible exceptions to the generalisation that *to every chemically distinct solid substance of other than perfect cubic symmetry there appertains a specific crystalline form, endowed with its own particular angles and morphological crystal elements, which are absolutely constant for the same temperature*, the law does really hold, and isomorphous substances are no exceptions. The law of progression of the crystal properties according to the atomic weight of the interchangeable elements affords indeed at the same time both an amplification of the generalisation and a precise explanation of its mode of operation in these cases.

The discovery of the local effect produced by the two kinds, positive and negative, of chemical replacement, has a profound bearing on crystal structure. For it is thereby rendered certain that the atoms are fixed in the crystal edifice, and therefore in the molecule in the solid state. It becomes obvious that the atoms—in their stereometric positions in the molecule, being thus fixed in the solid crystal when the molecules set themselves rigidly in the regular organisation of the space-lattice—form the points of the regular point-system of the crystal structure, which determines to which of the thirty-two classes of symmetry the crystal shall belong. Any movement of the atoms in the crystal, other than that which accompanies change of temperature, and possibly change of pressure, is thus improbable; and this experimental proof of their fixity, afforded by the fact that definitely orientated changes accompany the replacement of particular atoms, also doubtless indicates that the latter are located in the particular directions along which the changes of exterior angle and of internal structural dimensions are observed to occur. Stereo-chemistry, which has made such enormous advances during the last few years, thus becomes of even greater importance than Wislicenus and its other originators ever dreamt of.

Within the atoms in the crystal the constituent electronic corpuscles may be and probably are in rapid movement, and such physical effects as have hitherto been ascribed to movement of the atoms within the crystal are doubtless due to movement of the electronic corpuscles within them, the sphere of influence of the atom itself being fixed in space in the solid crystal, and being doubtless defined by the area within which the corpuscular movements occur.

Three illustrations of the law of change of the crystal properties with variation of the atomic weight of the determinative elements of an isomorphous series may be given, and will serve to render the practical meaning of the generalisation clearer. The first is a diagrammatic representation, in Fig. 60 (in a very exaggerated manner as the real change would be inappreciable on the scale drawn), of the change of angle on replacing the potassium in potassium sulphate, K_2SO_4, or selenate, K_2SeO_4, by rubidium or cæsium. The inner crystal outline, a vertical section, is that of the potassium salt. The vertical lines represent the intersections of the two faces of the brachypinakoid $b=\{010\}$ with a vertical plane parallel to the macropinakoid $a = \{100\}$; the horizontal lines represent the intersection of the two faces of the basal plane $c=\{001\}$ with the same vertical plane; and the oblique lines represent the intersection of the vertical plane with the four faces of the dome form $q=\{011\}$, which are inclined to both b and c planes. The diagram is thus designed to show the variation of the inclination of these latter dome faces to the two rectangular axial plane faces b and c. The outer crystal outline represents a similar section of a crystal of the corresponding cæsium salt, and the middle outline that of a crystal of the rubidium salt.

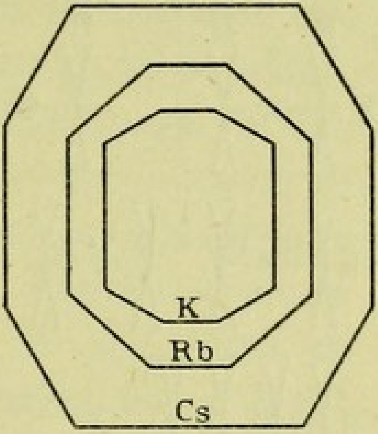

FIG. 60.—Diagram illustrating Progressive Change of Crystal Angles in Isomorphous Series.

The progressive alteration of the angle of the q-face will be obvious, the direction of the change being correct, but the amount of change, as already stated, being much exaggerated; in reality it never reaches a degree between the two extreme (potassium and cæsium) salts. It will be remembered that the respective atomic weights of potassium, rubidium, and cæsium are 38·85, 84·9 and 131·9, when hydrogen equals 1, that of rubidium being almost exactly the mean.

The second illustration is taken from the optical properties. Fig. 61 represents graphically the regular diminution of double refraction (the difference between the two extreme indices of refraction α and γ) which accompanies increase of the atomic weight of the metal present. The diagram exhibits the closing up of the two spectra afforded by three analogously orientated 60°-prisms, one of each of the three salts, such as was used in determining two of the refractive indices of the salt. Each prism produces two refracted rays from the single ray furnished by the collimator of the spectrometer, and consequently two images of the signal-slit of the collimator when monochromatic light is used, or two spectra if white light be employed. The Websky signal-slit is narrow at the centre to enable an accurate allocation to the vertical cross-wire of the telescope to be made, but wide at its top and bottom ends, in order to transmit ample light, and Fig. 61 shows four images of this signal produced by each prism, namely, one R in red C-hydrogen light and another B in greenish-blue F-hydrogen light belonging to each of the two spectra, in order to locate the two ends of each of the latter, coloured monochromatic light of each of the two colours in turn and of the exact

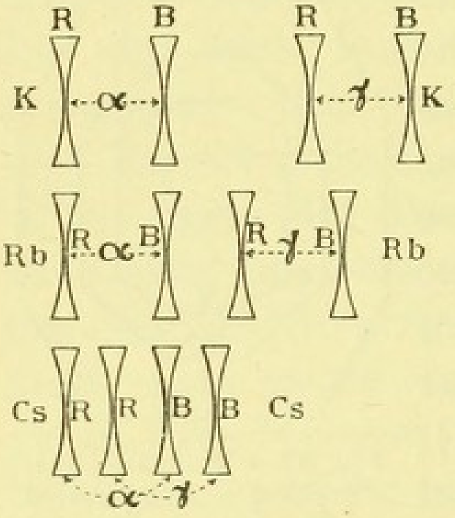

Fig. 61.—Diagram illustrating Progressive Change of Double Refraction in Isomorphous Series.

C and F wave lengths having been fed to the spectrometer from the spectroscopic illuminator. It will be observed in the case of the top row that the two spectra, each indicated by the adjacent red and greenish-blue images, are well apart, the relative distance being about that actually observed in the case of potassium sulphate. They are nearer together, however, in the second row, which indicates what is observed in the case of the analogous rubidium salt, and in the lowest row representing the relative distances of the two spectra apart in the case of the cæsium salt, they are so close together as to overlap; for in this latter case the greenish-blue image of the left-hand spectrum, corresponding to the α index of refraction, occupies the same position as the image for yellow sodium light of the right-hand spectrum corresponding to γ would occupy in the case of cæsium sulphate, the α refractive index for F-light being 1·5660 and the γ index for Na-light being 1·5662. The progression of the alteration of the amount of the double refraction is thus very striking, as the atomic weight of the metal is varied.

The third illustration of the law of progression with atomic weight is also an optical one, and is taken from the monoclinic series of double sulphates and selenates. It indicates the rotation, with increase of the atomic weight of the metal, of the ellipsoid which graphically represents the optical properties, about the unique axis of symmetry, which is likewise an axis of optical symmetry, of the crystal. In the potassium salt the ellipsoid occupies the position indicated by the ellipse drawn in continuous line in Fig. 62, the section of the ellipsoid by the symmetry plane; the outline of a tabular crystal parallel to the symmetry plane is also given, as well as the axes of the crystal and of the ellipsoid lying in that plane.

In the rubidium salt the ellipsoid has rotated over to the left, as indicated by the dotted ellipse, for a few degrees, the number of which varies slightly for the different groups of double salts; while in the cæsium salt it has swung over much more still, to the place marked by the ellipse drawn in broken line. In both this and the last illustration it will be remarked that the optical change is greater between the rubidium and cæsium salts than it is between the potassium and rubidium salts, the reason being that the optical properties are usually functions (of the atomic weight of the interchangeable elements) which are of an order higher than the first corresponding to simple proportionality.

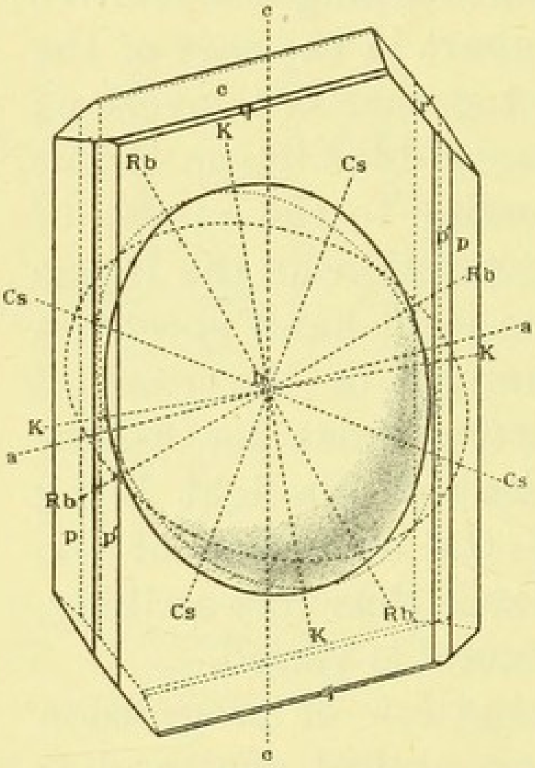

FIG. 62.—Diagram illustrating Progressive Rotation of Optical Ellipsoid in Monoclinic Isomorphous Series.

These three ocular illustrations may serve to render this interesting law of progression, according to the atomic weight of the interchangeable elements which give rise to the isomorphous series, clearer to the mind, by placing before it concrete instances of the operation of the law.

The generalisation itself may be very concisely expressed in the statement that:

The whole of the properties, morphological and physical, of the crystals of an isomorphous series of salts are functions of the atomic weights of the interchangeable chemical elements of the same family group which give rise to the series.

The fact that this law extends to the structural dimensions, equally with all other morphological properties, as stated under (3) at the beginning of this chapter, is of especial interest. For it has actually been found possible to determine the relations of the dimensions of the unit parallelepipeda of the space-lattices of the various salts, that is, the separation of the molecular points of the space-lattice in the directions of the three crystal axes, for the various salts of the isomorphous series. This is achieved by combining in suitable formulæ the volume of the unit cell of the space-lattice with the relative lengths of the three crystal axes, *a*, *b*, *c*.

The axial ratios $a : b : c$ are calculated from the measurements of the crystal angles, as explained in Chapter VI., page 68, and the volume is the physical constant long known as "molecular volume," but now for the first time understood as regards its meaning in the case of solid substances. It is the quotient of the chemical constant molecular weight (the sum of the atomic weights, taking into account the number of atoms of each element present) by the specific gravity of the substance, here the solid crystal. Very great care has been taken to obtain absolutely accurate determinations of the specific gravities of the salts, as much depends on this now very valuable physical constant, and all the values obtained were reduced to the constant reference temperature of 20°, as the density notoriously alters rapidly with change of temperature.

We have thus arrived at morphological constants of very considerable importance, which are best termed "*Molecular Distance Ratios,*" as they express the relative distances apart in the three directions of space of the centres of gravity or other representative points of contiguous chemical molecules. They are dependent on three experimental determinations, atomic weight, specific gravity, and crystal angles, all of which have now been brought to the highest pitch of refinement and accuracy; hence the molecular distance ratios are particularly trustworthy constants. If it were only known how much is matter and how much is space in the molecular parallelepipedal cell, we should actually have in these constants a relative measure of the sizes of the molecules. They do give us, however, the relative directional dimensions of the molecular unit parallelepipedal cells of the space-lattices of the various members of the isomorphous series, just as the molecular volumes give us the relative volumes of these cells. For in an isomorphous series we are absolutely sure that the plan on which the space-lattice is constructed, its style of architecture, is identical for all the members of the isomorphous series. Hence, the molecular distance ratios are in these cases absolutely valid and strictly comparable. The ratios are generally expressed by the Greek letters $\chi : \psi : \omega$.

On comparing the molecular distance ratios for a potassium, a rubidium, and a cæsium salt of any of the series of sulphates, selenates, permanganates, perchlorates, double sulphates or double selenates investigated, we invariably find that the values of χ, ψ, and ω for the rubidium salt (rubidium having the intermediate atomic weight) lie between the analogous sets of three values for the potassium and cæsium salts respectively, in complete accordance with the law.

For the generalisation to apply absolutely it is essential that the interchangeable elements shall belong strictly to the same family group of the periodic classification of Mendeleéff. Potassium, rubidium, and cæsium fulfil this condition absolutely, and so the law of progression of the crystal properties with the atomic weight of the interchangeable elements applies rigidly to their salts. Now there are two bases, the metal thallium and the complex radicle group ammonium NH_4, which are not thus related to the group of three alkali metals just mentioned, but which are yet capable of replacing those metals isomorphously in their crystals without more change of angle or of structural constants than is provoked by the replacement of potassium by cæsium; and often indeed the amount of change has been singularly like the lesser amount observed when rubidium has been interchanged for potassium. But although this is so, the directions of the changes are irregular, being sometimes the same as when rubidium or cæsium is introduced, and sometimes contrariwise, and in the case of thallium there are also striking optical differences, the thallium salts being exceptionally highly refractive. Still, morphologically the ammonium and thallium salts may legitimately be included in the same isomorphous series with the salts of potassium, rubidium, and cæsium, and a somewhat wider interpretation has to be given to the term "isomorphism" in order to admit these cases. To distinguish the inner group formed by family analogues, that is, the more exclusive group obeying the law of progression according to the atomic weight, the term "eutropic" is employed.

Thus the "isomorphous series" of rhombic sulphates, selenates, permanganates, and perchlorates, and the monoclinic series of double sulphates and double selenates, comprise the potassium, rubidium, cæsium, thallium and ammonium salts and double salts of sulphuric, selenic, permanganic, and perchloric acids, while the inner more exclusive "eutropic series," following the law absolutely, comprises in each case only the salts containing the family analogues, potassium, rubidium, and cæsium.

In this beautiful manner has the controversy between the schools of Haüy and Mitscherlich now been settled, the interesting law described in this chapter having definitely laid down the true nature and limitations of isomorphism, while at the same time absolutely proving as a law of nature the constancy and specific character of the crystal angles of every definitely chemically constituted substance.

CHAPTER XI

THE EXPLANATION OF POLYMORPHISM, AND THE RELATION BETWEEN ENANTIOMORPHISM AND OPTICAL ACTIVITY.

Polymorphism. It has been shown in Chapter VII. that Mitscherlich had in several instances proved the possibility of the occurrence of the same substance in two different forms, notably sodium di-hydrogen phosphate $NaH_2PO_4.H_2O$, calcium carbonate $CaCO_3$ (as calcite and aragonite), the metallic sulphates known as vitriols, and the chemical element sulphur, and that he gave to the phenomenon the name "dimorphism." Since that time large numbers of dimorphous substances have been discovered, and several which occur in three forms and even a few in no less than four totally distinct forms. Until the establishment of the geometrical theory of crystal structure, as expounded in Chapter IX., this phenomenon of polymorphism gave rise to endless fruitless discussion. It was most generally attributed to the different nature of the so-called "physical molecule," which was supposed to be an aggregate of chemical molecules and the unit of the space-lattice determining the crystal system; the different polymorphous varieties were supposed to be built up of structural units or physical molecules consisting of an aggregation of a different number of chemical molecules. Several attempts were made by various investigators, notably by Muthmann and by Fock, to determine the number of chemical molecules constituting the physical molecule.

All these efforts, however, ended unsatisfactorily, and in the year 1896 the author showed, in a memoir[1] on "The Nature of the Structural Unit," that in general the physical molecule is a myth, and that the chemical molecule is the only structural unit possessing the full chemical composition of the substance in question; and that its centre of gravity, or better, any representative point within it, such as a particular atom, is the unit point of the Bravais space-lattice of the crystal structure, while the atoms of which the chemical molecule are composed, arranged stereometrically identically similarly in all the molecules, are the points of the individual point-systems which make up the combined point-system. This does not imply a necessarily parallel and identically orientated arrangement of all the molecules, as at first postulated by Sohncke and which is a fact for his sixty-five point-systems; for in accordance with the conclusions of Schönflies, von Fedorow, and Barlow discussed in Chapter IX., cases are possible in which alternate molecules may be arranged as each other's mirror-images. Such are the cases of external molecular compensation or molecular combination, two oppositely enantiomorphous sets of molecules balancing each other within the structure, but by exterior compensation as regards the molecule itself. Moreover, the principle of mirror-image symmetry enters, as stated

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[1] *Journ. Chem. Soc.*, 1896, **69**, 507.

in Chapter IX, altogether into the constitution of no less than 165 of the 230 types of homogeneous structure possible to crystals.

Hence the conception of a physical molecule is totally unnecessary and, moreover, erroneous. The alkali sulphates and selenates exhibit dimorphism, one member of the series, ammonium selenate, having only hitherto been observed in the pure state in the second, monoclinic, form, and never in the ordinary rhombic form; and the author has conclusively proved for these salts, and also for the double salts which they form with the sulphates and selenates of magnesium, zinc, iron, nickel, cobalt, manganese, copper, and cadmium, that the chemical molecule is the only kind of molecule present, and that its representative points are, as just stated, the nodes of the Bravais space-lattice of the crystal structure, determining both the system of the crystal and its obedience to the law of rational indices.

The explanation of polymorphism thus proves, in the light of the results which have now been laid before the reader, to be a remarkably simple one. Special pains were taken in explaining those results to show that the temperature had a great deal to do with the conditions of equilibrium of the crystal structure, for it determines the intermolecular distances, that is, the amount of separation of the molecules, and thus controls their possibility of movement with respect to one another. Now the behaviour of the chemical molecules on the advent of crystallisation is undoubtedly largely influenced by the stereometric arrangement of the atoms composing them, and it is possible for the latter to be such that the molecules may take up several different parallel or enantiomorphously related positions; or as we have just seen, a regular alternation within the crystal structure of such mirror-image positions may be taken up. These different arrangements, whether parallel or enantiomorphously opposite, may be, and probably will be, of different degrees of stability, each of these different forms finding its maximum stability of equilibrium at some particular temperature, which is different for the different varieties. Hence, at a series of ascending or descending temperatures, assuming the pressure to remain the ordinary atmospheric, these different types of homogeneous crystal structures will be most liable to be produced, each at its own particular temperature, for which stable equilibrium of that crystal structure occurs.

These different assemblages are as a rule quite dissimilar, certainly in the crystal elements, often in class and not infrequently in system. Generally two such different crystalline forms are all that are possible within the life-range of temperature of the substance. But occasionally three or even as many as four such different forms are found to be capable of existence within the temperature life-limits of the substance.

Polymorphism is thus completely and simply explained as a direct result of the establishment of the geometrical theory of crystal structure as laid down in Chapter IX. The equilibrium of the homogeneous structure is a function of the temperature, and the stereometric arrangement of the atoms in the chemical molecule of a substance may be such as permits of two or more homogeneous arrangements of the molecules in assemblages of varying degrees of stability, but each of which has a maximum stability at a particular temperature. Hence, within any given range of temperature such a substance will assume that type of homogeneous arrangement of its molecules in a crystal which corresponds to the stablest equilibrium within these temperature limits, assuming the pressure constant within the bounds of the usual atmospheric variations. Employing the language of physical chemistry, such a substance will thus present two or more different solid "phases," each characterised by its specific crystalline form, the elementary parallelepipedon of which is quite a distinct one. Each phase possesses also its own specific optical and other physical properties, such as melting point, solubility, thermal expansion, and elasticity.

It would appear as if the element sulphur is also polymorphous in this sense, for the monoclinic prismatic form (Fig. 2, Plate I.)—the best known and most easily prepared, from the state of fusion, of all the forms other than the common rhombic form, in which sulphur is found in the neighbourhood of volcanoes and in which it is also deposited from solution in carbon bisulphide—is of distinctly lower stability, the crystals passing in a few days into powder composed of minute crystals of the stable rhombic variety. But in the case of carbon, with its totally different and apparently at ordinary temperatures equally stable varieties of octahedral-cubic diamond (Fig. 82, Plate XVI.) and hexagonal graphite, there is some doubt;

for although the diamond is converted into graphite at a red heat in the electric arc, it is doubtful whether we are not in the presence of a case of chemical polymerism or allotropy, like the case of ozone, where three atoms of oxygen compose the molecule, instead of the two atoms in the molecule of ordinary oxygen. The fact that the negatively electrified electronic corpuscles of the Crookes tube cause the same conversion of diamond into graphite, producing according to Parsons and Swinton a temperature of 4,890° C. in the act, is evidence in favour of allotropy, as the charged corpuscles are a very likely agent for breaking down such atomic combinations. Moreover, diamond is volatilised out of contact with air at 3,600° C. without liquefaction, and the vapour when cold condenses as graphite. But there is reason to believe, from experiments by Sir Andrew Noble and Sir William Crookes, that under great pressure carbon does liquefy at 3,600° C., and that the liquid drops on cooling crystallise as diamond.

The yellow and red varieties of phosphorus may also be due to a similar cause, the yellow variety, which forms excellent crystals, corresponding to P_4, while the red variety may correspond to a molecule composed of a different number of atoms than four.

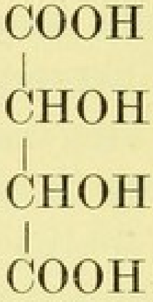
Another view of the nature of polymorphism has lately been brought forward by Lehmann, as the result of his remarkable experimental discovery of "liquid crystals," to which fuller reference will be made in Chapter XVI. This new view is, however, but an amplification of the foregoing explanation of polymorphism, indicating the possible mode in which the stereometric position of the atoms in the molecule does actually influence and even determine the particular homogeneous structure which shall be erected, and explains why the temperature plays such an important rôle. Lehmann's theory is that any one definitely stereometrically constituted chemical molecule can only display one particular homogeneous structure and form of crystal, and that when at a particular temperature the system or class of symmetry is altered, this occurs because the stereometric arrangement of the atoms within the molecule is altered, that is, a new form of molecule is produced, which naturally gives rise to a new form of crystal. As far as the author understands it, this does not mean an isomeric change from the chemical point of view, the chemical compound remaining the same, but that the stereometric positions of the atoms have been changed, without altering their chemical attachments, but sufficiently to change the nature of the point-system which they produce. A significant fact in support of this view is that the molecules of the substances forming liquid crystals are usually very complicated and extended ones, comprising a large number of atoms, the molecules, in fact, corresponding in length with the long names of the organic substances of which they are generally composed.

Lehmann's work has certainly proved that the molecule is endowed with more individuality than has hitherto been ascribed to it, and he even shows that there is some ground for believing that his liquid crystals are such because this directive orientative force resident in the molecules themselves maintains them in their mutually crystallographically orientated positions even in the liquid state, which may be and sometimes is as mobile as water. It thus appears that any general acceptance of Lehmann's ideas will only tend to amplify and further explain the nature of polymorphism on the lines here laid down, the temperature of conversion of one form into another being merely that at which either a different homogeneous packing is possible, or that at which the stereometric relations of the atoms in the molecule are so altered as to produce a new form of point-system without forming a new chemical compound.

Enantiomorphism of Crystalline Form and Optical Activity. It has already been stated that two supplementary forms which are similar but not identical, the one being the inverse or mirror-image reflection of the other, as a right-hand glove is to a left-hand one, are termed "enantiomorphous." Also it has been shown that all those crystal forms which have no plane of symmetry, either of simple symmetry or alternating symmetry (which is equivalent to saying that no centre of symmetry is present in addition to no plane of symmetry), are enantiomorphous, and that such forms belong to eleven specific classes. It has further been shown that the introduction of this principle of mirror-image symmetry or enantiomorphism into the conditions already laid down by Bravais and Sohncke for a homogeneous structure, by von Fedorow, Schönflies, and Barlow, enabled those investigators to derive the remaining 165 of the 230 possible types of homogeneous structures compatible with crystal structure, over and above the 65 already established by Bravais and Sohncke, and thus to complete the geometry of crystal structure, when the units of such structure are represented by points. Sohncke subsequently accepted the new principle, and modified his own theory so as to bring it into line with it. He exhibited some disinclination, however, at first, to accept the idea—which is a part of the assumption of the other three authors just referred to, and which appears to be absolutely necessary to explain one or two of the most complicated of the crystal classes—of the possibility of two enantiomorphous kinds of molecule being present in the crystal of the same single substance, the balancing of the two sets having the effect of producing mirror-image symmetry of the whole crystal, that is, the development of a plane of symmetry.

Now the whole subject is of deep interest, both physical and chemical as well as crystallographical, inasmuch as it is precisely such substances as show enantiomorphism,—and can thus exist in two forms, one of which is the mirror-image of the other and not its identical counterpart, the two being like a pair of gloves,—which are found to possess the property of rotating the plane of polarised light and which are therefore said to be " optically active." Moreover, the property may be displayed by both the crystals and their respective solutions, or by the crystals only. If, therefore, two optical antipodes of the same substance are known, one rotating the plane of polarisation to the right and the other rotating it to the same extent to the left, their crystals invariably exhibit mirror-image symmetry with respect to each other. The converse does not necessarily hold good, however, that a crystal possessing the symmetry of one of these eleven classes will always exhibit optical activity.

Pasteur [1] was the first to recognise this important relation between enantiomorphous crystalline form and optical activity, in the case of tartaric acid, which has the empirical formula $C_4H_6O_6$ and the constitution:



$$\begin{array}{l} \mathrm{COOH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{COOH} \end{array}$$

Tartaric acid was isolated by Scheele in 1769, and its discovery was described in the very first memoir of that distinguished chemist. Another very similar acid, as regards some of its more apparent properties, was afterwards, in 1819, described by John of Berlin, and investigated by Gay-Lussac in 1826; the latter obtained it from the grape juice deposits of the wine manufactory of Kestner at Thann in the Vosges. It was still more fully investigated by Gmelin in 1829, who called it racemic acid (Traubensäure). But it needed the genius of Berzelius to prove that it really had the same composition as tartaric acid, although so different to that acid in some of its properties.

We have here as a matter of fact, the first instance brought to light involving the principle of isomerism, the existence of two or more distinct

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[1] *Ann. de Chim. et Phys.*, 1848, **24**, 28 and 38; also 1850, **28**, 56; *Comptes Rendus*, 1848, **26**, 535; also 1849, **29**, 297; also 1850, **31**, 480; also 1853, **37**, 162, and 1858, **46**, 615.

compounds having the same chemical composition as regards the numbers of atoms of the same elements present, but differing in chemical or physical properties, or both, owing to the different arrangement of those atoms within the molecule. The "isomers" may be chemical or purely physical; the latter involves no alteration of the linking of the atoms, but merely of their disposition in space, and is the kind met with in the case of the tartaric acids.

Biot, so noted for his optical researches, showed afterwards that tartaric and racemic acids behave optically differently in solution, an aqueous solution of the former rotating the plane of polarisation to the right whilst that of racemic acid is optically inactive, not rotating the plane of polarisation at all. That is, if the dark field be produced in the polariscope, by crossing the polarising and analysing Nicol prisms at right angles, tartaric acid solution will restore the light again, and the analyser will have to be rotated to the right in order to reproduce darkness. In the case of tartaric acid, the crystals themselves also rotate the plane of polarisation, the amount being as much as 11°.4 in sodium light for a plate of the crystal one millimetre thick. On the other hand, neither the solution nor the crystals of racemic acid rotate the plane of polarisation at all.

Pasteur's discovery, made in the year 1848, consisted in finding that racemic acid is really a molecular compound of two physical "isomers," namely, of ordinary tartaric acid, which, as we have seen, rotates the plane of polarisation to the right, and of another variety of tartaric acid which rotates the beam of polarised light to the same extent to the left. The latter and ordinary tartaric acid he therefore distinguished as lævo-tartaric acid and dextro-tartaric acid respectively. Pasteur went even further than this, in discovering yet a fourth variety of tartaric acid, which is optically inactive like racemic acid, but which cannot be split up into two optically active antipodes.

Indeed, it has since been shown that there are three varieties of this truly inactive tartaric acid ; they are cases of isomerism of the chemical molecule itself, that is, the stereometric arrangement of the atoms in the molecule is different in the three cases. For the molecule of tartaric acid—in common with the molecules of all carbon compounds the solutions of which, or which themselves in the liquid state, rotate the plane of polarisation—possesses an asymmetric carbon atom, an atom of carbon which is linked by its four valency attachments to four different kinds of atoms or radicle groups ; indeed, the molecule of tartaric acid contains two such asymmetric carbon atoms, namely, the two in the pair of CHOH groups. For each of these carbon atoms is linked by one attachment to the carbon atom of the outer COOH group, by another to an atom of hydrogen, by a third to the oxygen of the group OH, and by its fourth attachment to the carbon atom of the other group CHOH, which carries the rest of the molecule, that is, this attachment is to the other half-molecule CHOH.COOH. Hence, it is quite obvious that there can be two different dispositions of the atoms in space, one of which would be the mirror-image of the other, while leaving the arrangement of the atoms about the two asymmetric carbon atoms dissimilar and not symmetrical in mirror-image fashion. That is, the two dispositions would render the molecules in the two cases enantiomorphous with respect to each other, and these two would be the arrangements respectively in the two optically active varieties. That this is the correct explanation of the ordinary dextro variety and the lævo variety of tartaric acid can now admit of no doubt.

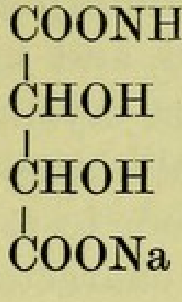
But if the groups round the two asymmetric carbon atoms are symmetrical in mirror-image fashion, there will be compensation within the molecule itself, and the substance will be optically inactive from internal reasons. This is the explanation of the optically inactive variety which is unresolvable into any components. The different varieties of this inactive form are doubtless due to the different possibilities of arrangement of the atoms in each half, while leaving the two halves round each asymmetric carbon atom symmetrical to each other.

We now know that the decomposable inactive variety, racemic acid, may be readily obtained by dissolving equal weights of the ordinary dextro and lævo varieties in water and crystallising the solution by slow evaporation at the ordinary temperature. For further investigation has fully borne out the conclusion of Pasteur, that racemic acid simply consists of a molecular compound of the two active varieties. It is thus itself inactive because it is externally compensated, the two kinds of enantiomorphous molecules being alternately regularly distributed throughout the whole crystal structure, the very case which von Fedorow, Schönflies, and Barlow assumed to be possible, and which Sohncke only tardily admitted. The crystalline form of racemic acid is, as was to be expected, quite different from the monoclinic form of the active tartaric acids, being triclinic ; and indeed it is not crystallographically comparable with the active form, inasmuch as the crystals of racemic acid contain a molecule of water of crystallisation, whereas the active varieties crystallise anhydrous.

Ordinary dextro and lævo tartaric acids crystallise in identical forms of the sphenoidal or monoclinic-hemimorphic class of the monoclinic system, the class which is only symmetrical about a digonal axis, the unique symmetry plane of the monoclinic system, which also operates when full monoclinic symmetry is developed, being absent in this class. Hence the interfacial crystal angles, the monoclinic axial angle, and the axial ratios are identical for the two varieties. But the crystals are hemimorphic, owing to the absence of the symmetry plane, and complementarily so, the dextro variety being distinguished by the presence of only the right clino-prism $\{011\}$, while the lævo variety is characterised by the presence only of the left-clino-prism $\{0\bar{1}1\}$, these two complementary forms, each composed of only two faces and which on a holohedral crystal exhibiting the full symmetry of the monoclinic system would both be present as a single form of four faces, being never both developed on the same optically active crystal.

This hemimorphism of the two kinds of crystals will be rendered clear by Figs. 63 and 64, representing typical crystals of dextro and lævo tartaric acids which are obviously the mirror-images of each other.

A remarkable discovery was made by Pasteur in connection with one of the salts of racemic acid, sodium ammonium racemate, $Na(NH_4)C_4H_4O_6$, or



$$\begin{array}{l} COONH_4 \\ | \\ CHOH \\ | \\ CHOH \\ | \\ COONa \end{array}$$

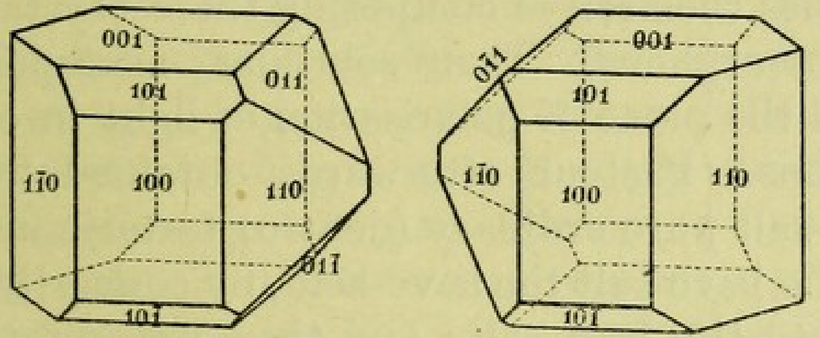


FIG. 63. FIG. 64.

Crystals of Dextro and Lævo Tartaric Acids.

which is obtained by adding ammonia to the readily procurable salt hydrogen sodium racemate. Sodium ammonium racemate was found by Pasteur to be decomposable into the salts of dextro and lævo tartaric acids, on crystallisation of a solution saturated at 28° C. by inoculation with a crystal of either of those active salts. The solution on cooling being in the state of slight supersaturation, which we now know from the work of Ostwald and of Miers as the metastable condition, corresponding to the interval between the solubility and supersolubility curves (see Fig. 98), if a crystal say of sodium ammonium lævo-tartrate be introduced, this variety crystallises out first and can be separated from the residual dextro-salt, which can then be subsequently crystallised. Moreover, in certain direct crystallisations of sodium ammonium racemate without such specialised inoculation, Pasteur found all the crystals hemimorphic, some right-handed and some left-handed, and he was actually able to isolate from each other crystals of the two varieties. On separate recrystallisation of these two sets of crystals, he found them to retain permanently their right or left-handed character, indicating that the molecules themselves composing these crystals were enantiomorphous. Their solutions correspondingly rotated the plane of polarisation of light in opposite directions. Pasteur afterwards obtained from the dextro-salt pure ordinary (dextro) tartaric acid, and from the lævo-salt the lævo-acid, by converting them first into the lead salts and then precipitating the lead as sulphide by sulphuretted hydrogen.

In the case of lævo-tartaric acid, this was its first isolation, as it had hitherto been unknown. Gernez afterwards independently found that a saturated solution of sodium ammonium racemate affords crystals of the lævo-salt just as readily as of the dextro-salt; if a crystal of either salt be introduced, crystals corresponding to that variety are produced.

Another most fruitful observation of Pasteur, the principle of which has since been the means of isolating one of the two constituents of many racemic compounds, was that when the spores of *Penicillium glaucum* are added to a solution of racemic acid containing traces of phosphates the ordinary dextro component is destroyed by the organism, while the lævo component is unattacked so long as any dextro remains ; hence, if the fermentation operation be stopped in time the lævo-acid may be isolated and crystallised. Why a living organism thus eats up by preference one variety only, possessing a particular right or left-handed screw structure, of a compound containing the same elementary constituents chemically united in the same manner, remains a most interesting biological mystery.

The crystals of both dextro and lævo tartaric acids prove to be pyro-electric, that is, develop electric excitation when slightly heated. The end which exhibits the development of the clinodome develops positive electricity in each case, when the crystal is allowed to cool after warming, so that the two varieties are oppositely pyro-electric, just as they are oppositely optically active. The most convenient method of demonstrating the fact is to dust a little of Kundt's powder, a mixture of finely powdered red lead and sulphur, through a fine muslin sieve on to the crystal as it cools. The sulphur becomes negatively electrified and the red lead positively by mutual friction of the particles in the sifting, and the sulphur thus attaches itself to the positively electrified part of the crystal and the red lead to the negatively electrified end. This phenomenon of the development by the two varieties of an optically active substance of opposite electrical polarity has since been shown to be a general one.

Finally, on mixing concentrated solutions containing equivalent weights of dextro and lævo tartaric acid Pasteur observed that heat was evolved, a sign of chemical combination, and the solution afterwards deposited on cooling crystals of racemic acid. Hence, the only conclusion possible is that racemic acid must be a molecular compound of the two oppositely optically active tartaric acids. It thus partakes of the character of a double salt, analogous to potassium magnesium sulphate for instance. Consequently the crystal structure is one in which alternating molecules of the two acids are uniformly distributed, and the case is actually presented of two oppositely enantiomorphous sets of molecules producing a homogeneous structure.

This interesting pioneer case of tartaric acid has been the cause of the term " racemic " being applied to the inactive form of a substance when it is decomposable into two oppositely optically active enantiomorphous varieties of the substance. No well authenticated exception has been found, in all the many instances which have been observed of the phenomenon since Pasteur's time, to the fact that optically active substances exhibit what was formerly termed hemihedrism ; that is, expressing the case in accordance with our later more accurate ideas of crystal structure as elucidated in previous chapters, such substances invariably belong to classes of symmetry possessing less than the full number of elements of symmetry possible to the system to which the class belongs. These classes are eleven in number, those possessing no plane of symmetry ; they are, namely, the asymmetric class of the triclinic system, the sphenoidal class of the monoclinic system (to which the two tartaric acids, dextro and lævo, belong), the bisphenoidal class of the rhombic system, the pyramidal and trapezohedral classes of the trigonal, tetragonal, and hexagonal systems, and the tetrahedral-pentagonal-dodecahedral and pentagonal-icositetrahedral classes of the cubic system.

The optical activity has been proved by Le Bel and Van t'Hoff to be due in most cases to enantiomorphism of the chemical molecules, that is, to the enantiomorphous stereometric arrangement of the atoms in the molecules, and therefore also,—as we have just seen, in accordance with the geometrical theory of crystal structure,—of the combined point-system in the case of each of the two varieties.

The point-systems are probably of a spiral screw-like character, either right-handed or left-handed, as has been shown by Sohncke to be the case for the two varieties of quartz, which crystallises in the trapezohedral class of the trigonal system, one of the eleven classes just enumerated. The example afforded by quartz will be developed fully in the next two chapters, as this beautifully crystallised mineral enables us to study and to demonstrate the phenomena of optical activity in a unique manner and on the large scale.

The solutions as well as the crystals are usually optically active in the cases where, as in the instance of the tartaric acids, the substances are soluble in water or other solvent. Occasionally, however, the optical activity is lost by dissolving in a solvent, and in such cases it is the point system only, and not the molecules themselves, which is enantiomorphous. Sodium chlorate, $NaClO_3$, is an instance of this kind, Moreover, a crystal can belong, as already mentioned, to one of the eleven above enumerated classes of symmetry without displaying optical activity, as all the point-systems possessing the symmetry of these eleven classes do not exhibit screw-coincidence movements. Barium nitrate, $Ba(NO_3)_2$, is such a case.

The two "optical antipodes," as the dextro and lævo varieties are conveniently termed, of an optically active substance thus possess an enantiomorphous crystal structure ; but they are alike in their physical properties such as density, melting point, optical refraction and optic axial angle, cleavage, and elasticity. The crystal angles are identical for the forms which are developed in common by them, and which are usually those which the particular low class of symmetry possesses in common with the holohedral class of the system. The crystallographic difference between the two varieties comes in with respect to the specific forms characteristic of the particular class of lower than full systematic symmetry, and these forms are never displayed in common by the two varieties, this being the essence of the enantiomorphism. When the crystals are not rich in faces, however, it frequently happens that only the common forms of higher symmetry just referred to are developed on the crystals, and the two varieties are then indistinguishable in exterior configuration ; it is only on testing their rotatory power, either by means of a section-plate of the crystal or by means of a solution, or their pyroelectric properties, or, lastly, their etch-figures afforded by a trace of a solvent (which etchings on the crystal faces are enantiomorphous and an excellent indication of the true symmetry), that their real character can be ascertained. Many mistakes have been made in the past, and crystals assigned to a higher than their true class of symmetry, owing to the investigation of only a single crop of crystals fortuitously poor in the number of forms displayed.

In the racemic form, if one should be deposited from the mixed solutions of the two optical antipodes as a molecular compound of the latter, we have an occurrence akin to polymerism, that is, the combination into a single whole entity of a number of molecules, essentially two in the case of racemism. Just as polymeric varieties of organic substances are always found to have quite different crystalline forms, so an optically inactive racemic form of a substance is generally quite different crystallographically to the dextro and lævo varieties. But there is usually some similarity along specific zones of the crystals, a kind of isogonism or morphotropy being developed, such as has been shown to occur, for instance, by Armstrong and Pope in the case of the substance sobrerol.[1]

Besides the true racemic form it is often observed that under certain conditions crystals are obtained which appear to combine the characters of both the dextro and lævo varieties, exhibiting both series of distinguishing hemimorphic or hemihedral forms on the same crystal; that is, they show the full, holohedral, symmetry of the system. This has been shown by Kipping and Pope[2] to be due to repeated twinning, thin layers of the right and left-handed varieties being alternated, just, in fact, as in the interesting

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[1] *Journ. Chem. Soc.*, 1891, 315.

[2] *Ibid.*, 1897, 989.

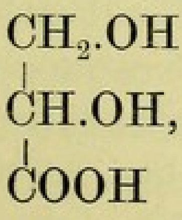
form of quartz known as amethyst, to which reference with experimental demonstration will be made in Chapter XIV.; the whole structure assumes in consequence the simulated higher symmetry which usually accompanies laminated twinning. Such forms have been termed "pseudo-racemic." In their memoir (*loc. cit.*, p. 993) Kipping and Pope summarise a large amount of highly interesting work on this chemico-crystallographic subject which has been carried out by them, and it may be useful to quote their precise definition of the relationship between racemic and pseudo-racemic substances. They say:

"We define a pseudo-racemic substance as an intercalation of an equal, or approximately equal, proportion of two enantiomorphously related components, each of which preserves its characteristic type of crystalline structure, but is so intercalated with the other as to form a crystalline individual of non-homogeneous structure. A solid racemic compound, on the other hand, may be defined as a crystalline substance of homogeneous structure which contains an equal proportion of two enantiomorphously related isomerides.

"The relations holding between a mere mixture of optical antipodes, a pseudo-racemic substance, and a racemic compound, are closely parallel to those existing between a crystalline mixture, an isomorphous mixture, and a double salt. The crystallographic methods, by which a double salt can be distinguished from an isomorphous mixture, may be directly applied to distinguish between racemic and pseudo-racemic substances. Thus, according as the crystalline substance obtained from a mixture of two salts resembles or differs from either of its components crystallographically, it is regarded either as an isomorphous mixture or a double salt; similarly, an inactive externally compensated substance, which closely resembles its active isomerides crystallographically, is to be considered as pseudo-racemic, whereas when the contrary is true, it is to be regarded as racemic."

The work of Kipping and Pope may be regarded as having finally vindicated and substantiated the law of Pasteur, that substances of enantiomorphous molecular configuration develop enantiomorphous crystalline structures, and that the crystal structures assumed by enantiomorphously related molecular configurations are themselves enantiomorphously related.

This subject, the main results and principles of which have now been elucidated, may well be closed with a reference to an interesting case of enantiomorphism and optical activity which the author has himself investigated,[1] and which is very similar to the case of the tartaric acids. It had been previously shown[2] by P. F. Frankland and W. Frew, that when calcium glycerate was submitted to the fermenting action of the *Bacillus ethaceticus* one-half only of the glyceric acid was destroyed, and that the remaining half was optically active, rotating the plane of polarisation to the right.



Now glyceric acid, $\begin{array}{l}CH_2.OH\\ |\\ CH.OH\\ |\\ COOH\end{array}$, has manifestly one

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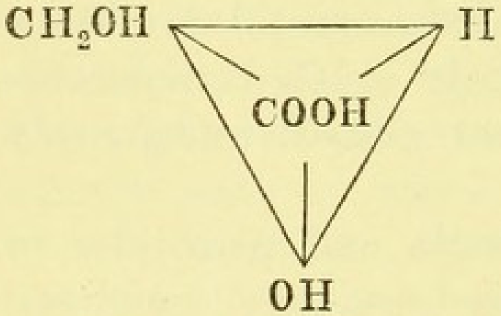
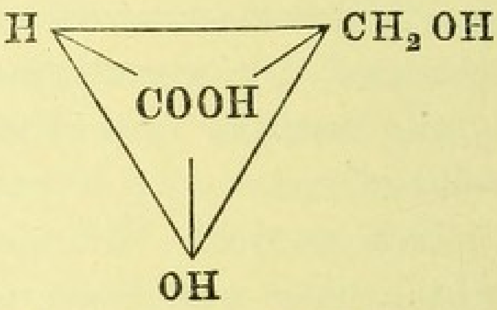
[1] *Journ. Chem. Soc.*, **1891, 59, 233.**

[2] *Ibid.*, **1891, 59, 96.**

so-called asymmetric carbon atom (that is, a carbon atom the four valencies of which are satisfied by attachment to four different monad elements or groups), that belonging to the CHOH group. There are consequently two possible arrangements of the molecule in space, probably corresponding to the two optically active varieties, namely, those represented, as far as is possible in one plane, as below, the asymmetric carbon atom (not shown in the graphic representation) being supposed to be at the centre of the tetrahedron, which is usually taken to represent a carbon atom with its four valencies.





Dextro-glyceric acid itself proved to be an uncrystallisable syrup, but the calcium salt, $Ca(C_3H_5O_4)_2.2H_2O$, was obtained in crystals sufficiently well formed to permit of a complete crystallographic investigation, which the author undertook by friendly arrangement with Prof. Frankland. Although the acid itself is dextro-rotatory, aqueous solutions of the calcium salt are lævo-rotatory to the extent of −12.09 units of "specific rotation" for sodium light.

The crystals were colourless well-formed prisms which proved to be of monoclinic symmetry, the best individuals being formed by very slow evaporation of the aqueous solution. They were terminated at both ends by pyramid and dome faces, and sometimes grew to the length of a centimetre. The actua crystal elements found after a full series of measurements were as under :—

CALCIUM DEXTRO-GLYCERATE.

Crystal-system : monoclinic.
Class of Monoclinic System : sphenoidal or monoclinic-hemimorphic.
Habit : prismatic.
Monoclinic axial angle : $\beta = 69° 6'$.
Ratio of axes : $a : b : c = 1.4469 : 1 : 0.6694$.
Forms observed :
$a = \{100\}$, $c = \{001\}$, $r' = \{\bar{2}01\}$, $p = \{110\}$,
$m = \{011\}$, $o = \{111\}$ $s = \{\bar{1}\bar{1}1\}$, $n = \{\bar{2}\bar{1}1\}$.

It will thus be seen that the system and the class are precisely those of the two active tartaric acids, which renders the case the more interesting. The usual appearance of the crystals is shown in Fig. 65, and the stereographic projection is given in Fig. 66, which will elucidate the symmetry more clearly, the plane of projection being the plane of symmetry The latter, however, in this class is inoperative, the two ends of the digonal symmetry axis, which runs perpendicularly to the plane of the paper, being differently terminated, as in the tartaric acids. The faces of the forms $o = \{111\}$ and $m = \{011\}$ were never found developed on the left side of the symmetry plane, that is, on the left side of the crystal as drawn in Fig. 65, the symmetry plane running perpendicularly to the paper vertically from front to back ; they were only present on the right. Conversely, the faces of $s = \{\bar{1}\bar{1}1\}$ and $n = \{\bar{2}\bar{1}1\}$ were never found developed on the right, but only on the left of the plane of possible symmetry.

Moreover, it was frequently observed that the right-hand faces (110) and $(\bar{1}10)$ of the primary prism-form *p* were much more brilliant and truly plane than those on the left hand, $(1\bar{1}0)$ and $(\bar{1}\bar{1}0)$, which were usually dull and often curved, as were also frequently the faces of the left-hand forms *s* and *n*. The right-hand distinguishing forms *m* and *o*, on the contrary, were generally most brilliant and gave admirable reflections of the goniometer signal-slit.

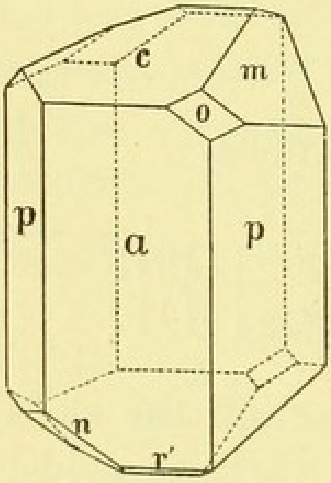


Fig. 65.—Crystal of Calcium Dextro-Glycerate.

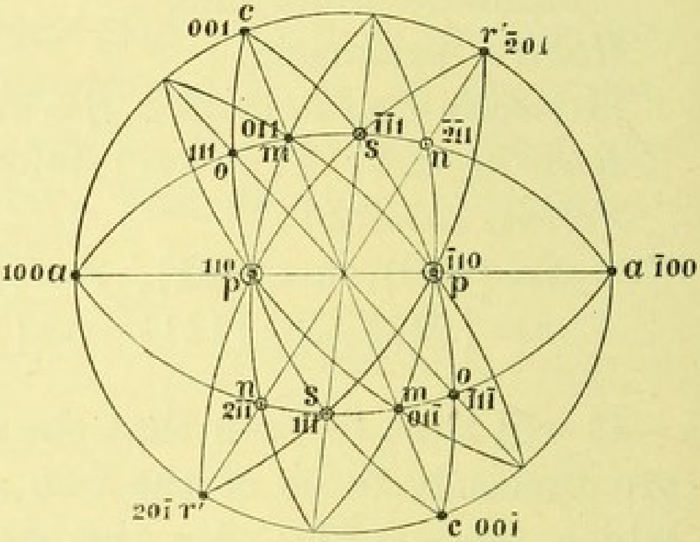


Fig. 66.—Stereographic Projection of Calcium Dextro-Glycerate.

The following table represents the results of the angular measurements, twelve different well-formed individual crystals having been employed. The angles marked with an asterisk were the important angles the mean observed values of which were accepted as correct, being the best measured angles, and which were therefore used as the basis of the calculations.

Table of Interfacial Angles of Calcium Glycerate.

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
$ap = 100:110$	42	52° 32′— 54° 16′	53° 29′	*
$pp = 110:\bar{1}10$	20	72 7 — 73 33	73 4	73° 2′
$ac = 100:001$	13	68 22 — 69 42	69 3	69 6
$cr' = 001:\bar{2}01$	13	52 4 — 52 31	52 13	*
$r'a = \bar{2}01:\bar{1}00$	13	58 35 — 58 46	58 41	*
$cm = 001:011$	10	31 47 — 32 19	32 3	32 2
$r'n = \bar{2}01:\bar{2}\bar{1}1$	2	29 43 — 29 48	29 45	29 47
$ao = 100:111$	7	53 59 — 54 10	54 3	53 54
$om = 111:011$	7	18 20 — 18 35	18 26	18 29
$ma = 011:\bar{1}00$	13	107 22 —108 24	107 41	107 37
$an = \bar{1}00:\bar{2}\bar{1}1$	11	62 32 — 63 44	63 6	63 10
$ns = \bar{2}\bar{1}1:\bar{1}\bar{1}1$	1	—	21 35	21 27
$sa = \bar{1}\bar{1}1:100$	3	94 49 — 95 34	95 18	95 23
$po = 110:111$	9	43 51 — 44 44	44 35	44 38
$oc = 111:001$	9	32 56 — 33 15	33 7	33 7
$cs = 001:\bar{1}\bar{1}1$	7	41 32 — 43 2	42 10	42 17
$sp = \bar{1}\bar{1}1:\bar{1}\bar{1}0$	7	59 15 — 60 54	59 59	59 58
$pc = \bar{1}\bar{1}0:00\bar{1}$	14	77 2 — 78 21	77 42	77 45
$cp = 00\bar{1}:110$	16	101 39 —103 36	102 16	102 15
$pm = 110:011$	9	52 15 — 53 25	52 42	52 41
$mn = 011:\bar{2}\bar{1}1$	5	79 5 — 79 26	79 15	79 12
$np = \bar{2}\bar{1}1:\bar{1}\bar{1}0$	5	47 41 — 48 23	48 4	48 7
$pr' = 110:\bar{2}01$	14	106 35 —108 42	108 5	108 1
$r'p = \bar{2}01:\bar{1}\bar{1}0$	26	70 54 — 73 32	71 55	71 59
$ps = \bar{1}\bar{1}0:1\bar{1}\bar{1}$	5	66 42 — 67 17	67 4	67 5
$sr' = 1\bar{1}\bar{1}:20\bar{1}$	6	40 36 — 41 29	41 5	40 56
$pm = \bar{1}10:011$	3	75 5 — 76 21	75 37	75 45

There is a moderately good cleavage parallel to the basal plane $c = \{001\}$.

The optical properties afford conclusive proof of the monoclinic nature of the symmetry. The plane of the optic axes is perpendicular to the possible symmetry plane, $b = \{010\}$, and the first median line makes an angle of 23° with the vertical axis c, emerging consequently nearly normal to the basal plane $c = \{001\}$, so that a section-plate parallel to the c-faces, or a tabular crystal or cleavage plate parallel to c, shows the optic axial rings and brushes well. The values of the apparent optic axial angle in air, 2E, and of the true optic axial angle within the crystal, $2V_a$, the latter measured with the aid of a pair of accurately ground section-plates perpendicular to the first and second median lines and immersed in oil, are given in the next table.

	2E	$2V_a$
For lithium light .	51° 35′	34° 56′
,, sodium ,, .	52° 30′	35° 28′
,, thallium ,, .	53° 50′	36° 16′

The intermediate refractive index β was found to be as under—

For red lithium light . .	1.4496
,, yellow sodium ,, . .	1.4521
,, green thallium ,, . .	1.4545

The double refraction was also determined and found to be of positive sign.

The optical properties of calcium dextro-glycerate thus confirm absolutely the monoclinic nature of the symmetry, as regards the crystal system. And it was conclusively demonstrated by the goniometrical part of the investigation that the exterior symmetry was not such as agreed with holohedral monoclinic symmetry, but with that of the sphenoidal class, in which the only one of the two elements of monoclinic symmetry (the plane of symmetry and the digonal axis of symmetry) in operation is the digonal axis, thus leaving the two terminations of that axis, at opposite sides, right and left, of the possible symmetry plane, unsymmetrical. And this is precisely the symmetry which is characteristic of an enantiomorphous optically active substance.

Unfortunately, the corresponding lævo-salt has not yet been obtained in measurable crystals, but there can be no doubt that whenever such are forthcoming they will display enantiomorphism in the precisely opposite and complementary sense, the facial forms characteristic in this dextro-salt of the right termination of the digonal axis being absent on that side of the systematic symmetry plane but developed on the left side instead, and *vice versa*, and that the two enantiomorphous forms will together make up the whole of the faces required by the full symmetry of the monoclinic system.

A concrete instance like this, worked out practically in the laboratory, brings home the precise nature of this interesting relationship, between crystallographic and molecular enantiomorphism on the one hand and optical activity on the other hand, in a particularly clear and forcible manner. It is hoped that this brief account of it will also consequently have been of assistance to the reader, in more clearly appreciating the main points of this chapter.

CHAPTER XII

EFFECT OF THE SYMMETRY OF CRYSTALS ON THE PASSAGE OF LIGHT THROUGH THEM. QUARTZ, CALCITE, AND GYPSUM AS EXAMPLES.

The action of transparent crystals on the rays of light which they transmit is a subject not only of the deepest interest, but also of the utmost importance. For it is immediately possible to detect a cubic crystal, and to discriminate between two groups, optically uniaxial and biaxial respectively, of the other six systems of symmetry, three systems going to each group, by this means alone. For a cubic crystal is singly refractive in all directions. A 60°-prism, for instance, cut from a cube of rock-salt, for the purpose of obtaining the refractive index of the mineral by the ordinary method of producing a spectrum and arranging it for minimum deviation of the refracted rays, affords but a single spectrum, or a single sharp image of the spectrometer slit when the latter is fed by pure monochromatic light instead of ordinary white light. This is true however the prism may have been cut, as regards its orientation with respect to the natural crystal faces.

But a 60°-prism cut from a crystal belonging to the optically biaxial group, composed of the rhombic, monoclinic, and triclinic systems of symmetry, will always afford two images of the slit or two spectra, corresponding to two indices of refraction; and, when the orientation of the prism is arranged so that the refracting angle is bisected by a principal plane of the ellipsoid which represents the optical properties, and the refracting edge is parallel to one of the principal axes of the optical ellipsoid, the prism, when arranged for minimum deviation of the light rays, will at once afford two of the three refractive indices, α, β, γ, corresponding to light vibrations along two of the three principal axial directions of the ellipsoid. The two indices which the prism affords will be (1) the one which corresponds to vibrations parallel to the refracting edge, and (2) that which corresponds to undulations perpendicular to the edge and to the direction of transmission of the light through the prism (the third axis of the ellipsoid). For the vibrations of the light in the two rays into which the beam is divided on entering the crystal are both perpendicular to the direction of transmission and to each other; the two images or spectra produced owing to the double refraction, that is, owing to the different velocities of the two mutually rectangularly vibrating rays, thus correctly afford the means of determining two of the three principal (axial) refractive indices.

Gypsum, the monoclinic hydrated sulphate of lime, $CaSO_4.2H_2O$, already referred to in connection with the Mitscherlich experiment in Chapter VII., is an excellent substance to employ for the demonstration of this fact, by cutting and polishing a 60°-prism out of a clear transparent crystal of the mineral as above described; and if a Nicol prism be introduced in the path of the rays, one spectrum or monochromatic image will be extinguished when the

Nicol is arranged at its 0° position, and the other when the Nicol is rotated 90° from this position. This proves that the two rays affording the two refractive indices are polarised in planes at right angles to each other, and, moreover, enables us to verify that the planes in which the vibrations of the two rays occur are actually parallel and perpendicular respectively to the refracting edge of the prism. For the two extinctions occur when the vibration plane of the Nicol is either vertical, parallel to the prism edge, or horizontal, perpendicular thereto.

If a second prism be cut complementarily to the first, that is, so that the refracting edge is parallel to the third axis of the ellipsoid (the direction of transmission through the first prism) and the bisecting plane again parallel to one of the three axial planes of the ellipsoid, such a prism will also yield two refracted images corresponding to two indices; one of them, that particular image the vibrations of which are parallel to the refracting edge, will correspond to that one of the three principal indices which was not given by the first prism, while the other one will afford a duplicate determination of one of the two indices afforded by the first prism. Hence, a couple of such axially orientated prisms of a rhombic, monoclinic, or triclinic crystal will enable us to determine all three refractive indices, and one of them in duplicate, which latter fact will enable us to check the accuracy of our work.

If the 60°-prism be cut from a crystal of the uniaxial group, that is, from a hexagonal, tetragonal, or trigonal crystal—quartz or calcite being admirable examples of the latter and particularly suitable for demonstration purposes—it will generally afford two spectra in the same manner as a crystal of the three birefringent systems of lower symmetry. But there is one special mode of cutting which results in the prism exhibiting only a single spectrum, namely, when the hexagonal, tetragonal, or trigonal axis of symmetry, which is also the unique "optic axis" of the crystal along which there is no double refraction, is arranged to be perpendicular to the bisecting plane of the 60°-prism. For then the light is transmitted along this unique axial direction when the prism is arranged for the minimum deviation of the refracted rays out of their original path, and as it may vibrate in any direction perpendicular thereto with equal velocity there is no separation into two rays, that is, no double refraction, and thus only a single spectrum is afforded by such a prism in white light, or a single image of the slit in monochromatic light, and this latter will at once yield the refractive index which is generally indicated conventionally by the letter ω, corresponding to light vibrations perpendicular to the axis.

Spectroscopists take advantage of this interesting fact, when they employ a train of quartz prisms so cut in order to explore the violet and ultra-violet region of the spectrum ; for quartz transmits many of the ultra-violet rays which glass absorbs. Each prism gives only a single image like glass, whereas if it were otherwise cut it would give two spectra, which would so complicate matters as to render quartz useless for the purpose.

When the prism of quartz or calcite, or of any hexagonal, tetragonal, or trigonal substance, is cut so that the rays of light are transmitted through it perpendicularly to the axis, and so that the refracting edge is parallel to the axis, the light is broken up into two rays, one of which is composed of light vibrating parallel to the edge and therefore to the axis, and the other of light vibrating perpendicularly to the axis. Such a prism consequently affords the two principal extreme refractive indices of the crystal, ω and ϵ, the latter letter being always assigned to the refractive index of a uniaxial crystal corresponding to vibrations parallel to the axis.

A uniaxial crystal, one belonging to the hexagonal, tetragonal, or trigonal systems, has thus two principal refractive indices, ω and ϵ, while a biaxial crystal, one belonging to the rhombic, monoclinic, or triclinic systems of symmetry, has three, α, β, γ, corresponding to vibrations respectively parallel to the three rectangular axial directions of the optical ellipsoid, which are also the crystallographic axial directions in the case of a rhombic crystal. The index α is the minimum, and γ the maximum refractive index, the β index being intermediate; when the latter lies nearer to α in value, the crystal is said to be a positive one, but when nearer to γ the crystal is conventionally supposed to be negative. Similarly, when in a uniaxial crystal ϵ is the greater, as it is in the case of quartz, the crystal is termed positive, but if ω be the greater index, as happens in the case of calcite, then the crystal is by convention considered negative.

Just as in the case of gypsum, which is a positive biaxial crystal (the reason for the term biaxial will presently be more fully explained), when the two spectra afforded by a prism of calcite or quartz cut to afford both ϵ and ω are examined in plane polarised light, by introducing a Nicol prism somewhere in the path of the light, the two images corresponding respectively to ϵ and ω will be found to be produced by light polarised in two planes at right angles to each other. For when the Nicol is at its 0° position one will be extinguished, and when it is at 90° the other will be quenched. At the 45° position of the Nicol both images will be visible with their partial intensities, as happens also in the cases of biaxial prisms.

This behaviour of 60°-prisms of crystals belonging to the seven different styles of crystal architecture, as compared with a prism of glass or other transparent non-crystalline substance, is extremely instructive. For not only is the optical constant refractive index—the measure of the power exhibited by the crystal of bending light, corresponding to its effect in retarding by the nature of its internal structure the velocity of the light vibrations—the most important of all the optical constants, but also in the course of its determination we learn more of the behaviour of crystals towards light than from any other type of optical experiment.

In Fig. 67 is shown a convenient mode of demonstrating the experiment with the aid of the electric lantern and one of the large Nicol prisms of the projection polariscope, already briefly described in Chapter VII. in connection with the Mitscherlich experiment. The 60°-prism is arranged on a small adjustable stand nearest the screen ; then comes the Nicol polarising prism of $2\frac{1}{2}$ to 3 inches clear aperture, behind which is the projecting lens, at the focus of which is placed the adjustable slit on a separate stand. The slit is filled with light from the condenser of the electric lantern, and in the lantern front a thick water cell is arranged, in order to remove sufficient of the heat rays which accompany the light beam to avoid damage to the balsam joint of the calcite Nicol. When all the parts are properly arranged a sharp image of the slit should first be thrown on the screen directly, in the temporary absence of the 60°-prism, and then on replacing the latter at the proper angle for minimum deviation,

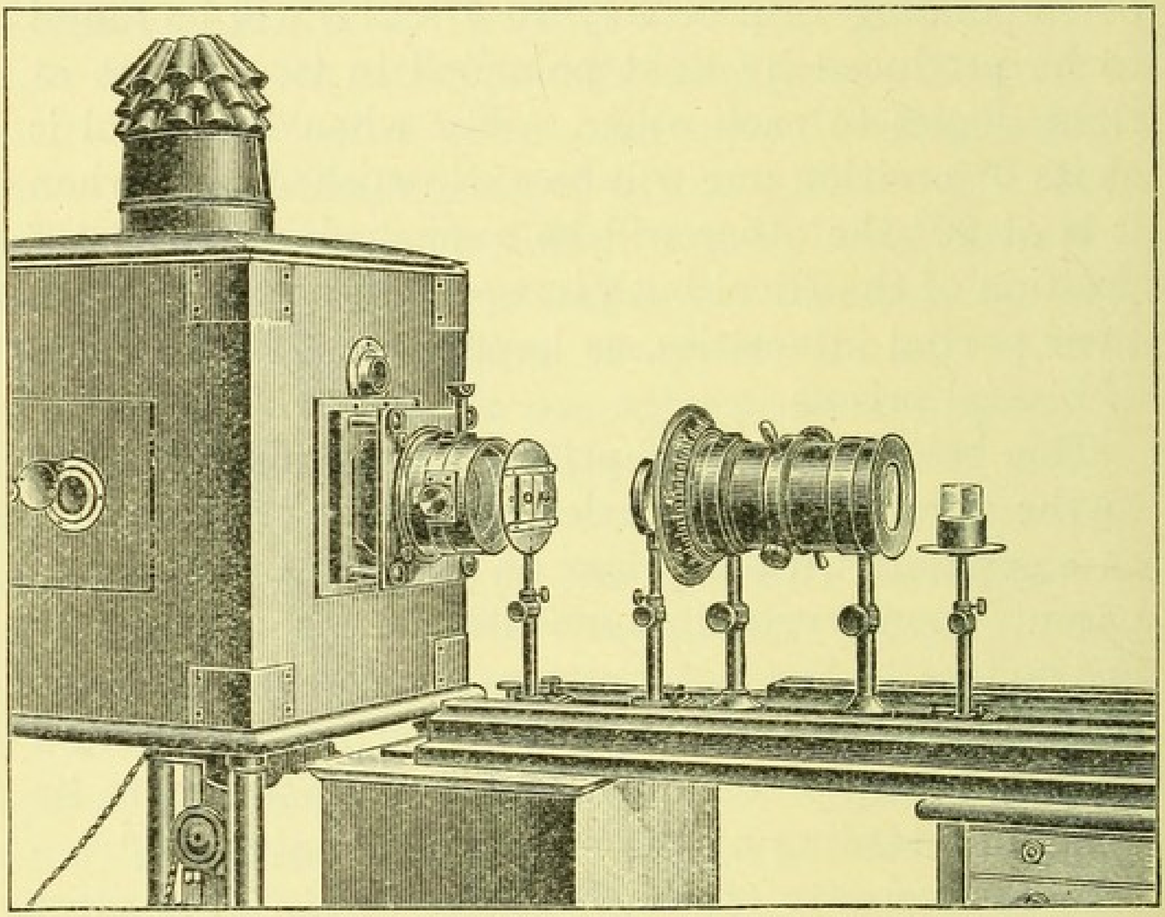


Fig. 67.—Experiment to show Rectangular Polarisation of the two Spectra afforded by a 60°-Prism of a Doubly Refracting Crystal cut to afford two Indices of Refraction.

when the light traverses the prism parallel to its third unused side, a spectrum or pair of spectra—according to the position of the Nicol and to the nature of the 60°-prism as explained in the foregoing discussion of the possibilities—will be projected on a second screen (or the same one if movable) arranged at the proper angle to receive the refracted rays.

If a single spectrum be afforded, which remains single on rotation of the Nicol, the prism is of glass or of a uniaxial crystal cut so that the light passes along the optic axis. If two spectra be shown when the Nicol is arranged in the neighbourhood of its 45° position, the crystal is a doubly refracting one, and if orientated so that the single optic axis, if the crystal be uniaxial, is parallel to the refracting edge, or, if the crystal be biaxial, so that the refracting edge is parallel to one of the three principal axes of the optical ellipsoid and its bisecting plane is parallel not only to this but also to a second principal axis, then one spectrum, corresponding to one principal refractive index, will extinguish when the Nicol is rotated to its 0° position, and the other spectrum, corresponding to a second principal refractive index, will be quenched on rotation of the Nicol to its 90° position.

The separation of the two spectra on the screen depends on the amount of the double refraction, and in the case of calcite this is exceptionally large, so that the two spectra are widely separated on the screen. They differ also considerably in dispersion. In the case of quartz the double refraction is very small, and the spectral images of the slit are consequently so close together as almost to touch one another.

The pair of spectra afforded by gypsum are similarly very close together, owing also to weak double refraction. The amount of the double refraction is measured by the difference between the uniaxial indices ϵ and ω, or that between the minimum and maximum biaxial indices α and γ. The two spectra given by quartz and calcite will correspond to ϵ and ω, and the greatest separation of spectra occurs in the case of gypsum when the spectra are those corresponding to α and γ, and not to α and β or β and γ.

It will now be useful and very helpful to examine more closely into the nature of the beautiful mineral quartz, in order that a series of interesting experiments may be described with it, which will assist largely in rendering the optical characters of crystals clear to us.

Quartz, rock crystal, although perhaps the commonest and best known of all crystallised substances, the naturally occurring dioxide of silicon SiO_2, is yet one of the most remarkable and fascinatingly interesting. To begin with, as explained in the last chapter, quartz belongs to one of the eleven enantiomorphous classes of lower than full systematic symmetry, those which exhibit two mirror-image forms related to one another like a pair of gloves. The particular class of the eleven to which quartz belongs is the trapezohedral class of the trigonal system, and two typical left-handed and right-handed crystals are shown in Fig. 68 and Fig. 69 respectively.

There is one principal form which is common to both the hexagonal and trigonal systems, namely, the hexagonal prism, and this is the chief form exhibited by quartz crystals. They are terminated by an apparently hexagonal pyramid, but which really consists of a pair of complementary rhombohedra, which are purely trigonal forms ; three upper faces of each rhombohedron are developed at one end of the prism which may be regarded as the upper, and the three lower faces of each of the two individual rhombohedra likewise at the lower end of a fully developed doubly terminated crystal. The rhombohedron is the characteristic form of the trigonal system of crystal symmetry, the systematic crystallographic axes being parallel to its edges. It is like a cube deformed by extension or compression along a diagonal, which latter is arranged vertically, and becomes the trigonal axis of symmetry (not a crystallographic axis), as shown in Fig. 70.

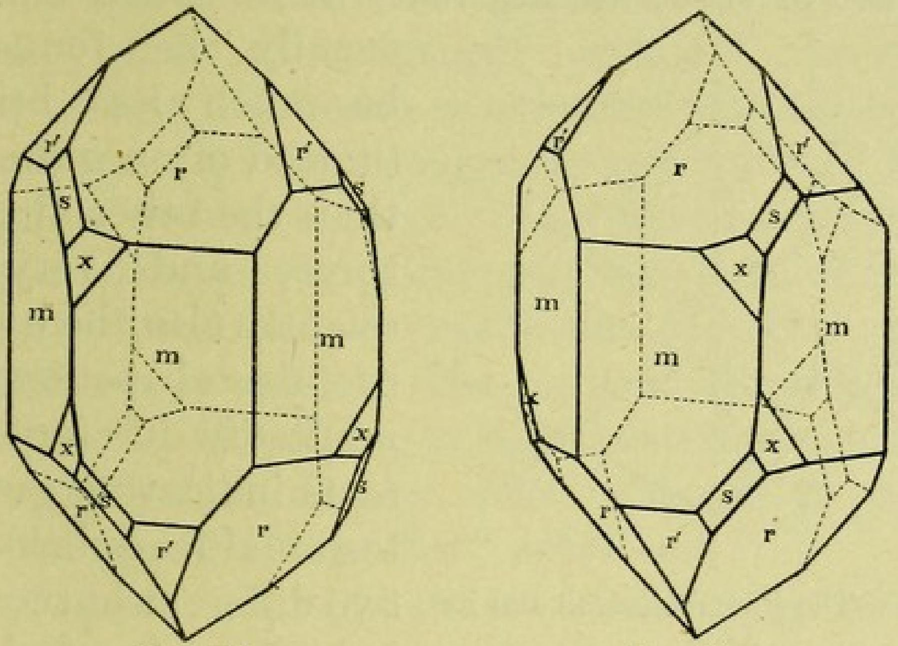


FIG. 68. FIG. 69.
Left-handed and Right-handed Crystals of Quartz.

When two rhombohedra are equally developed, one being rotated with respect to the other 60° round the vertical trigonal axis of symmetry, they together resemble a hexagonal pyramid, and crystals of quartz thus terminated at both ends are not uncommon, so that at first sight a quartz crystal might be mistaken for a hexagonal prism doubly terminated by the hexagonal pyramid, and the mineral considered, in error, to belong to the hexagonal system.

But one alternate set of three faces of the hexagonal pyramid at one end, and the oppositely alternate set of three similar faces at the other end, will usually be found to be much less brilliant (indeed often quite dull) than the other alternate three, and very frequently also the amount of development is markedly different, both facts indicating that the terminal faces belong to two different but complementary rhombohedral forms, and that the system of symmetry is the trigonal and not the hexagonal.

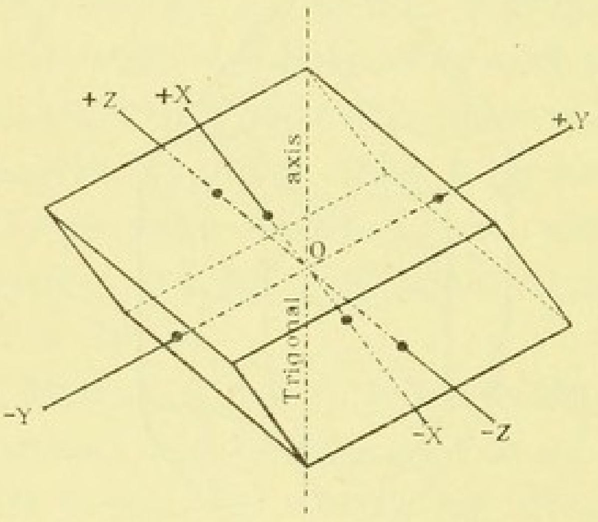


Fig. 70.—The Rhombohedron and its Axes.

But there is much stronger evidence than this for trigonal symmetry. For the little faces marked *s* and *x* on Figs. 68 and 69 are characteristic of the trapezohedral class of the trigonal system, and it will be observed that on one crystal, Fig. 68, these faces occupy and modify a left-hand corner or solid angle on the crystal, while on the other crystal, Fig. 69, they occupy and replace a right-hand solid angle. Now, if a plate be cut out of the former crystal perpendicularly to the axis of the hexagonal prism, that is, to the optic axis of the trigonal uniaxial crystal, it will be found to rotate the plane of polarisation to the left, the direction in which the small faces are situated ; while if a similar plate be cut out of the right-handed crystal shown in Fig. 69, that is, one which has the small faces on the right, it will be observed to rotate the plane of polarisation to the right.

As quartz possesses the symmetry of the trigonal system and is thus optically uniaxial, its optical properties are expressed, in common with those of all trigonal, tetragonal, and hexagonal crystals, by an ellipsoid of revolution, an ellipsoid the section of which perpendicular to the principal axis—that of revolution, the maximum or minimum diameter of the ellipsoid—is a circle. The optical properties are consequently the same in all directions round this axis, which has already been referred to by its common appellation of the "optic axis."

The optic axis is identical in direction with the trigonal axis of symmetry in the case of quartz or other trigonal crystal, and in the cases of hexagonal and tetragonal crystals with the axes of hexagonal and tetragonal symmetry, these three axes of specific symmetry being the distinctive property of these three respective systems, which are thus known in common as optically "uniaxial."

Consequently, no double refraction is suffered by a ray transmitted parallel to the optic axis, and the refractive index is equal in all directions perpendicular to the optic axis, that is, for all rays vibrating perpendicularly to the axis ; hence the value of the refractive index obtained along any such direction is one extreme value for the whole crystal, and as already mentioned is distinguished by the letter ω. The refractive index along the direction of the axis itself is the other extreme value, and is labelled ϵ. It must be clearly appreciated, however, that it is not the direction of transmission but that of vibration perpendicular thereto, that is meant when it is said that, for instance, the direction of the axis corresponds to the index ϵ. That is to say, a ray the *vibrations* of which occur parallel to the optic axis of a uniaxial crystal is refracted to an amount which corresponds to the refractive index ϵ, while a ray the vibrations of which occur perpendicularly to the axis affords ω. The difference between ϵ and ω is the measure of the double refraction of the crystal.

In the case of quartz ϵ is the greater, being 1.5534 for sodium light, quartz being thus positive according to the convention already alluded to; while ω is the smaller, namely, 1.5443. In the case of the other widely distributed trigonally uniaxial mineral calcite, carbonate of lime $CaCO_3$, the opposite is the case, ω being the greater, having the value 1.6583 for sodium light, and ϵ the less, namely, 1.4864, calcite being thus a negatively uniaxial substance. The amount of the double refraction in the cases of the two minerals is very different, ϵ-ω for quartz being 0.0091, and ω-ϵ for calcite being as much as 0.1719. Calcite is indeed a mineral endowed with an especially large amount of double refraction, a property which renders it so eminently suitable for use in demonstrating the phenomenon, and for the construction of the Nicol polarising prism, in which one of the two mutually perpendicularly polarised rays, that which affords the index ω, is got rid of by total reflection at a balsam joint, a large rhomb of calcite being cut in half along a particular diagonal plane and the two halves cemented together again with Canada balsam; the other ray, which affords ϵ (but not at its minimum value), is transmitted as a beam of perfectly polarised light.

The result of this difference in the amount of the double refraction of the two minerals quartz and calcite is very interesting as regards their behaviour with polarised light. A thin plate of quartz, such as is often found in the slices of rock sections employed for microscopic investigation, of muscovite granite or quartz porphyry for instance, and which is usually about one-fiftieth of a millimetre in thickness, shows brilliant colours in a parallel beam of polarised light, the Nicol prisms of the polarising microscope being crossed for the production of the dark field before the introduction of the section plate on the stage. This is only true, however, when the plate has not been cut perpendicularly to the axis, for such a thin plate thus cut does not perceptibly affect the dark field, there being no double refraction of rays transmitted along the axis, and the interference colours afforded by crystal plates in polarised light being due to the interference of the two rays produced by double refraction, one of which is retarded behind the other so as to be in a different phase of vibration. Also, the plate, even when cut obliquely, and best of all parallel, to the axis, has to be rotated in its own plane (perpendicular to the optical axis of the microscope), to the favourable position for the production of the most brilliant colour. This especially favourable position is half-way between (at 45° to) the positions at which darkness is afforded by the plate. For on rotating the plate between the crossed Nicols it becomes four times dark during a complete revolution, and at places exactly 90° apart, known as the "extinction positions," whenever, in fact, that plane perpendicular to the plate which contains the optic axis is parallel to the plane of polarisation of either the polarising or analysing Nicol. At the intermediate 45° positions the maximum colour is produced.

The colour owes its origin, as already mentioned, to the interference of the two rays, corresponding to the two refractive indices, into which the light is divided on entering the crystal in any direction except along the axis. For one of the rays is retarded behind the other owing to the difference in velocity which is expressed reciprocally (inversely) by the refractive indices, and thus a difference of phase is produced between the two light-wave motions, with the inevitable result of interference when the vibrations have been reduced to the same plane by the analyser ; light of one particular wave-length is then extinguished, and the plate therefore exhibits a tint in which the complementary colour to that extinguished predominates. The light which leaves the polarising Nicol is vibrating in one plane, but on reaching the crystal this is resolved into two rays vibrating at right angles to each other, and at 45° on each side of its previous direction of vibration, supposing the crystal to be arranged for the production of most brilliant colour. On reaching the analysing Nicol, the function of which is to bring the two vibrations again into the same plane, these two rays are each separately resolved back to the planes of vibration of the two Nicols, and that pair (one from each ray) vibrating parallel to the analysing Nicol are transmitted, while the other pair are extinguished. The two former rays thus surviving, one individual ray of the two having one refractive index and the other individual the other index, are thus in a position to interfere ; for they are composed of vibrations in the same plane and of practically the same intensity, and differ only in phase. Extinction occurs when this amounts to half a wave-length, or an odd multiple of this, to which, however, requires to be added half a wave difference of phase which is introduced by the operation of the analyser. This explanation is a general one, applicable to thin plates of crystals belonging to all the six systems of symmetry other than the cubic. For plates of the latter, unless they are in an abnormal condition of strain, do not polarise.

When we take a plate of calcite of the same small thickness as that of the quartz in a rock section, thinner than a sheet of thin paper, we find that the calcite does not polarise. So great is the retardation of one of the two rays behind the other in calcite, that a plate excessively thin is required in order that colour shall be observed. For the colours of crystal plates under the polariscope, due to double refraction, are subject to the same laws as the colours of thin films, namely, that as the thickness increases—introducing more and more retardation in the case of a crystal, just as in a thin film greater length of path is introduced with increase of thickness — the various tints of all the seven orders of Newton's spectra are exhibited in turn, each spectrum differing by one further wave-length of retardation, and after the seventh the white of the higher orders (white light mixed with colour, the latter thus appearing only as a faint tint) gives place to true white light, colour being no longer perceptible. Hence with calcite, owing to the extremely powerful double refraction, and therefore very considerable retardation of the slower ray behind the quicker, a plate a fiftieth of a millimetre only in thickness already shows the white of the higher orders, that is, appears only very feebly tinted with colour, and a plate of calcite very much thinner still is required to show brilliant colours. A plate of calcite, therefore, cut obliquely or parallel to the optic axis, of the thickness of a rock section or thicker, simply appears four times dark and four times light alternately, at positions 45° apart, as the section-plate is rotated in its own plane perpendicular to the axis of the polariscope.

When a plate of either quartz or calcite one-fiftieth of an inch thick, cut perpendicularly to the optic axis, is examined under the polariscope or polarising microscope, the dark field is unaffected by its introduction on the stage, remaining dark on a complete rotation of the crystal plate in its own plane. Moreover, the calcite plate continues to behave similarly however much the thickness is increased, the field remaining dark. But when quartz is examined as regards the effect of thickness an extraordinary thing happens. As the plate is thickened, that is, as a series of plates of gradually increasing thickness are successively placed on the stage, the dark field begins to brighten, and eventually colour makes its appearance. Moreover, rotation of the plate in its own plane—supposing the latter to be strictly perpendicular to the axis of the polariscope and the plate itself to have been truly cut perpendicularly to the optic axis of the quartz crystal—produces no change whatever, the colour remaining the same and evenly distributed over the plate, thus differing from the previous phenomena of interference due to double refraction. When monochromatic light is employed, yellow sodium light for instance, it is found that if the plate be not too thick, say a millimetre in thickness, the dark field is restored when the analyser is rotated in a particular direction, either to the right or to the left, for a specific angle, which is 21° 42′ for a plate of quartz one millimetre thick. Moreover, if the plate has been cut from a crystal showing the distinctive trapezohedral-class faces *s* and *x* on the right (Fig. 69) the analysing Nicol requires to be rotated to the right; whereas if the plate has been cut from a crystal showing these little determinative faces on the left (Fig. 68) the analyser has to be rotated to the left in order to quench the light.

It is obvious, therefore, that the colours of these thicker plates of quartz are due to the phenomenon of "optical activity." The original plane of polarisation of the light received from the polarising Nicol is rotated by the quartz plate, and to an extent which is directly proportional to the thickness. When white light is used a particular colour is extinguished for each position of the analyser, and the complementary colour therefore predominates in the tint actually exhibited. Now the most intensely luminous part of the spectrum is about wave-length 0.000550 millimetre in the yellow, and in the case of a plate of quartz 7.5 millimetres thick this colour is extinguished when the Nicols are crossed, while a plate of half this thickness, 3.75 mm., actually exhibits the colour under crossed Nicols and extinguishes it under parallel Nicols. For the angle of rotation of the plane of polarisation for light of this wave-length is 90° for a plate 3.75 mm. thick, so that the analyser has to be turned through a right angle from the crossed position, that is, placed parallel to the polariser, in order to extinguish this colour. A plate of double the thickness, 7.5 mm., will require the analyser to be rotated through 180°, the angle of rotation for this thickness of plate, in order to extinguish this yellow ray. But 180° rotation simply brings the Nicol again to the crossed position, so that no rotation is really necessary at all.

Now the complementary colour to the yellow of wave-length 0.000550 mm. is the transition violet tint, the well-known " tint of passage " between the brilliant red end of the first order spectrum of Newton and the deep blue of the beginning of the second order. Hence, this violet tint is afforded by a plate of 7.5 mm. thickness when the Nicols are crossed, and by a plate of 3.75 mm. thickness when they are parallel. When, therefore, these plates are examined respectively under crossed and parallel Nicols, and the analysing Nicol is turned ever so little, the tint changes remarkably rapidly into brilliant red or blue, according to the direction of the rotation of the Nicol and the nature, whether right or left handed, of the quartz. Moreover, when two complementary plates of each thickness are thus examined, one of each pair being cut from a right-handed crystal and the other from a left-handed one, the colour will be red in one case and blue in the other for the same direction of rotation of the analyser.

A composite plate is frequently found very useful in work in connection with optical rotation, and is known as a "biquartz," two plates of opposite rotations being cemented together by Canada balsam, the plane of junction being made perpendicular to the plate so as to be almost invisible when the plate is examined normally. When polarised light is employed, the least rotation of the analyser from exact crossing with the polariser, for which the violet transition tint is evenly produced over the whole composite plate, causes the half on one side of the plane of junction (appearing as a fine line) to turn red and the other half to turn blue or green.

This, in essence, is the nature of the optical activity of quartz, and the secondary effects derived from it influence all the optical phenomena afforded by this interesting mineral. Owing to the fact that quartz crystals are practically unendowed with any facility for cleavage, the natural rhombohedral cleavage being very imperfectly developed and rarely seen, it is possible to cut, grind, and polish large plates of this beautiful, colourless, and limpidly transparent mineral without a trace of flaw. Such quartz plates of large size, adequate to fill the field of a large projection polariscope, the stage aperture of which is nearly 2 inches in diameter, form magnificent polarising objects for the projection on the screen of the effects observed in polarised light. As many of the optical properties of crystals may be illustrated with their aid, it is proposed in the next two chapters to describe a few of the more interesting screen experiments which can be performed with quartz, first (Chapter XIII.) in convergent polarised light, and then (Chapter XIV.) in parallel polarised light, and thus to illustrate the facts relating to the connection between optical activity and the internal structure of crystals in a manner which will at the same time be interesting and will lead to their much clearer comprehension.

The experiments described are largely those with which the author illustrated his lecture to the British Association for the Advancement of Science during their 1909 meeting at Winnipeg.

CHAPTER XIII

EXPERIMENTS IN CONVERGENT POLARISED LIGHT WITH QUARTZ, AS AN EXAMPLE OF MIRROR-IMAGE SYMMETRY AND ITS ACCOMPANYING OPTICAL ACTIVITY.

It has already been shown that crystals are optically divisible into two classes characterised respectively by single and by double refraction. Singly refractive crystals belong exclusively to the system of highest symmetry, the cubic. They afford obviously only one index of refraction, which is generally symbolised by the Greek letter μ, the value of this constant being the same for all directions throughout the crystal. Crystals of the other six systems of symmetry are all doubly refractive. Those of the trigonal, tetragonal, and hexagonal systems have been shown in the last chapter to possess two refractive indices, a maximum and a minimum, one represented by ϵ corresponding to light vibrating parallel to the singular axis of the system, the trigonal, tetragonal, or hexagonal axis of symmetry, and another signified by ω corresponding to light vibrations perpendicular to that axis. For the properties are identical in all directions around this axis, which is thus the optic axis as well as the predominating crystallographic one. Such crystals are consequently known as "uniaxial." When ϵ is the larger refractive index the crystal is positive, while if ω be the maximum the crystal is said to be negative. It has been shown in the last chapter that quartz belongs to the positive category, while calcite is negative. Along the one direction of the optic axis these uniaxial crystals behave like singly refractive crystals do in all directions.

Crystals of the rhombic, monoclinic, and triclinic systems of symmetry have also a minimum refractive index, symbolised by α, and a maximum index indicated by γ, corresponding to light vibrating parallel to two directions at right angles to each other ; the third direction perpendicular to both these and normal to their plane does not afford an index of refraction equal to either of these, however, as in the case of a uniaxial crystal, but one of an intermediate value, for which the second letter β of the Greek alphabet is reserved. Whether this value β is nearer to the minimum α or to the maximum γ determines the conventional optical sign of the crystal, whether positive or negative. In the case of the rhombic system the three rectangular directions in question are identical with the three rectangular crystallographic axes. In the monoclinic system the single symmetry axis normal to the unique plane of symmetry is identical in direction with either the α, β, or γ optical direction, but in the triclinic system there are no coincidences between the crystal axes and those of the optical ellipsoid. Along none of these axial directions of the optical ellipsoid which can be imagined to express graphically the refractive index—an ellipsoid known as the optical "indicatrix," and which has been shown by Fletcher to be a more convenient mode of expressing the optical characters of a crystal than the vibration-velocity ellipsoid of Fresnel—do the optical properties resemble those of a uniaxial crystal along the optic axis, or of a cubic singly refractive crystal, the crystal being doubly refractive along all three axes.

But it is a remarkable fact, nevertheless, that there are two directions in such a crystal along which the latter is apparently singly refractive, and these two directions are known as the "optic axes," and the crystals of the three systems of lower symmetry are consequently said to be "biaxial." These two singular directions are symmetrical to two of the three rectangular axes of the ellipsoid, those corresponding to the extreme indices α and γ, in the plane containing which two axes they lie, and they are perpendicular to the third β. For if we draw the ellipse of which the minimum and maximum axes are represented in length by α and γ, there will obviously be four symmetrical positions on the curve where a line drawn to the centre of the ellipse would be equal to the intermediate value β. If we join opposite pairs of these four points by diameters (lines passing through the centre of the ellipse) we have two directions each of which, together with the perpendicular direction of the β axis, lies on a circular section of the ellipsoid, for all radii from the centre lying in each of these sections are alike equal to β. Consequently, light transmitted along the two directions in the crystal normal (perpendicular) to these two circular sections will suffer no apparent double refraction, the refractive index being the same, namely β, and the velocity of vibration equal in all directions in the crystal parallel to the two circular sections. Hence, we have two directions in biaxial crystals in which the optical properties are similar to those of uniaxial crystals along their singular optic axis. But the optical properties along the two optic axes of a biaxial crystal are advisedly stated to be "similar" to, and not "identical" with those along the optic axis of a uniaxial crystal; for although they are identical to all ordinary experimental tests, they are not quite so when we come to ultimate details, which, however, are beyond the purview of this book, but an account of which will be found in the author's "Crystallography and Practical Crystal Measurement" (Macmillan & Co., 1911).

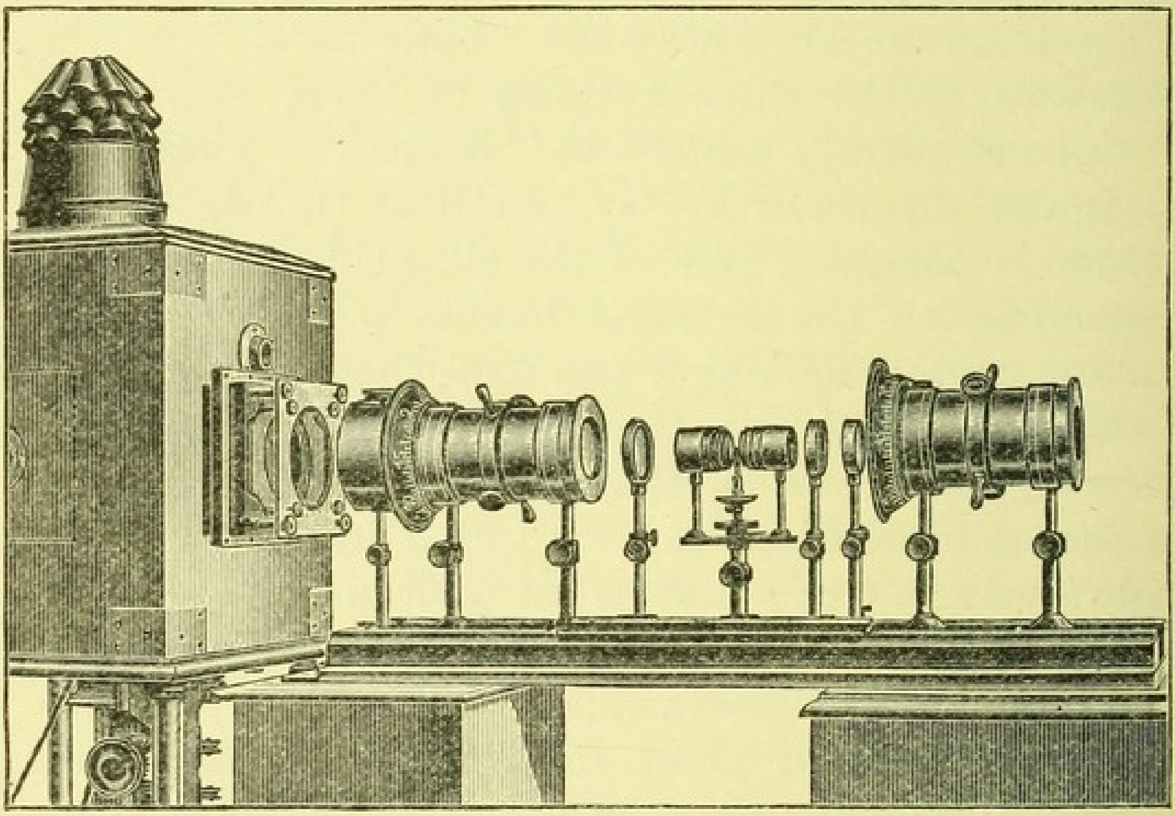


Fig. 71.—Projection Polariscope arranged for Convergent Light.

With these prefatory theoretical remarks, which are necessary in order that the experiments now to be described should be understood, we may proceed to consider a graduated series of experimental demonstrations which it is hoped will render clear some of the more important features of crystal structure which have been dealt with in previous chapters. Our principal agent will be polarised light, that is, light which has been reduced to vibration in a single plane by means of the well-known Nicol's prism. This latter is a rhomb of calcite which has been cut in two parts along a specific diagonal direction, and the two parts of which have been re-cemented together with Canada balsam, in such a manner that one of the two rays, known as the "ordinary" and which corresponds to the ω refractive index, into which the doubly refracting calcite crystal divides the ordinary light which it receives from the lantern or other source of light, is totally reflected at the layer of balsam, while the other ray, known as the "extraordinary" and corresponding to a refractive index of intermediate value between ω and ϵ, and composed of vibrations at right angles to those of the totally reflected ray, is alone transmitted, as a ray of plane polarised light.

We employ a pair of such Nicol prisms (a very large pair being shown in Fig. 71), together with a convenient system of lenses for focussing either the object-crystal or the phenomena displayed by it, as a "polariscope," which is the most powerful weapon of optical research on crystals which has ever been invented. When the two prisms are arranged so that the vibration planes of the polarised light which they would singly transmit are parallel, we speak of them as "parallel Nicols," and light is transmitted unimpeded through the pair thus placed in succession ; but when one of them is rotated the light diminishes, until when the vibration planes are at right angles no light escapes at all if the Nicols are properly constructed, there being produced what is known as the " dark field " of the " crossed Nicols." For the plane polarised light reaching the analyser from the polariser cannot get through the former, its plane of possible light vibration being perpendicular to that of the already polarised beam.

The phenomena exhibited by crystals in polarised light are of two kinds, namely, those observed when a parallel (cylindrical) beam of light is passed through the crystal, and those exhibited when a converging (conical) beam of light is employed and concentrated on the crystal, the centre of which should occupy the apex of the cone. The disposition of apparatus in the former case of parallel light will be described in the next chapter and illustrated in Fig. 79. The arrangement for convergent light, as employed for projections on the screen, has already been referred to in connection with the Mitscherlich experiment with gypsum, and illustrated in Fig. 51 (page 92). The arrangement is shown again here for convenience, in Fig. 71. The parts of the apparatus are briefly as follows : (1) the electric lantern with self-adjusting Brockie-Pell or Oliver arc lamp and a 4½ or 5-inch set of condensers ; (2) the water cell ; (3) the polarising Nicol with a parallelising concave lens at its divided-circle end ; (4) a condensing lens ; (5) the convergent system of three lenses closely mounted in succession ; (6) the crystal ; (7) the collecting system of three lenses equal and similar to the convergent system; (8) the field lens; (9) the projection lens; and (10) the analysing Nicol. The ten parts are separately mounted in the author's apparatus, which confers greater freedom in experimenting and more power of varying the conditions; the converging and collecting lens systems, however, are mounted in a separately adjustable manner on a common standard, which carries in the centre complete goniometrical adjustments for the crystal.

When we place on the stage of the polariscope, the Nicols being crossed, a plate of a uniaxial crystal cut perpendicularly to the optic axis, and subsequently a similar plate of a biaxial crystal cut perpendicularly to that axis of the optical ellipsoid, either α or γ, which is the bisectrix of the acute angle between the two optic axes, and use the system of lenses which converges the light rays received from the polarising Nicol prism on the crystal, as shown in Fig. 71, we observe in the two cases quite different and very beautiful interference phenomena, which at once distinguish a uniaxial from a biaxial crystal. The two appearances are illustrated in Plate XIV., by Figs. 72, 73, and 74, which are reproductions of the author's direct photographs. Fig. 72 shows the interference figure afforded by uniaxial calcite, which is the same for all positions of the crystal plate when rotated in its own plane by the rotation of the stage. Figs. 73 and 74 represent the interference figures given by biaxial aragonite, the orthorhombic form of carbonate of lime, calcite and aragonite being the two forms of this substance, which has been shown in Chapter VII. to be dimorphous. The effect shown in Fig. 73 is afforded when the line joining the two optic axes is parallel to the plane of vibration of either of the crossed Nicols, and the interference figure represented in Fig. 74 is given when the stage and crystal (or the two Nicols simultaneously) are rotated 45°.

The uniaxial calcite figure (Fig. 72) consists of circular spectrum-coloured rings resembling the well-known Newton's rings, but with a dark cross, fairly sharp near the centre but shading off towards the margin of the field, marking the directions of the vibration planes of the Nicols.

The biaxial aragonite figures (Figs. 73 and 74) show two series of rings surrounding the two optic axes and thus locating the positions of their emergence, equidistant from the centre of the field, where the bisectrix emerges. They are not circular, but are curves known as lemniscates, which are complete rings nearest to the two optic axes, but soon pass into figure-of-eight loops, and eventually into ellipse-like lemniscates enveloping both optic axes, and more and more approaching circles in their curvature as the margin of the field is approached. Moreover, when the direction of the line joining the two optic axes is parallel to the vibration plane of either of the Nicols, as was the case when Fig. 73 was produced and photographed, a black rectangular cross is seen, one bar, which is much the sharper one, passing through the optic axes and the other lying between them at right angles to the first bar, the centre of the cross being in the middle of the field.

On rotating the crystal plate in its own plane, while no change occurs with the calcite, the aragonite

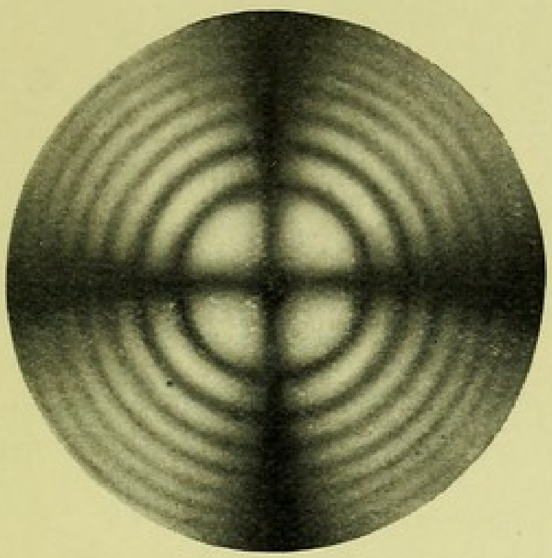


FIG. 72.—Crystal Plate cut perpendicularly to the Axis.

Uniaxial Interference Figure afforded by Calcite (Trigonal) in Convergent Polarised Light, with Crossed Nicols.

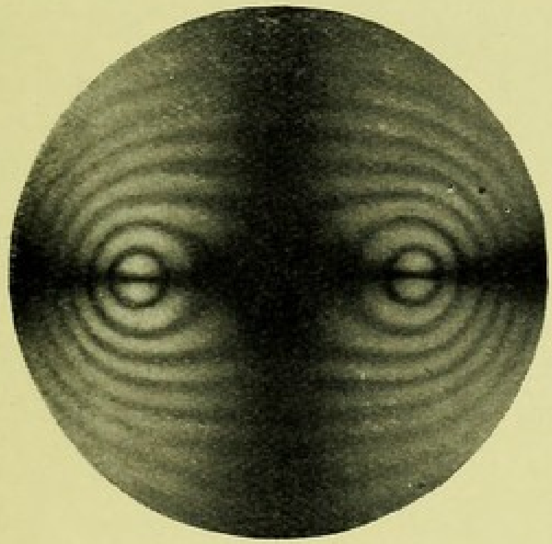


FIG. 73.—Crystal Plate cut perpendicularly to the Bisectrix of the Acute Optic Axial Angle.

Biaxial Interference Figure afforded by Aragonite (Rhombic) in Convergent Polarised Light, with Nicols crossed and parallel to the Vibration Directions of the Crystal.

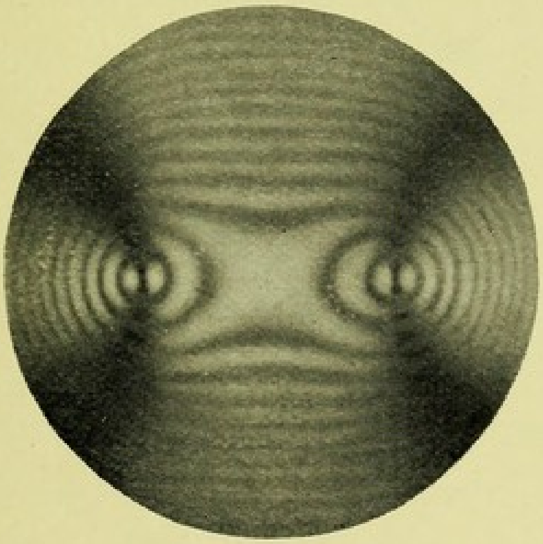


FIG. 74.—The same Plate as for the previous Figure.

The same when the two Nicols have been rotated in the same direction for 45°, still remaining crossed.

CHARACTERISTIC UNIAXIAL AND BIAXIAL INTERFERENCE FIGURES IN CONVERGENT POLARISED LIGHT.

(Reproductions of direct Photographs by the author.)

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figure changes as regards the black cross, which breaks up into hyperbolic curves currently spoken of as " brushes," until when the plate has been rotated 45° the appearance is that shown in Fig. 74, the eye being supposed to have followed the rotation. Or, keeping the eye still, the effect shown in Fig. 74 is equally produced by the simultaneous rotation of both Nicols for 45°. The vertices of the hyperbolæ now mark the positions of the optic axes, and the angle between them is the apparent angle of the optic axes as seen in air, which is considerably different from the true angle between the optic axes within the crystal, owing to the very different refraction of light in air and in the crystal substance.

Now some crystals exhibit a very different optic axial angle at different temperatures, and one of the most beautiful experiments which have ever been performed is the Mitscherlich experiment with gypsum, which has already been described in Chapter VII. in connection with the work of Mitscherlich, and illustrated in Plate XII., Figs. 52 to 55. Other substances, on the other hand, show a marked change of optic axial angle as the wave-length of the light is changed, and such a case has already been described in Chapter VIII. and illustrated in Plate XIII., Fig. 58. The figure afforded by such a substance in ordinary white light is, however, a complicated one, quite different from the normal one of Fig. 73 afforded by aragonite, as will be clear on reference to the interference figure shown at *f* in Fig. 58, which represents the figure given by ethyl triphenyl pyrrholone in white light.

In order to understand such biaxial interference figures thoroughly, they should be studied in monochromatic light, when one obtains a clear and sharp figure consisting of black curves as well as the cross or brushes, and very sharp vertices to the brushes when the crystal is arranged as in Fig. 74. The optic axial angle can then be measured for each important wave-length of light in turn, and the variation for wave-length followed throughout the whole spectrum. For this purpose it is very convenient to have a source of monochromatic light of any or every wave-length always at hand, and the author some years ago devised a spectroscopic monochromatic illuminator,[1] for use with any observing instrument, and which is particularly convenient for use with the polariscopical goniometer which is employed in practice for the measurement of optic axial angles. It is shown, along with the latter instrument, in Fig. 75. The spectroscope has a single but very large prism of heavy but colourless flint glass, and the spectrum produced—the electric lantern being the source of light, its rays being concentrated on the slit—is filtered through a second slit at the other end of the spectroscope, where the detachable eye-piece is situated when the instrument is used as an ordinary spectroscope, and for the calibration (with the Fraunhofer solar lines) of the circle on which the prism is mounted. The escaping narrow slit of monochromatic light includes only the 250th part of the spectrum, so is monochromatic in a high sense of the word. It impinges on a little ground glass diffuser carried in a very short tube in front of this exit slit, and the optic axial angle polariscope is

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[1] *Phil. Trans. Roy. Soc.*, 1895, A, 185, 913.

brought up almost into contact with the ground glass, and is thus supplied with an even field of pure monochromatic light. With this apparatus it is easy to observe the exact crossing wave-length in all cases of crossed-axial-plane dispersion such as that illustrated in Fig. 58; for the reading of the graduated circle on which the prism is mounted, and which is rotated in order to cause monochromatic light of the different wave-lengths in turn to stream through the exit slit, affords the exact wave-length with the aid of the calibration curve once for all prepared. This calibration of the graduations is readily carried out by using sunlight, and determining the readings corresponding to the adjustment

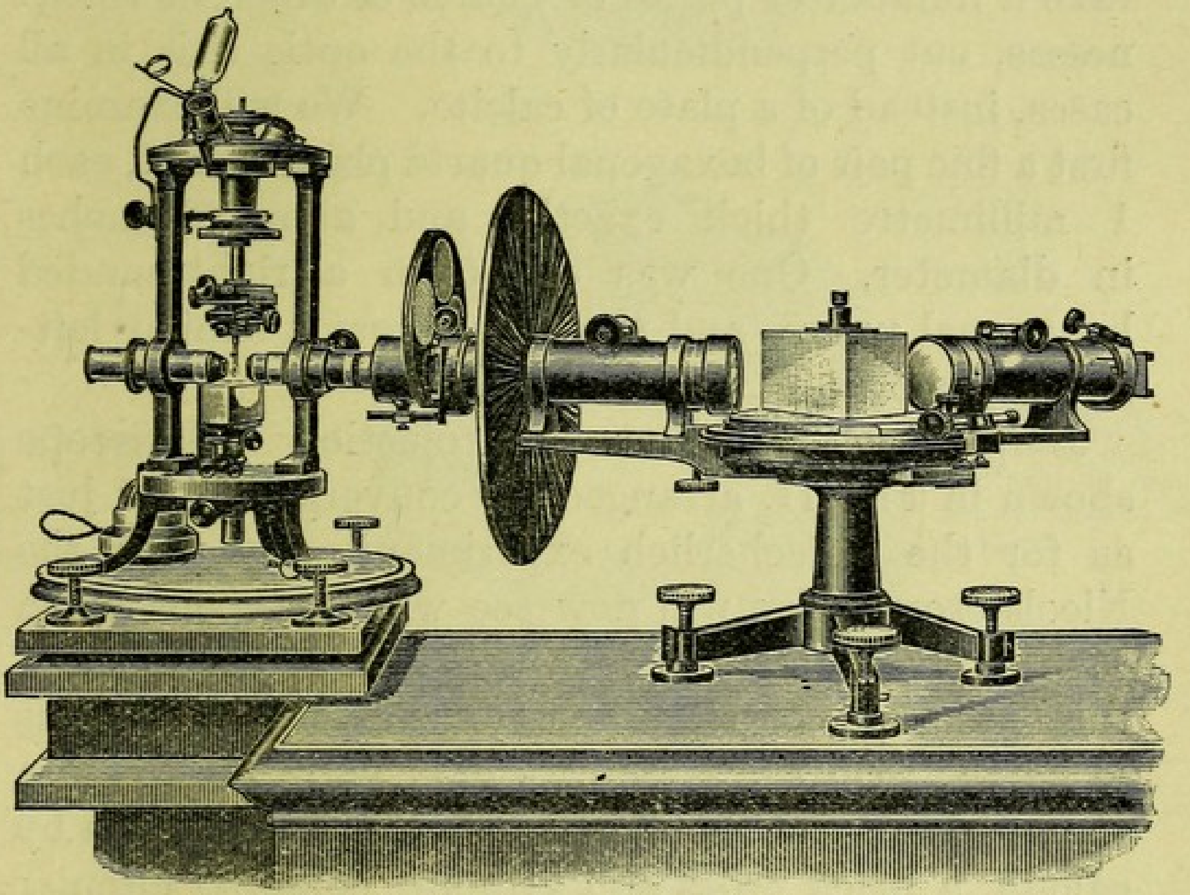

Fig. 75.—Optic Axial Angle Goniometer and Spectroscopic Monochromatic Illuminator.

of the principal Fraunhofer lines in the middle of the exit slit.

Having thus rendered clear the nature of ordinary interference figures afforded by crystals of the two types, uniaxial and biaxial, in convergent polarised light, we may pass on to see what happens when we take a number of plates of quartz of different thicknesses, cut perpendicularly to the optic axis in all cases, instead of a plate of calcite. We will examine first a fine pair of hexagonal quartz plates so cut, each 1 millimetre thick exactly, and about 2 inches in diameter. One was cut from a right-handed hexagonal prism, and the other from a similar left-handed one.

Employing the lantern projection polariscope shown in Fig. 71, arranged for convergent light just as for the Mitscherlich experiment, and with the Nicols crossed, we will now see what happens when each of these plates in turn is placed at the focus of the light rays, between the two convergent systems of lenses. On the screen we observe in each case a somewhat similar interference figure to that given by calcite, a black cross and rainbow coloured circular rings, the smallest ring, however, being very large relatively to the innermost ring given by calcite, and the other rings being also further separated from each other. Moreover, the black cross appears broadened out, this spreading of both rings and cross being due to the thinness of the plate combined with the low double refraction of quartz. Further, the right-handed and left-handed plates both afford apparently identical figures. In order to obtain a sharp figure like that of calcite we require to add

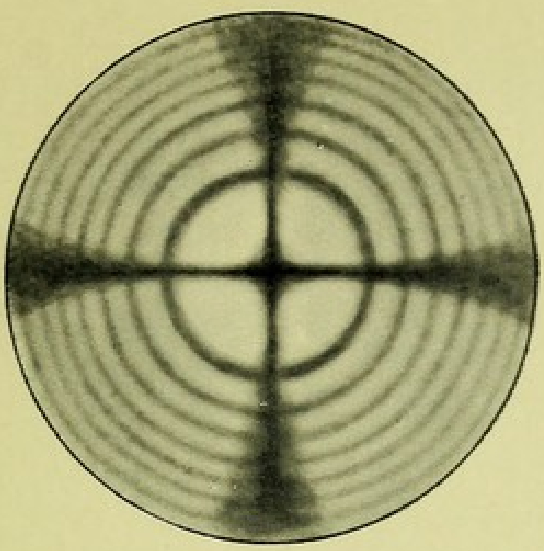

Fig. 76.

Interference Figure afforded by a Quartz Plate, 1 Millimetre thick, in strongly Convergent Polarised Light.

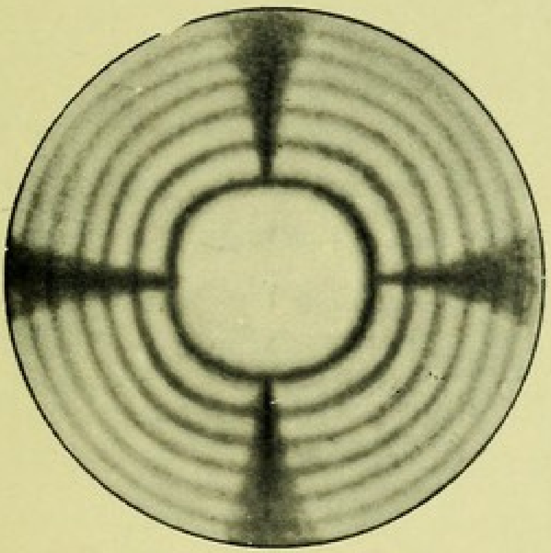

Fig. 77.

Interference Figure afforded by a Quartz Plate, 3·75 Millimetres thick, in moderately Convergent Polarised Light.

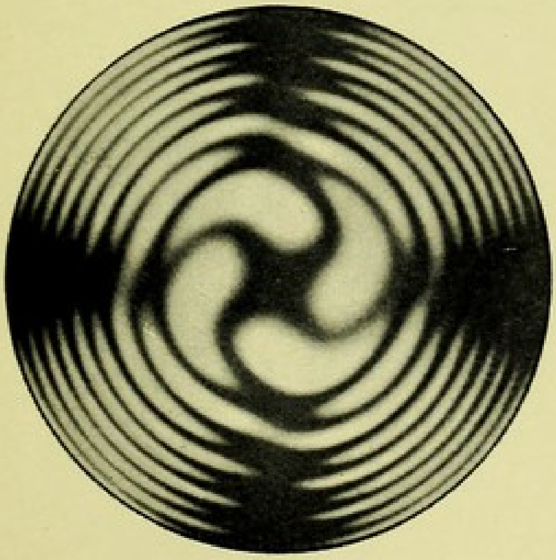

Fig. 78.

Interference Figure (Airy's Spirals) afforded by two superposed Quartz Plates, 3·75 Millimetres thick, one of Right-handed Quartz and the other of Left-handed Quartz, in moderately Convergent Polarised Light.

Interference Figures in Convergent Polarised Light afforded by Quartz Plates cut Perpendicularly to the Axis.

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a fourth lens, kept in reserve for such cases, to each of the two similar convergent lens-systems, one on each side of the crystal-plate, in order to increase the convergence of the light rays. The figure then obtained with one of the two plates is reproduced in Fig. 76, Plate XV.

Let us now observe, however, what occurs when a thicker plate of quartz is used. Taking one of 7.5 mm. thickness, and placing it in the focus of the converging rays, after removing the two extra lenses, we see on the screen quite a different effect, an attempt to reproduce which photographically in black and white is made in Fig. 77 on the same Plate XV. The rings are closer together (using the same degree of convergence), and the innermost is smaller; moreover, within it all signs of the central part of the black cross have disappeared, and instead a brilliant violet colour is shown, which alters to bright red of the first order spectrum with the least rotation of the analysing Nicol in one direction from its crossed position with respect to the polarising Nicol, while if the rotation be in the opposite direction the deep blue of Newton's second order is produced. The arms of the cross, however, appear towards the margin of the field. The violet colour shown for the exact position of crossing of the Nicols is the tint of passage between the first and second orders of Newton's spectra, and this illumination of the central part of the interference figure is obviously the effect of the optical activity of quartz, for the tint is the same as is produced with the plate in ordinary parallel plane-polarised light, and is, in fact, due to the central axial rays of the convergent cone being practically parallel.

On rotating the analysing Nicol for a few more degrees to the right we observe that the innermost ring widens out and that the red passes into orange and yellow, the quartz plate being a right-handed one. But when a similar plate cut from a left-handed quartz crystal is used instead, the inner ring closes up somewhat for the same rotation of the analyser, moving inwards instead of outwards, and the blue colour given with the first slight rotation passes into green and yellow as the rotation is continued. Moreover, the circular character of the rings is altered, and so much so that when the rotation has proceeded as far as 45° the shape of the rings has changed almost to a square. These alterations in the interference figure are characteristic of the two varieties of quartz crystals. A useful rule to remember is, that for a right-handed crystal rotation of the analyser to the right causes the colours to appear in the order of their refrangibility, namely, the least refrangible red first, then orange, yellow, green, blue and violet in their order; while for a left-handed crystal the converse is true when the direction of rotation of the analyser is the same, that is, to the right, clockwise; obviously also the colours appear in the opposite order when the rotation of the analyser is to the left.

It will now prove of interest to examine the effects produced by two plates of opposite varieties of quartz of half this thickness, namely, 3.75 mm. The phenomena are very similar to those just described, but the rings are a little wider, and the larger area within the innermost ring is now filled with yellow light instead of violet, when the analyser is exactly crossed to the polariser. It passes into a bright green when the analyser is rotated slightly on one side, and into orange when the Nicol is rotated in the reverse direction. But the most interesting thing of all is to observe what occurs when these two plates of 3.75 mm. thickness, one of right-handed quartz and the other of left-handed, are superposed and placed in contact together as one plate, of double the thickness, 7.5 mm., at the convergent focus. A beautiful spiral figure is produced on the screen, composed of the celebrated "Airy's spirals" as if the black cross were being reproduced in the central part, but with each of its bars distorted into the shape of the letter S, as shown in Fig. 78 at the foot of Plate XV. The contrary effects of the two opposing rotations are thus extraordinarily indicated visually in the interference figure afforded by the composite plate.

Now, it is of great practical interest that certain quartz crystals are found in nature which show Airy's spirals directly, on cutting a plate 7.5 mm. thick or thereabouts, perpendicular to the optic axis. For instance, one in the author's collection of quartzes, a single plate of an apparently homogeneous and perfectly limpid crystal, shows the spirals exceedingly well and clearly defined. As a matter of fact, it is a twin, a right and a left-handed crystal being twinned together with an invisible plane of composition, which is only revealed on examining the crystal in polarised light, as will be demonstrated in the next chapter by the use of parallel polarised light. The fact of such a plate of quartz affording Airy's spirals in convergent polarised light is, however, of itself an excellent proof of the twinning of two crystal individuals of the opposite varieties.

Now the very shape of these spiral figures suggests screw action of the molecular structure of the crystals on the waves of light passing through them, and moreover, of the action of two screws of opposite directions of winding, one clockwise and the other anti-clockwise, thus remarkably confirming the supposition that the point-systems of the structure of the right and left-handed varieties of quartz are of a helical nature and respectively of opposite modes of winding.

Another experiment, devised by Reusch, which still further enhances the probability that this supposition as to the structure of quartz crystals is correct, may next be introduced. A thin film of biaxial mica has been cut into twenty-four narrow strips, which have been laid over each other at angles of 60°, so that a screw-shaped pile has been formed of the central overlapping parts, consisting of four complete rotations; that is, there are four repetitions of the "pitch" of the screw, each composed of six films. On placing this composite plate of mica at the convergent focus of the lantern polariscope, so that the overhanging ends of any four identically superposed strips occupy the focus, the ordinary biaxial interference figure of mica—two sets of rings and hyperbolic brushes, very much like Fig. 52, Plate XII.—is observed on the screen. But when the plate is moved so that the central part comes into the focus, where all the twenty-four films overlap in their six different orientations 60° apart, and so that all the light rays have to traverse the whole helical pile of the twenty-four films, a uniaxial figure exactly like that of quartz is produced, namely, one composed of circular rings, with a black cross only visible, however, at the marginal part, and with the inner ring filled with brightly coloured light. Moreover, on slightly rotating the analysing Nicol the innermost ring moves outwards or inwards and the colour changes to blue or red, according to the direction in which the helix had been wound, in exact accordance with the rule stated above for quartz.

If now a second such helical pile of mica films, but one for which the opposite manner of winding has been adopted, anti-clockwise if the first had been clockwise, be examined at the convergent focus, precisely the same appearance will be observed with crossed Nicols, but the opposite changes will occur on rotating the analyser. Finally, to complete the interesting proof of the helical nature of quartz crystals, when these two oppositely wound composite mica plates are superposed—each being marked carefully to indicate the direction of the helix and the proper mode of superposition in order to effect precise oppositeness of arrangement, mirror-image symmetry, in fact, about the plane of contact—and placed in the convergent beam near its focus, there is at once seen on the screen a magnificent display of Airy's spirals, as perfect as those afforded by the fine natural twin last experimented with. Hence, there can be no doubt whatever that the remarkable optical behaviour of quartz is due to its point system being of a helical nature, a right or a left-handed screw structure being apparently produced in nature with equal facility. The circumstances of environment during the formation of the crystal probably determine which variety shall be produced, and when the nature of the environment becomes changed during the operation of formation either twins are produced of the two varieties, or separate individual crystals.

This may well conclude our experiments in convergent polarised light, which—including the beautiful Mitscherlich experiment described in Chapter VII., of exhibiting the crossing of the optic axial plane in the case of gypsum, and the production of all the types of interference figures in succession, as the crystal becomes warmed by the heat rays accompanying the beam of convergent light—will have introduced the reader to a typical series of such experiments, and such as were actually exhibited by the author to the British Association at Winnipeg. We may pass, therefore, in the next chapter to the consideration of an equally interesting series in which a parallel beam of polarised light will be used, which will still further elucidate the internal structure in the especially instructive case of quartz crystals, and that of crystals in general.

CHAPTER XIV

EXPERIMENTS WITH QUARTZ AND GYPSUM IN PARALLEL POLARISED LIGHT. GENERAL CONCLUSIONS FROM THE EXPERIMENTS WITH QUARTZ.

In order to rearrange the projection polariscope for experiments in parallel light, we simply remove the three lenses on separate stands (Fig. 71), and the convergent systems of lenses on their special adjustable stand with goniometrical crystal holder, from between the two Nicol prisms, and replace them by two other separately mounted lenses, acting together as an achromatic projecting objective, and a rotatable object stage. The whole arrangement as thus altered for experiments in parallel polarised light is shown in position in Fig. 79. The change is readily made, a gap in the plinth-bed guides near the analysing Nicol enabling it to be effected without removing either of the prisms, the analyser being simply drawn along a few inches nearer the end in order to expose the changing gap. The pair of lenses consists of a plano-convex lens of 5 inches focus and 2¼ inches diameter, and another plano-convex lens of 8½ inches focus and 2 inches aperture, with their convex faces turned towards each other. Together they produce on the screen an excellent image of the object on the stage, and the size of the image can be varied at will by regulating the relative positions of the two lenses with respect to each other and to the object stage. If found more suitable for the particular screen distance available, the 5-inch lens may be replaced by a 6-inch lens also provided as an alternative.

When the analysing Nicol is arranged with its vibration direction parallel to that of the polariser, we obtain bright light on the screen on actuating the electric lantern, and the image of an object on the stage can thus be projected on the screen on a bright ground. But when the analyser is crossed to the polariser, that is, rotated to the position 90° from this parallel position, the two planes of vibration of the Nicols being then at right angles, the screen is quite dark. Before continuing in this dark field our experimental study of quartz, which is obviously a

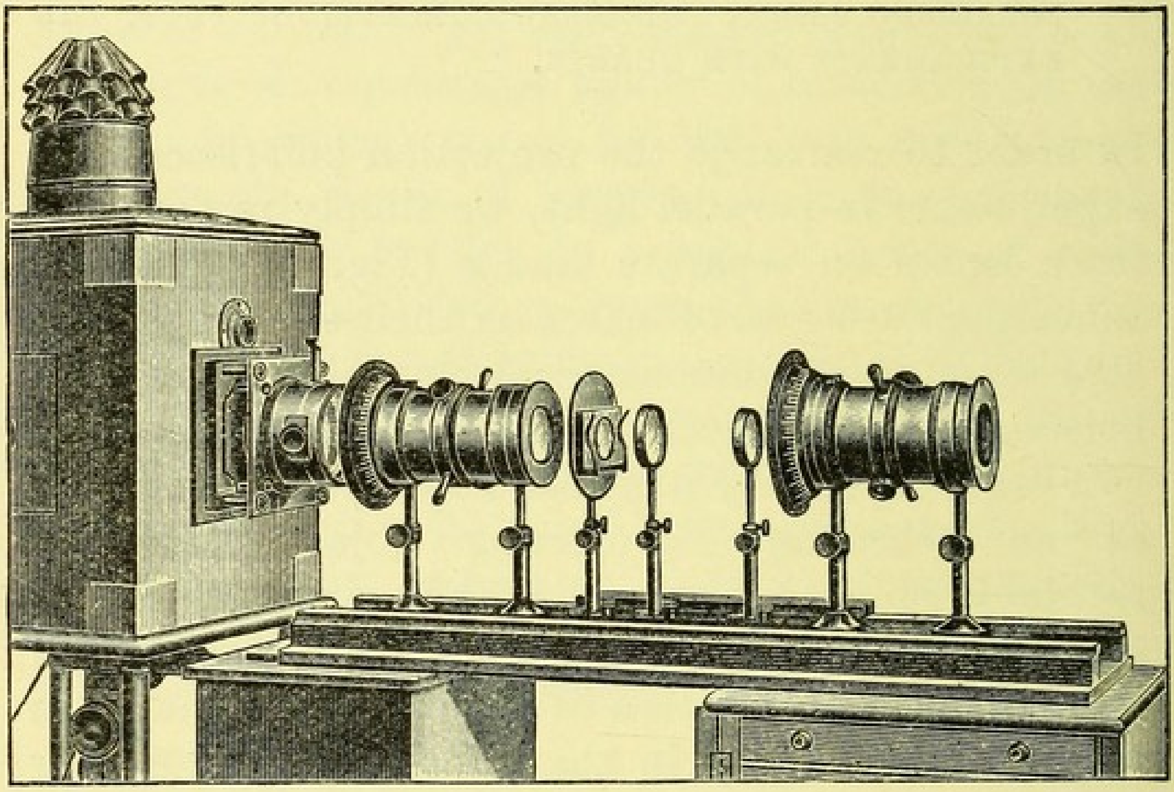

Fig. 79.—Projection Polariscope arranged for Parallel Light.

type of the more exceptionally behaving substances owing to its special structure, it will be wise to examine a more ordinary kind of crystalline substance. For this purpose gypsum—better known in optical work as selenite, hydrated sulphate of lime, $CaSO_4.2H_2O$, crystallising in beautifully transparent and often large crystals belonging to the monoclinic system, a typical one of which has been illustrated in Fig. 9 (page 14), and which we have already referred to in connection with the Mitscherlich experiment described in Chapter VII.—is especially suitable, on account of its clear and colourless transparency, the large size of crystals available, and the brilliancy of the polarisation colours which they afford when adequately thin. A very perfect cleavage being developed parallel to the symmetry plane, the clinopinakoid $\{010\}$, such thin films, of even thickness throughout, can be readily prepared.

Such a very thin cleavage plate, about $1\frac{1}{2}$ inches in its longest dimension, is mounted with Canada balsam between a pair of circular glass plates $1\frac{7}{8}$ inches in diameter, the standard size of object plates for the projection polariscope; the double plate is then supported in a mahogany frame also of the standard size —4 by $2\frac{1}{4}$ inches, with clear aperture of $1\frac{5}{8}$ inches diameter and supporting rabbet for the plate $1\frac{7}{8}$ to 2 inches diameter—on the rotating stage by a pair of spring clips. The Nicols being arranged with their vibration directions parallel, in order to permit light to travel to the screen, and the lenses being arranged properly for a sharply focussed picture of suitable size, the outline of the crystal plate will be seen on the screen, and the whole area of the crystal will either at once appear coloured, or will do so on more or less rotation of the stage carrying the crystal, which rotates the latter in its own plane. The crystal outline is of the character shown in Fig. 80, which also gives the positions of the crystal axes *a* and *c*, and a simple stereographic projection of the faces of the crystal, from which the nature of the faces bounding the section-plate will be clear.

On rotating the Nicol analyser the colours change, and appear at their maximum brilliancy when the field is dark and the Nicols crossed. Leaving the analyser crossed to the polariser, and rotating the stage and therefore the crystal, the colours again change, and at certain positions 90° apart during the rotation, marked by the two strong lines in Fig. 80, they disappear altogether, and the crystal becomes dark like the rest of the field, while the positions of maximum brilliancy of colour are found to be situated at the 45°-positions intermediate between these positions of "extinction." When the quenching occurs the vibration planes of the two rays, travelling by virtue of double refraction through the crystal, are parallel to the planes of vibration of the rays transmitted through the two Nicols, and the fact is a very important one, enabling us to determine

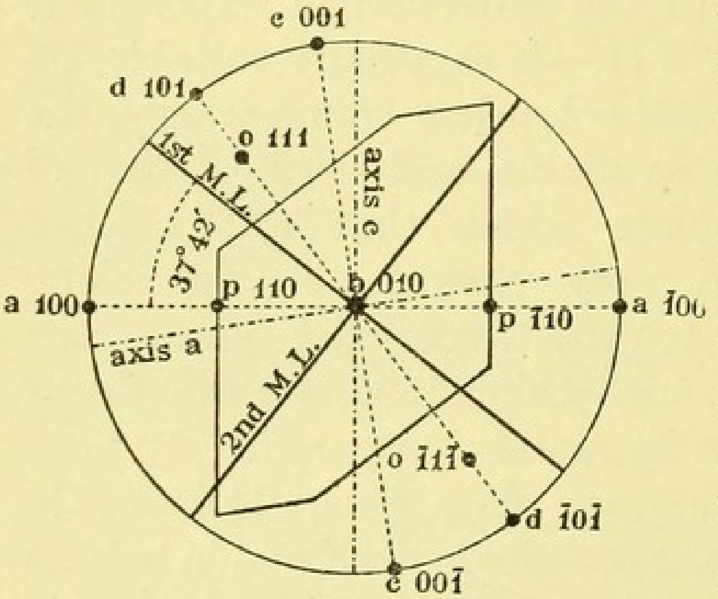

Fig. 80.—Section of Gypsum Crystal showing the Extinction Directions.

the directions of light vibration in the crystal. In the case of our gypsum plate, the cleavage of gypsum being parallel to the unique plane of symmetry of the monoclinic crystal, these two positions are the directions of the two axes of the optical ellipsoid which lie in the symmetry plane, and they correspond to the vibration directions of rays affording the refractive indices α and γ. The direction corresponding to γ is that of the "first median line," the bisectrix of the acute angle between the optic axes; while α corresponds to the obtuse bisectrix or "second median line." These directions are clearly marked by the strong lines in Fig. 80. The third axis of the optical ellipsoid is obviously perpendicular to the plate and to the symmetry plane, and corresponds to the intermediate refractive index β. Thus this simple observation of the extinction directions in such a case as gypsum enables us at once to fix completely the orientation of the optical ellipsoid, a fundamental optical determination.

A second thin plate of gypsum may next be examined, similarly prepared and mounted. It is clearly a composite one, being composed of a pair of twins. For when placed on the stage in the dark field of the crossed Nicols, and rotated to the position for maximum brilliancy of colour, it shows different colours in the two halves, as indicated by different shading in Fig. 81. If, however, the analysing Nicol prism be withdrawn from the plinth-bed and removed altogether the crystal appears in its natural colourless condition as a single one, with no indication whatever of any line of division.

Some exceedingly brilliant polarisation effects are afforded by a number of objects exhibited by the author in his lecture at Winnipeg, composed of selenite (gypsum) twins and triplets, some arranged to cross one another like the mica films of Reusch described in the last chapter, but only for a single rotation, three twin strips going to a rotation, at angular distances of 120°; others are arranged in geometrical patterns, and in circles overlapping one another, and the whole series afford the most gorgeous and variegated display of colour imaginable, the colours, moreover, altering either on rotation of the stage or of the analysing Nicol, and thus passing through every tint conceivable.

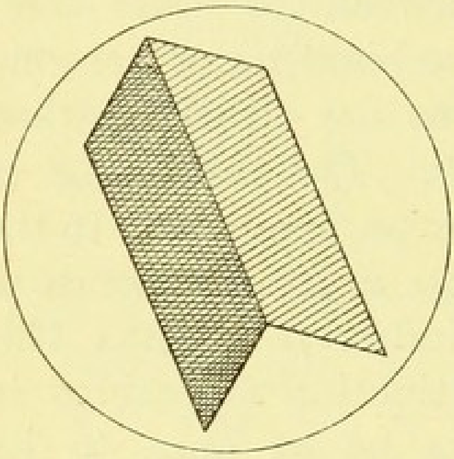

FIG. 81.—Twin of Gypsum as seen in Parallel Polarised Light.

Having thus demonstrated the usual effect afforded by a doubly refracting crystal plate in parallel polarised light, we may next illustrate two special cases, which will lead us up to the case of quartz once more. The first relates to a crystal belonging to the cubic system, which is theoretically singly refractive or "isotropic"; the second concerns a plate of a uniaxial crystal cut perpendicularly to the optic axis, the unique direction of single refraction of such a crystal. A plate of fluorspar affords a good example of the first case. When placed on the stage of the polariscope it shows no colour at all in polarised light, whatever be the position of the two Nicols with respect to each other, and the field remains dark when they are crossed, the crystal, in fact, behaving just like so much glass.

A word of caution, however, is here necessary, for natural mineral crystals are not unfrequently formed under conditions of considerable strain, at high temperatures or under great pressure, as in the case of the diamond for instance. So that we must be careful to choose a normal and well formed crystal of fluorspar for our experiment. This point may be well illustrated by placing on the stage a thick circular plate of glass, an inch or more in diameter, which has been purposely heated and then suddenly cooled in order to evoke such a condition of strain. Crossing the Nicols so as to obtain the dark field, there is at once produced on the screen a black cross and circular concentric spectrum-coloured rings, resembling with wonderful simulation the interference figure, shown in Fig. 72, Plate XIV., afforded by calcite or other uniaxial crystal in convergent polarised light. Artificial double refraction has been produced in the glass by the strained conditions, in a fashion concentrically symmetrical to the axis of the cylinder, an interference figure being afforded symmetrical about the axis of the cylinder as if it were an optic axis.

The diamond crystallises in the cubic system, in octahedra, hexakis octahedra, or hexakis tetrahedra, and should, therefore, theoretically be without effect on polarised light. Yet it is rare to find a diamond which does not show more or less colour in the dark field, owing to the condition of strain in which it exists. It is notorious that the strain is occasionally so great that a diamond explodes into powder shortly after removal from its enveloping matrix of blue clay. The author, by the great kindness of Sir William Crookes, was enabled to show on the screen, both in a lecture at the Royal Society and in the Evening Discourse to the British Association at Winnipeg, the images of ten magnificent large diamonds, natural, perfectly formed crystals uncut and unspoilt by the lapidary. They were mounted between two circular glass plates of the usual $1\frac{7}{8}$ inches diameter, the diamonds being attached by balsam to one of them; each plate was held in a mahogany frame of $1\frac{5}{8}$ inches circular aperture, the two frames being then attached face to face to form a single one, an enclosing cell, which could be placed on the rotating stage as an object-slide for the projection polariscope. The appearance of the diamonds on the screen in ordinary light is reproduced in Fig. 82, Plate XVI., as well as is possible without their natural colour, for while several of them are brilliantly colourless, others are tinted, one being a bright green diamond. On producing the dark field by crossing the analysing Nicol with respect to the polariser, the darkness was dispelled by brilliant polarisation colours, at once revealing the diamonds and outlining them clearly against the dark background. On rotating the analyser the colours changed in the usual manner of polarising objects, and bright colours were shown by all the diamonds even when the Nicols were parallel.

It is obvious, then, that both a transparent non-crystalline substance such as glass, and a cubic crystal, must be free from strain in order that it shall exhibit no colour in polarised light and, indeed, no polarisation effects whatever, and behave as an isotropic substance.

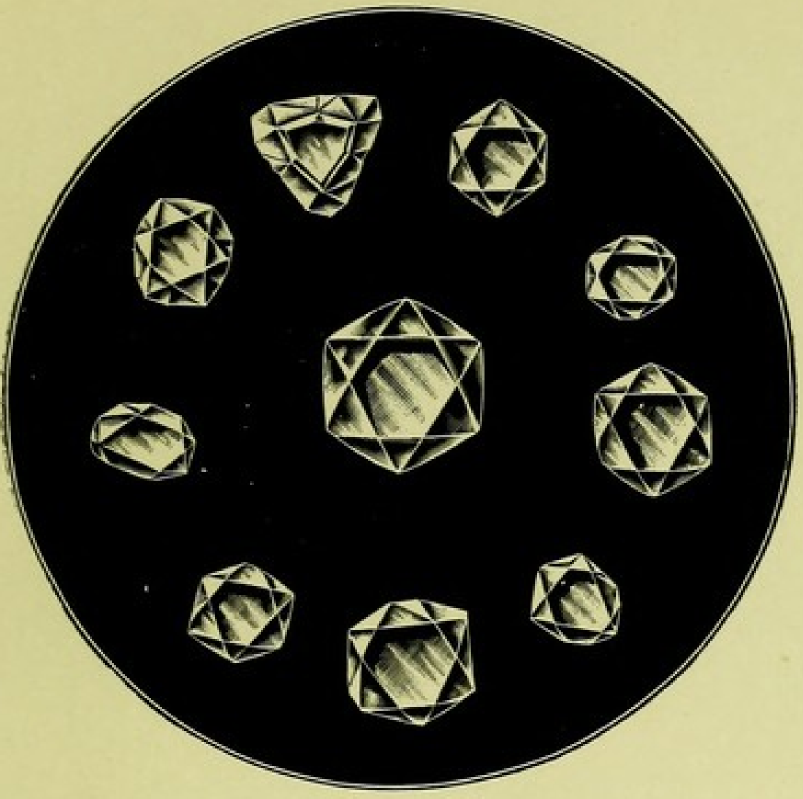

FIG. 82.—Ten Diamonds exhibiting Natural Faces, mounted for the Lantern Polariscope, to show Polarisation Colours due to Internal Strain.

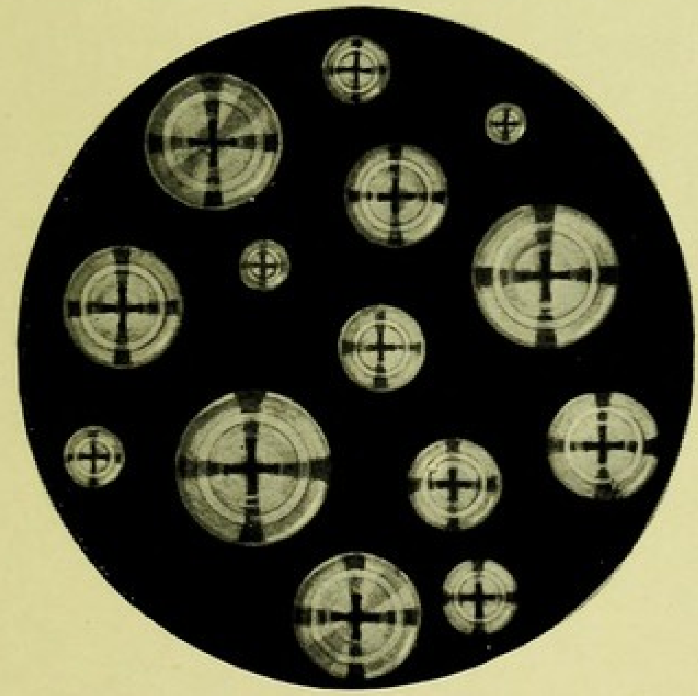

FIG. 121.—Doubly Refracting Liquid Crystals of Cholesteryl Acetate, projected on the Screen in the Act of Growth (see p. 281).

TWO FIGURES ILLUSTRATING THE HARDEST (DIAMOND) AND THE SOFTEST (LIQUID CRYSTALS) OF CRYSTALS.

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The second special case to which attention may be called, that of a plate of an ordinary uniaxial crystal such as calcite, cut perpendicularly to the optic axis, is also obviously subject to the same proviso, that the crystal must be free from strain in order to exhibit the normal phenomena. Such a perfectly normal plate remains quite obscure in the dark field in parallel light, producing neither colour nor interference figure, even on rotation of the object stage with the crystal, in its own plane. For the light traverses the crystal along the optic axis, the axis of single refraction, and the vibrations occur with equal velocity in all directions perpendicular to it. Hence there is no division into two rays, one retarded behind the other on account of less velocity of vibration, and therefore no interference colour.

And now this leads us back to quartz, for this mineral is also uniaxial, and we will investigate in the same manner in parallel polarised light the plates of the mineral cut perpendicularly to the optic axis, which have already been referred to in connection with the experiments concerning the interference figures produced in convergent polarised light. Suppose we take first the large plate of quartz 7.5 mm. thick and over 2 inches in diameter. Placing it on the stage—instead of finding the dark field to be unaffected by the introduction of the plate, and to remain so on rotation of the latter in its own plane, as should theoretically be the case if quartz were a normal uniaxial crystal, and as calcite has been actually shown to do—we observe that it polarises in brilliant colour, the whole hexagonal outline of the plate, clearly focussed on the screen, being filled with an evenly brilliant violet tint, the tint of passage, just as the central part of the interference figure, within the innermost ring, had been coloured in the convergent light experiment with the same plate. The colour changes with the slightest rotation of either of the Nicols, passing into red for one direction of rotation and into blue and green when the Nicol is rotated in the other direction. The tint also alters when the section-plate is rotated about its vertical diameter, by rotating the upper adjustable part of the supporting column of the stage within its outer fixed tubular column; this latter change is equivalent to a thickening of the plate, the light beam having to traverse a longer path through the quartz during such oblique setting of the plate.

This colour is due to the same fact which produced colour in the central part of the interference figure, namely, the optical activity of quartz, the fact that the plane of vibration of a beam of plane-polarised light transmitted along the axis of quartz is rotated to the right hand or to the left. The amount of this rotation is precisely equal, although opposite in direction, for the two varieties of quartz, but the rotation varies very considerably for different rays of the spectrum. It also varies directly proportionally to the thickness of the plate. A plate one millimetre thick cut perpendicularly to the axis rotates the plane of polarisation for red hydrogen light (C of the spectrum) to the extent of 17° 19′, for yellow D sodium light 21° 42′, and for greenish blue F hydrogen light 32° 46′. The rotation is a maximum for plates perpendicular to the axis, and the effect is inappreciable in directions at right angles thereto. It is clearly due to the oppositely spiral winding of the regular-point-system of the crystal structure, round the direction of the optic axis, the trigonal axis of symmetry of the crystal, a structure which we have proved to be characteristic of quartz by the beautiful experiments with the helical piles of mica plates, absolutely reproducing the polarisation effects with quartz, as described in the last chapter.

The opposite optical rotation of the two varieties of quartz can be well shown by constructing a "biquartz." Two plates of equal thickness, preferably either 7.5 mm. or 3.75 mm., are cut, one from a right-handed and the other from a left-handed crystal, each exactly perpendicular to the optic axis. The two edge-surfaces to be subsequently joined together are also cut, ground and polished as true planes perpendicular to the plate surfaces, and the two plates are then cemented together with Canada balsam by these two prepared edge-surfaces, taking care that the broad plate-surfaces of the two halves are absolutely continuous as if the whole were a single parallel-surfaced plate of quartz. Such a composite plate or "biquartz," is one of the most useful aids to the study of optical activity, being much used for enhancing the sensitiveness of the determination of the angle of rotation.

When the image of such a 7.5 mm. biquartz, mounted in the usual mahogany frame and placed on the object stage of the projection polariscope, is thrown on the screen—the Nicols being crossed for production of the dark field, and the stage and crystal plate being strictly perpendicular to the parallel beam of polarised light—the whole of the screen covered by the image of the plate appears uniformly coloured with the violet tint of passage. But the moment the analysing Nicol is rotated for a very few degrees, one half turns red and the other blue and then green. If the Nicol be turned back again to the crossing position with the polariser, and then rotated further in the opposite direction to the former rotation, the appearances on the two sides of the sharply focussed fine line of demarcation between the two halves are inverted, the side which formerly turned red now becoming green, and *vice versa.* The two varieties of quartz are thus oppositely affected, and it will be obvious that the biquartz is a very delicate test for the exact crossing of a pair of polarising prisms, or for the determination of the mutual extinction of two rectangularly polarised beams of light in general.

A very striking and beautiful mode of exhibiting this opposite and equal rotation of the plane of polarisation by the two varieties of quartz may next be described, an experiment which we owe to Prof. S. P. Thompson. A composite plate of mica is constructed out of 24 sectors of 15° angle each, the whole making up a complete circular plate. They are cemented between two circular glass plates of the usual $1\frac{7}{8}$ inch size, with balsam; the sectors are laid down in succession on one of the plates first, side by side, with the edge of every one in turn in close contact with the edge of the next in order, so as to radiate from a common centre. The second glass plate is only cemented after the arrangement has been allowed to set for some days, when there is less risk of disturbing the mounting of the sectors. The latter have all been cut from the same film of mica, which has a thickness corresponding to a retardation of one of the two rays produced by the double refraction of the crystal behind the other equal to one and a half waves. Each sector is so cut that the line bisecting the 15° angle is parallel to the line joining the positions of emergence of the two optic axes of the crystal.

On placing this wheel of mica on the polariscope stage, the Nicols being crossed, the effect shown at *b* in Fig. 83 is observed on the screen. The four sectors 90° apart, the bisecting lines of which are vertical and horizontal respectively, parallel to the vibration planes of the Nicols, appear as a jet black cross; the sectors next to them appear pale brown, and the next again a still paler delicate shade of sepia, while the central diagonal ones of each quadrant, at 45° to the black cross, are brilliantly white.

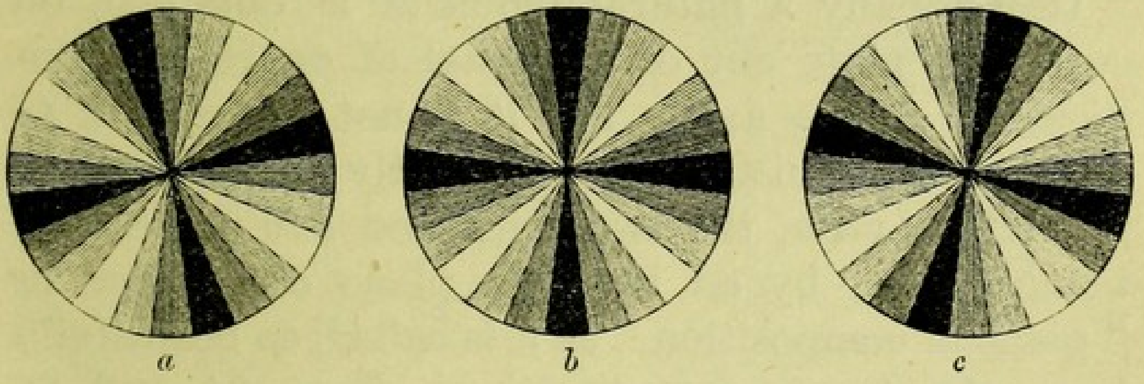

Fig. 83.—A Disc *b* of 24 Mica Sectors under Crossed Nicols, showing Effects at *a* and *c* of Introduction of Left and Right-handed Quartz Plates.

On now introducing behind or in front of the stage a right-handed quartz plate one millimetre thick, one of the pair of large ones described in one of the convergent light experiments of the last chapter, the black cross is observed to be deflected one sector to the right, as shown at *c* in Fig. 83; whereas when the left-handed companion plate is introduced in like manner the cross moves over one sector to the left, as indicated at *a* in Fig. 83. The two quartz plates are mounted on the same mahogany object frame, a specially long one with two large apertures carrying the quartzes, so that first one and then the other can be placed in or out of position, and when this is done rapidly the movement of the cross from right to left and back again is very marked.

Occasionally a natural biquartz is obtained, on cutting a plate out of a crystal of quartz perpendicularly to the axis. For it is not uncommon to find a crystal which, while apparently a single crystal, is really a twin, the two right and left individuals being joined by an invisible plane of contact, or "plane of composition" as it is called, so beautifully have the two grown together. Figs. 84 and 85 show two kinds of twins of quartz. The former consists of two obviously different individuals, with the little *s* and *x* faces indicating right or left handedness clearly developed in an opposite manner. The crystal shown in Fig. 85, however, appears to be a single individual, yet differs from either a right-handed or a left-handed crystal in showing the *s* and *x* faces developed on both right and left solid angles. It is a case of complete interpenetration.

In both cases the plane of twinning is parallel to the optic axis, and to a pair of faces of the hexagonal prism of the second order, perpendicular to a pair of the actual first order prism faces shown by the crystal. They are examples of the well known

" Brazilian twinning " of quartz, so called because many quartz crystals found in Brazil display it.

A natural biquartz of 3.75 millimetres thickness cut from such a crystal as is shown in Fig. 85, the plate having a hexagonal outline just as if the crystal were really a single one, may next be projected on the screen. The Nicols being crossed, the outline of the crystal is seen sharply defined, the whole area of the crystal being coloured a uniform yellow, there being absolutely no trace of any dividing line. But the moment one commences to turn the analysing Nicol different shades, orange and green respectively, begin to develop on the two sides of the line indicating the plane of composition of the twin, the hexagon being divided by a diametral line joining two corners, which have been arranged in mounting the plate in its carrier frame to be above one another, so as to bring the line of composition vertical, as will be

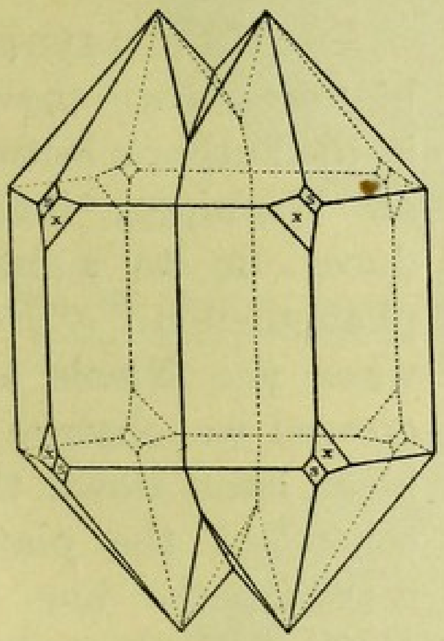

FIG. 84.—Pair of Brazilian Twins of Quartz.

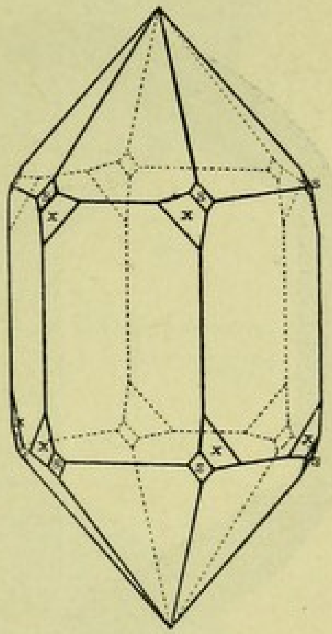

FIG. 85.—Completely Interpenetrated Brazilian Twins of Quartz.

clear from Fig. 86. On rotating the analyser further the difference is still more marked, and we have blue on one side and orange red on the other, developing still deeper into red and purple as the analyser approaches the parallel position with respect to the polariser; when this latter position is attained the transition violet tint is developed evenly over the whole plate, and the dividing line has again disappeared.

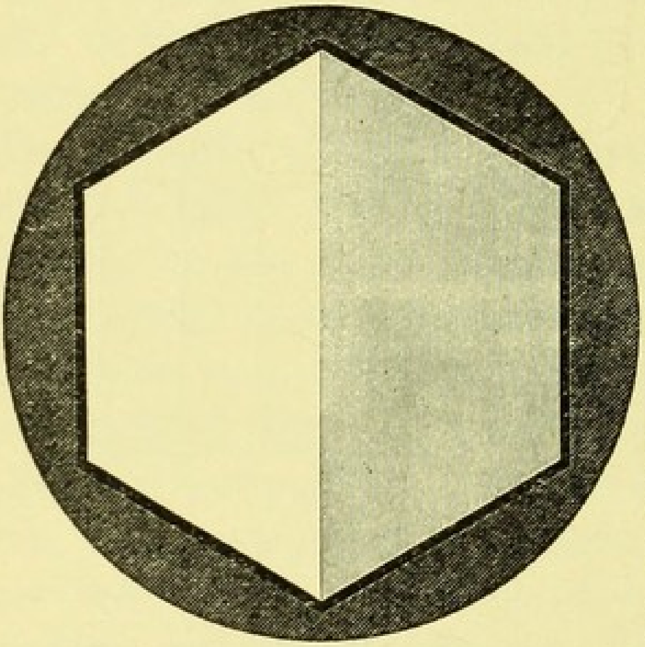

Fig. 86.—A Natural Biquartz in Parallel Polarised Light.

Another natural biquartz, also shown in the author's lecture at Winnipeg, introduces us to a new phenomenon. For when the Nicols are crossed we observe a black band down the centre of the plate, marking the line of division of the twins. When the analyser is rotated until it is parallel to the polariser this black band changes to a white one, the sequence of colours on the different sides of the band, that is, in each half of the plate, being the same as just described. The effect with crossed Nicols is more or less simulated in Fig. 87, Plate XVII., which is a reproduction of a direct photograph of the screen picture. The reason for this black band in the dark field, and for the white one in the bright field, is that the two halves of the twin overlap at the centre, the plane of junction of the two

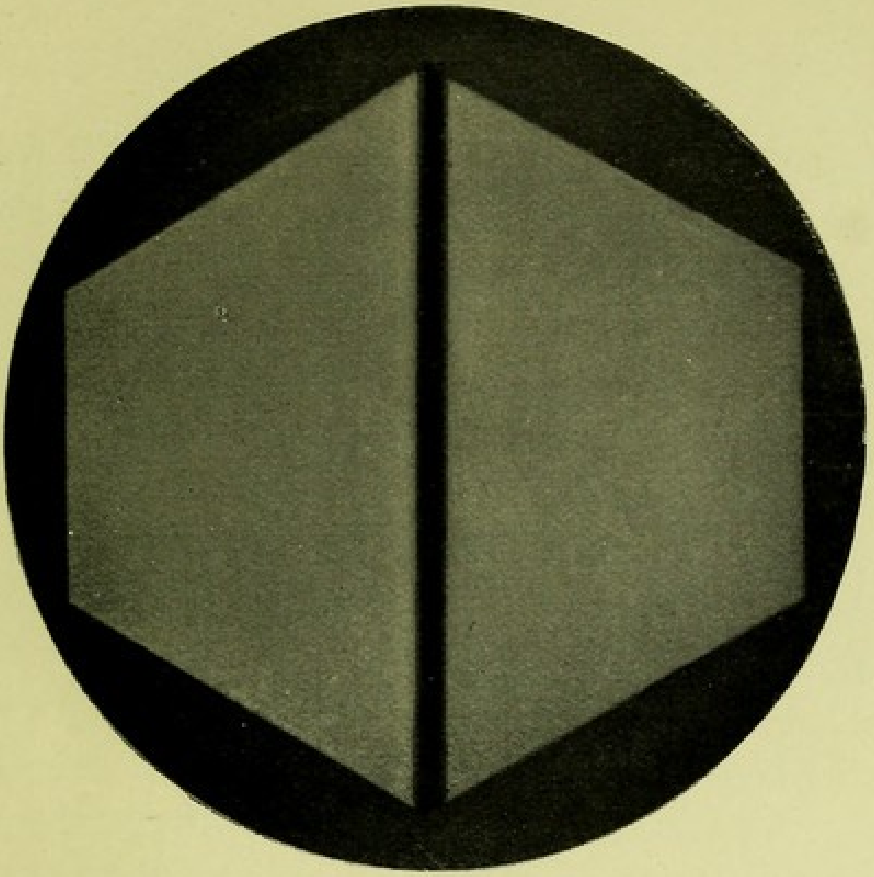

FIG. 87.—Natural Biquartz exhibiting the Black Band (Nicols crossed) at the Oblique Junction of the Right-handed and Left-handed Parts.

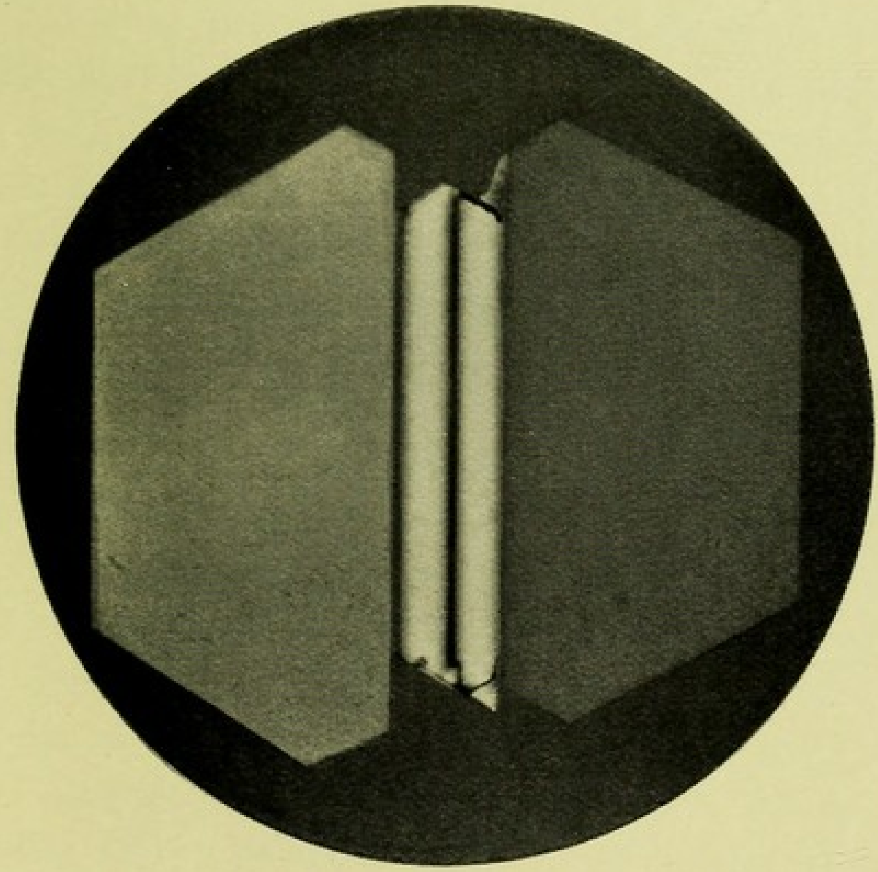

FIG. 88.—Artificial Biquartz, the two parts being obliquely joined in order to produce the Black Band.

DIRECT PHOTOGRAPHS OF PICTURES PROJECTED ON THE SCREEN BY THE LANTERN POLARISCOPE, USING PARALLEL LIGHT.

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individual crystals being oblique to the plate, instead of exactly perpendicular thereto as was the case with the first natural biquartz. We are, in fact, beginning to get the effect of two superposed wedges of quartz.

When the obliquity is greater, or the crystal thicker, a white band appears on each side of the black central one, the Nicols being crossed, and when the thickness is as great as 6 to 7.5 mm. a spectrum band appears on each side of the white one.

That this obliquity of the surface of contact of the two intergrown individuals (not the plane of twinning, which remains parallel to a pair of faces of the hexagonal prism of the second order) is the true explanation can be readily proved by reproducing the effect artificially. A thick double plate of quartz is constructed, as shown in Fig. 88, composed of two halves of respectively right-handed and left-handed quartz, each 6 to 7 millimetres thick, and each of which has had the edge-face of junction ground and polished obliquely at an angle of 30° or so, and oppositely so, instead of perpendicularly to the plates ; the two halves are then cemented together in the usual manner for a biquartz, with Canada balsam, in order to make a continuous plate. On placing the plate of this construction possessed by the author on the stage of the projection polariscope, the two halves exhibit on the screen respectively brilliant red and green colour, with a vertical central black band, and on each side of it first a white strip and then a spectrum band, all the bands being parallel to each other, and the whole effect being precisely what was observed with the thickest natural biquartz.

Thus, we have imitated the oblique junction of the twin parts of the second and third biquartzes, and proved that this obliquity is the reason for the phenomena of bands, the black band occupying the centre where the two opposite rotations of the right and left quartz are precisely neutralised. The dark field of the crossed Nicols consequently prevails along this central strip, for the rotatory effect of the first individual crystal on the light passing through it is exactly undone by the subsequent passage of the rays through the other individual. On either side of this neutral strip there is a little preponderance of right-handed quartz on one side, and of left-handed quartz on the other, and the usual effect of a thin plate of quartz is therefore seen, namely, no colour but a little light, while further accretions of thickness of the preponderating variety give all the colours of the spectrum in turn, as with growing thicknesses of ordinary single quartz plates, thus producing the spectrum band.

The black band is also afforded when the plate is cut somewhat obliquely, out of a twin crystal with a junction plane truly perpendicular to the equatorial section, instead of cutting it truly perpendicularly to the axis, the junction plane being then oblique to the plate. The polarisation colours are not so strong, however, unless the plate be made thicker.

This effect of a black band with flanking spectra is very similar to that obtained, due to double refraction and not to optical activity, when two thin wedges of quartz are cemented together to form a parallel plate, one wedge being cut so that the optic axis is parallel to the edge of the wedge,

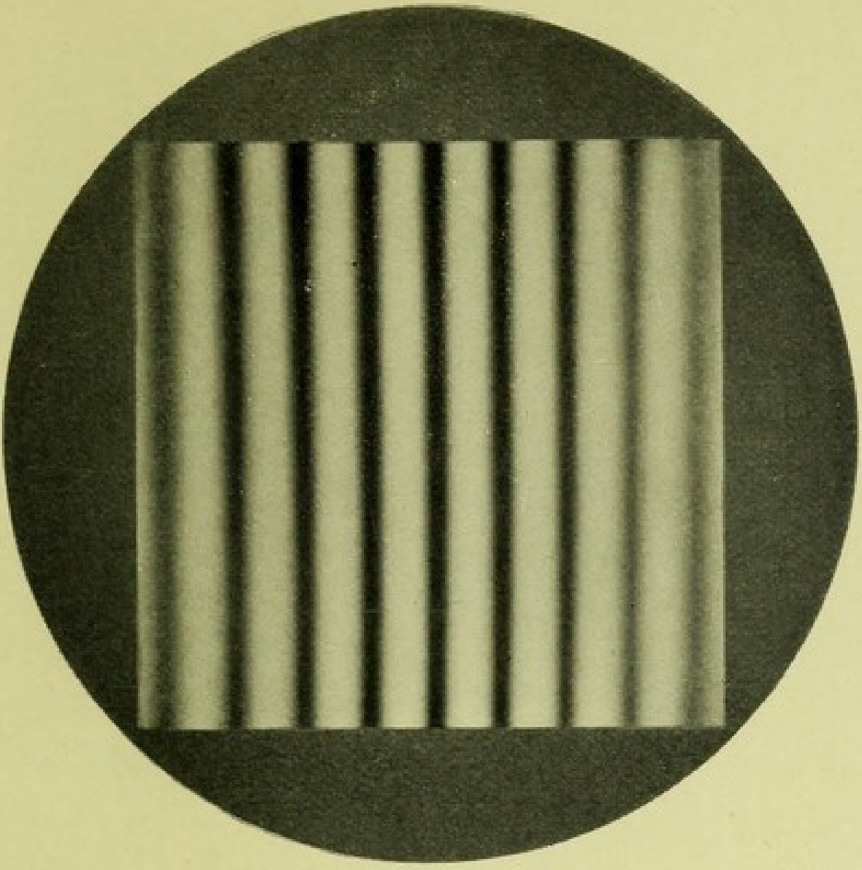

FIG. 89.—Black Central Band and equidistant Spectrum Bands on each side, afforded by Babinet's Composite Plate of two Quartz Wedges, one parallel and the other perpendicular to the Axis. (Direct Photograph of Screen Picture as projected by Lantern Polariscope.)

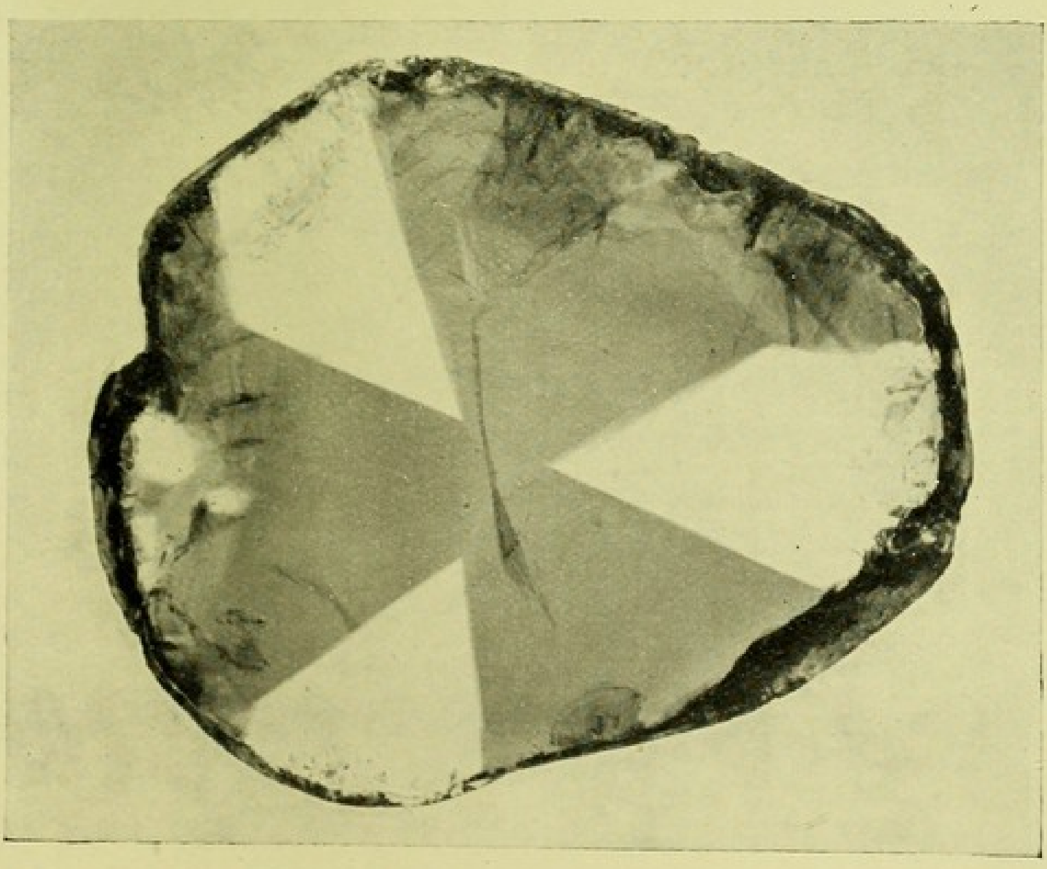

FIG. 94.—Section-plate of Amethyst, natural size, as seen directly in Ordinary Light, showing Alternate Violet Sectors (see p. 223).

and the other with the optic axis perpendicular to the edge. When such a composite plate of quartz, often known as a Babinet plate from the name of its first constructor, is placed on the stage of the polariscope, and rotated to the 45° position with respect to the planes of vibration of the crossed Nicols, there is observed on the screen a deep black band in the centre parallel to the edge of the wedge, and a number of spectrum bands on each side, separated by white equal interspaces, the rainbow coloured bands showing the orders of Newton's spectra. The effect, as seen on the screen, is reproduced photographically in black and white in Fig. 89, Plate XVIII.

These experiments lead us naturally to the study of a great variety of quartz twins, involving some of the most beautiful and gorgeously chromatic phenomena which it is possible to produce on the screen with the projection polariscope. They will eventually bring us to the study of amethyst quartz, in which the twinning is repeated so often that the laminations of alternate right and left quartz are sometimes countless, and almost approach molecular dimensions.

The Brazilian twinning of quartz, parallel to a pair of faces of the second order hexagonal prism $\{11\bar{2}0\}$, often occurs in a very erratic manner, as regards the arrangement of the portions of the composite crystal belonging to the two varieties, the surfaces of contact and character of the interpenetration being frequently very irregular, and often remarkably so. Thus Fig. 90, the upper figure of the coloured frontispiece, gives some faint idea of the appearance presented on the screen by a very beautiful quartz plate, one-half of which is entirely composed of left-handed quartz, giving a rich even rose-red colour when the Nicols are crossed, not very far from the violet transition tint, the plate being nearly 7.5 mm. thick, while the other half consists of an alternation of strips of right and left-handed quartz, joined obliquely to the surface of the plate, the black band and its accompanying white ones and spectrum bands being repeated two or three times before the edge is reached. This is a very instructive case, for it shows in this half of the plate, on a large scale, what occurs in amethyst in a more minutely structural manner, the broad strips, the sections of plates upwards of a quarter of an inch thick, of alternating character becoming in amethyst thin lines, the sections of laminæ or films of microscopic tenuity, their number being correspondingly enormously increased.

It may be interesting to state how this Fig. 90, and the lower Fig. 97 of the frontispiece representing the projection on the screen of benzoic acid in the act of crystallisation, were produced. The pictures on the screen were directly photographed on the latest Lumière autochrome plates, a transparency in the actual natural colours being thus obtained in each case. These transparent colour-photographs were then used as originals wherewith to reproduce the effects on paper by the most recent improved three-colour photographic process.

Two other typical cases of irregular quartz twinning may also with advantage be demonstrated. The first is a plate in which there are repeated 60° V-shaped or 120° wedge-shaped intrusions of one

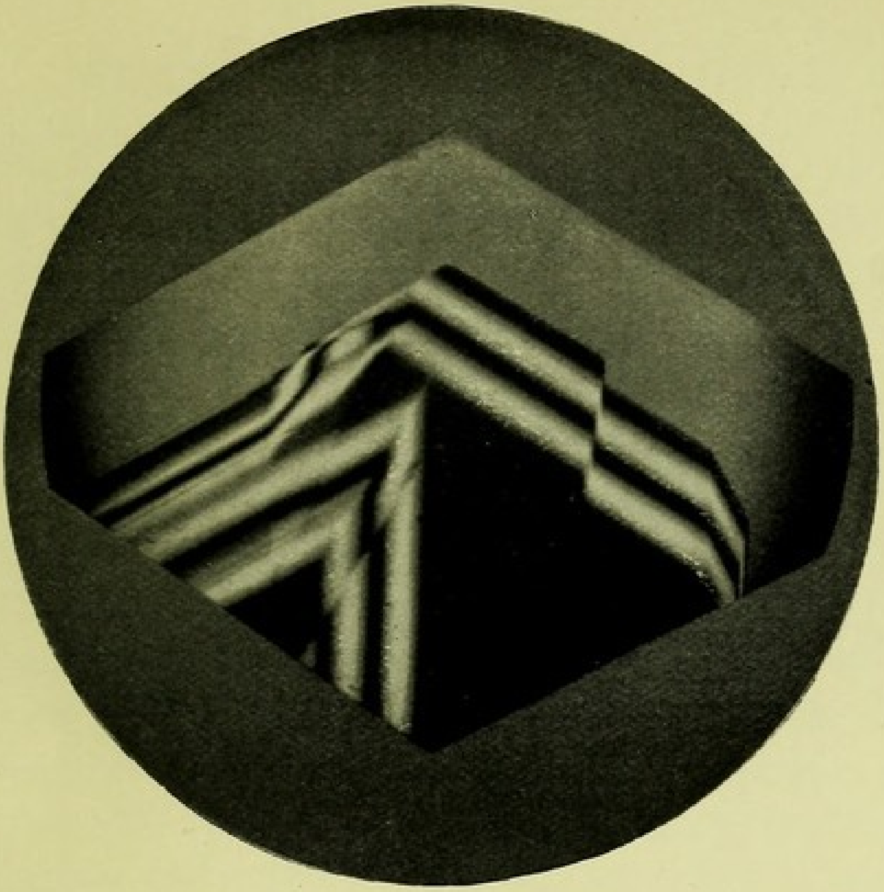

Fig. 91.—Sectorial 60° or 120° Intrusive Twinning of Right and Left-handed Quartz, showing Ribbons with Central Black Band where Oblique Overlapping occurs.

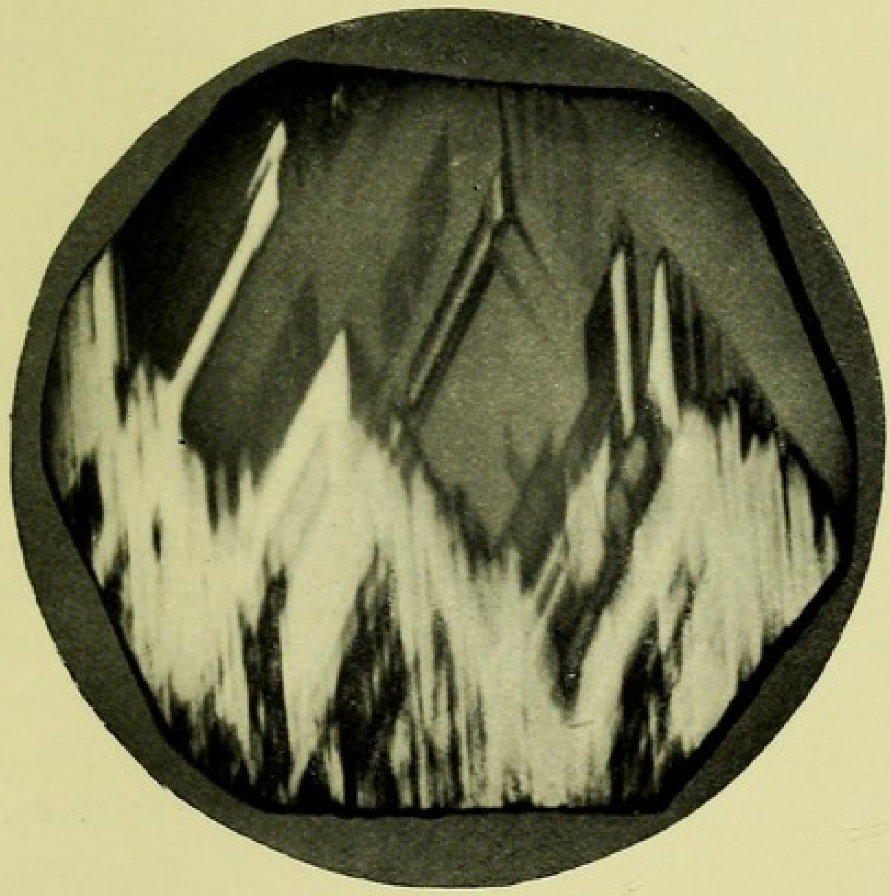

Fig. 92.—Irregular Intrusive Twinning of Right and Left-handed Quartz.

Direct Photographs of Remarkable Screen Pictures afforded in Parallel Polarised Light by Sections of Twins of Right and Left Quartz.

To face p. 220.

variety into a greater mass of the other variety. The border of the V or 120° wedge is composed of a ribbon, the outer edges of which are spectrum-coloured and the central line of which is formed by the deep black band, which is separated on each side from the spectra by a white strip. Some idea of the beauty of this quartz plate, which was generously lent to the author by Prof. S. P. Thompson, as projected on the screen under crossed Nicols, may be gathered from Fig. 91, Plate XIX., the upper homogeneous part of the plate being coloured a brilliant green, and the lower part red.

The second is an irregular interpenetration of one variety into the other, in repeated V-shapes occupying the lower half of the image of the plate as seen on the screen in the dark field of the projection polariscope, like a range of sharp mountain peaks, the black bands being so rapidly repeated as to be nearly continuous. These darker portions thus appear to form the bulk of the mountains, while the upper untwinned half of the crystal shows a clear and even sky blue; to make the resemblance to a range of Alpine mountains even more complete, the wavy line of demarcation between the twinned and non-twinned portions of the plate is bordered by a white ribbon, of varying width, giving the appearance of a snow-cap to each peak, which shows up clearly against the blue sky. It will be obvious that this quartz plate affords an altogether very beautiful series of phenomena in parallel polarised light on the screen, for the colours change with every movement of the analysing Nicol from the crossed position, the appearance for which has just been described.

Fig. 92, Plate XIX., gives only the faintest idea of the beauty of the screen picture afforded by this section-plate. The effect chosen as best for photographic reproduction purposes is one afforded when the analysing Nicol is rotated somewhat away from the crossed position with respect to the polariser.

And now we arrive finally at amethyst quartz, three very beautiful hexagonal plates of which—cut perpendicularly to the optic axis as usual for quartzes intended to display optical activity, from an apparently single hexagonal prism in each case—will be taken as typifying the phenomena exhibited by this especially interesting variety of quartz on the screen in parallel polarised light. The smaller one affords a screen picture, with Nicols not quite crossed, such as is portrayed in Fig. 93, Plate XX. We observe that the area of the hexagon is roughly divisible into six 60°-sectors, and that alternate ones are uniformly coloured, indicating that they belong to wholly right-handed or left-handed quartz; whereas the other alternate sectors are most beautifully marked, as if by line shading parallel or inclined at 30° to the edges of the hexagon, by a considerable number of equally spaced dark or slate coloured bands, close together but separated by white bands, with a trace of spectrum colours along the middle of the latter. If we rotate the analysing Nicol somewhat we can readily find a position, which is not always that of crossed Nicols, for which these parallel bands of laminar twinning are most clearly defined, as shown in the illustration, the colours of the other sectors ever changing during the rotation.

It is obvious that we have here to do with the

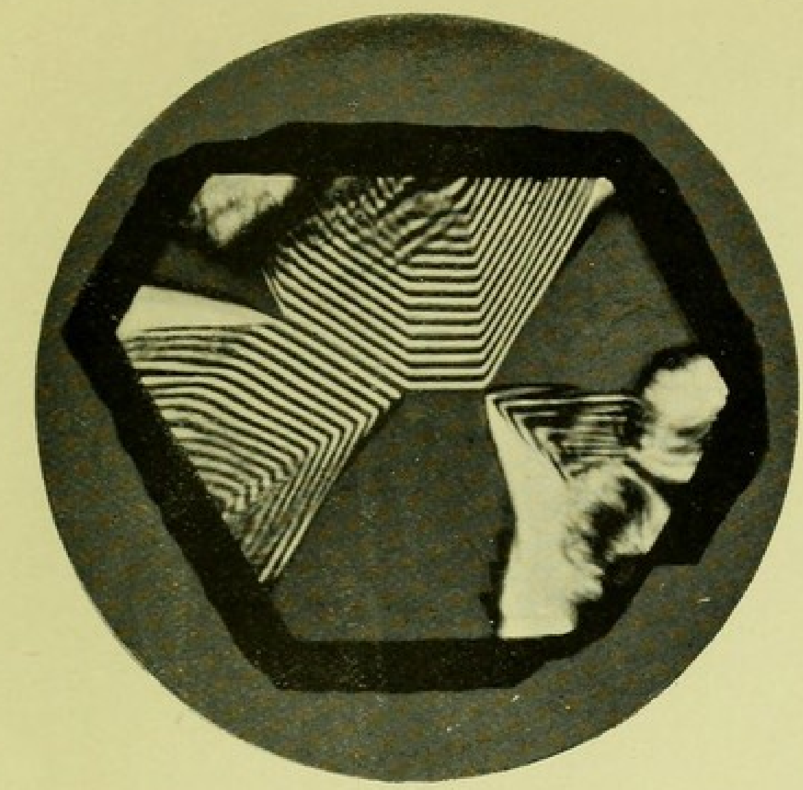

FIG. 93.—Section-plate of Amethyst Quartz, showing Sectorial Repeated Twinning of the Right and Left Varieties.

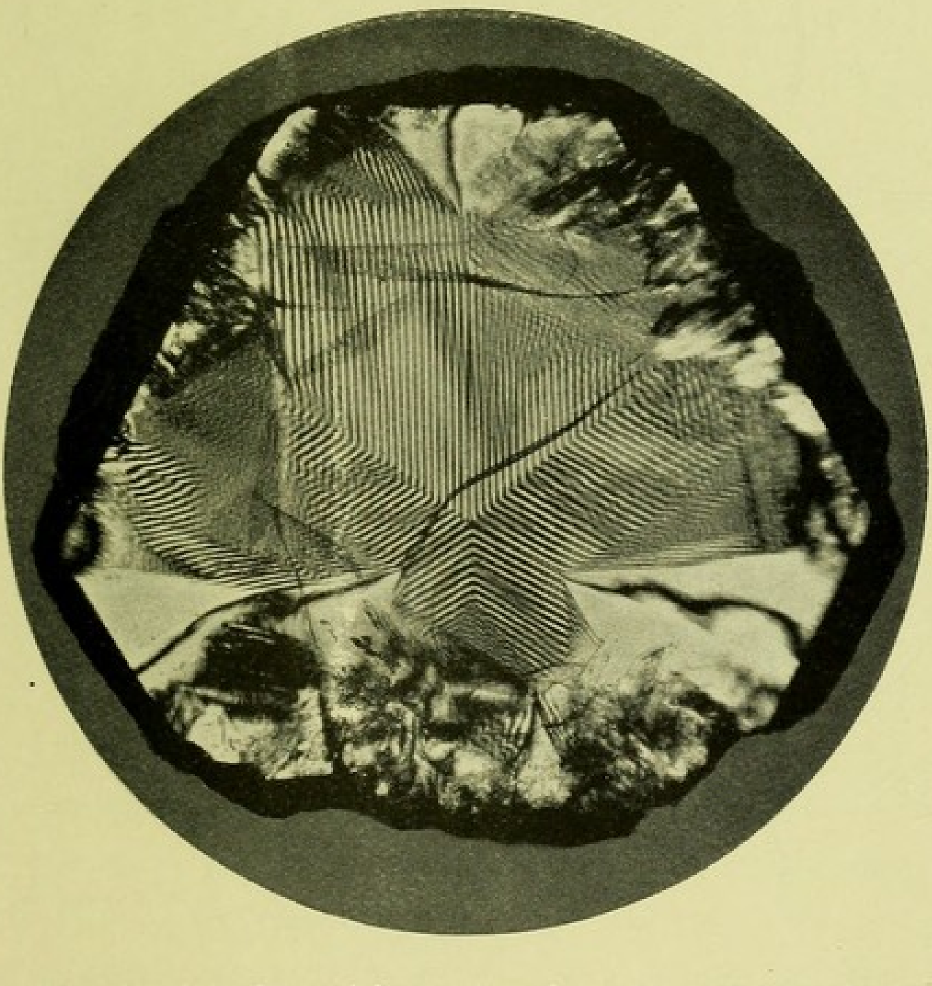

FIG. 95.—Section-plate of large Amethyst Quartz Crystal, showing relatively large Area of Sectorial Repeated Twinning of Right and Left-handed Quartz (see p. 225).

DIRECT PHOTOGRAPHS OF SCREEN PICTURES OF AMETHYST PROJECTED BY THE LANTERN POLARISCOPE IN PARALLEL LIGHT.

To face p. **222.**

same phenomenon as was illustrated by the parallel bands shown on the large scale by the section illustrated in Fig. 90 of the coloured frontispiece, the black, white, and spectrum-coloured bands being simply repeated very many more times in the same space, and in alternate sectors of the crystal.

The twinning of amethyst in 60°-sectors is very characteristic of this variety of quartz, and it is an interesting fact that the sectors which show the laminar bands in polarised light often appear purple coloured in ordinary light, the tint from which amethyst derives its name. This is not necessarily or always so however, and the section just described and illustrated in Fig. 93 appears quite colourless throughout on casual inspection in ordinary light, in fact as a clear colourless hexagonal section of ordinary simple quartz ; a trace of the amethyst colour becomes, however, apparent on closer examination when held obliquely, in the sectors where the bands become visible in polarised light.

The second plate of amethyst is a magnificent section 9 millimetres thick and 2½ inches in diameter, of which alternate 60°-sectors are deeply amethyst coloured, the tint being a pure violet of about the wave-length of the hydrogen line near G of the spectrum. Moreover, even to the naked eye when the specimen is held in the hand up to the light, in certain positions the laminæ become visible as more deeply shaded violet line markings. On placing it on the stage of the polariscope but with the analysing Nicol removed, so as to observe the natural appearance of the section in white light (for, although polarised by the polarising Nicol, being unanalysed the section exhibits no polarisation effects), these facts become clear to everyone in the room. The violet staining of alternate sectors appears very deep, and traces of lamination in the violet parts are just apparent on close scrutiny, the other alternate sectors appearing colourless and unmarked except by a few flaws almost always present in so large a section-plate of amethyst. The natural appearance of this plate is shown in Fig. 94, Plate XVIII. (facing page 218), as far as is possible photographically, the violet sectors being clearly demarcated.

On replacing the analysing Nicol the colourless sectors are seen to polarise uniformly in brilliant colours, indicating a homogeneous variety of quartz in each, either right or left-handed. Moreover, whenever two of these naturally colourless parts touch each other, which they do as the margin of the plate is approached, an irregular ribbon is produced, composed of the black band in the centre, with first white and then spectrum coloured flanking strips on each side, the spectra forming the edges of the ribbon. The violet sectors show the laminated twinning, but, owing to the great thickness of this plate, in too complicated (overlapping) a manner to be easily followed, a thinner plate being required to show such fine laminations clearly.

Finally, the third section is such a thinner plate, about 3.5 mm. thick and nearly 1½ inches in diameter. This section of amethyst is probably the most beautiful of all, for it not only shows the laminated twinning to perfection, in three alternate 60°-sectors and in all six in the middle part of the plate, but also these alternate sectors are distinctly violet even to the eye when the specimen is held in the hand against a white background; and the laminations are likewise also clearly visible on holding the section obliquely up to the light. In polarised light, either with crossed or parallel or anyway arranged Nicols, the phenomena on the screen are of the most superb character. The whole of the middle part of the plate appears made up of six sectors, *all* showing the fine laminar bands parallel to the edges of the second order hexagonal prism $\{11\bar{2}0\}$, that is, at 30° to the edges of the section, the crystal being a first order hexagonal prism $\{10\bar{1}0\}$. Some idea of the arrangement will be afforded by Fig. 95, Plate XX. The marginal parts develop into alternately right and left-handed sectors or half-sectors, polarising in different and very brilliant colours, and showing the ribbon bands at every junction. On rotating the analysing Nicol the changes are remarkably beautiful, particularly for the positions of the analyser when the laminar bands take on their deep slate colour, with white and marginally spectral interstrips. The whole phenomena, indeed, afforded by this plate of amethystine quartz, are the most magnificent which the author has ever seen on the screen, in the whole of his crystallographic experiences.

The Brazilian twinning law of quartz, according to which the plane of twinning is parallel to a pair of faces of the second order hexagonal prism $\{11\bar{2}0\}$, appears capable of explaining all these varieties of right and left-handed twins, the interpenetration of the intimate kind shown in Fig. 85 (page 215) usually resulting in sectorial portions of space being occupied by each kind, the surfaces of junction of oppositely optically active parts being, however, very varied in their distribution and character. Where they happen to be more or less horizontal, a plate cut perpendicularly to the axis to include both kinds would show Airy's spirals in convergent polarised light, as may readily be demonstrated by such a plate, one of several, in the author's collection. Where they are oblique, a plate cut at right angles to the axis would, as we have seen experimentally, afford the black, white and spectral ribbon bands in parallel polarised light. Where, however, the mode of interpenetration is still more intimate, we have the rapidly alternating laminæ of the two varieties, right and left-handed, building up the beautiful structure of amethyst in thin layers. A section plate of such an intimate blending of the two varieties, cut as usual perpendicular to the axis in order that any phenomena of optical activity shall be exhibited at the maximum, affords no indication whatever of optical rotation, the two varieties simply neutralising each other's effects, and the plate behaves as an ordinary uniaxial crystal, affording in convergent polarised light a black cross like calcite, complete to the centre. In parallel polarised light it shows of course the laminated structure, but the tendency to remain dark under crossed Nicols is shown by the fact that the tints exhibited by the laminations are slates, greys, and even black, when the Nicols are crossed, the delightful other colours only making their appearance when the analysing Nicol is rotated. Thus the simple law of Brazilian twinning is quite capable of explaining the whole of the phenomena exhibited by composite crystals of the two varieties of quartz, and such an explanation is the one accepted by von Groth, in the excellent description of quartz in the last edition of his *Physikalische Krystallographie*.

An interesting crystal of amethyst very similar to the third of those just described, the one illustrated in Fig. 95, was described by Prof. Judd in the year 1892 to the Mineralogical Society.[1] The plan of the crystal is given in Fig. 96. The wedges marked *x*, *y*, *z*, are of a pale yellow colour, as are also the three strips, sections of plates, proceeding from the wedges and meeting at the centre

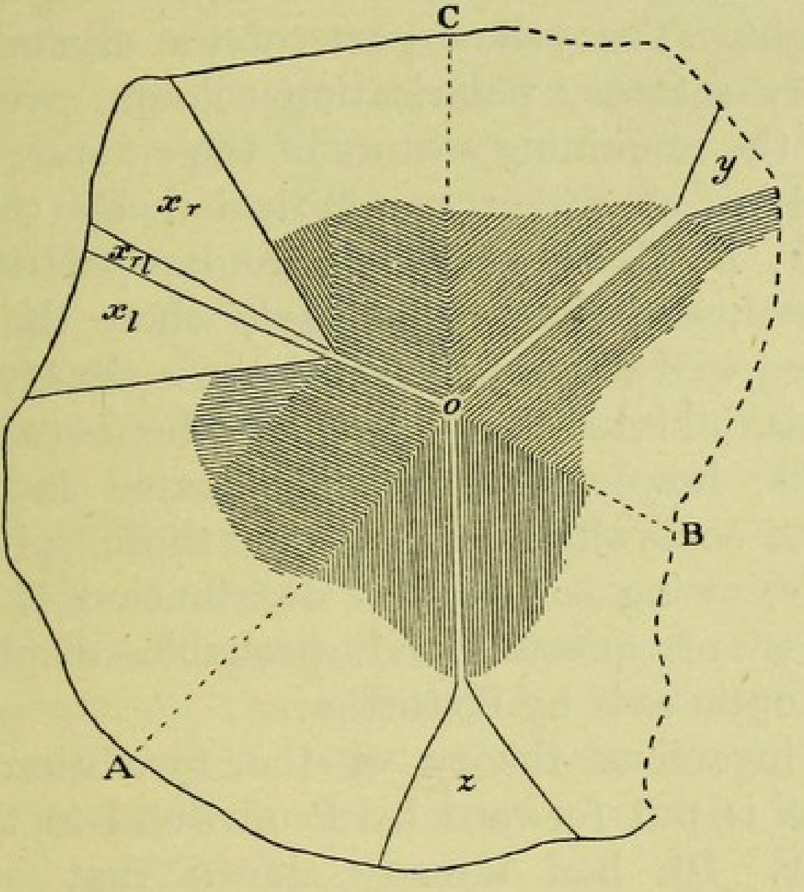

FIG. 96.—Plan of Amethyst Crystal.

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[1] *Mineralogical Magazine*, 1892, **10**, 123.

o. The wedge y exhibits left-handed polarisation, and the wedge z right-handed. The large wedge x is composite, the part marked x_r being right-handed and that marked x_l left-handed. The surface of junction of the two parts is not perpendicular to the plate, so where the two varieties overlap, the part marked x_{rl}, a ribbon band is shown in parallel light and Airy's spirals in convergent polarised light. The yellow parts of the crystal exhibit ordinary rotatory polarisation colours, even tints; but in the remaining sectors of the crystal, the lines of division of which are indicated by the radial lines A, B, C, no trace of circular polarisation is displayed, and the central part, where the lamellæ are very well developed, gives the ordinary calcite-like uniaxial interference figure. The more marginal portions, however, show complicated interference figures, somewhat resembling those of biaxial crystals, owing to irregular distribution of the two varieties of quartz, and probable displacement of the optic axis by distortion.

An ingenious theory of the formation of the lamellæ is put forward by Prof. Judd in the same memoir. He had already shown that quartz is endowed with planes of gliding, parallel to the rhombohedral faces, and suggests that the lamellation is the result of the effect of high pressure and possibly high temperature on the quartz crystal after its formation. The lamellæ appear to be frequently parallel to the rhombohedral terminal faces of the crystal, as if they were indeed glide plane effects. It is quite conceivable that the gliding of layers of molecules, which when permanent usually involves rotation and inversion of the molecules, might result in alternately right and left structural arrangements, and there is considerable evidence that the development of the purple tint occurred subsequently to the growth of the crystal. It is probably due to change in the state of oxidation of the trace of manganese present as a minute impurity in the quartz crystal, and which is concentrated between the lamellæ, just as the yellow tint is due to a slight trace of iron (ferric) oxide. The theory is an interesting one, and throws considerable light on the possible nature of intimate lamellar twinning.

One last experiment may now be referred to, the concluding experiment of the Winnipeg lecture, and which is very reminiscent of the beautiful slate-colour of the lamellæ of amethyst. It is the actual crystallisation, projected on the screen, of a thin film of melted benzoic acid, which affords radiating closely packed long and narrow crystals, shooting out on the screen from centres near the margin of the field, very much like the individual crystals of repeatedly twinned quartz in the beautiful amethyst crystal illustrated in Fig. 95. Provided the film of melted benzoic acid be thin enough, the crystals appear on the screen in parallel polarised light, under crossed Nicols, tinted with the same beautiful shades of slate colour as amethyst, the intermediate low-order tint between the black and the grey of Newton's first order spectrum. Some idea of the appearance on the screen is afforded by Fig. 97, the lower of the two coloured figures in the frontispiece. As in the case of Fig. 90, the screen picture was photographed directly on a Lumière autochrome plate, and the transparency in the actual colours thus obtained was employed as an original wherewith to reproduce the picture on paper by the latest three-colour photographic process.

In carrying out the experiment a few of the flaky crystals of benzoic acid are placed on one of the circular glass object plates of the standard $1\frac{7}{8}$-inch size for the projection polariscope ; they are covered by a second similar one, and the two plates are then held in a pair of tongs and gently warmed over a small spirit lamp, or miniature Bunsen lamp. As soon as the crystals have fused, and the melted substance is evenly spread as a thin film between the two glass plates, the latter are rapidly transferred to a special mahogany object frame, fitted with a side slide to press the double-plate edge just sufficiently to hold it in position in the frame, which is then at once placed on the rotating stage of the polariscope. The screen appears quite dark at first, the Nicols being crossed, but in a second or two as the slide cools the benzoic acid begins to crystallise out at the sides, brilliant colours and the deep greys being both developed, the former chiefly near the edges of the crystals, rendering the crystallisation wonderfully distinct and beautiful on the black background. Then long needle crystals shoot out from various quarters one after another or simultaneously, in lovely shades of slate or grey tinted with brilliant colours at the margins and tips, the growing point cutting its way along like a sharp brilliantly coloured arrowhead. Eventually an arch is formed of such acicular crystals, radiating simultaneously from many centres, gorgeously coloured in parts, but showing the yet more æsthetic slates and greys in the main. Finally, the whole screen picture fills up with a mass of interlacing yet ever distinct crystals, the last few to crystallise in the centre usually doing so with a burst of especially bright colour, as the thickness increases adequately for the double refraction retardation to reach the more brilliant second order spectrum, a concluding effect which evokes the emphatic delight of even the most phlegmatic philosopher, inured to scenes of beauty in natural phenomena.

The series of experiments with quartz described in this and the previous chapter, culminating with those revealing the alternate repetition of extremely fine layers of right and left-handed quartz in amethyst, will, it is hoped, have illustrated and rendered intelligible the important structural principle of enantiomorphism or mirror-image symmetry. We have only to imagine the layers to become thinner and thinner until we approach ultimately the neighbourhood of the minute dimensions of the chemical molecule, without as yet penetrating within the range of the molecular forces; the two such oppositely constructed and intimately blended structures, built up by atoms arranged oppositely screw-wise, clockwise and anti-clockwise, will now form an ultra-microscopic mixture of the two varieties in equal quantities, that is, in equal molecular proportions.

Such a structure will exhibit the symmetry of the system to which the two individuals belong, but instead of only displaying that of the enantiomorphous class of that system, possessing lower than the full symmetry, as each variety does when crystallised alone, it will now display the full holohedral symmetry of the system. That is, the symmetry is enhanced by this intimate blending of the two complementary enantiomorphous forms, the two together supplying all the possible elements of symmetry of which the system is capable. Moreover, as we have seen in the case of the lamellar portion of the amethyst crystals represented in Figs. 95 and 96, there will now be no sign of optical activity, for the two opposite rotations are equal and destroy each other.

Hence, such a compound crystal shows the holohedral symmetry of the system, and is optically inactive. In such cases we are, in fact, confronted with the phenomenon of pseudo-racemism, as defined in Chapter XI. For we know that the two varieties are still present intact, polarised light revealing them in the case of their grosser development such as is found in amethyst, and the system of symmetry being clearly the same, the forms developed being merely the sum of those of the two individual varieties.

Amethyst thus affords us a gross demonstration of the nature of pseudo-racemism, and as such has proved an exceedingly illuminating study.

We can carry the process further, however, in imagination, until the two differently helical molecules are themselves juxtaposed face to face, right molecule to left molecule. When, however, this occurs, we have entered into that most fascinatingly interesting region, the range of molecular forces, a mysterious sphere of activities of which we are only just beginning to learn something. Within this region of larger activity the two oppositely constructed molecules are often known to combine chemically to produce a molecular compound, just as potassium sulphate molecules, for instance, will combine with those of magnesium sulphate to form the well known double salt. The double molecule now furnishes the representative point of the space-lattice, in other words, a new space-lattice is now erected, the units of which may be taken to be the representative points of the double molecules. Such a space-lattice will of necessity be of a totally different character to the old one corresponding to the single molecule of either variety (for each variety has the same space-lattice, the points, however, representing differently, enantiomorphously, orientated atomic details). That is to say, we shall have an entirely new kind of crystal produced, in all probability belonging to a different crystal system. It is known as a racemic compound, as described in Chapter XI.

This is exactly what happens in the case of tartaric acid, the two varieties, dextro or right-handed tartaric acid and lævo or left-handed tartaric acid, not forming pseudo-racemic crystals of like but enhanced (holohedral) symmetry, but a truly molecular compound, the well-known inactive racemic acid, in which the phenomenon of "racemism" was first discovered and from which it took its name.

Now a molecular compound is notoriously regarded by chemists as a type of chemical compound of low stability, molecular attraction or affinity not being nearly so powerful as atomic affinity. Hence, under suitable conditions it may be possible to induce the two component varieties to crystallise out separately from the solution of the racemic compound. In the case of racemic acid itself this does not readily happen, but in the cases of certain of its metallic salts, sodium ammonium racemate, for instance, specific conditions are known under which the two varieties of crystals, right and left handed respectively, may be separately crystallised out from the solution, some of which conditions were referred to in Chapter XI. Racemic acid itself, however, crystallises quite differently to the two tartaric acids, namely, in triclinic prismatic crystals. These are, in fact, absolutely different from the monoclinic crystals of the dextro and lævo varieties of ordinary tartaric acid, for racemic acid takes up also a molecule of water of crystallisation on separating from its aqueous solution. There are certain chemical differences also, due to the chemical union of the two enantiomorphous molecules into a single double molecule, such, for instance, as greater facility of reduction by hydriodic acid to succinic acid.

Thus our experiments with quartz have afforded us the means of acquiring a clear idea of the nature of this most interesting type of crystal structure which involves the principle of mirror-image symmetry. Racemic acid and its similar structures, racemic compounds in general, are known as "externally compensated" structures, the reflective principle here acting externally to the single enantiomorphous molecule. It is but another step, however, to imagine internal compensation of enantiomorphous parts of a molecule, by mirror-image combination of such parts, such as in all probability occurs in the case of the truly inactive fourth variety of tartaric acid, in order to comprehend how the principle enabled the 165 types of homogeneous structure involving this kind of repetition to be arrived at, and thus, together with the 65 regular point systems already known, to afford us the complete set of 230 types of homogeneous structures possible to crystals.

CHAPTER XV

HOW A CRYSTAL GROWS FROM A SOLUTION.

One of the most deeply interesting aspects of a crystal, especially from the point of view of the history of crystallographic investigation, concerns the mysterious process of its growth from a solution (in a solvent) of the substance composing it. The story of the elucidation, as far as it has yet been accomplished, of the nature of crystallisation from solution in water is one of the most romantic which the whole of scientific progress can furnish. Again we are struck with the parallelism between crystals and living objects. For just as the discovery of bacteria, the infinitesimal germs of life, has given an immense impetus to our knowledge of disease and been blessed with most beneficent effects in combatting the ravages of the latter, so the discovery that crystal germs of most common crystallised substances, of no larger size than bacteria, are floating about in our atmosphere, and ready at any time to drop into our solutions and, if the latter are in the proper receptive condition, to set them crystallising, is little less marvellous, and has had as profound an effect on our knowledge of the process of crystallisation. A true story, told to the Royal Society the other day, may serve to illustrate the point. A new chemical compound had been discovered, and at the time there could obviously be no crystal-germs, minute crystallites of the dimensions of possibly only a comparatively few chemical molecules, of this hitherto unknown substance floating about in the air. It was found impossible to obtain the deposition of crystals in the ordinary way, from solutions of the substance in its ordinary solvent, although they were in the condition of proper receptivity above referred to, on account of the absence of such germs in the air. But later on, when the air of the laboratory had become impregnated with such germs, on account of the daily handling of the substance in the laboratory, no difficulty was any longer found in obtaining good crystals quite readily from these solutions.

We are at first inclined to wonder whether such extraordinary statements can possibly be sober facts. Yet such is, indeed, the case, and it will be very well worth devoting a chapter to the story of how we have at length arrived at definite knowledge concerning the process of crystallisation from the state of solution in water. For water is the ordinary solvent from which we obtain our crystals, that is, such as are prepared artificially in the laboratory. The laws which have been discovered to hold for aqueous solutions are, however, equally applicable to the cases where other solvents are used, such for instance as the usual organic solvents like alcohol, ether, chloroform, and benzene.

The conditions under which crystallisation occurs from the liquid state, or from solution of the substance in a solvent, have been accurately determined experimentally by H. A. Miers,[1] and they bear out in the main the predictions from theoretical considerations which were made by Ostwald.[2] Taking first the case of crystallisation from solution, there are two distinct curves representing the degree of solubility of the solid substance and of supersolubility. The well-known ordinary solubility curve is obtained by taking the temperature for abscissæ and concentration for ordinates, so that any point on the curve indicates the amount of the solid substance which the solvent can hold in solution at that particular temperature. Now the fact that supersaturation may occur has long been established, the phenomenon being of frequent occurrence; and it is common knowledge that a supersaturated solution may be preserved for a long time without crystals being deposited from it, provided the liquid be maintained quietly at rest. Obviously, therefore, this condition of supersaturation ought to be represented by a second curve a few degrees lower as regards temperature than the solubility curve, and its conditions were fairly fully predicted by Ostwald, after collecting together and analysing the results of the experiments of Gernez, Lecoq de Boisbaudran, J. M. Thomson, de Coppet, Lefebvre, and Roozeboom. It was reserved for Miers, however, to discover a means of experimentally tracing this curve, by observations of the refractive index of the solution. The point at which the deposition of crystals from

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[1] *Journ. Chem. Soc.*, 1906, **89**, 413; *Proc. Roy. Soc., A*, 1907, **79**, 322.

[2] "Lehrbuch der Allgemeinen Chemic," vol. 2, part 2, p. 780.

the supersaturated solution occurs is immediately indicated by a sudden change in the refraction of the liquid, the refractive index attaining its maximum value at the temperature of spontaneous crystallisation, and then dropping suddenly the moment the crystals begin to fall. Moreover, the solution at the same time records its own strength, for the refractive index varies directly as the amount of salt dissolved. The determination of the strength of the solution at the critical moment itself had previously proved an impossibility by ordinary methods.

Fig. 98 gives a general diagrammatic representation of Miers' results for a typical crystalline substance soluble in water. S is the ordinary solubility curve, which may also be termed the "curve of crystallisation by inoculation." For as soon as the solution reaches this condition of normal saturation it is liable to be caused to commence crystallising if a germ crystal, that is, a miniature crystallite floating in the air as dust, of the substance itself or of one isomorphous with it or capable of forming parallel growths with it, fall into the solution from the air. It has been a revelation to us that such minute crystallites of all common substances are scattered broadcast in our atmosphere, and that sooner or later one will introduce itself into any solution set to crystallise which is not sealed up or placed in a vessel with a filtering plug of cotton-wool in its neck or other aperture.

SS is the supersolubility curve, situated approximately 10° to the left of the solubility curve as regards temperature, but about as much above as regards concentration, so thàt the two curves usually run diagonally and more or less parallel to each other across the diagram. This supersolubility curve may be also called the "curve of spontaneous crystallisation," for it represents the conditions under which alone crystals may begin to form without the initiating impulse of inoculation by a germ-crystallite. On the suggestion of Ostwald it is also termed the "metastable limit," and the whole area between the solubility and supersolubility curves is named the area of metastability, that which represents the "metastable" condition of the solution. Within this area the conditions

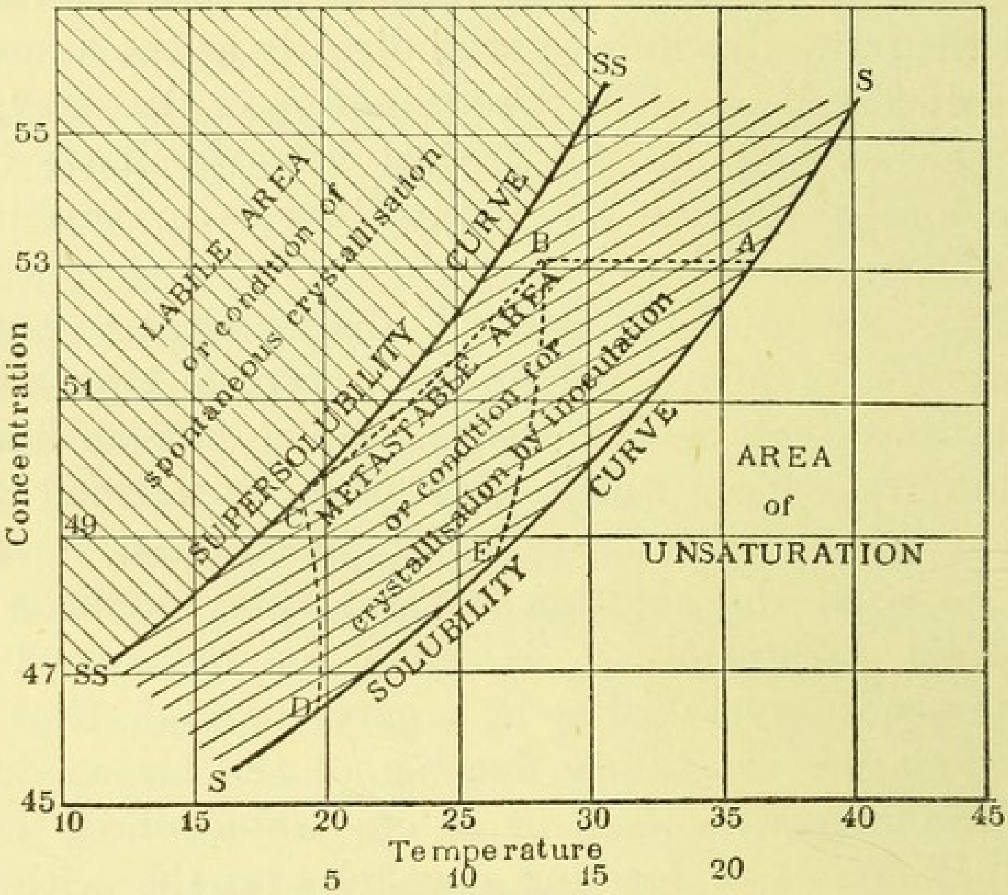

FIG. 98.—Diagram illustrating the Conditions for Crystallisation from Solution or the Liquid State.

are those for the start of crystallisation by inoculation. The area beyond the supersolubility curve represents the "labile" state, in which the conditions are those for spontaneous crystallisation, inoculation being no longer necessary. These precise results will, it is hoped, be quite clear with the aid of Fig. 98.

Hence, when a cooling solution not quite saturated at the higher starting temperature is stirred in an open vessel a slight shower of crystals, started by inoculation, appears when the saturation point is reached, which Miers calls a "metastable shower," corresponding to the ordinary solubility curve; the liquid then goes on cooling without depositing the main bulk of the excess which that curve indicates ought to be deposited, if it represent the whole truth. But when the temperature of the supersolubility curve about 10° lower is reached, a much more copious shower falls by spontaneous crystallisation, the "labile shower."

In a closed vessel, such for instance as a glass tube sealed with the aid of the blowpipe after the introduction of the solution, on cooling after heating to a temperature superior to that of saturation, the first shower never falls at all, no amount of shaking inducing the deposition of crystals at the ordinary saturation point, proving that the slight shower of the experiment in the open vessel is due to crystal-germs introduced from the atmosphere. The second shower of crystals falls at the lower temperature just as before, however, at the temperature of the supersolubility curve, indicating that this shower is due in both cases to spontaneous crystallisation. Solutions thus enclosed in sealed tubes, to which inoculating dust crystals cannot have access, can never be made to crystallise at any temperature higher than that given by the supersolubility curve, however agitated, although they immediately do crystallise, if shaken, as soon as that temperature is reached during the cooling. If allowed to remain absolutely quiet, however, the temperature may fall considerably lower before any crystallisation occurs, the labile region being frequently well penetrated before this happens. When crystallisation does supervene, the temperature usually rises somewhat. After the labile shower has been deposited, the crystals continue to grow steadily further, until the metastable region has been traversed, and the saturation state is eventually reached, when final equilibrium is produced.

The proof that the crystals deposited in the metastable condition were started by the advent of atmospheric germ-crystals—that is, by infinitesimal but perfectly structurally developed crystals, carried by their very lightness like the particles of dust which are only revealed in the path of a sunbeam as seen against a dark background—was afforded by a series of experiments with a mixture of two rare organic chemical preparations, salol (phenyl salicylate) a substance melting at 42°.5, and betol (β-naphthol salicylate) another melting at 92°, which Miers assumed were not likely to be present in ordinary air. The assumption proved well grounded, and the first shower never fell at all in the earlier experiments in which mixtures of these two substances were allowed to cool in open vessels, from the state of fusion. But very soon the air of the laboratory became impregnated with crystallites of both substances, due to the very operations themselves being carried on in contact with the air, and in the later experiments the first shower of crystals did fall. The experiments were really designed to effect the determination of the solubility curve for salol and betol in each other, that is, the freezing-point curve of their mixtures, and the discovery of the so-called "eutectic" point at which a mixture of constant composition solidifies at a definite temperature. But incidentally the experiments also served to establish similar laws for the production of crystals from the liquefied state, by cooling below the melting point, to those applying to crystallisation from solution. In the case of the mixtures of the substances the one of lower melting point acted as a solvent for the one of higher melting point, just as water does for salt. Two curves corresponding to the ordinary freezing point and to the limit of superfusion were established, analogous to the solubility and supersolubility curves. Pure salol alone proved to crystallise spontaneously at 33°, $9\frac{1}{2}$° below its melting point, and the refractive index attained a maximum for this temperature. Betol spontaneously crystallised at 79°, 13° below its melting point.

Two general cases of crystallisation are shown by the dotted curves ABCD and ABE in Fig. 98. The first, represented by ABCD, is the case of a supersaturated solution, made by adding the salt to hot water, being allowed to cool slowly while stirred. The solution cools from A to B without anything visibly happening, no crystal-germ falling into the solution until B is reached, somewhere well within the metastable region. When the germ has fallen in, however, crystals begin to appear as a slight shower at B, and from B to C they continue to grow slowly. On reaching the labile condition at C a cloud of crystals, the heavy shower, is deposited, and the concentration falls rapidly to D on the solubility curve, generally with slight rise of temperature.

The second case is the important one employed by the author in the investigations which will be found described in his "Crystalline Structure and Chemical Constitution" (Macmillan & Co., 1910), for the purpose of producing crystals of high perfection for goniometrical investigation. The method can be confidently recommended as the one best adapted to afford good measurable crystals, and is of quite general application. The solution is made up so as to be in the metastable condition, that is, only slightly supersaturated for the ordinary temperatures. Eventually, while the solution is at rest in a protected place, free from draughts or vibration, and after it has cooled to the temperature of the air, a crystal-germ enters, followed probably by others; each forms a centre of crystal growth, which proceeds very slowly and deliberately, keeping pace with the evaporation in such a manner that the labile condition is never reached. The natural result is the production of very well-formed crystals bounded by excellent faces, truly plane and free from striation or distortion.

When the operation is arranged to occur during the night, as will usually be the case, the solution being set out to crystallise in a quiet and protected place on the previous afternoon or evening, the slight fall of temperature during the night gently assists the process and almost ensures a good crop of a few well-formed crystals large enough for goniometrical purposes next morning. They should be removed before the temperature begins to rise again with the advent of the sun, dried with blotting paper and by air exposure for a short time, and stored in a miniature bottle labelled with the name or formula of the substance and the date of collection of the crop. In such cases the labile state is never reached, and the course of the crystallisation is represented by the curve BE. The whole conditions for the curve ABE, however, would correspond to much lower temperatures, such as those given at the foot of the diagram below the word "temperature," rather than to the upper row of temperature abscissæ suitable for the other purposes of the diagram already referred to. Crystallisation might well begin about 13° or 14°, as shown at B, and the liquid would cool a couple of degrees or more during the night while crystallisation was steadily proceeding, until equilibrium was reached at E on the solubility curve.

The diagram does not represent any substance in particular, but is a perfectly general one, corresponding to the facts observed with most of the very varied salts worked with by Miers and those of which the author has had experience. The exact temperatures and concentrations will, of course, differ for each substance.

A beautiful experimental demonstration of crystallisation from the metastable and labile conditions of solution respectively is afforded by potassium bichromate, $K_2Cr_2O_7$. When deposited slowly from a metastable solution under conditions of quietude, this salt is slowly deposited in bright orange coloured and excellently formed crystals, often of considerable size, belonging to the triclinic system of symmetry; they are bounded by good pinakoidal (pairs of parallel) faces intersecting in sharp edges. But when the crystallisation occurs from a labile solution, being much more rapid, it takes the form of feathery or arborescent branching skeletal growths, there being inadequate time for the formation of well-developed crystals.

Fig. 99, Plate XXI., is a photographic reproduction of well-formed crystals of potassium bichromate, grown from a solution in the metastable condition on a microscope slip, just as they are seen through the microscope in the slow act of formation, employing a $1\frac{1}{2}$ inch objective. The crystallisation had been started by germ crystals of the salt falling in from the air, after which the drop, placed within the ring of hardened gold size on the slide, had been covered with a cover-glass, under which the crystallisation had proceeded with sufficient slowness to enable a successful photograph to be taken, when the camera was subsequently attached above the vertically arranged microscope. An upright micrographic apparatus had been designed by the author specially for this photography of growing crystals, many of the results of which are reproduced in this book.

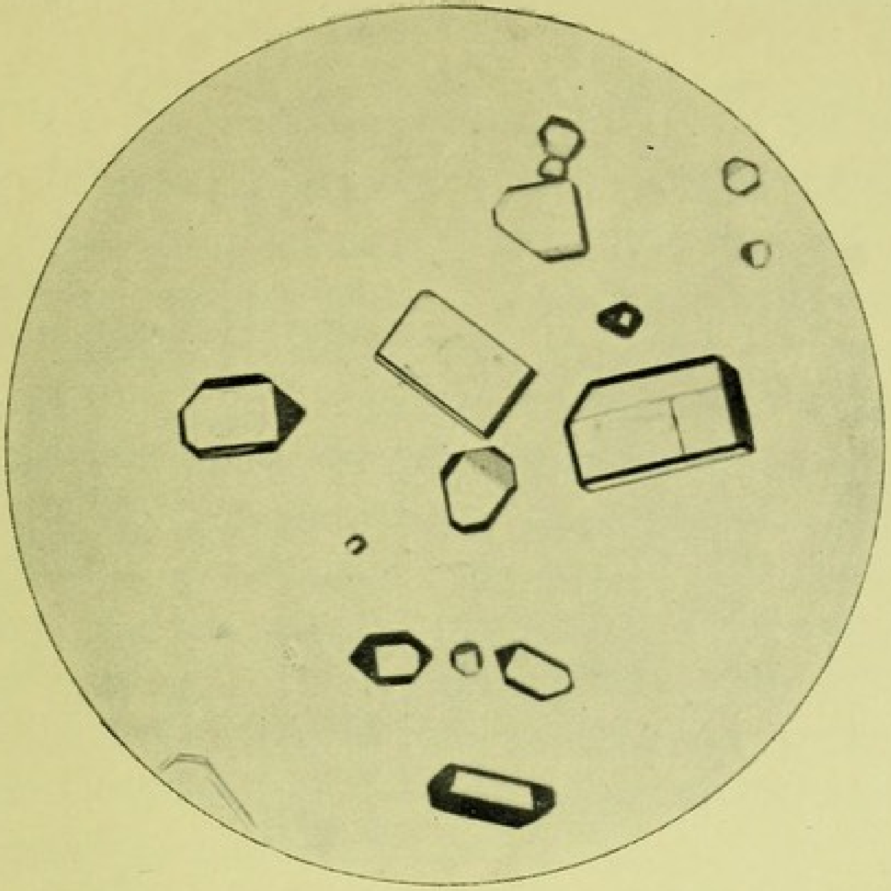

FIG. 99.—Potassium Bichromate slowly crystallising from a Metastable Solution.

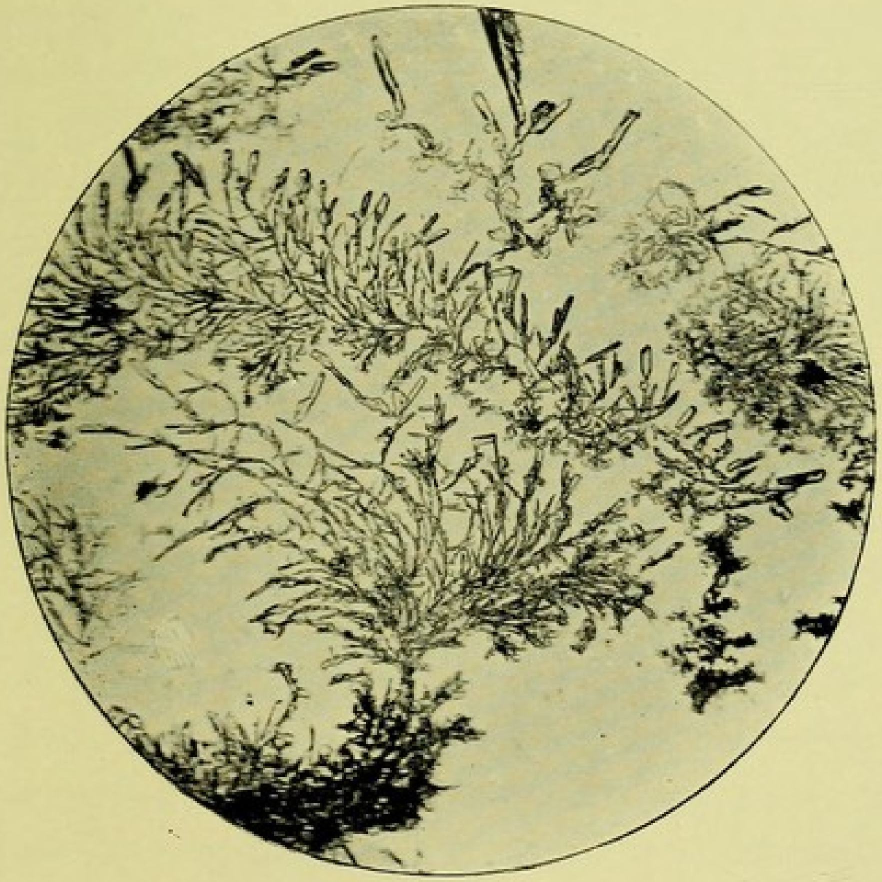

FIG. 100.—Potassium Bichromate rapidly crystallised from a Labile Solution.

CHARACTERISTIC DIFFERENCE IN THE CRYSTALS DEPOSITED FROM METASTABLE AND LABILE SOLUTIONS.

To face p. 246.

Fig. 100 is the reproduction of another photograph taken under similar conditions, but employing a hot and somewhat more concentrated solution of potassium bichromate, and making the exposure at the moment when, in the particular field chosen, a rapid labile crystallisation was just completing itself, the rapidity of growth of the feathery skeletal crystals having just become arrested. Indeed, the branches are frequently terminated by small well-formed crystals, the rapid growth having been succeeded by a final slow crystallisation where the solution had discharged its labile excess and attained once more the metastable condition.

This experiment with potassium bichromate lends itself admirably to lantern demonstration with the projection microscope. When the drop of hot concentrated solution is first placed on the warmed microscope slip, and the latter laid on the stage, nothing visible on the screen happens for a minute or two, the solution becoming, however, more or less rapidly cooled. But suddenly, the drop having cooled sufficiently to bring the solution to the labile condition of supersaturation corresponding to the conditions for spontaneous crystallisation indicated by the supersolubility curve, arborescent or feathery growths begin to shoot out from various points in the field, often near the margin, and traverse the screen so rapidly that in a moment or two it is filled with them. The crystallisation then slows down once more, the labile shower of excess having become exhausted, and the terminations of the branches and ramifications begin to develop into good little crystals, which thus hang like fruit on a tree. The experiment is rendered the more brilliant and beautiful by the bright orange colour of the crystals.

In Fig. 101, Plate XI., facing page 88, a reproduction of a photograph of a similar crystallisation from a labile solution of ammonium chloride is given. This salt is also particularly suitable for screen demonstrations. The beautiful skeletal ramifications follow the axial directions of the cubic axes, ammonium chloride crystallising in the pentagonal-icositetrahedral class of the cubic system. Good crystals may, however, be very slowly grown from metastable solutions, and they usually exhibit as the principal forms the icositetrahedron (predominating), cube, octahedron, rhombic dodecahedron, and the class-distinguishing pentagonal icositetrahedron. The rapid growths by spontaneous crystallisation of labile solutions, however, invariably take the form of the rectangularly branching feathery crystals shown in Fig. 101.

Further light has been thrown on the act of crystallisation by another most interesting research of Miers concerning "vicinal faces,"[1] such as the three very low pyramid faces (forming a very flat triakis octahedron) which often replace each octahedron face on a crystal of alum which has been grown somewhat rapidly. The author has frequently observed this phenomenon in the course of the numerous crystallisations required for the investigation of the sulphates and selenates. It may be described in general terms as the replacement of primary faces possessing the simplest rational indices by faces having such high indices that it is

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[1] *Phil. Trans.*, 1903, A, **202**, 459.

doubtful whether they ought really to be represented by indices at all. The number of such vicinal faces which replace the simple face depends on the symmetry of the crystal, to which, of course, they conform. Thus, while three such vicinal faces replace an octahedral face, and two replace the face of a tetragonal prism, the simple primary prism face of a rhombic or monoclinic crystal would only be replaced by one, which may have a deformation of as much as even 30′ from the correct position of the prism-face, and on either side of it. Indeed it is possible for a whole succession of such vicinal faces to be developed within the degree of arc which may in extreme cases separate the limiting values on each side of the prism face, and such are often seen and make up the well-known bundle of images afforded on the goniometer by a bad face, a face which would cause the author at once to reject the whole crystal for measurement purposes. One of the faces, even in cases such as alum or a tetragonal crystal, where three or two might have equal values as regards the symmetry, generally predominates, and affords a very much more brilliant image of the goniometer signal than the others in the bundle, so that an unwary observer might easily come to the conclusion that this was the really valid image corresponding to the octahedron face or to the simple primary prism face, or whatever particular face was expected in the neighbourhood indicated by the bundle of images. Obviously, however, it might only be one of three or two equally valid faces of a vicinal form, which had grown predominatingly during the last period of growth previous to removal from the mother liquor.

The explanation of this interesting phenomenon of the production of vicinal faces is one intimately connected with the structure of crystals, and it forms one of the strongest confirmations of the correctness of the theory of crystal structure the basis of which is the molecular space-lattice. Miers is in full agreement with the author in emphasising the importance of the space-lattice formed by the "points" representative of the molecules, and analogously chosen in the molecules. He says: "Whatever structures may be necessary to account for other features of crystals, there is little doubt that we are justified in regarding their faces as the planes of a space-lattice."[1] Now Wulff,[2] who has contributed very considerably to our knowledge of the nature of the act of crystallisation, has proved, from his own investigations and those of Weyberg, carried out at his suggestion in his laboratory at Warsaw,[3] that faces of greatest reticular density, that is, those along which the points of the space-lattice are most thickly strewn, are those which grow the most slowly, and therefore are the best developed. This latter will be obvious on a little consideration, for the faces of less reticular density which grow more, tend in doing so to extend the boundaries of the faces of greatest reticular density, and thus to enlarge those faces. Hence the usual planes on a crystal must be those of high reticular density; and these are such as are represented by

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[1] *Phil. Trans.*, 1903, A, **202**, 519.

[2] *Zeitschr. für Kryst.*, 1901, **34**, 449.

[3] *Loc. cit.*, p. 531.

the simplest indices, the faces most dense of all in points being the primary ones.

But it has been shown from the researches of Miers that vicinal faces are often produced in preference to these simple-index planes of high density, and such vicinal faces, although the nearest (in angular position) of all possible faces to those simple index planes, are themselves of excessively low reticular density, so much so that if represented by indices at all they can only be indicated by very high numbers, not such as we are accustomed to consider as in keeping with the simple spirit of the law of rational indices. Taking the example worked out most fully by Miers, the octahedral crystals of alum, it is a fact that the cubic faces of highest reticular density are those of the cube itself, then come in order those of the rhombic dodecahedron and those of the octahedron. Hence, the density of octahedral faces is very high. But those of the very low triakis octahedron, which Miers finds to replace the octahedron faces so frequently as vicinal faces, are of excessively low reticular density.

Miers explains the appearance of the latter instead of octahedral faces by assuming that the supersaturated liquid in contact with the growing crystal consists of the particles (molecules) of salt uniformly mingled with those of water, the solvent, and that the act of crystallisation consists of the escape of the water and solidification of the salt. Consequently, the salt particles just before crystallisation cannot be so dense as they are along primary planes of the crystal, as they are separated by the water particles, which are presumably much more numerous.

Hence it is that they are not deposited along the planes of high reticular density, but along vicinal planes of low density of points. For instance, he shows that the shower of salt particles upon a cube face would have to be so dense that there would be insufficient room for the water particles. The density in a cube face is 114 times as great as that in one of the vicinal planes observed. Now, 100 cubic centimetres of solid alum weigh 172 grammes, and 100 c.c. of the solution depositing crystals contain 9·74 grammes of alum. Thus the density of the growing crystal of alum is nearly 18 times that of the alum in the adjacent saturated solution.

Consequently the deposition of the salt particles, in a moderately quick crystallisation, when insufficient time is afforded for the deliberate escape of the water particles and for the orderly rearrangement of the salt particles, occurs along vicinal planes instead of along the primary planes. For it must not be forgotten that whenever it has the opportunity of coming into operation there is a directive molecular force of some kind, which controls the operation of crystallisation, and which undoubtedly attempts to cause, and given adequate time and scope succeeds in causing, the production of faces of high reticular density, the fundamentally important primary faces of lowest indices, and which are often those along which cleavage occurs. Wulff emphasises this in saying (*loc. cit.*, p. 461): "Bei der Krystallisation orientiren sich die Molekeln auf den Flächen des Krystalles ganz gleichförmig durch den Einfluss der Richtkraft der Krystallisation." The more rapidly the crystallisation occurs, however, the less chance is there for this force to attain its ultimate object. More will be said about this directive force in the next chapter, after we have studied the remarkable "liquid crystals" discovered by Lehmann.

This highly interesting explanation of Miers, supported as it is by the work of Wulff, and confirmed also in many respects by the observations of the author, whose great aim throughout his investigations has been to avoid the production of such vicinal faces, throws an important light on the nature of the act of crystallisation. It renders the reason clear why crystals which are very slowly grown from solutions only feebly supersaturated and under conditions of absolute rest, protected from either air currents or preventable earth tremors—conditions which the author has taken quite exceptional pains to procure for the preparation of the crystals used in the investigation of the sulphates and selenates of the rhombic simple salt series and monoclinic double salt series—are occasionally obtained quite free from any sign of such vicinal faces. They are small perfect individuals exhibiting primarily the faces of high reticular density, that is, the faces of the simple forms of low rational indices; and these faces are absolutely plane, affording one single brilliant image of the goniometer signal, which can be adjusted with great precision to the cross-wires of the telescope. For the slower the growth, the more time is afforded for the escape of the water molecules, and for the salt molecules to deposit themselves as directed by the molecular guiding force of crystallisation, along the planes of high reticular density. In many of his experiments Miers expressly stirred the solution, to prevent concentration currents, which had been considered by Wulff of importance in the process, from coming into play and causing unknown effects. Hence his experiments in which vicinal faces were produced are not comparable with the author's slow growths.

The work of Miers assists in the proof that the constancy of angle to within one or two minutes of arc is a real property of the crystals of a substance. For previously the frequent presence of vicinal faces rather than the simple forms of high reticular density, and which had been mistaken for the latter, had caused Pfaff in 1878[1] and others to conclude that variations from the true crystal angle amounting to as much as 30′ were of common occurrence as the result of strain during deposition.

Brauns[2] in 1887 made a careful series of measurements of very good octahedral crystals of lead nitrate, and found 13′ 20″ the largest deviation of a good image from the theoretical position. He imputed it to the action of gravity as a disturbing cause during deposition. The researches of Miers have cleared away all this misconception, in proving that the bright images referred to, taken for those of the simple primary form, are not such at all, but vicinal faces of very low reticular density.

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[1] *Sitzungsber. d. Physik. Med. Soc.*, Erlangen, 1878, **10**, 59.

[2] *Neues Jahrbuch*, 1887, 138.

CHAPTER XVI

LIQUID CRYSTALS.

We have seen in the foregoing pages that a crystal is usually a solid, highly organised in a homogeneous manner, and, unless the symmetry be developed to its highest extent, the crystal then belonging to the cubic system, it is also in general anisotropic, that is, it exhibits double refraction. Section plates of it, more or less thin according to the strength of the double refraction, exhibit colours in parallel polarised light, and show the phenomenon of a single optic axis, or of two optic axes, in convergent polarised light. Every variety of hardness, however, is displayed, from that of the diamond down to that of a crystal as soft as gypsum, and even softer. Moreover, many of the softer crystallised substances develop the property of permitting one layer to glide over another by gentle side pressure with a knife blade, when inserted in an edge or face in an attempt to cut the crystal. Calcite and ice, for instance, both possess such planes of gliding of the structural units over one another in layers. There are also the border line cases of crystals so soft as to be readily bent, and many well known viscous substances crystallisable only with great difficulty, some of which form pliable crystals.

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But in the year 1876 Lehmann discovered a new property in an already remarkable substance, iodide of silver, AgI, namely, that at temperatures superior to 146° C. it can flow like a viscous liquid, while exhibiting several of the properties which are characteristic of crystals. Silver iodide is dimorphous, exhibiting a hexagonal form at the ordinary temperature, which persists up to 146°. But during the heating to the latter temperature a regularly accelerating diminution of volume occurs, the feeble expansion in directions perpendicular to the axis being overbalanced by a considerable contraction along the axis, both quantities having been accurately measured so long ago as the year 1867 by Fizeau, by means of his delicate interference dilatometer. This contraction, so unusual an occurrence with increase of temperature, culminates at 146°, according to Mallard and Le Chatelier, in a sudden change of condition into a cubic modification, accompanied by absorption of heat. Now Lehmann, studying this cubic modification of silver iodide under a microscope which he had devised—specially adapted for observations at temperatures higher than the ordinary, by being supplied with the means of heating the object under observation—found that it was not only plastic, but actually a liquid.

The form of Lehmann's "Crystallisation Microscope," as now constructed by Zeiss, is shown in Fig. 102. Its essential features are that the glass object-plate, which is somewhat wider than the usual microscope 3 by 1 inches slip, is supported by little metallic columns at a height an inch or more above the ordinary stage, and may be heated from below by a miniature Bunsen burner, which is provided with a delicate graduated gas-tap and is adjustable for its position, swinging in or out as desired. The small Bunsen flame may be converted into a blowpipe flame if necessary, an air blast attachment to a mixing reservoir being provided, to which the arm of the burner is hinged. Two cooling blasts, con-

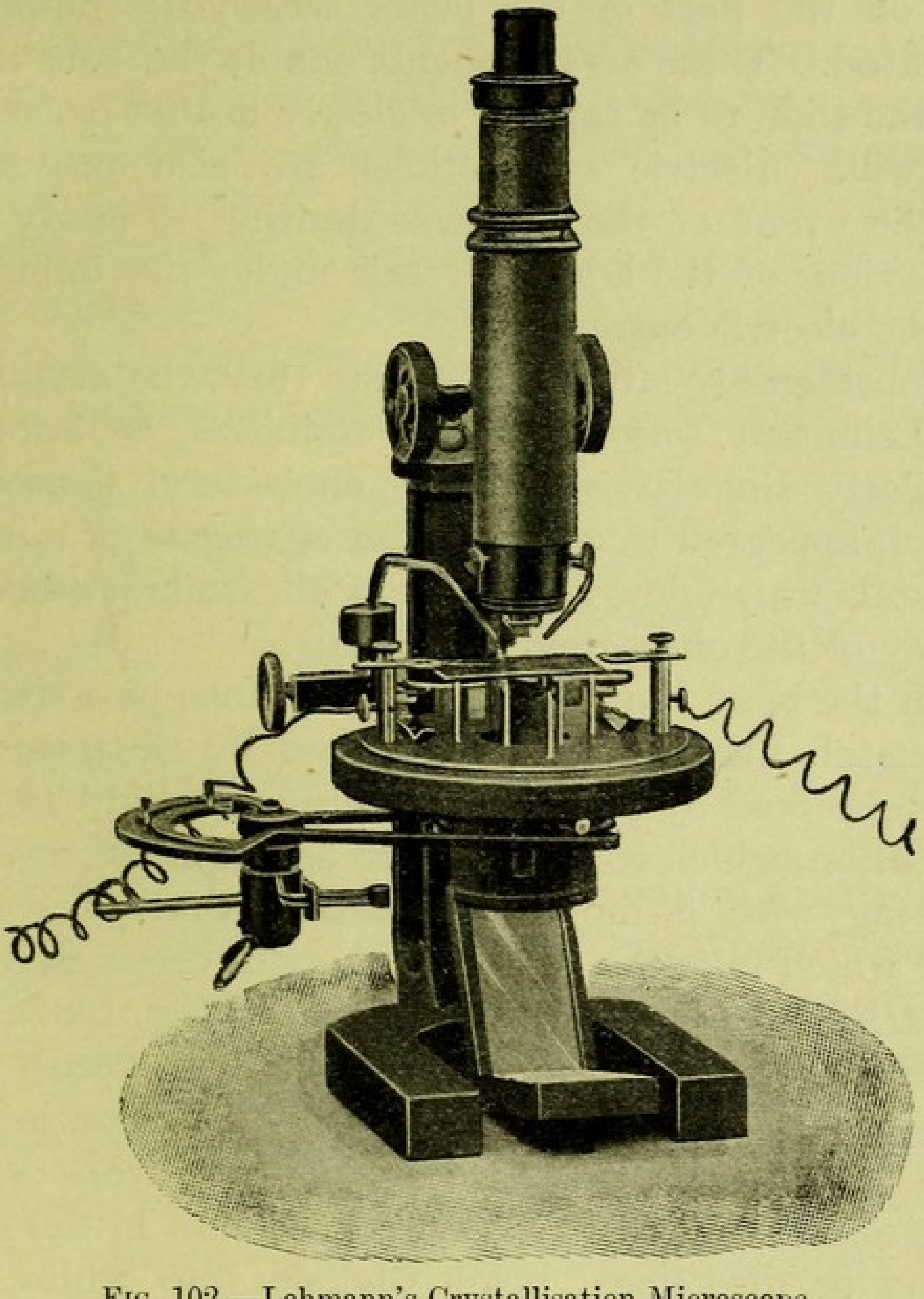


FIG. 102.—Lehmann's Crystallisation Microscope.

nected with a gas-holder of air, are also provided, and are adjustable to the most suitable symmetrical positions above the slide for directing the cooling air on the part of the latter where the liquid is situated. These arrangements enable the substance on the slide to be rapidly or slowly heated or cooled at will. Electric connections are also provided, in the event of the observer desiring to study the behaviour of the liquid crystals under the influence of the electric current.

Considerably later, in the year 1889, the attention of Lehmann was called by Reinitzer to another similarly singular substance, cholesteryl benzoate, which appeared to consist of an aggregate of minute crystals which flow as readily as oil, while preserving many of the characters of crystals.

In the next year, 1890, the substance para-azoxyphenetol, then recently discovered by Gattermann, was observed by Lehmann to form a turbid " melt " on fusion, which consisted of an aggregate of crystals flowing with a mobility equal to that of water, and which take the form of spherical drops showing a dark kernel inside, as shown at *a* in Fig. 103, quite unlike a drop of ordinary liquid. The kernel disappears on shaking, but reappears on coming to rest again. In polarised light the drops show dichroism, that is two different colours in different parts or directions, being divided into white and yellow parts, the yellow as a pair of opposite approximately 60°-sectors, as indicated at *c* in Fig. 103. Under crossed Nicols they show a black cross, as represented at *d* in Fig. 103.

Now obviously these drops are doubly refractive, and their whole optical behaviour corresponds to the arrangement of the molecules in concentric circles, such as that suggested at *b* in Fig. 103.

Another substance of like character, para-azoxy-anisol, was subsequently found to behave similarly, and forms an excellent substance to use for demonstration purposes. A reproduction of a photograph, kindly sent to the author by Prof. Lehmann, of a slide of this substance is given in Fig. 104, Plate XXII. It shows a characteristic field of such drops, exhibiting white parts and yellow sectorial parts which photograph dark, of para-azoxy-anisol mixed with a little para-azoxy-phenetol, oil and resin (colophony), as seen under the polarising microscope with crossed Nicols.

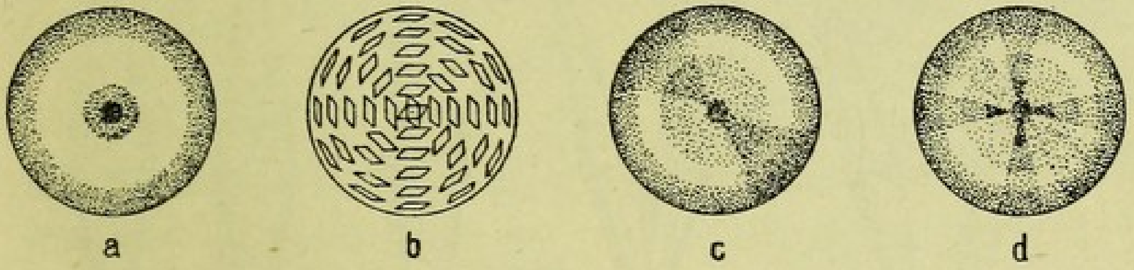


FIG. 103.—Liquid Crystals of Para-azoxy-phenetol arranged in Spherical Drops.

The next and possibly most interesting step in this remarkable series of discoveries was made by Lehmann himself in the year 1894. He alighted on the fact that ammonium oleate, crystallised from solution in alcohol, affords a splendid example of flowing crystals, which are sufficiently large to enable their habits to be studied in detail. The individuals are almost invisible in ordinary light, owing to the refractive index of the crystals and of the mother liquor being approximately the same. But in polarised light, using crossed Nicols, they are clearly revealed as steep double pyramids with more or less rounded edges. Their section is nearly circular in consequence, and they exhibit optical properties of a uniaxial character, the optic axis being that of the double cone or bipyramid. A characteristic individual is shown at *e* in Fig. 105. When two of these flowing crystals approach each other, as at *a* in Fig. 105, they coalesce to form a larger single individual, as is indicated in stages at *b*, *c*, and *d* in the illustration.

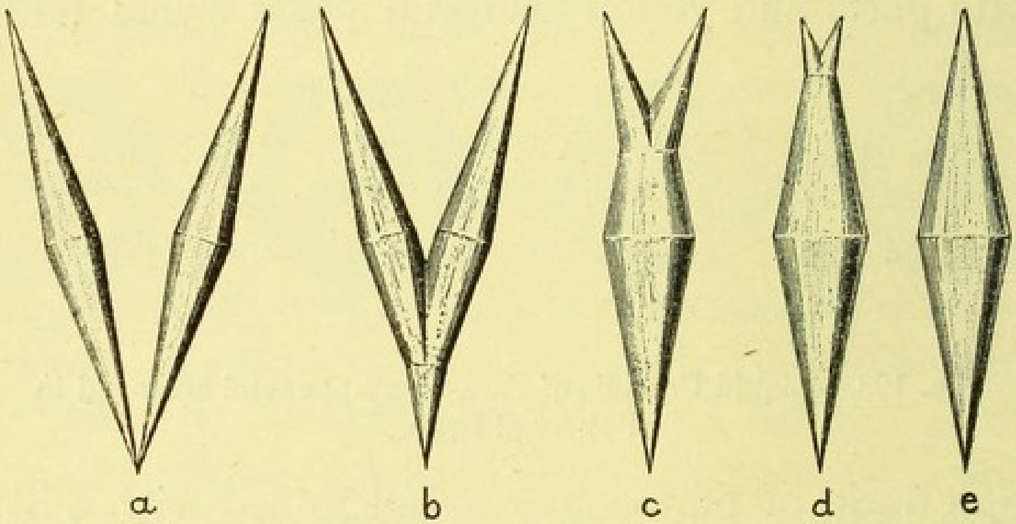


Fig. 105.—Liquid Crystals of Ammonium Oleate.

When the cover glass, under which they are growing on a microscope 3 by 1 inch slip, is moved to and fro so as to distort these remarkable bodies, which we may well hesitate to call crystals, the singular effect is produced of causing them all to become similarly orientated, for the extinction directions follow the direction of the pressure. They at once seek to regain their original form, however, on cessation of the disturbance. A slide of the bipyramids under pressure is shown in Fig. 106. In the black extinguished portions of the field the flowing crystals are flattened, according to Lehmann, and arranged so that the optic axis is in all cases perpendicular to the tabular crystals and the glass plates and parallel to the axis of the microscope. The black parts are separated by oily strips, as shown in another slide under considerable pressure, represented in Fig. 107, which are composed of the tabular crystals standing on end, with their optic axes parallel to the plates. These strips polarise the more brightly the more truly the crystals stand perpendicularly to the plates. The two conditions are shown diagrammatically at *a* and *b* in Fig. 108.

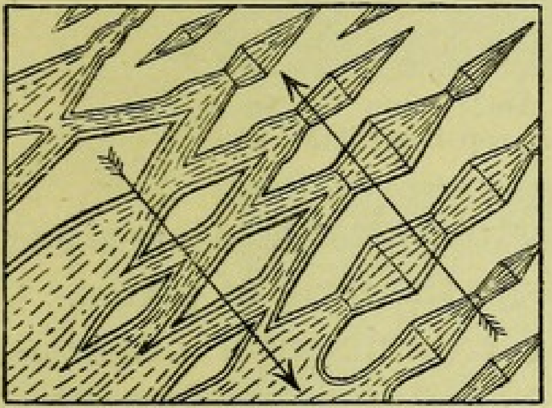


Fig. 106.—Liquid Crystals of Ammonium Oleate under slight pressure.

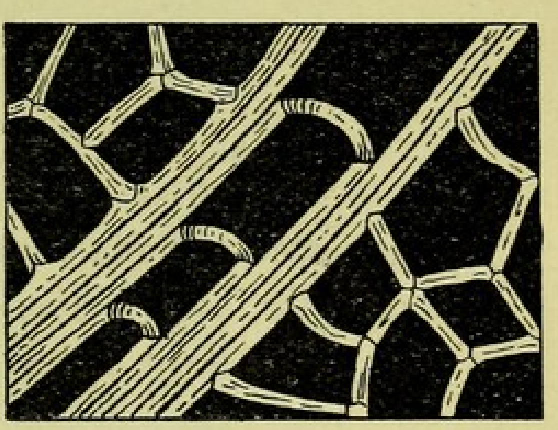


Fig. 107.—Ammonium Oleate under considerable pressure.

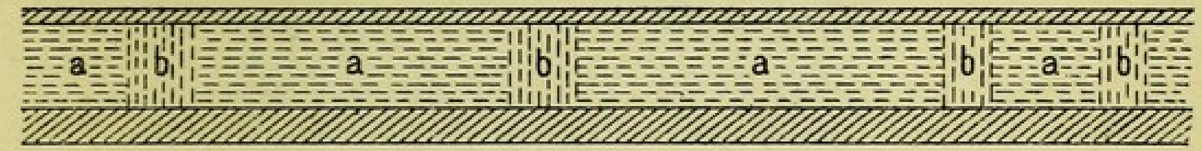


Fig. 108.—Diagrammatic Representation of Arrangement of Molecules.

Lehmann believes the explanation of these singular phenomena to be that the "liquid crystals" of ammonium oleate are composed of piles or layers of thin plates perpendicular to the optic axis. Disturbance detaches the plates from their piled positions over one another, and sets them parallel to the glass plate, except in places, the oily strips, where the plates stand upright, perpendicularly to the microslip and cover glass. Lehmann, indeed, goes further, and asserts that the molecules themselves are anisotropic, and probably take the form of plates.

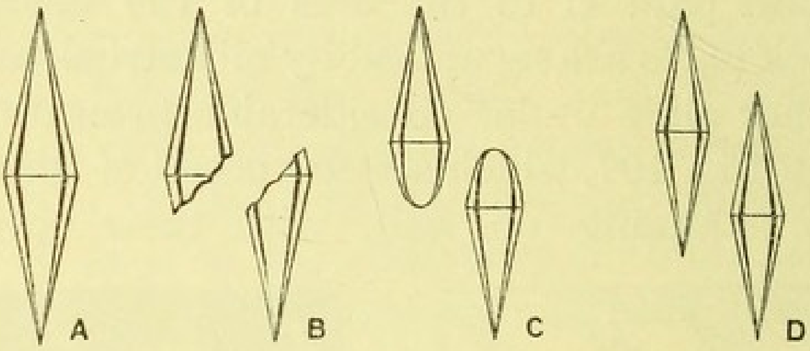


Fig. 109.—A Crystal of Ammonium Oleate A, broken at B, each part repairing itself at C, perfect again at D.

An extremely interesting experimental observation of Lehmann's with the bipyramids of ammonium oleate is, that if one of them, for instance A in Fig. 109, be broken into two parts, as at B, each part grows again and completely repairs itself, becoming once more a perfect double pyramid, as indicated in stages at C and D in the figure.

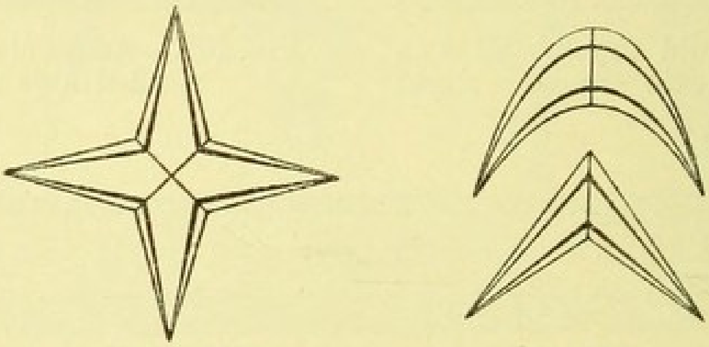
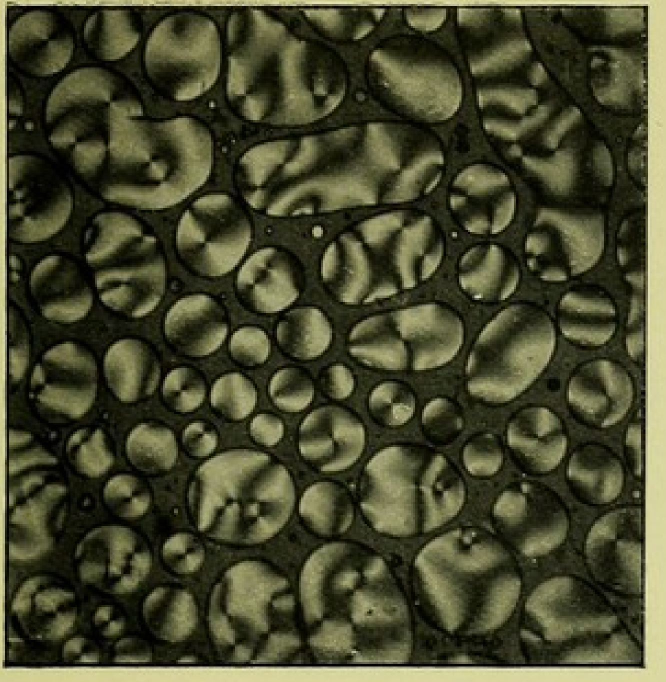


Fig. 110. Fig. 111.
Cruciform, Boomerang, and Arrow-head Twins of Ammonium Oleate.

Twins of ammonium oleate are also shown in Figs. 110 and 111, the former figure representing a twin of cruciform character, and the latter exhibiting

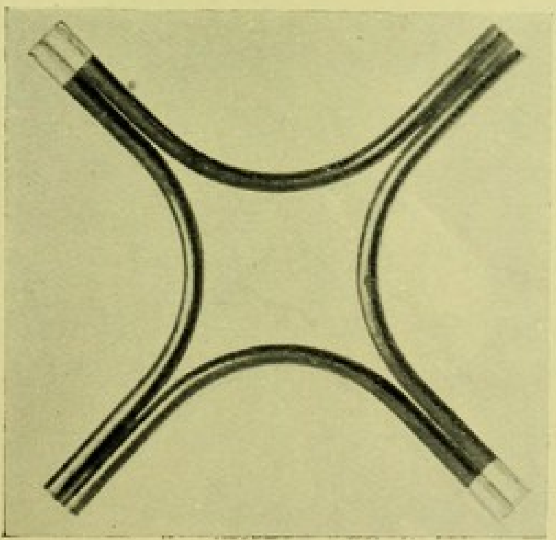
Fig. 104.



Dichroic Crystal Drops of Para-azoxy-anisol.

Fig. 112.

Rectilinear Liquid Prisms of Para-azoxy - benzoic Acid.



ig. 115.—Tetragonal Astatic Magnet-system.

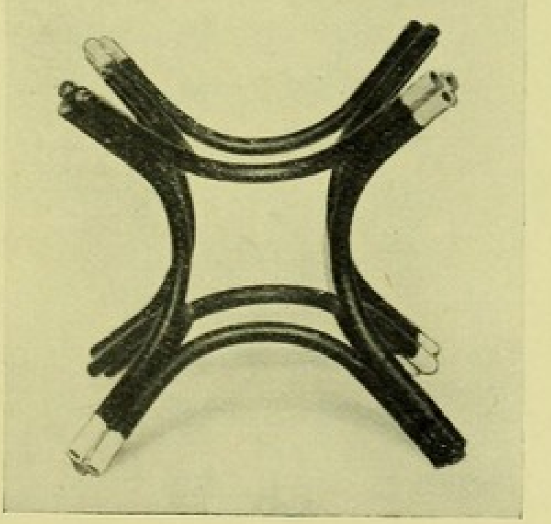


Fig. 116.—Cubic Astatic Magnet-system.

To face p. 262.

twins resembling a boomerang and an arrow-head respectively.

This substance, ammonium oleate, thus appears to be one of the most remarkable and interesting of all the bodies yet observed to afford liquid crystals. Many other oleates produce liquid crystals also, but the ammonium salt is by far the most striking, and very convincing as to the reality of Lehmann's discovery.

Another substance of a different nature was discovered by Vorländer in the year 1904, namely, the ethyl ester of para-azoxy-benzoic acid. A characteristic microscope slide of it in ordinary light is shown in Fig. 112, Plate XXII., which is a reproduction of an actual photograph most generously sent to the author by Prof. Lehmann.

The individuals are described by Lehmann, who further studied the nature of the substance, as almost perfectly rectilinear prisms with nearly sharply defined basal-plane end faces. A singular fact about this substance is, that when two individuals approach each other they arrange themselves parallel with a jerk, and then flow into each other, producing a single larger liquid crystal, and often with such rapidity that the eye can scarcely follow the movements. These coalescences appear to be occurring all over the field at once, with the production of larger and larger crystals. Indeed, Lehmann likens it to a struggle between the innumerable individuals, in which the smaller ones are being continually eaten up by the larger.

Vorländer also prepared the ethyl ester of para-azoxy-cinnamic acid, and Lehmann found it to be similarly interesting. The substance separates from a solution in monobromonaphthalene in uniaxial prisms or hemimorphic pyramids, the edges and solid angles of which are more or less rounded, and which appear colourless in the direction of the axis and yellow in all other directions. When pressed between the cover-glass and the micro-slip on which the crystallisation is proceeding, extinction of the light occurs throughout the whole mass when polarised light is being employed and the Nicols are crossed. For throughout the entire substance the particles—whether they are the molecules themselves as Lehmann asserts or aggregations of them in the form of ultramicroscopic crystals—arrange themselves with their optic axes (the crystals being uniaxial) perpendicular to the cover-glass and micro-slip, as in the case of ammonium oleate. Lehmann's theory is that the molecules themselves are tabular perpendicular to the axis, as in the case just referred to, and that they are thus readily coerced by the pressure of the flat cover-glass to take up positions parallel to it.

Two further reproductions of photographs, taken in polarised light, of a somewhat remarkable character, which have been placed at the author's disposal by the courtesy of Prof. Lehmann, are given in Figs. 113 and 114, Plate XXIII. Fig. 113 represents numerous doubly refractive and dichroic strips marking the boundaries of elongated individual crystals of the substance dibenzal benzidine, and affords a graphic idea of the real character of the double refraction displayed by liquid crystals.

Fig. 114 represents the effect of compression on

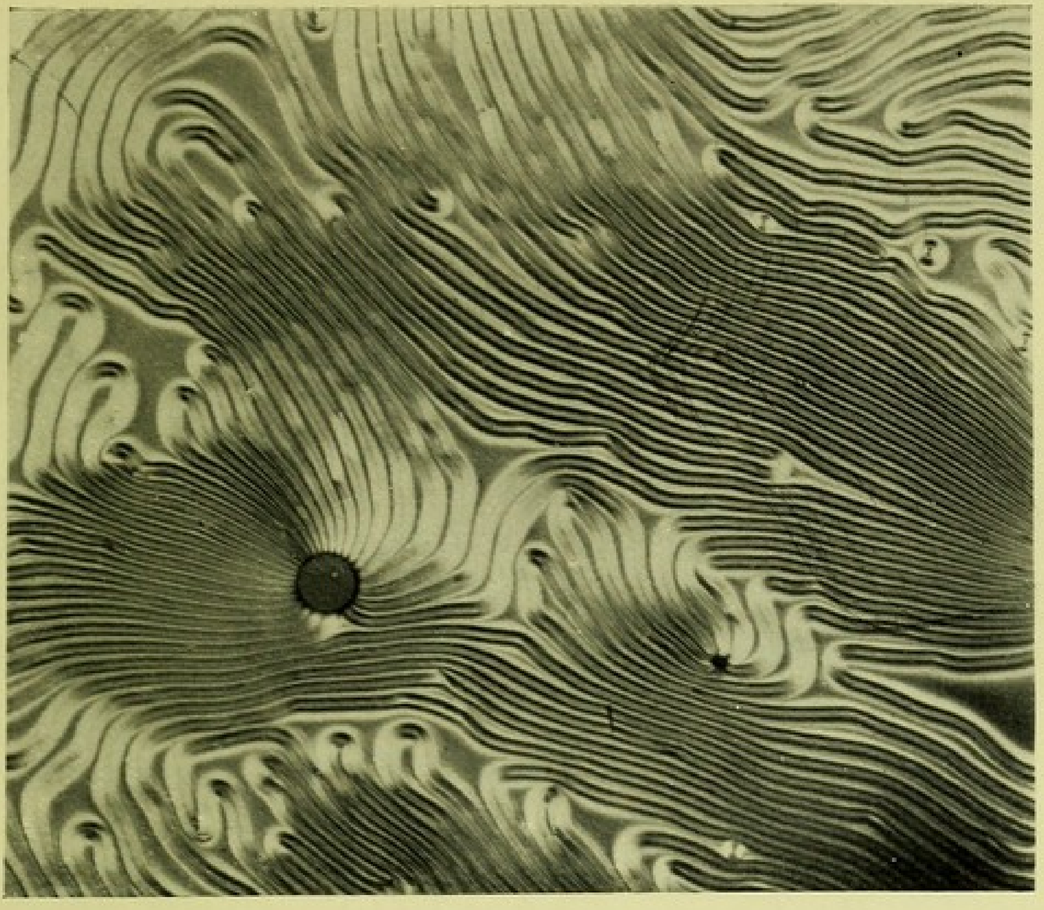


FIG. 113.—Elongated Liquid Crystals of Dibenzal Benzidine, showing Double Refraction and Dichroism.

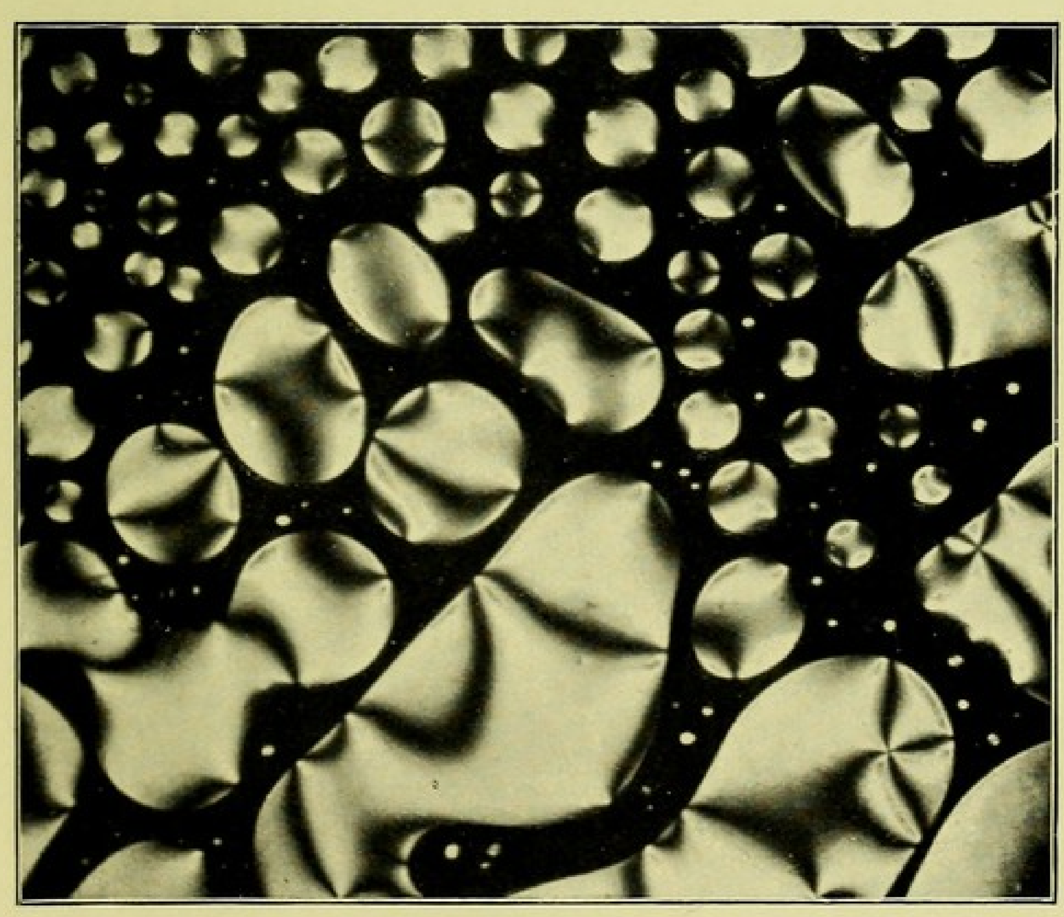


FIG. 114.—Spherical Liquid Crystals of Para-azoxy-anisol, showing Interference Colours under Crossed Nicols as the Effect of Compression.

To face p. 264.

para-azoxy-anisol, and demonstrates very clearly the distribution of the interference colours due to double refraction.

We are thus face to face in these remarkable experiments with some new facts concerning the nature of crystals. For we pass here into the borderland between ordinary liquids—singly refractive and structureless, in which the molecules are rolling over each other with every possible orientation—and solid true crystals possessing homogeneous structure, and the basis of which is a space-lattice arrangement of the chemical molecules, determinative of the system of symmetry displayed. In this wonderful borderland we certainly have had revealed to us, by the genius and persistency of Lehmann, liquids which possess many of the attributes of crystals, such as definite orientation of the ultimate particles, double refraction, and optic axes. These are undoubtedly solid facts which require to be faced.

Whether Lehmann's theory is to be accepted in full can only be decided after much more investigation by several independent investigators. We are now becoming familiar with the phenomena, as they have naturally excited immense interest in all scientific circles, and demonstrations of many of the experiments of Lehmann have been given in this country by Dr. Miers, Prof. Pope, and others, and particularly by Messrs Zeiss, with their new high temperature microscope, a description of the use of which for the projection of liquid crystals on the screen will presently be given. Prof. Lehmann himself has described the phenomena so clearly and fully that it is quite easy for others to repeat his experiments, and doubtless time would often be much better spent in doing so than in criticising points of theory without observing the phenomena at first hand. It frequently happens, in the inevitable march of scientific progress, that striking new facts, such for instance as the discovery of the composite nature of the chemical atom, are apt to cause either alarm, even panic, as to cherished theories, or else unreasoning scepticism. The happy mean between these two modes of receiving such facts, the open philosophic mind, ever ready to widen the scope of the horizon when a novel supposition is indubitably proved to be a real fact, and to assimilate that truth into the theory, widening correspondingly the scope of the latter if needful, is obviously the ideal thing to cultivate, and one which eventually finds itself in harmony with the authenticated final results of the new discoveries. It usually happens that too sweeping conclusions are at first drawn from such new facts, but time, with its further wealth of experience, especially the accumulation of experimental *data* which it brings in its train, soon levels these down and relegates the facts to their proper positions in the great scheme of natural knowledge.

Lehmann's view is that the ordinary effect of surface tension to cause truly liquid particles to assume the spherical " drop " form is resisted by a special force, which he terms " Gestaltungskraft," and which we may perhaps translate " Configuration-determining force." This force he considers is not identical with that of elasticity, but is that force by virtue of which a " flowing crystal " continually seeks, while freely swimming in the mother liquor or fused liquid, to take up its normal configuration. Even if a spherical drop could be cut out of it, the sphere would at once become a rod, prism, or pyramid or whatever the normal configuration of the flowing crystals of the substance in question might be.

The much debated term " liquid crystal " has been given by Lehmann to the normal configuration of each of the now considerable number of substances which have been discovered to exhibit the phenomena of flowing crystals. The latter appellation " flowing crystal," which Lehmann also uses, appears to the author to be in many ways more suitable, however, and would avoid much of the criticism which has been levelled at the term " liquid crystal."

As already indicated, Lehmann attributes the whole phenomena to a fundamental cause, namely, anisotropy (optical dissimilarity in different directions) of the molecules themselves, which he considers must cause self-restoration of the structure after disturbance, a process which he terms " spontaneous homœotropy." He considers that it is the molecular configuration-producing force, connected with the tabular form of, and directionally differentiated distribution of energy and force in, the single chemical molecules, which maintains the inner structure of the flowing crystal in position. The polyhedral outward form thus appears to be a necessary consequence of the inner structure, on this basis that it is a force resident in the molecules themselves which produces the structure.

Now the revelation of new facts, as startling as those which are now experimentally fully confirmed concerning flowing crystals, must inevitably cause searching reflection as to whether the magnificent geometrical work on the 230 homogeneous structures, and their development in actual fact in the 32 classes of crystals, is to stand or to be seriously affected. Again the author ventures to express the opinion, that just what happened in regard to the historic differences beween the schools of Haüy and Mitscherlich, will in all probability again occur, namely, both extreme views will be shown to depend more or less on real facts, and other connecting facts will eventually be revealed which will completely reconcile the two series with each other. In the author's opinion, the geometrical work will stand, as the grand generalisation it really is. But it will be interpreted in the future without the somewhat arbitrary assumptions which have more or less accompanied it. From these it will be freed, and then rise purified and elevated to its real dominating position in regard to crystal morphology.

Lehmann, with the natural enthusiasm of the discoverer of one of the most remarkable facts for which the last few decades have been famous, may have carried his theory too far, and particularly in that part of his work, to which the author has not hitherto referred, in which he describes certain phenomena of flowing crystals as akin to the movement of living organisms such as bacteria, and thus brought even some of the sound facts under the criticism of the sceptic more than might otherwise have been the case. He may also have made his theory far more revolutionary than is essential.

But the one incontrovertible thing stands out plainly, namely, that the "flowing crystals" with which he has made us acquainted are an indubitable experimental fact. Flowing crystals are produced, however, by a relatively few substances of very complex molecular constitution, involving a large number of atoms in the molecule; they are mostly compounds of carbon, and in number possibly not one per cent. of the innumerable substances known to produce ordinary solid crystals. That the theory of crystal structure can eventually be made to include these few remarkable substances is highly probable, when many more facts have been accumulated.

Lehmann would appear to have made one point very clear, which at once removes an objection long felt by the author to the theory of crystal structure as it stands at present, namely, that the chemical molecule is endowed with a directive orientative force, which is certainly concerned in crystallisation. To assume, as has been done, just because it is not necessary from the point of view of the geometrician in developing his possible homogeneous structures, that no directive force is operative in crystallisation, and that all is a mere question of the most convenient mechanical packing of the molecules, is, in the author's opinion, going beyond what the experimental facts justify. If Lehmann's discovery of flowing crystals does nothing more than return to the molecule the property always hitherto attributed to it, of possessing in itself some directive force by reason of which it arranges itself homogeneously by mutual accommodation with its similarly endowed fellow molecules, when its motion in the liquid state has been sufficiently arrested by its approach to its fellows within the range of molecular action (four or five molecular diameters), either by cooling or the falling out of previously separating solvent molecules, it will have achieved a notable thing.

What does occur at the moment of crystallisation is at the present time one of the most interesting unsolved questions in crystallography, and one calling most urgently for solution. Attention was directed to the problem in the last chapter, in connection with the suggestive work of Miers on vicinal faces. It was shown that it was only when the directive force had time to come properly into operation that the primary faces of fundamental importance were produced, and that when the crystallisation was rapid vicinal faces formed instead. Lehmann believes that a single kind of chemical molecule is only capable of producing a single specific space-lattice, and that polymorphism is due to alteration of the molecules themselves at the critical temperature of transformation. He showed so far back as 1872 that this limit could be actually observed under the microscope, as a definite line of demarcation between the two varieties as the temperature fell, one side of the field attaining the critical temperature slightly before the other, and the defining line between the two kinds thus travelling over the field. Internal friction did not appear to Lehmann to enter into the question at all, as he considered it would have done if a rearrangement of the molecules were the sole cause of the change. The molecules themselves, he states, must have been undergoing change, and such re-

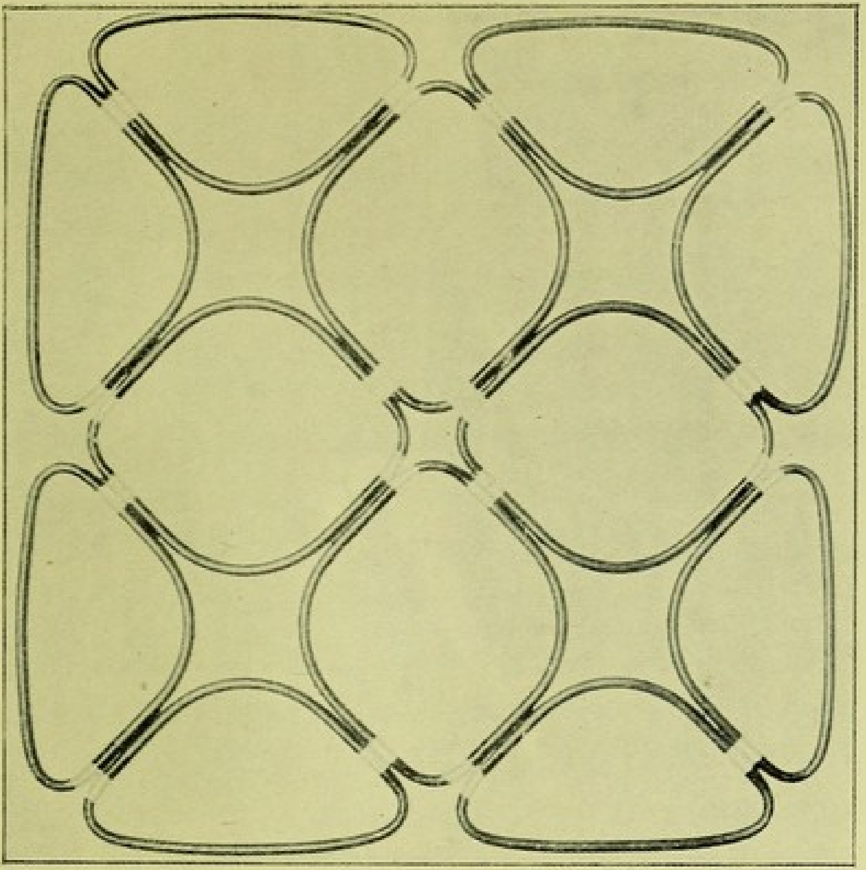


FIG. 117.—Arrangement of Astatic Magnet-systems in a Plane.

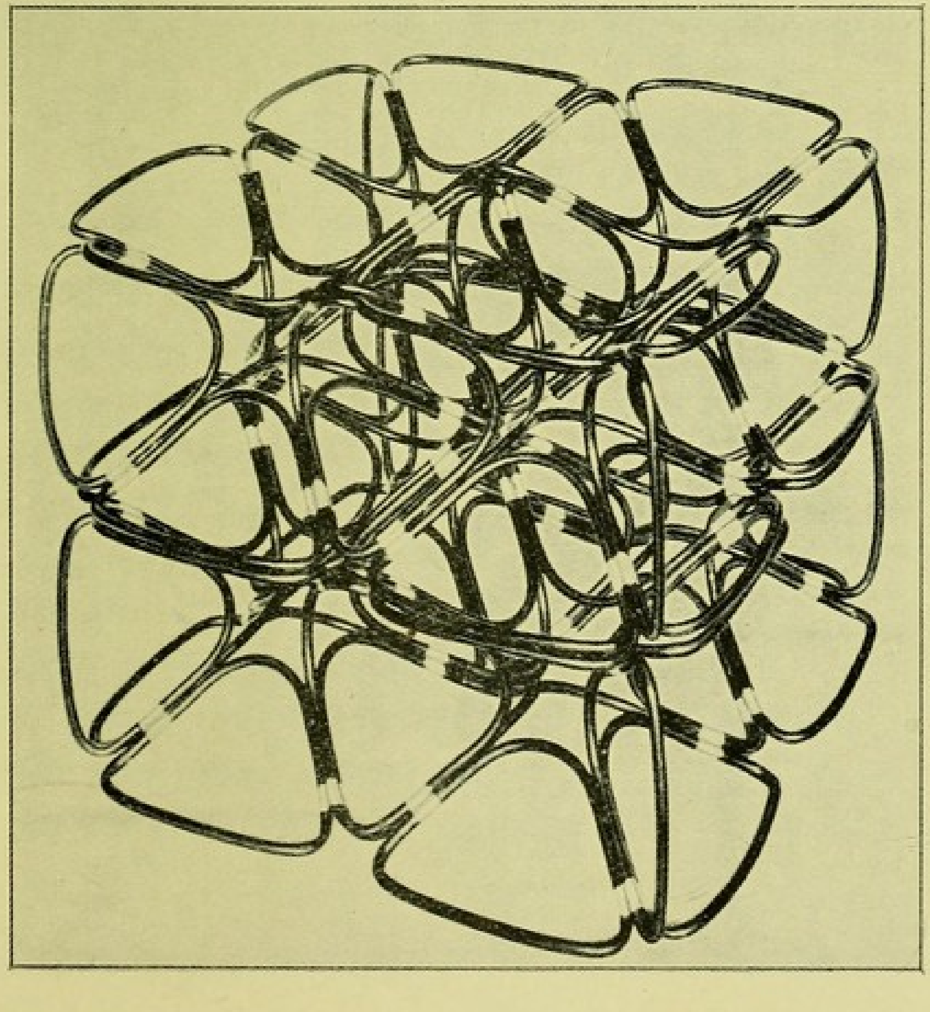


FIG. 118.—Arrangement of Astatic Magnet-systems in Space.

To face p. 270.

arrangement of them as occurred must have been due to that fact.

Lehmann suggests a very interesting explanation of the molecular orientative force of configuration, namely, that it is due to the action of the electronic corpuscles (forming the elementary atoms) rotating in the molecule. For the molecules of flowing crystals behave like freely suspended astatic systems of magnets, which are constantly setting themselves, even while moving about, in a crystalline space-lattice. He suggests that the molecules are really magnets the poles of which mutually attract and repel one another; that two equal magnetic molecules are arranged alongside with opposite poles against each other, thus mutually binding each other, or that four horse-shoe magnets may be arranged with opposite poles together, in a tetragonal astatic system, as shown in Fig. 115, Plate XXII. The latter may be grouped in space in a cubic astatic system, as represented in Fig. 116 on the same Plate; while Figs. 117 and 118, Plate XXIV., are further suggestive of how a homogeneous structure of such astatically distributed molecules can be built up, Fig. 117 representing a single plane of them, and Fig. 118 the complete arrangement in space.

An astatic system of molecules of this nature would have lost all power of attraction by a magnet, and the fact would thus be accounted for that no striking crystallographic results have ever attended experiments on crystallisation in a magnetic field. Astatic systems, however, such as that shown in Fig. 115, would certainly arrange themselves in space-lattices. For such parallel arrangements would, in general, involve differences in different directions, with regard both to internal friction and to the power of thermal expansion and of such regular dilatational or other deformational changes as we know are provoked by different physical conditions of environment. These differences would naturally, in turn, give rise to external polyhedral form.

Lehmann then goes on to point out that either electric currents or mechanically moved quantities of electricity, such as moving negative electronic corpuscles, can give rise to just such magnetic effects, and he suggests that these corpuscles are the true cause. He supposes that the directive forces result in astatic combinations which find their equilibrium when the latter have taken up their positions at the eight corners of a cube or other elementary parallelepipedon of one of the fourteen possible space-lattices, the positive atoms being encircled spiral-wise by the negative electronic corpuscles in alternately opposite directions. Such parallelepipeda would seek homogeneous repetition by virtue of the fact of the corners exhibiting alternating polarity.

These theoretical ideas of Lehmann have naturally called forth much discussion, criticism, and scepticism. But, so far, his experimental facts have been fully substantiated by further investigation. Much more practical work is urgently required, however, before the subject can be considered as laid on a secure foundation. So much may be said, however, that it is clear that we must concede the existence of a directive force of crystallisation, and not be led by the pure geometry of the subject of crystal structure to ignore facts of such interest and undoubted importance as have been brought into prominence by the remarkable work of Lehmann.

A further interesting contribution has recently been made by Vorländer[1] to the facts regarding the relationship between chemical constitution and the formation of liquid crystals. It must have already struck the reader that most of the substances which exhibit liquid crystals are composed of a large number of chemical atoms, being either long-chain compounds of the fatty acids or complex derivatives of the hydrocarbon benzene, C_6H_6 ; also that many of the latter are " para " compounds, that is, derivatives in which the substitution groups are inserted in the benzene ring of six carbon atoms in the " para " position, which is that at the opposite corner of the hexagon to the carbon atom to which a substitution group has already been attached. This renders the para compounds the most extended in a straight line of all the benzene derivatives. Now Vorländer finds that a particularly favourable condition for the production of liquid crystals is a linear structure of the molecule. As the para substitution products of benzene derivatives possess this elongated structure, many of them exhibit the development of liquid crystals. The more linearly extended the structure becomes, that is, the longer the straight chain of atoms is, the more favourable become the conditions. The advent of a third substitution group, however, which would have the effect of producing a kink in the chain, or of bending it, appears to destroy the

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[1] *Ber der deutsch. Chem. Ges.*, 1907, **40**, 1970.

possibility of the production of liquid crystals. This interesting observation may afford the key to many of the extraordinary phenomena of liquid crystals which have been described, and is undoubtedly one of prime importance. Further favourable conditions for the formation of liquid crystals, according to Vorländer,[1] are the aromatic character, and the presence of the doubly-linked carbon and nitrogen groups C : C, C : N, and N : N, which are usually so rich in energy.

The idea of the formation of a specific crystalline homogeneous structure, merely because the mechanical fitting-in of the molecules occurs with the minimum of trouble or maximum of ease for this particular type of all the 230 possible types, is certainly not applicable to the case of Lehmann's liquid crystals. With this, moreover, is also connected the question of softness or hardness of crystals, which was referred to at the opening of this chapter. For the so-called liquid crystals are extreme cases of softness, and yet in these cases the molecules must still be arranged in accordance with the internal structure of a crystal, either parallel or enantiomorphously definitely orientated with respect to each other, for otherwise it is not possible to account for the optical properties resembling the orientated ones of a crystal. Yet the condition being that of a liquid, the molecules must be able readily to pass and roll over each other, and hence cannot be at the close quarters where mere "fitting-in" comes into play.

Again, as has been pointed out earlier, many soft

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[1] *Zeitschr. f. Phys. Chemie.*, 1907, 57, 357.

crystals, even such as calcite, which are only relatively soft, attaining the position of as much as four in the scale of hardness, readily exhibit the property of being deformable upon glide-planes. The molecules in these cases have been shown to undergo a movement which has two components, a transference and a rotation, a fact which has been thoroughly substantiated by optical investigations of the parts of the crystal concerned before and after gliding. There cannot, therefore, have been merely "fitting-in" of the molecules, but their orientated positions must have been determined and maintained by the organising force, which is probably purely physical and not chemical, but is nevertheless the cause of crystallisation; it draws the molecules within a certain range of each other, corresponding to and dependent upon the temperature, causes or enables them to arrange themselves in the marshalled order of the particular type among the 230 possible arrangements, and keeps them at the same time from approaching nearer to each other than within these prescribed limits corresponding to the temperature. It is doubtless within these limits that gliding can occur parallel to such planes as leave the molecules most room for the purpose, and which are directions of least resistance.

Connected with this important question is the principle enunciated by Bravais, as a result of his discovery of the space-lattice, that cleavage occurs most readily parallel to those net-planes of the space-lattice which are most densely strewn with points. The force just referred to, whether we term it cohesion or otherwise, is obviously at a maximum within such a plane, and at a minimum in the perpendicular direction where the points are further off from each other. Moreover, it has been fairly well proved also, from the experiments

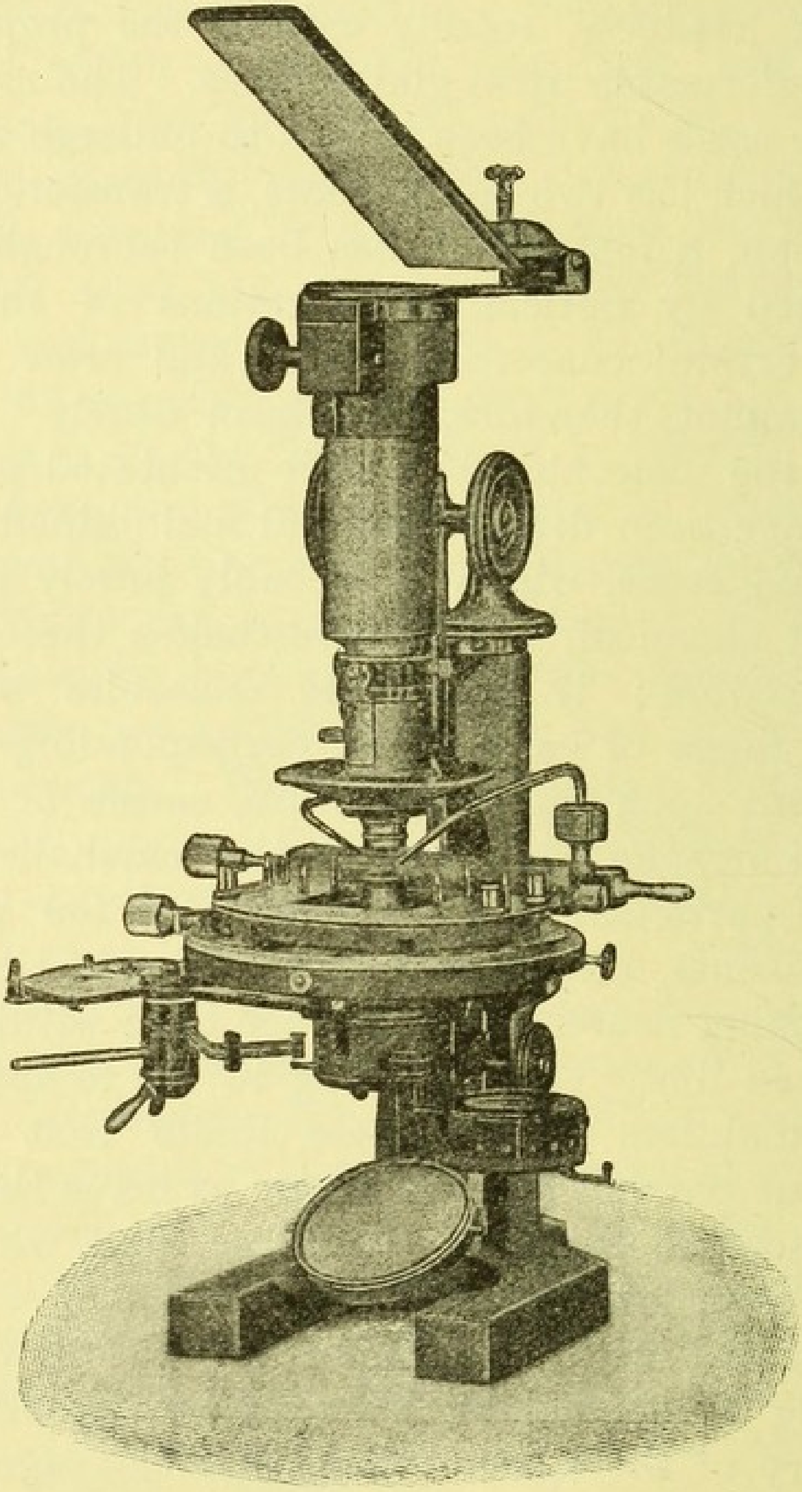

FIG. 119.—Lehmann's Crystallisation Microscope arranged for Projection.

of Wulff, described in the last chapter, that the direction or directions of maximum cohesion are those of slowest growth of the crystal; so that faces parallel to those directions become relatively more extended owing to the more rapid growth of other faces on their boundaries, and thus become the most largely developed and confer the "habit" on the crystal. All these are facts so important as evidences of a controlling force at work in crystallisation, that a *purely* geometrical theory of the formation of crystals which would make "facility of fitting-in" of the molecular particles its chief tenet, obviously does not tell us the complete story. Hence the author desires to utter a warning against going too far with the pure geometry of the subject. The geometricians have done a grand work in providing us with the thoroughly well established 230 types of homogeneous structures, as a full and final explanation of the 32 classes of crystals, and so far their results are wholly and unreservedly acceptable.

The phenomena of "liquid crystals" lend themselves admirably to screen demonstration, for which purpose an excellent improved form of the crystallisation microscope of Lehmann, shown in Fig. 119, is constructed by Zeiss, and its actual use in the projection, with the aid of the well-known Zeiss electric lantern, but specially fitted for the purpose, is shown in Fig. 120.

A magnification of 600-700 diameters on the screen is very suitable, employing a Zeiss 8-millimetre objective without eyepiece. This objective affords directly a magnification of 30 diameters. For ordinary eye observation an eyepiece magnifying

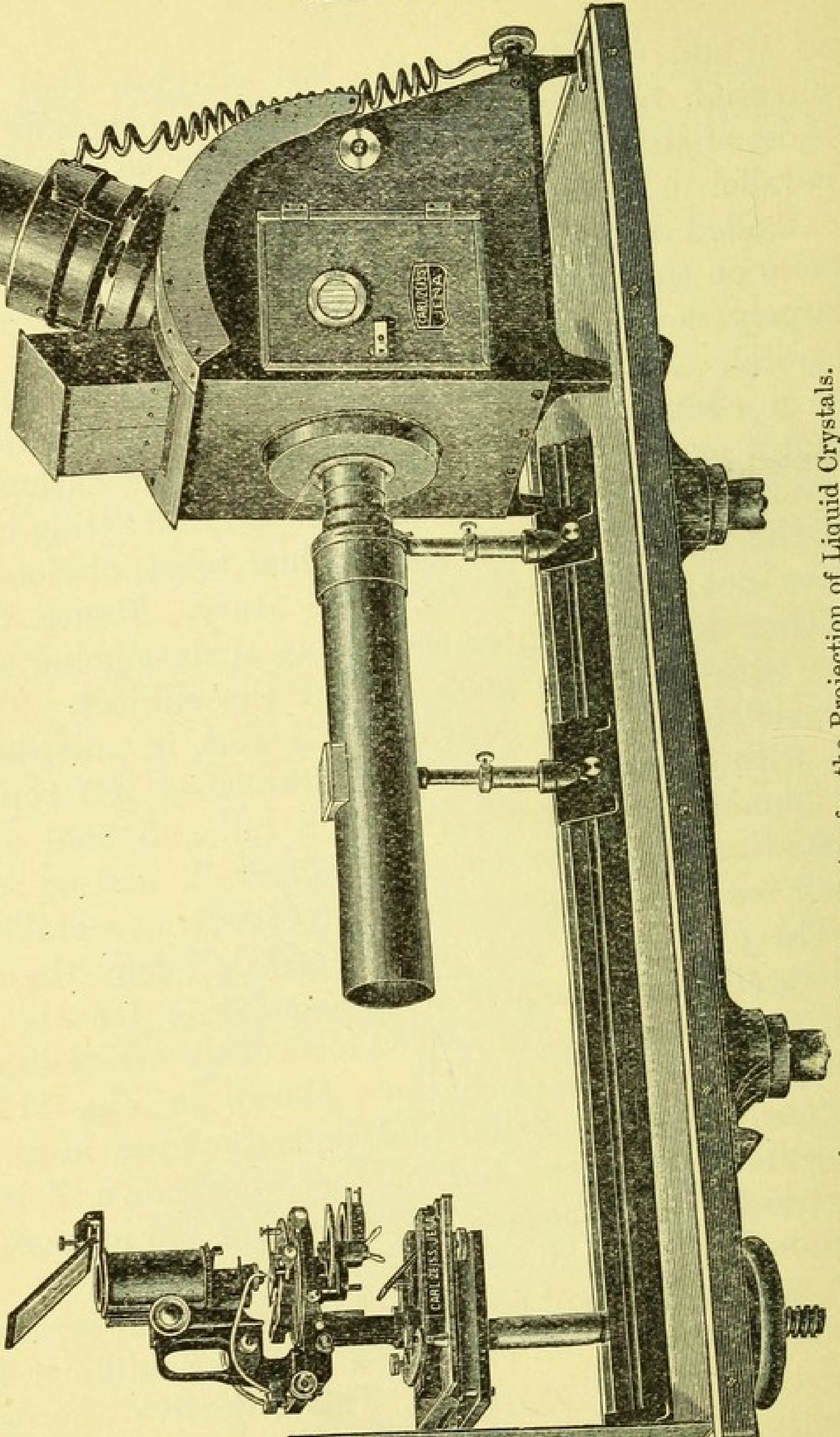

FIG. 120.—Zeiss Apparatus for the Projection of Liquid Crystals.

6-8 times is added, thus affording to the eye a magnification of about 200 diameters.

The lantern is supplied with a self-feeding electric arc lamp, ensuring a steady light. A collective lens of extra light-gathering power is fitted in front as condenser, and from it proceeds a light-tight tube provided with a water cell to filter out most of the heat rays which accompany the light. The electric lantern with Brockie-Pell or Oliver self-feeding arc lamp, shown in Figs. 71 and 79 (pages 186 and 202), is also equally suitable, and with the water cell, and parallelising concave lens removed from the large Nicol polariser, affords a parallel beam of the same character as the Zeiss apparatus. The microscope stands on a sole plate provided with levelling screws, and is naturally employed in the vertical position for such work with fused substances. A mirror inclined at 45° at the foot of the microscope directs the parallelised rays from the optical lantern through the microscope, and another above the optical tube reflects them to the screen.

The heating apparatus consists of a form of miniature Bunsen burner fitted with blow-pipe blast, the respective pressures of gas and air being regulated by means of two taps with graduated arcs for obtaining greater delicacy of adjustment. The tabular plate seen to the left in Fig. 119 is the graduated semi-circle of the two taps ; below it is seen the cylindrical mixing chamber for gas and air, in the event of the necessity for using the Bunsen as a blowpipe. There are two separate attachments for indiarubber tubes to this cylinder, conveying respectively gas and air. Above the object stage a double air-blast is fitted, each tube of which is hinged with a universal joint, so that it can be readily adjusted to any desired position on either side of and above the glass plate (supported on little metallic uprights) on which the experiment is being conducted. A polarising Nicol prism and an analysing Nicol, both constructed in a manner which protects them from the effects of heat more effectually than is the case with the usual form, are provided for obtaining the projections in polarised light. The objective and analysing Nicol, as well as the substage condenser, are also specially protected from injury by heat, by being surrounded with a water jacket, supplied with running water, and a disc-like screen just above the objective assists in deflecting the heat rays from the optical tube and its Bertrand lens and other usual fittings. The miniature Bunsen flame is usually brought about an inch below the object plate, and the size of the flame can be regulated with the utmost precision, so that a fairly constant temperature can be obtained for a considerable time. With the aid of the blowpipe air-blast temperatures up to 700° C. can be safely employed.

The microscope shown in position on the projection apparatus in Fig. 120 is a still more recent form introduced by Zeiss, embodying several further conveniences and improvements.

The following substances lend themselves particularly well to projection purposes. Para-azoxyanisol with resin, which exhibits the phenomenon of rotating drops; cholesteryl acetate, which affords a fine example of spherical liquid crystals; para-azoxy-phenetol with resin, which gives beautiful interference colours ; and the acetyl ester of para-azoxybenzoic acid with resin, which shows the uniting of crystals to form larger and larger individuals.

Perhaps the most interesting and beautiful of all is cholesteryl acetate, a characteristic field of which is shown in Fig. 121 on Plate XVI., facing page 208. It is interesting that on this Plate XVI. there are represented the very hardest and the softest of crystals, namely, diamonds and liquid crystals. In order to obtain the finest effect the heating and cooling should be carried out very slowly. The little Bunsen burner, with a very minute flame, is first placed under the slide, and allowed to act until the substance melts and forms a clear liquid. The gas jet is then removed and the air-blasts, both of which are simultaneously actuated when the tap controlling them is turned, are very gently brought into operation, one on each side of the centre of the slide, there being a good working distance of a quarter of an inch or more between the slide and the objective. The cooling is thus brought about very slowly. The Nicols should be crossed, and at this time the field is quite dark, the liquid substance being at this temperature (well above 114°.5 the ordinary melting point) an ordinary singly refractive liquid.

As soon as the temperature has become reduced to that at which the particular modification of cholesteryl acetate is produced which forms liquid crystals, spots of light make their appearance at various points in the field, and each expands into a beautiful circular and more or less coloured disc marked by a rectangular sectorial black cross, which latter is well shown in the illustration (Fig. 121). These beautiful apparitions continue to occur, and each to expand to a certain size, which is rarely exceeded, until the whole field becomes filled with the wheels or crossed discs, the general effect very much in some respects resembling that afforded by a slide of the well-known polarising substance salicine. These discs, however, are liquid, being spherical drops, of the structure already described and illustrated in Fig. 103, and that this is so is at once made apparent on touching the cover glass with a pen-knife or other hard pointed substance, which immediately causes them to become distorted. They recover instantly their shape again when the pressure is removed. When the cooling, moreover, has proceeded still further, there is a sudden change, and acicular solid crystals shoot over the screen, tinted with all the colours of the spectrum, until the field is full of them, the ordinary solid modification of the substance having then been produced. The experiment may be repeated with the same specimen of the substance, mounted on the same slide, covered with the usual thin cover-glass, time after time for months, at reasonable intervals.

In concluding this chapter it may be mentioned that absolute proof of the double refraction of the liquid crystals of several different substances, derivatives of cinnamic acid, has been afforded during the year 1910. For direct measurements have been carried out by two independent investigators, Dorn and Stumpf, of the two refractive indices corresponding to the ordinary and extraordinary rays in each case, the crystals being uniaxial.

CHAPTER XVII

THE CHEMICAL SIGNIFICANCE OF CRYSTALLOGRAPHY. THE THEORY OF POPE AND BARLOW—CONCLUSION.

NOTHING in connection with the subject of crystallography is more surprising than the neglect and apathy with which it has been for long treated by the chemical world. That crystalline structure is intimately related to chemical constitution will have been made abundantly plain during the course of this book. Yet in spite of the great work of Mitscherlich, essentially a chemist, and of a large amount of striking work which has been steadily accumulating during the last thirty years, with results of vital importance to chemistry, it is only at the eleventh hour that chemists are really awakening to the vast significance which crystal structure has for them.

The explanation undoubtedly is, that the long interregnum of conflicting investigations, doubt, and controversy, which followed the work of Haüy and Mitscherlich, and preceded the beginning of really accurate and painstaking investigation of an organised and systematic character, had caused chemists to regard with more or less of indifference the work of the crystallographers. Added to this we must remember that the subject of crystallography has hitherto been taught, when taught at all, merely as an appanage of mineralogy, although the pure chemical substances which crystallise well infinitely outnumber the naturally occurring minerals, and the results afforded by them frequently possess a much greater value by reason of the purity of the substances and their more definite chemical constitution. Also the mathematical and geometrical side has usually been unduly emphasised, and carried on in lectures without any practical goniometrical work at all. Moreover, the current text-books have often proved forbiddingly full of calculations and formulæ, and of the obsolete and unenticing symbols of Naumann.

At last we have come to see that the subject is one of fascinating interest when its study is commenced in a practical manner from the beginning, armed from the very first lesson with the goniometer. The crystal itself is then our main and highly interesting study; its exterior form unravels itself in a most delightfully simple manner when we follow the arrangement of its faces in zones on the goniometer itself; and its symmetry becomes immediately patent to our eyes in all ordinary simple cases, when we construct for ourselves its plan in a stereographic projection, drawn at first in freehand while still at the goniometer. The calculations also become perfectly simple when we have learnt that only the simplest of the very easy formulæ of spherical trigonometry are required, and which a knowledge of only elementary plane trigonometry enables us to apply. Aided by a few very helpful rules, such as those of Napier for calculating right-angled spherical triangles, and the rule of the anharmonic ratio of four poles in a zone—which, when the positions of three crystal faces of the zone are known, at once enables us to calculate the situation of any fourth face of the zone—we have at once a stock-in-trade which carries us over all difficulties in the way of calculation, and relegates this side of the work to an altogether subordinate position, although accuracy in carrying it out is, of course, absolutely essential and even vital.

Especial interest has recently been attracted on the part of chemists to the bearing of crystallography on their science by a remarkable theory which has been advanced by Pope and Barlow, connecting the internal structure of crystals with chemical valency, the power which the atom of a chemical element possesses of combining with the atoms of other elements, and which is generally expressed by the number of atoms of a monad element, such as hydrogen or chlorine, with which it is capable of combining chemically. Thus the electro-positive metal potassium is said to have monad valency because it is capable of combining with one atom of the electro-negative element chlorine to form the salt potassium chloride, KCl; calcium possesses dyad valency because it can unite with two atoms of chlorine to form calcium chloride, $CaCl_2$; aluminium is triadic as it can combine with three atoms of chlorine producing aluminium chloride, $AlCl_3$; carbon is a tetrad because it can take up four chlorine atoms, forming carbon tetrachloride, CCl_4, and phosphorus a pentad as it can fix five with production of phosphorus pentachloride, PCl_5; while sulphur is a hexad because it can take up as many as six atoms of chlorine, forming sulphur hexachloride, SCl_6.

Occasion has already been taken in Chapter XI. to refer to the able work of Prof. Pope with regard to optically active carbon compounds, and in Chapter IX. the important contribution of Mr Barlow to the completion of the theory of the homogeneous partitioning of space has likewise been discussed. In collaboration these two investigators have now propounded a theory which connects the chemical and geometrical sides of crystallography in a somewhat startling manner, which has naturally aroused very considerable discussion, and which, whether right or wrong, cannot fail to have the best results in attracting investigators to the subject.

Starting from the facts which have now been laid down in this book as having been firmly established by the most careful measurement and experimental investigation—notably the constancy of the interfacial angles of the crystals of the same substance, the fixed positions of the atoms or their spheres of influence in the molecule and in the crystal, and the arrangement of the molecules in space-lattices and the atoms in point-systems—Pope and Barlow assume that valency, the expression of the relative combining power of the chemical elements, is a question of the size of the sphere of influence of the atom of an element, and that the relative sizes of such spheres of influence determine the modes in which they can be packed, that is, the nature of the homogeneous crystal structure which they can build up. The theory consequently renders the chemical phenomenon of valency and the physical phenomenon of crystalline form mutually interdependent.

It will thus be apparent that the essence of their conception is that the chemical molecule may be considered as made up of a number of spheres corresponding to, and representing, the spheres of influence of the atoms composing it, and that the volume of each sphere is roughly proportional to the valency of the atom which it represents. They then assume that the sum of the valencies of the atoms present in the molecule may be substituted for the molecular volume, and the quantity thus arrived at is termed by them the "valency volume." By using the valency volume instead of the molecular volume in the author's formulæ for calculating the molecular distance ratios, which have been shown in Chapter X. to afford the relative dimensions of the unit-cell of the space-lattice, and the distances of separation of the centres of gravity of the molecules from each other along the directions of the crystal axes, Pope and Barlow arrive at new ratios, which they term equivalence parameters. By the use of these latter they have attempted to account for the crystalline structure of a number of substances—chiefly organic compounds, in the investigation of which Prof. Pope has proved so adept—which are connected morphotropically in the manner described in Chapter VIII., and of others which are still less intimately connected.

Unfortunately, the equivalence parameters do not make clear the relationships in an isomorphous series, as do the molecular distance ratios; for they are, from their very nature and mode of derivation, almost identical for all the members of an isomorphous series, the valencies of the interchangeable elements being the same. The molecular distance ratios have also the great advantage of being derived from the three measurements which have now been brought to the highest pitch of experimental accuracy, namely, atomic weight determinations, density determinations by the Retgers immersion method, and goniometrical and physical measurements (optical and thermal) with instruments now available of the utmost refinement. Structural constants thus derived are obviously of especial value. It would thus appear that the theory requires modification so as to take account of the experimentally proved regular increase in volume and in the directional dimensions of the structural unit cell of the crystal space-lattice, when one element of the same family group and of the same valency is interchanged for another. Indeed, as the theory stands at present it entirely ignores and fails to offer any explanation of the highly important physical property of density, specific gravity. That this physical constant, and the equally important constant molecular volume, derived by dividing the molecular weight by the density, possess a real and significant meaning in isomorphous series, formed by the interchange of elements of the same family group, has been clearly proved in Chapter X. This fact is, indeed, so obvious that any further development of the theory must of necessity take account of it.

A precise statement of their conception has recently been made by Prof. Pope in an excellent Report on the Progress of Crystallography, issued by the Chemical Society early in the year 1909. He states that they (Pope and Barlow) " regard the whole of the volume occupied by a crystalline structure as partitioned out into polyhedra, which lie packed together in such a manner as to fill the whole of that volume without interstices. The polyhedra can be so selected that each represents the habitat of one component atom of the material, and are termed the spheres of atomic influence of the constituent atoms. Up to this point no assumption is made other than that clearly indicated by the result of crystallographic measurements, namely, that each atom present in a crystalline structure exerts a distinct morphological effect—or, what is the same thing, appropriates a certain definite volume. The assumption is next made that the crystalline structure, which is resolvable into individual molecules and ultimately into individual atoms, exists as such by reason of equilibrium set up between opposing attractive and repulsive forces operating between the component atoms, and that this equilibrium results in the polyhedra representing the spheres of atomic influence assuming shapes which are as nearly as possible spherical. . . . The polyhedra thus arrived at may be regarded as derived by compression of a close-packed assemblage of deformable, incompressible elastic spheres,[1] the compression sufficing for the practical extinction of the interstitial space. When such an assemblage

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[1] This apparent contradiction in terms the author takes to mean that, whatever compression is produced by pressure on one part of the sphere, is counterbalanced by a corresponding protuberance produced in the part not confined under pressure, the total volume being incompressible.

is released from pressure it is evident that in place of polyhedra, the shapes of which approximate as closely as possible to the spherical, closely packed spheres are presented; the distances between the sphere centres can be substantially in the same ratios as the distances between the centres of the corresponding polyhedra in the unexpanded mass, and the equilibrium condition of maximum sphericity of the polyhedra will be presented in the expanded mass of spheres by the existence of the maximum number of contacts between spheres. The whole method of treating the primary assumption thus resolves itself into finding close-packed assemblages of spheres of various sizes representing by their relative volumes the spheres of influence of the component atoms of any particular crystalline structure."

Some very interesting evidence of the validity of their fundamental assumption of spheres of influence of the component atoms as the ultimate structural units is brought forward. They show that there are two modes of closely packing equal spheres, which give rise respectively to a cubic and a hexagonal crystal structure, the latter having a specific axial ratio of the vertical to the three equal equatorial horizontal axes; and that the chemical elements which are solids and crystallise, and the structural units of which can naturally be assumed to be equal spheres, being those of the similar atoms of the same chemical element, do practically all crystallise either in the cubic system or in the hexagonal system with the specific axial ratio indicated by them. The theory as it concerns chemical valency is obviously not affected by these interesting facts, as the spheres of influence present are those of the identically similar atoms of the same element. But the theory has received considerable support from the results of the investigation of a number of carbon compounds, chiefly derivatives of benzene.

Thus, in spite of the very wise decision of Barlow at the time of developing his theory of the homogeneous partitioning of space, to keep quite clear of attributing shape to the structural unit atoms or molecules, and to consider them as points, he, in common with the other contributors to that splendid geometrical work, appears driven to consider the question of shape when, in collaboration with his chemical colleague, he endeavours to apply his geometrical results to the practical problems of chemistry. It may be inevitable that we cannot get away from the idea of shape of the fundamental structural units. Yet the moment we do admit the idea, and begin to talk of polyhedra, or even of spheres, in close or any other packing, we enter the debatable land, concerning which the experimental evidence is as yet but shadowy and liable to many interpretations. Hence it is that we have the parallelohedra of Von Fedorow, having volumes proportional to the molecular volumes, the more general plane-faced cell of fourteen faces, the tetrakaidecahedron of Lord Kelvin and its deformed derivatives, and now the polyhedra of Pope and Barlow. The more indefinite "Fundamentalbereich" of Schönflies appears to be left behind, and we have embarked on a definite course of attributing shape to the component atoms or their regions of influence in the crystal structure. Von Fedorow has developed his particular theory in a very masterly manner, and with the aid of it professes, and with very considerable success in many cases, to determine the correct mode of setting up a crystal for truly comparative descriptive purposes, and has derived therefrom a remarkable method of crystallochemical analysis.

Moreover, there is yet another view, that of Sollas,[1] that the packing of the molecules is a more open one altogether, a view to which he has been guided by consideration of the molecular volume. Sollas has offered some remarkable explanations of crystal structure, notably in the case of the dimorphous forms of silver iodide. The abnormal contraction which occurs on heating this interesting substance, and its sudden transformation at 146° from the ordinary hexagonal into a cubic modification as discovered by Lehmann, appear capable of very clear explanation on the basis of his theory. According to this theory of Sollas the volumes of the spheres of influence of the atoms of the different elements of the same family group, such as those of the group of alkali metals or those of the halogens, chlorine, bromine, and iodine, vary progressively in a manner which is dependent on the atomic volumes of the elements, which have a real comparative significance when the elements belong to the same family group.

It is probable that there is a considerable substratum of truth behind these various apparently conflicting views, and what is now required is that the germ of real fact shall be winnowed from the

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[1] *Proc. Roy. Soc.*, 1898, **63**, 270, 286, and 296; 1901, **67**, 493.

husk of fallacious speculation, just as occurred in the happy recent settlement of the old issue between Haüy and Mitscherlich. As in that case, moreover, it will be experimental work of superlative accuracy which can alone offer the desirable evidence on which a satisfactory arbitration can be founded.

It is thus obvious that we have now arrived at a stage in the history of crystallography when more experimental data, and many more measurements of the most carefully conducted character, on pure materials and excellently developed crystals, are most urgently needed, in order to decide these important, indeed fundamental, questions, the present state of which the author has endeavoured to present with judicial impartiality. When one looks around, and sees the almost complete lack of opportunities for the training of investigators in this rapidly growing branch of science, the importance of which to chemistry and physics is increasing every day, while the field is ripe for the harvesters, one is inclined to feel depressed with the thought of the opportunities which are being lost. Our country has, in this science at any rate, a fine record, having with few breaks led the van of progress from the time of Wollaston, the inventor in the year 1809 of the reflecting goniometer, and of Miller, the originator of our method of describing crystals and the pioneer of accurate experimental work, down to the present day. It may be, also, that our country's reputation is safe at this moment. But it is in the hands of a band of investigators so small, and often of the private and not professional nature, carrying on the work for sheer love of it and deep interest in it, that the wonder is that so much has been done, and it is the provision for carrying on our national tradition of leadership in crystallography in the future that is a matter for the deepest concern.

If the perusal of this book should have awakened sufficient interest in the minds of some of its readers to prompt them to offer themselves as recruits to this small band of investigators, and especially if it should have inspired the zeal and enthusiasm of a few young students looking around for a promising and fascinating field of work, and, finally, if it should prove to be of assistance in obtaining the means of training such recruits with the help of the best and most accurate experimental apparatus which can be obtained, the author's main objects in writing it will have been attained.

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