CRYSTALS AND THE FINE-STRUCTURE OF MATTER

FRIEDRICH RINNE

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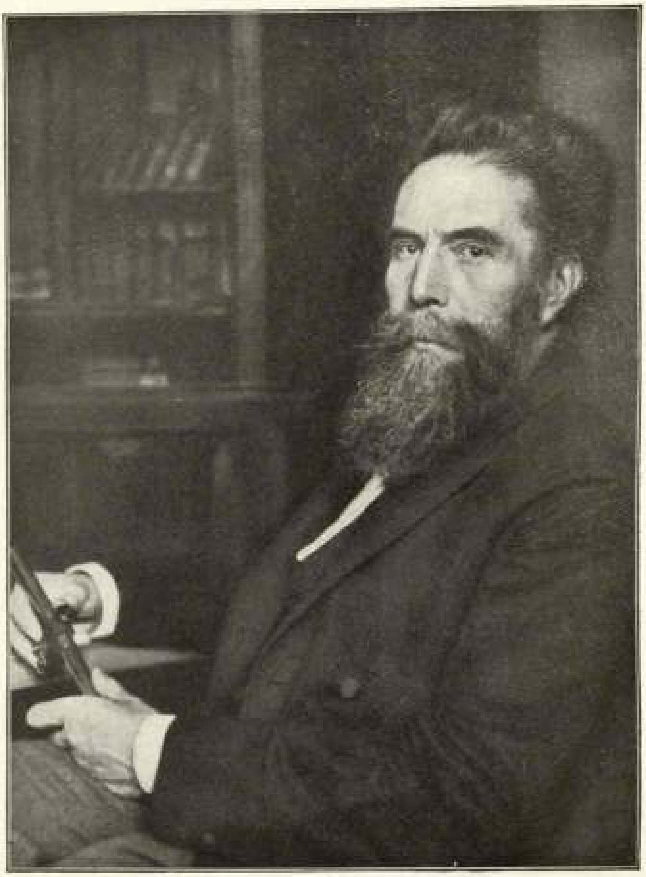

DR. W. C. RÖNTGEN

CRYSTALS AND THE FINE-STRUCTURE OF MATTER

BY

FRIEDRICH RINNE

PROFESSOR OF MINERALOGY IN THE UNIVERSITY OF LEIPSIC

TRANSLATED BY

WALTER S. STILES

WITH A DRAWING BY A. DÜRER, AND PORTRAITS OF THE LEADING INVESTIGATORS IN THE STUDY OF FINE-STRUCTURE AND 202 FIGURES

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PREFACE

THE first edition of this work was submitted to the scientific public a year ago. The book set out to consider experiments on the fine-structure of matter from a new and essentially crystallographic standpoint, corresponding to its title "Crystals as types of the fine-structure of matter."

The friendly communications I have received, the reviews in the press, and the fact that translations of the book have been prepared, will testify to the good reception given to the work by the public. The demand for the first edition being so great, I have thought it well to extend the work considerably for the new issue.

Historical details are introduced, the treatment of crystallography is amplified, tabular summaries and sections on the atom domain and stereochemical axes are added. Instructive cases of polymorphism are also described. In addition, the book contains many new explanatory figures, and portraits of some leading scientists. By these changes the work is not, I think, increased in size by more than half of its previous bulk, without at the same time being enriched by many glimpses into the interesting relations of the science of fine-structure.

The need for a treatment of the subject easily understood by the general reader is, however, constantly observed. For those more closely interested a list of text-books on crystals has been included. An index is appended.

I hope that this new and much enlarged edition, the preparation of which has been a labour of love for me, will help, as did its predecessor, both by its text and diagrams, in placing in the right light the physical, or, rather, the natural philosophical side of crystallographic science, and in acquiring new friends for the very fertile study of the fine-structure of matter.

To these preliminary remarks I add my thanks for the advice offered to me by the reviewers, whose suggestions have been willingly followed, together with the expression of my gratitude to my assistants, Dr. K. H. Scheumann and Dr. E. Schiebold, for friendly help in the editing of this new edition. The Saxon Academy of Sciences facilitated the publication of the book by the loan of a large number of printing blocks.

INSTITUTE OF MINERALOGY AND PETROGRAPHY
IN THE UNIVERSITY OF LEIPSIC
IN THE SPRING OF 1922

NOTE

THE translator wishes to tender his best thanks to Professor Rinne for very kindly reading through the proofs, and offering many helpful suggestions. Most of these have been adopted and have materially assisted in the work of translation.

W. S. STILES

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MELANCHOLY

FROM AN ENGRAVING BY ALBERT DÜRER

CRYSTALS AND THE FINE-STRUCTURE OF MATTER

I. INTRODUCTION

THE reader sees before him a reproduction of a drawing by the great German master, Albert Dürer, whose art has here represented the problems of natural science and technical practice, together with the simple means available in his time for their elucidation. Among the symbols in the picture we observe in a very prominent place a gigantic crystal, which is surely an indication that Dürer saw a scientific problem of the first importance in the solution of the riddle of this regular form.

Over the whole scene rests a gloomy air of speculative resignation, the Faust-like expression of the feeling that we, ultimately and in spite of fervent endeavour, " nothing *can* know." The artist has called his picture " Melancholy."

A Dürer of our own day would certainly have drawn more hopefully. It would seem as though the darkness enveloping the great mysteries of nature were lifting a little. By studying crystals and using them in other investigations much light is thrown on the ultimate significance of matter and on the nature of the forces which, acting from one minute particle to another, result in the coherence of the universe.

Crystals are proving themselves more and more the ideal substances of physics and chemistry. Even before the last great discoveries in this branch of knowledge the late Woldemar Voigt, Professor of Theoretical Physics at Göttingen, who had a unique knowledge of this subject, drew attention to the exceptional regularity of the crystalline parts of matter in a fine simile, which is quoted below:

"Imagine a couple of hundred picked violin players in a large room, all playing the same piece of music on faultless instruments, but beginning simultaneously at widely different places, and starting afresh each time they reach the end. The finest ear would be unable to recognise the piece actually played in this uniform medley of sound. Now such music is presented to us by the molecules of gaseous, liquid, and ordinary solid bodies. A crystal, on the other hand, corresponds to the orchestra described above when it is guided as a whole by one able conductor, so that all eyes hang on his slightest gesture, and all hands play the same bar. In this way the melody and rhythm of the piece presented become completely effective, the number of the performers not hindering but intensifying the result."

This picture makes it clear how crystals can present a large series of phenomena which are absent in other bodies, and that, in them, certain characteristics are developed in wonderful variety and elegance, which elsewhere occur only as monotonous mean values. This fact is briefly referred to in Voigt's text-book at the end of the chapter on the æsthetic side of crystal science as follows:—

"In my opinion the music of physical laws in no other branch achieves harmonies so full and rich as in crystal physics." The full truth of his view has been strikingly proved in the last ten years ; it could not have been brought to notice in more impressive fashion than by the results of the researches initiated by M. v. Laue on the action of X-ray impulses in crystals. The fine-structure of crystals acts like a grating diffracting the X-rays. In this "Laue effect," which will be discussed later, crystalline substances are seen to be the best ordered materials. It is easily understood that, since these experimental demonstrations of the constitution of crystals, the investigations not only of mineralogists but also of physicists and chemists have been especially concentrated on the crystal form. Further magnificent results have been obtained which are extensions of the discovery of M. v. Laue and his fellow-workers, W. Friedrich and P. Knipping. These matters certainly merit the widest dissemination in scientific circles. Many expositions with this object have already appeared. Besides taking a share in the work of research, I have frequently done my best to promote the same end by means of notes in journals and papers.

The present small work has, in addition, a wider purpose. In a treatment which aims at being comprehensible, as far as possible, to general readers, while at the same time offering much new material to fellow-students, the attempt is also made to deduce from the properties of crystals the main characteristics of the fine-structural constitution of matter.

With this in view the title has been slightly altered from that of the first edition. The aim of this book is thus to show that crystals exemplify not only the morphological but also the physical and chemical constitution of matter. The crystal is therefore treated from the standpoint of its fine-structure, and a discussion of amorphous bodies (for example gases and liquids) is included.

II. THE STUDY OF FINE-STRUCTURE (LEPTOLOGY)

I INTRODUCE the expression fine-structure-study, or leptology, because the customary term stereochemistry does not cover completely the field of the inquiry intended. In stereochemistry we study the form and arrangement of the particles comprising various substances in order to explain thereby their chemical properties. Alongside this science, another has arisen, which may justly be termed stereophysics, and this also is concerned with the constitution and association of the particles of matter, dealing especially with their movements and physical properties (e.g. crystal optics). Finally, a third allied subject is included, namely, crystal structure, or the study of the fine-structure of crystalline bodies from the point of view of their geometrical relations.

Thus from the trunk of Greek Atomic Theory, which is more than two thousand years old, three branches of knowledge have sprung forth and blossomed—stereochemistry, stereophysics, and crystal structure. Their intimate relations to one another justify a name to include them all. If now the particles of matter, the electrons, atoms, ions, and molecules which constitute gases, liquids, and crystals are termed collectively fine-structure-particles or leptons (from λεπτος, fine, delicate), the name suggested above, fine-structure-study or leptology indicates precisely the end in view.

III. CRYSTALLOGRAPHY AND LEPTOLOGY

HISTORICAL

NEARLY two thousand five hundred years ago, in ancient Greece, where Babylonian, Persian, and Egyptian wisdom was associated with the Greek genius, philosophical theories as to the fine-structure of matter were extant. These theories were due to Democritus and to his friend Leucippus, and also to Epicurus, who lived some hundred years later. Their writings have not come down to us; their ideas, however, are preserved in the poem "De rerum natura" of Lucretius (96-55 B.C.).

According to this they assumed all matter, considered in its finest state, to have a granular structure, and to consist invariably of aggregates containing large numbers of atoms. These very small particles are, in their opinion, extended but indivisible, unchangeable, and for different substances, of different shape, magnitude, and weight. They oscillate and move about at random. Between them is empty space.

Under the influence of Aristotle this theory retreated into the background, and it found no favour in intellectual circles of the Middle Ages until scientists, such as P. Gassendi (1592-1655), and the great physicist, I. Newton (1642-1726), endowed the old fundamental idea with a new validity. As a consequence, closer relations between leptology and crystallography were soon established. In this connection Ch. Huygens (1629-1695) was able to explain the form of calc-spar, its cleavage, and the variation of its hardness and double refraction with direction, by assuming a regular packing of spheroidal particles (a conception which later Barlow and Pope also employed successfully). Later, the principal founder of scientific crystallography, Abbé René Just Haüy (1743-1822,) endeavoured to establish his expositions on a fine-structural basis. He thought of crystals as "additive molecules" constructed of, for the most part, contiguous building stones, the form of which determined the cleavage, and he deduced by means of "decrescence" (i.e. regular, step-like reduction in the size of molecular plates on a nucleus) the crystalline forms from such "Primitive Bodies." The extraordinary fineness of the staircase structure renders the boundary planes perfectly smooth to the eye, and even to the most sensitive optical tests.

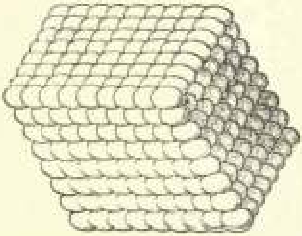

Fig. 1.—Fine-structure of calc-spar according to Ch. Huygens.

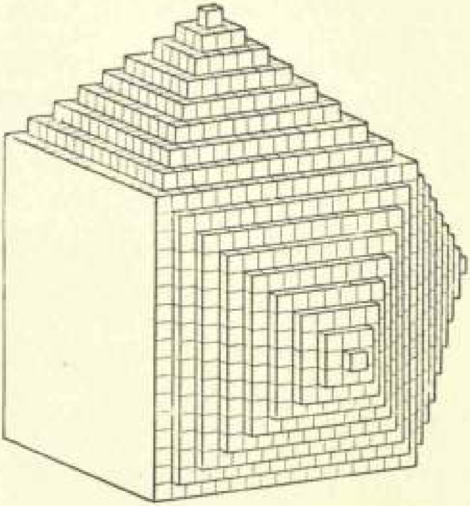

Fig. 2.—Crystalline fine-structure according to R. J. Haüy.

An experimental law of crystallography, that of the "simple rational axial sections of the crystal faces,"[1] found in the above its obvious explanation. We understand by this law that in the external form of crystals, surfaces arbitrarily placed do not occur, but only those which stand in a definite relation to one another. In contrast to the freedom of an architect who, in building a house with the roof D, as shown in Fig. 3, can at will give a small or large value to its angle of inclination, in crystal structure (Fig. 4) only certain slopes are possible, such as those

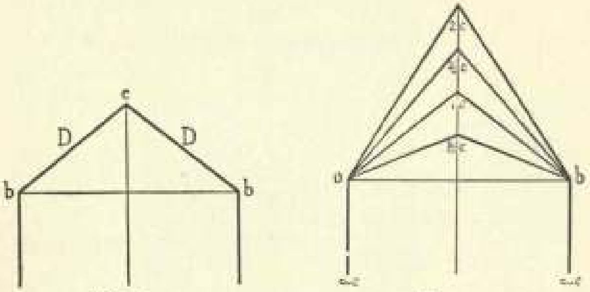

FIG. 3. FIG. 4.

Illustration of the law of simple rational axial sections of crystal faces.

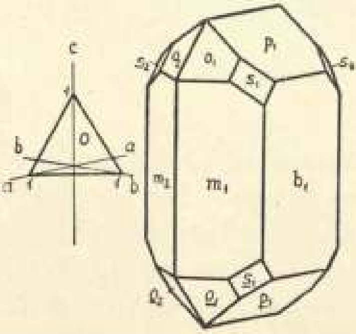

FIG. 5.—The relationship of the faces of an aragonite crystal on three intersecting axes.

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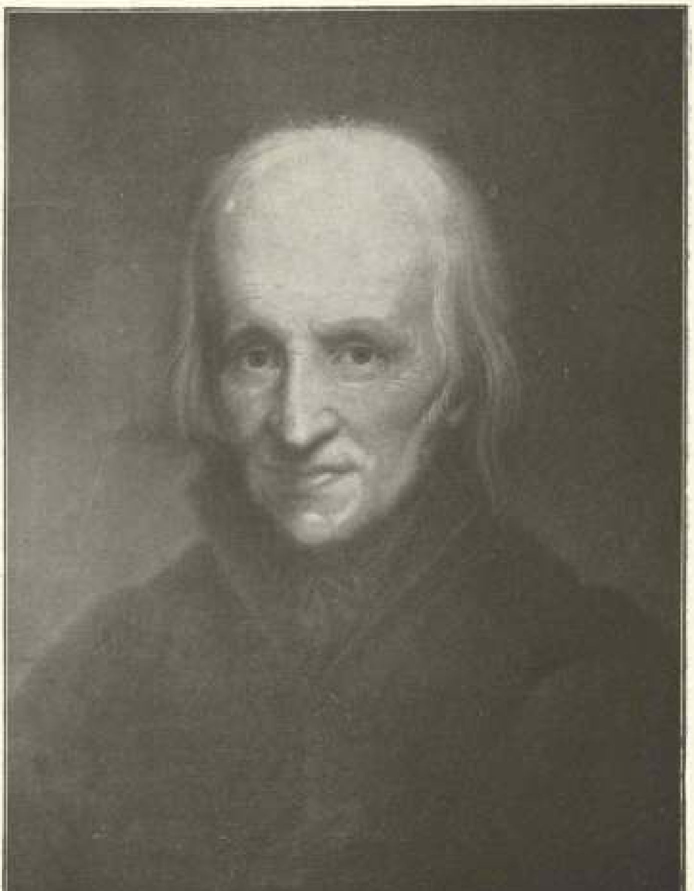
[1] Commonly known as the "Law of Rational Indices."



RENÉ JUST HAÜY
Born 28th February, 1743, Died 3rd June, 1822

from b to c, from b to $\frac{1}{2}c$, $\frac{3}{2}c$, $2c$, ∞c, or, in other words, according to simple rational ratios. Similar remarks hold for the other external faces of the crystal with respect to the points of section on the spacial axes a, b, c. If the units of these are marked out, say, for aragonite (Fig. 5), by means of the axial points of the face $O_1 = a : b : c$ in which ratio the length of b is set equal to unity, and each of the other surfaces be imagined displaced parallel to itself till it passes through the end point $1b$, then experimentally all such surfaces cut the axes a and c in the manner discussed above. For example, the face b cuts these axes in $\infty a : \mathrm{b} : \infty c$; m_1, in $a : b : \infty c$; p_1, in $\infty a : b : c$; s_1, in $2a : b : 2c$, and so on.

A consideration of Fig. 6 renders this law of crystallography, which restricts in a far-reaching fashion the external form of crystals, immediately intelligible according to the ideas of R. J. Haüy.

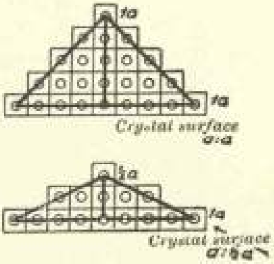


Fig. 6.—Deduction of crystal forms by "decrescence."

Against the great advantage of the agreement between the Haüy theory and crystallographic practice several considerations, especially those of a physical nature, must be advanced. The compressibility of the crystals, and their volume changes, with change of temperature, make their structure according to the Haüy scheme improbable. However, these difficulties could easily be got over, as the founder of the theory himself pointed out, if the closely-packed "additive molecules" are replaced at their centres by particles freely oscillating, which mutually maintain each other in this arrangement.

Thus we arrive at the idea of space-lattices as systems of particles, arranged periodically in three dimensions (Fig. 7).

Such a system is formed by the points of intersection of three families of planes, each family consisting of parallel planes, the distance between consecutive members being constant. According to A. Bravais (1811-1863), the space-lattice particles consist of chemical molecules, the symmetry of which is determined by crystallographic considerations (Fig. 8). The Munich physicist, L. Sohncke (1842-1897), and his mineralogical colleague, P. v. Groth, on the other hand, replace the Bravais molecular lattice by what they call point systems, which are atom lattices placed regularly one inside the other, as indicated in Fig. 9, where the scheme includes only two types of atom.

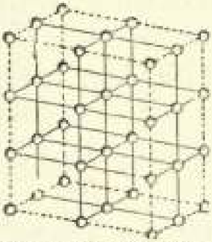


FIG. 7.—Space-lattice.

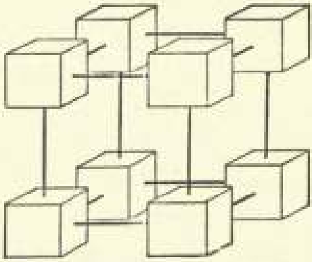


FIG. 8.—Molecular lattice according to A. Bravais.

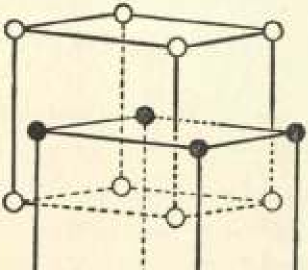
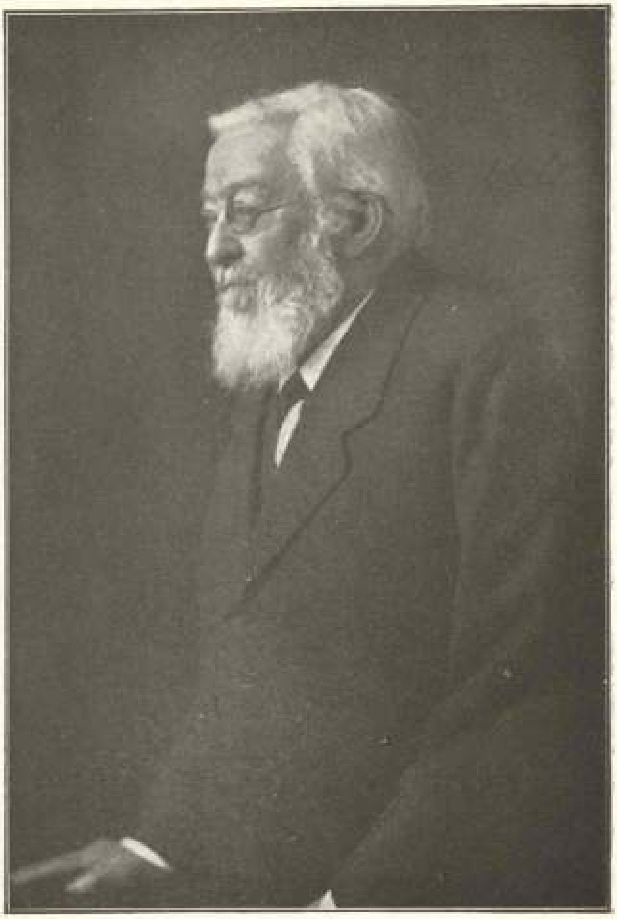


FIG. 9.—Point system according to L. Sohncke and P. v. Groth.

At the same time, the necessary geometrical



Prof H. Groß.

A. Schoenflies

representation of all space groupings possible in accordance with crystallographic laws was carried out. A. Schönflies[1] has given in a classical treatise the whole system of space-lattice arrangements. The same work has also been accomplished by the Russian investigator, E. v. Fedorow.

THE "LAUE EFFECT"

The year 1912 came as the great harvest year in the physics of space-lattice ideas. This led to the ever-memorable researches instituted by M. v. Laue, and carried out jointly with P. Knipping and W. Friedrich, in Munich, on the use of crystals as diffraction gratings for X-rays. A polychromatic impulse of the radiation is split up by diffraction at the particles of the crystal grating into a spectrum of monochromatic rays. These, received on a photographic plate, give rise after development to a figure symbolic of the atomic arrangement, in the form of a Laue diagram (Fig. 10). This diffraction effect can be considered[2] formally as a reflexion

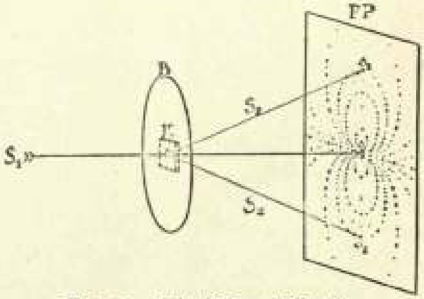


FIG. 10.—The "Laue Effect."

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[1] A. Schönflies, "Kristallsysteme and Kristallstruktur," 1891.

[2] Thus each point in a Laue diagram is to be regarded as the point of impact of X-rays which have been reflected at a structure plane in the crystal. Fig. 12 makes this clear for two planes, E_1E_1 and E_2E_2. The primary ray P is reflected at E_1E_1 to R_1, and at E_2E_2 to R_2. R_1 and R_2 are thus the points of impact of secondary rays on the photographic plate. Rhythmic arrangements of structure planes are emphasised in the radiogram by corresponding

of the incident rays at the planes of atoms in the crystal, in which case, however, a reflected ray is obtained only if the condition $n\lambda = 2r \sin a$ is fulfilled[1] (Fig. 11). This aspect was especially emphasised by W. H. and W. L. Bragg.

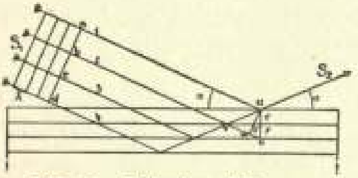

FIG. 11.—Reflexion of X-rays.

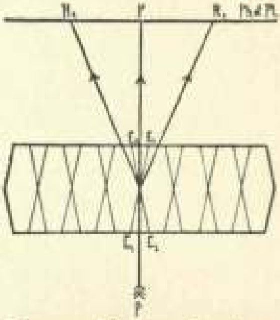

FIG. 12.—Diagram showing reflexion of an X-ray at two structural planes of a crystal.

In this way the space-lattice idea of crystallography became the starting-point of an extraordinary development of physical science; for not only the nature of X-rays as wave phenomena, but also the actuality of the atom was experimentally proved,

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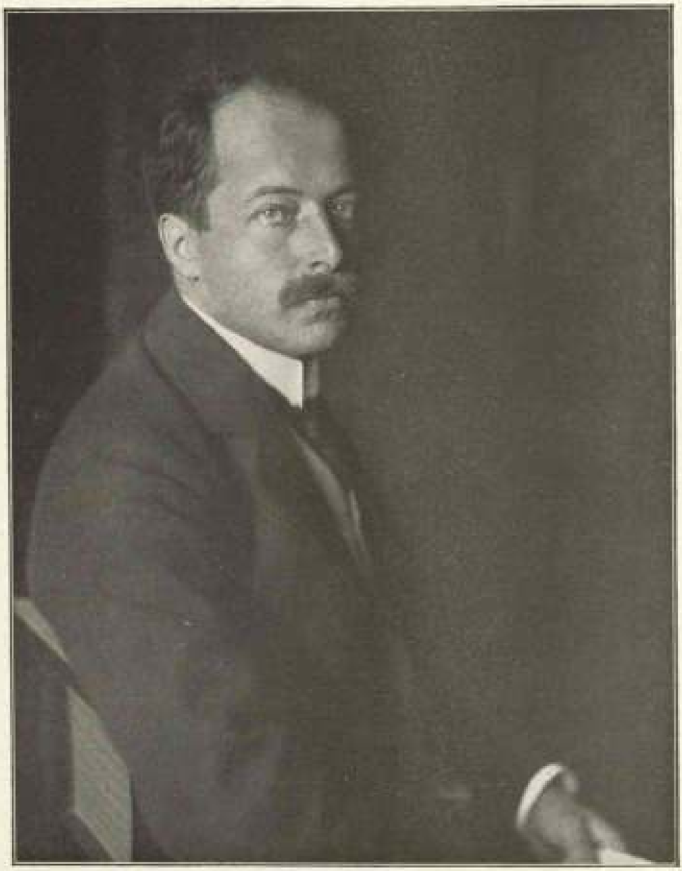
repetitions of reflected rays of the same intensity; the Laue diagram of beryl (Fig. 14) is an especially beautiful example of this.

The customary arrangement of the points on elliptical curves is easily explained with Fig. 13. In this S_1s_1 is the primary ray, which is reflected along Ks_2 by a plane cutting the plane of the paper at right angles and in the line Kz. If this plane be rotated about Kz, the reflected ray traces out a conical surface with Kz as axis. The receiving photographic plate PP cuts this cone in an ellipse s_1s_2. For other inclinations of the line Kz, parabolas, hyperbolas, or straight lines are obtained for the series of reflexions from those planes which run parallel to some one direction (corresponding to Kz); or which, as the crystallographer says, lie in a "zone."

[1] $n = 1, 2, 3 \ldots \lambda =$ wave lengths. $r =$ distance between reflecting planes. $a =$ glancing angle. The path difference for the two rays 1 and 2 is obviously equal to wu, thus it equals $2r \sin a$ (Fig. 11).

E. v. FEDOROW



Dr. M. v. Laue

once and for all, by the Laue effect. The existence of atoms is as certain now as that of the macrocosm of the starry heavens. Laue's experiment may with justice be described as a solemn deposition of nature concerning its most intimate structure.

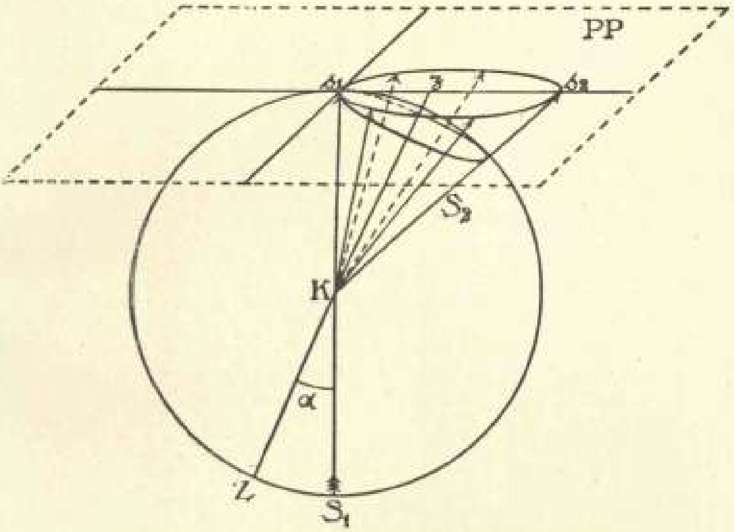


FIG. 13.—Formation of zone curves in Laue diagram.

M. v. LAUE

Under these circumstances it will be of interest to the reader to hear something more of the young German scientist and his celebrated researches, which opened up an unlimited field for investigation in the fine-structure of matter by the application of X-rays.

M. v. Laue was born on the 9th October, 1879, at Pfaffendorf, near Coblenz. While a student in Berlin he received the greatest encouragement in his scientific work from the creator of the quantum theory, M. Planck, whose assistant he was from

1906 to 1909. When v. Laue removed to Munich in 1909, stimulated by the work of Röntgen and the keen interest of Sommerfeld in X- and γ-rays, his attention was directed to the question of the nature of these rays. Moreover, it chanced that at Munich Uni-

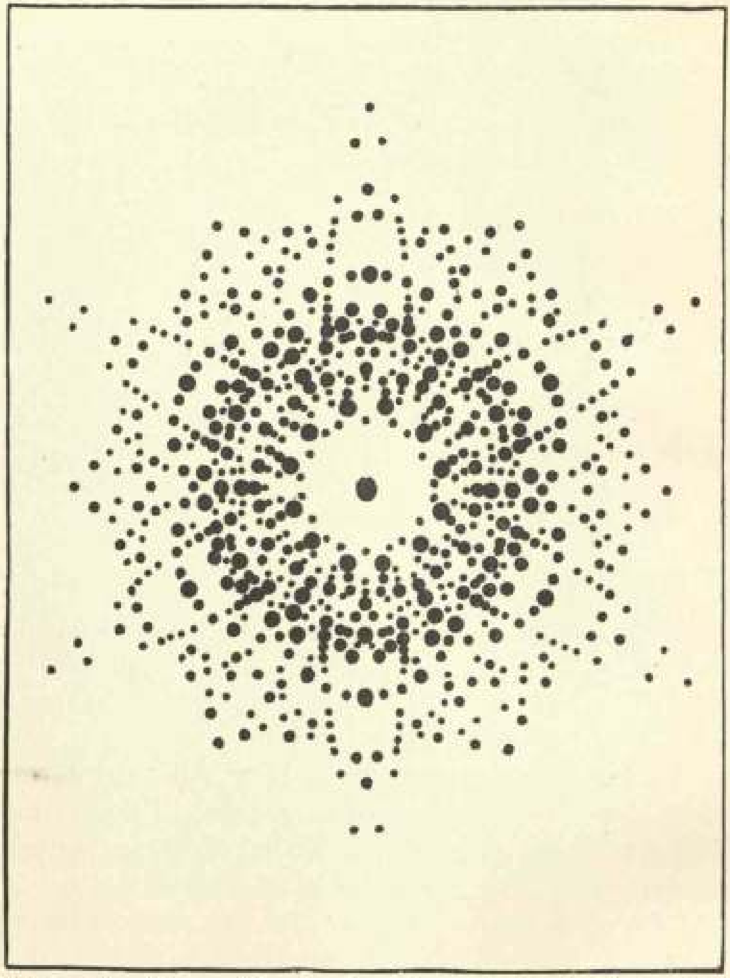


FIG. 14.—Laue diagram of the end surface of a crystal or beryl. Photographed by F. Rinne.

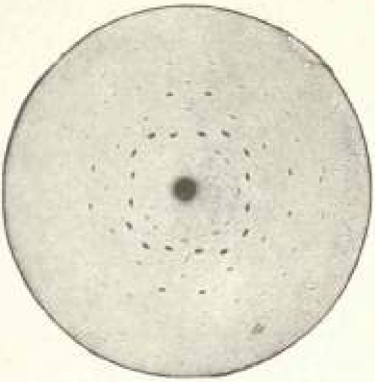


FIG. 15.—Laue effect for a zinc-blende plate parallel to a cubic surface

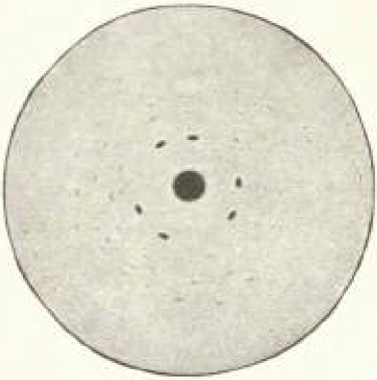


FIG. 16.—Laue effect for a zinc-blende plate parallel to a tetrahedral surface

versity, P. v. Groth, in his lectures and writings, was emphasising the space-lattice idea, and this ultimately took its place in the circle of ideas of the physicists there. In this way it happened that, when v. Laue was visited in February, 1912, by his colleague, P. P. Ewald, they discussed the studies of the latter as to the relations of long electro-magnetic waves in a space-lattice, and the question occurred as to the action of such waves, which are short compared with the dimensions of the lattice. Laue's optical knowledge told him that grating spectra must arise ; he expected interference phenomena in the passage of X-rays through crystals, and mentioned this to Ewald. Copper vitriol served as the material for the first experiment, large regular pieces of this being easily obtained. Friedrich and Knipping left the direction of the incident beam to chance. On the photographic plate behind the crystal there appeared in the first experiment the expected grating spectra. In the continuation of the work, Friedrich and Knipping investigated regular crystals having the highest possible symmetry, such as zinc-blende, and illuminated them in the direction of the crystallographic axes, with the beautiful results submitted to the reader in the original figures 15 and 16.

By applying here the results for the ordinary and the crossed grating the theory of the phenomena was immediately obtained, and Professor Sommerfeld was able, on the 8th June, 1912, to lay before the Munich Academy the joint work of Friedrich, Knipping, and v. Laue on the interference of X-rays.

In 1912 M. v. Laue obtained the Professorship of Theoretical Physics at Zurich University. From 1914 to 1919 he acted as Professor in the same subject at Frankfurt University; a summons to Berlin University brought him to his present position. A further recognition was accorded him in the Nobel Prize for physics for the year 1914.

FURTHER METHODS IN X-RAY WORK ON CRYSTALS

It is to a number of investigators, happily an increasing number, that we owe extensions of the method of the fundamental research of Laue, Friedrich, and Knipping. W. H. and W. L. Bragg[1] used plates cut in known directions from crystals, and rotated then on a spectrometer about an axis lying in the surface of the specimen. As soon as the angle between the plane of the specimen and one of the incident X-rays satisfied the equation $n\lambda = 2r \sin a$ reflexion occurred. The reflected ray lying in the plane of incidence was detected by means of a cylindrical ionisation chamber, and its inclination determined. The quantity of

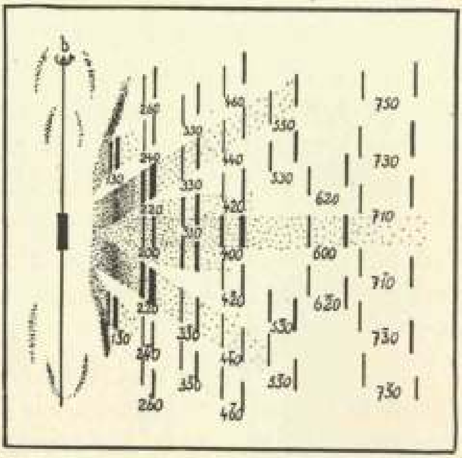


Fig. 17.—Rotation spectrogram of adularia. After E. Schiebold.

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[1] W. H. and W. L. Bragg, "X-Rays and Crystal Structure."

ionisation served as a measure of the intensity of the reflected radiation.

Other rotation methods with photographic determination of the direction of the reflected rays have been elaborated, especially by H. Seeman and E. Schiebold.

Interesting researches on substances possessing a fibrous or flaky structure, such as occur in nature, in plants, and animals, or can be prepared by drawing or pressing metals, have been carried out by members of the Research Institute in the Chemistry of Fibrines at Dahlem, near Berlin ; among these, Polanyi and his collaborators, Becker, Herzog, and Jancke, may be specially mentioned.[1]

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[1] Substances built up of fibres or flakes, which lie with all their fibre axes or flake normals parallel, but otherwise indifferently, give on the passage of X-rays perpendicular to this direction an X-ray effect similar to that of a crystal plate which is rotated about an axis passing through it. The series of reflexions, one after the other, produced by the latter, as a result of the rotation, are shown by the pack of fibres or flakes simultaneously. All fibres or flakes the structure planes of which satisfy the equation $n\lambda = 2r \sin \alpha$ give rise to reflected rays. As was shown by H. Seeman and E. Schiebold, in particular for rotating plates, and by M. Polanyi for fibrous substances and stretched metals, we get in this way characteristic diagrams. The reader more closely interested is referred to Fig. 18. In this PSt denotes the primary ray. It is reflected at surfaces whose normals N_1, N_2, etc., corresponding to various positions of rotation about the rotation axis DA (or the axis of the fibres, as the case may be), are shown in the figure. The incident ray, the normal to the surface, and the reflected ray, lie in every case in one plane, e.g. the ray S_3, corresponding to $N3$ lies in the plane E_3. If monochromatic radiation be used and only reflexions of a given order be considered (i.e. if we assume definite values for λ and n in $n\lambda = 2r \sin \alpha$), then reflected rays arise which pass through the intersections of the α-circle with the great circles corresponding to various planes of incidence. Take, for example, $N = 3$. In this case the intersections on the circle E_3 are, on the sphere, $S_3S'_3$; on the photographic plate PhPl, $S_3S'_3$. For other values of n, and therefore of α, other

Of the greatest importance is a method emanating from P. Debye and P. Scherrer, in Göttingen, which

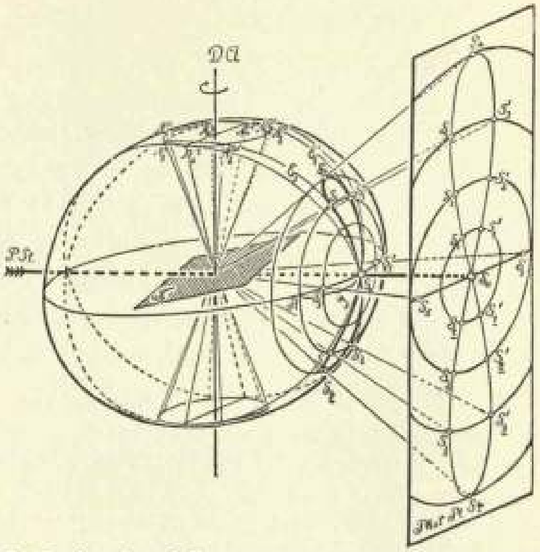

FIG. 18.—Explanation of the rotation spectrogram. After E. Schiebold.

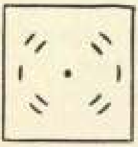

FIG. 19.—Reproduction of a Polanyi diagram.

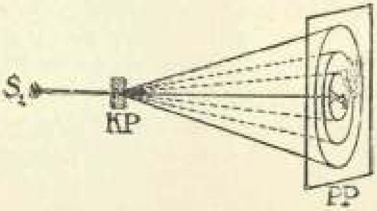

FIG. 20.—Reflexion cone of X-rays obtained with crystal powder.

renders the investigator independent of the possession of oriented plates or of crystals with any regularity at all.

reflexions will arise. Taking all the intersections into consideration, they lie on the curve similar to a lemniscate, shown in the figure. In general, of course, there are four reflected rays; in special positions of the reflecting planes, only two. Compare S_1 and S'_4, S_2 and S'_3, in Fig. 18, also Fig. 19.

These scientists employed powders of the finest crystalline particles, such as can be obtained by precipitation from solution or by continued pulverisation. In such a case the structure planes reflecting the X-rays lie at random in all directions. Those of them, however, which are inclined to the primary rays at the glancing angle α, satisfying the equation $n\lambda = 2r \sin \alpha$, give rise to a reflected ray; and since such positions occur all round the primary ray, a cone of rays is produced, as P. Debye and P. Scherrer showed, instead of the single reflected ray obtained in the Laue diagram. This effect is that which would be obtained if a Laue diagram were rotated about its central normal. Since monochromatic light is employed, the hollow cones of reflected rays obtained are thin, and cut the interposed photographic plate in separate circles (Fig. 20).

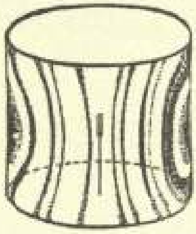

FIG. 21.—Camera for the Debye-Scherrer method.

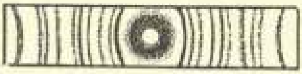

FIG. 22.—Unrolled film with Debye-Scherrer diagram.

In order to make the distance travelled by all the reflected rays to the receiving surface the same, and to facilitate photographic registration, a cylindrical camera, with the specimen as a small roll at its centre, is employed, following the suggestion of P. Debye and P. Scherrer. A film is placed round the inner wall of the camera; after exposure and photographic development this is unrolled, examined, and measured (Figs. 21 and 22). Independently of Debye and Scherrer, the American investigator Hull, has devised a similar method. W. H. Bragg has also combined the Debye-Scherrer with his spectrometric ionisation method.

With respect to the manipulation of the experimental results, the reader interested further is referred to the more detailed works on the subject.[1]

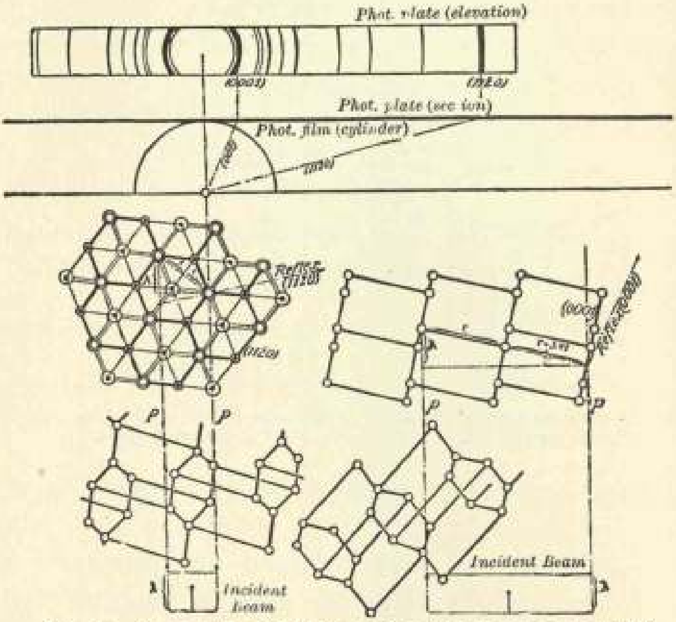

Fig. 23.—Construction of the Debye-Scherrer diagram of powdered graphite.

X-RAY RESULTS IN THE DOMAIN OF CHEMISTRY

The X-ray spectra of H. Moseley (1888-1915) provided chemistry with the natural series of the

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[1] W. H. and W. L. Bragg, "X-Rays and Crystal Structure." E. Marx, "Handbuch der Radiologie, Band 5 (Kathodenstrahlen und Röntgenstrahlen)." P. Niggli, "Geometrische Kristallographie des Diskontinuums." F. Rinne, "Einfuhrung in die Kristallographische Formenlehre sowie Anleitung zu Kristallographisch-optischen und röntgenographischen Untersuchungen," 5th edition, published by Dr. M. Jaenecke, Leipsic. Works by P. P. Ewald and E. Schiebold on X-rays and Crystals are in course of preparation.

DR. P. DEBYE
Professor of Physics in the University of
Zurich

P. Debye

DR. P. SCHERRER
Professor of Physics in the University of
Zurich

P. Scherrer.

elements according to their "atomic numbers," an arrangement to which there are no exceptions up to the present time. In L. Meyer's and D. J. Mendeléeff's "Natural System of the Elements," where they are set down in the order of increasing atomic weight, the arrangement being broken at certain points and so split up into series, there were several very awkward anomalies. Contrary to the guiding principle of the arrangement according to increasing weight, the properties of argon necessitated its being placed before potassium in spite of its higher atomic weight. For similar reasons cobalt came before nickel, and tellurium before iodine. This anomaly has now been removed. The spectrometric diffraction of X-rays, using crystal plates as gratings, with anticathodes of the various substances, proved that the elements are ordered by their X-ray spectra in complete accordance with the corrected Meyer-Mendeléeff table. The square root of the frequency of the spectral lines is a linear function of the atomic number in the system. Accurate determinations in particular by the Lund physicist, Manne Siegbahn, have definitely fixed this extremely important scientific result, "the atomic number," which constantly characterises the elements. In addition, these X-ray investigations rendered possible determinations of exact stereochemical formulæ by a physical method. W. H. and W. L. Bragg have led the way in this with remarkable ingenuity. They measured the r values of crystals, for example, of fluor-spar, for various directions, such as perpendicular to the cubic, rhombododecahedral and octahedral surfaces, and were able to conclude therefrom, with the help of the intensity relations of the appropriate spectra, the positions of the atoms. Later the fine-structural constitutions of rock-salt, fluor-spar, zinc-blende, diamond, calc-spar, and other important crystal types were elucidated, not only as regards general structure, but including the absolute magnitudes of their *r*-values.

Distinguished scientists, including P. Debye, P. Scherrer, P. Vegard, A. W. Hull, R. W. Wyckoff, and L. W. Mackeehan, carried on the investigation of such atomic point lattices.

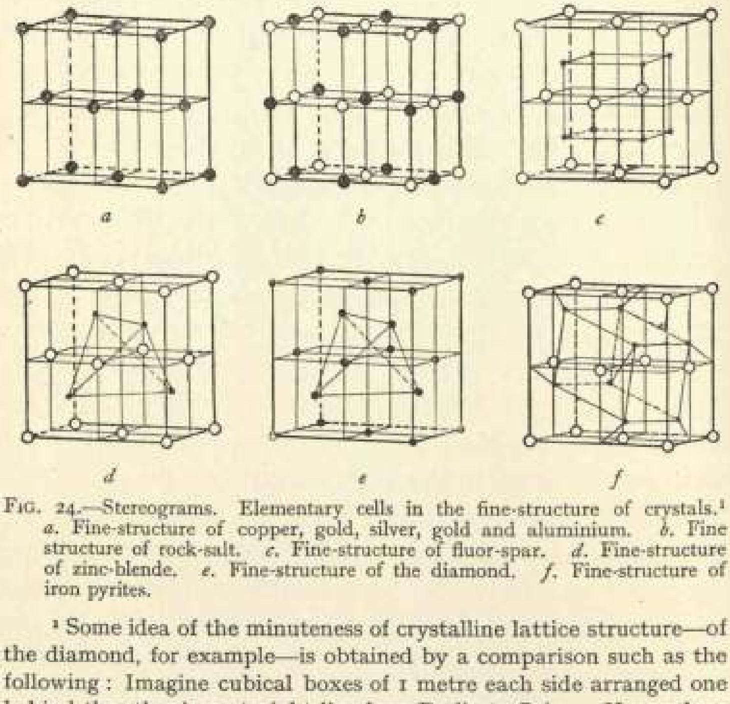

FIG. 24.—Stereograms. Elementary cells in the fine-structure of crystals.[1] *a*. Fine-structure of copper, gold, silver, gold and aluminium. *b*. Fine structure of rock-salt. *c*. Fine-structure of fluor-spar. *d*. Fine-structure of zinc-blende. *e*. Fine-structure of the diamond. *f*. Fine-structure of iron pyrites.

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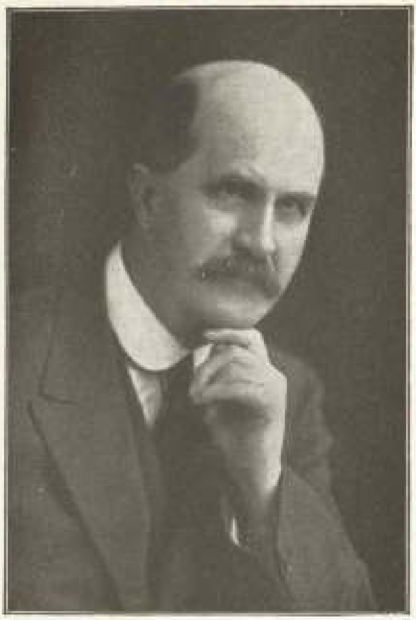
[1] Some idea of the minuteness of crystalline lattice structure—of the diamond, for example—is obtained by a comparison such as the following: Imagine cubical boxes of 1 metre each side arranged one behind the other in a straight line from Berlin to Cairo. Now reduce this enormous length of nearly 3000 kilometres to 1 millimetre; a measure of the actual size of the elementary cells is obtained in the proportionally reduced boxes. There are about 2,837,000 of these to the millimetre, and a similar number of carbon atoms lie on 1 millimetre of the edge of a diamond cube (Fig. 24*e*). In a cubic millimetre of the gem there are 178 trillion carbon atoms.

In considering the question further, it is noticed that in Fig. 24*a* the



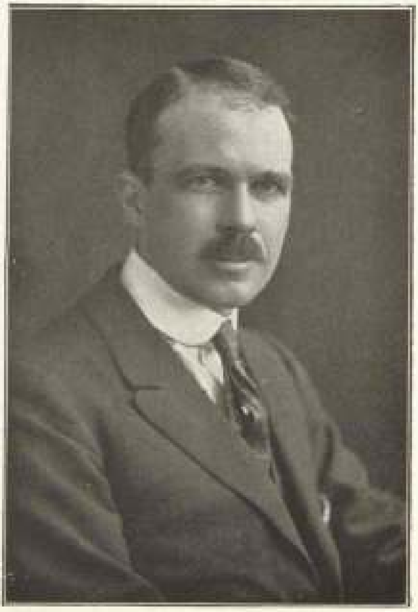
SIR WILLIAM HENRY BRAGG

Professor of Physics in the University of London

W H Bragg

WILLIAM LAWRENCE BRAGG

Professor of Physics in the University
of Manchester



W L Bragg

If, however, it were immediately assumed that already a comprehensive idea of the microcosm

copper atoms are to be thought of as being at the corners and at the centres of the sides of an elementary cube. Its length of side *a* is equal to $3{\cdot}61 \times 10^{-8}$ cm., i.e. 0·000,000,0361 cm.

For silver this length amounts to 4·06, for gold 4·07, and for aluminium 4·07, all multiplied by 10^{-8} cm. The sodium atoms in rock-salt NaCl are arranged in exactly similar fashion (Fig. 24*b*). The corresponding chlorine atoms occur at the mid-points of the edges and at the centre of the cube; $a = 5{\cdot}8 \times 10^{-8}$ cm. In Fig. 24*c* the calcium atoms of fluor-spar CaF_2 are placed in the same way as the copper and sodium atoms in Fig. 24*a* and *b* respectively. Now divide up the elementary cell into eight smaller cells by three planes, parallel to the sides and passing through the centre, and instal in each a fluorine atom. These atoms, owing to their positions at the centres of the cells, form a small cube inside the larger one; $a = 5{\cdot}44 \times 10^{-8}$.

For zinc-blende ZnS (Fig. 24*d*) the metal is arranged as in the previous types, and like fluor-spar, the cubic structure is divided into eight compartments; in this case only every other one contains a sulphur atom. The value of *a* for the zinc sulphide cube is $5{\cdot}4 \times 10^{-8}$ cm. The structure of the diamond (Fig. 24*e*) is obtained from that of zinc-blende, if both the zinc and sulphur atoms of the latter are replaced by carbon atoms; $a = 3{\cdot}53 \times 10^{-8}$ cm. Finally, iron pyrites FeS_2 (Fig. 24*f*) reproduces the earlier arrangements in the positions of the metallic atoms. Its sulphur particles set themselves on the diagonals of the eight smaller cells mentioned above, each one being about a quarter of the diagonal length from either the cube edge or the cube centre. Taken together the sulphur atoms form a rhombohedron, as Fig. 24*f* indicates. If the corners of this were moved along to the mid-points of the diagonals, the sulphur atoms would reproduce the arrangement of the fluorine atoms in fluor-spar CaF_2 (Fig. 24*c*); $a = 5{\cdot}37 \times 10^{-8}$ cm.

It is necessary that the joining lines shown in the figure should be constantly kept in view. Moreover, it must be remembered that each atom represented by a point is itself a kind of planetary system with central body and satellites.

Regarded in this way it is more than ever obvious that we have here a marvellous microcosmic system; the particles hover in the crystal space like stars in the heavens, all mutually supporting one another in their regular arrangement, which we have learnt to measure accurately to a ten-millionth of a millimetre.

of the crystalline world had been obtained, our jubilation would be premature. Only a comparatively small number of crystal stereochemical formulæ are available to-day, ten years after the first Laue research on the subject. This is to be attributed to the unsettled state of the times, and, in addition, to the indirect nature of the experiments.[1] Indirect methods must be used which, in complicated cases of atomic arrangement, are extremely difficult mathematically.

This applies especially to the case of the compounds of organic chemistry.[2]

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[1] The atomic world is not disclosed by the microscope. As E. Abbé showed, the microscope is, in a certain sense, blind to objects smaller than about ·0005 mm. (5×10^{-5} cm.). The wave length of light visible to the eye, or of light such as can be used in photography, is coarse compared with the fineness of the leptons. The atoms are a thousand times smaller (only about 10^{-8} cm.), and can therefore no more act on light waves, which are large in comparison, than a leaf can influence the waves on which it floats. The wave lengths of X-rays, however (10^{-8} to 10^{-9} cm.), correspond well with such minuteness.

A leptoscope using these fine waves has, however, not yet become possible, for no substance is known which would serve optically as a lens. We thus must rely on the original diffraction effect as in the case of the ultramicroscope with ordinary light. Probably at some time an image of the fine-structure will be obtained with X-rays by making use of the reflecting power of the structure planes in the crystal. M. Wolfke called attention to the possibility of separating in practice, as is done in theory, the formation of the image into the production of, first, a diffraction figure, and then, by further diffraction, the actual image. The production of the first diffraction figure would be assigned to the X-rays; it would be photographed and then transformed by repeated diffraction, using ordinary light, into the image of the sub-microscopic object. With regard to several restricting conditions, those interested might read the "Physikalische Zeitschrift," vol. xxi, p. 495, 1920. The suggestion has not, so far, matured sufficiently to give practical results.

[2] Recently W. H. Bragg, and also K. Becker and W. Jancke, have made some very welcome contributions to our knowledge of

CRYSTALS AS STEREOCHEMICAL TYPES

This being the case, it is obvious that, in the difficult work of establishing stereochemical formulæ, any external assistance is welcome. Crystal morphology makes its appearance in such a capacity. When carefully considered, this subject, in a certain sense, is merely macrostereochemistry. Of course, we must not conclude that a crystal is an enormous molecule similar to sub-microscopic molecules. That would be a false conception, being inconsistent with two actual properties of molecules, namely, constant form and constant weight. In this respect we may compare the scheme for the benzene ring with the protean multiplicity of calc-spar (Fig. 25), and the exclusiveness of the molecule with the capacity of the crystal to grow and so to increase its magnitude and weight. A crystal form, however, is definitely characterised as a stereochemical symbol in the sense that it is a visible, and therefore easily examined, sample of the leptonic structure Its

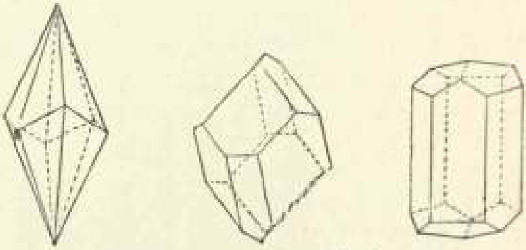

FIG. 25.—Variety of forms of calc-spar.

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such substances. The dimensions of the elementary cells, and the number of molecules in each, are now known for indigo, anthracene, urea, succinic acid, hydroquinone, anthraquinone, naphthalene, and many other organic compounds, although the precise positions of the atoms are still uncertain.

principal surfaces represent series of planes through the leptocosm occupied by a network of atoms, and Fig. 26 shows clearly that in this way surfaces with rational axial sections arise; for the planes densely packed with matter form stable boundaries. The principal edges of a crystal indicate the directions of rigidly set lines of atoms, and its morphological symmetry is symbolic of the arrangement of its fine-structure particles.

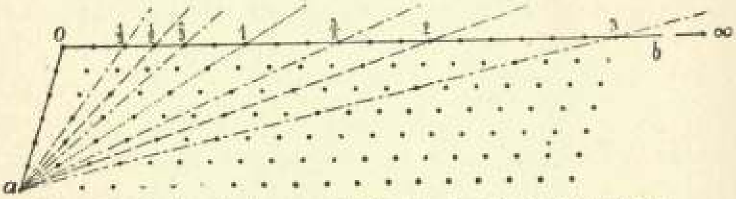


FIG. 26.—A plane in the space-lattice showing edges and surfaces.

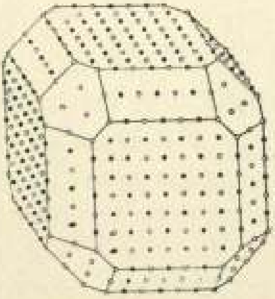


FIG. 27.—Rock-salt. Fine-structure of the crystal faces and edges. Circles represent Na, dots Cl.

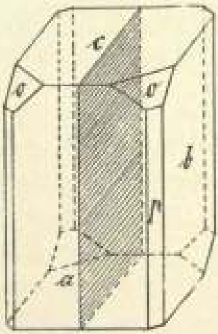
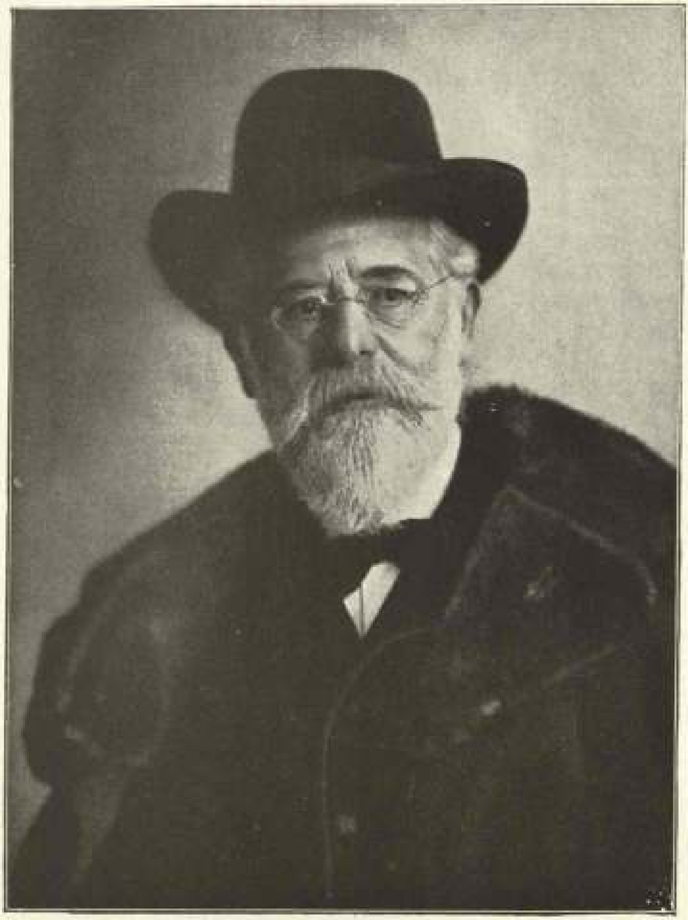


FIG. 28.—Mirror symmetry of pyroxene.

The explanatory Fig. 27, which represents the known fine-structure of rock-salt, enables this to be clearly understood. In this way substances not yet investigated will be in great part determined from their external forms alone, and thus macrostereo-



G. Tschermak

chemistry will play the part which was emphasised as early as the year 1903 by G. v. Tschermak.

In this sense Fig. 28, for example, gives us hints as to the structure of pyroxene, which is still unknown. Fig. 29, in the same way, provides definite indications as to the structure of that remarkable silicious material, quartz, for it exhibits in the crystal form, and therefore, we may assume, in its fine-structure (not yet experimentally investigated), not mirror, but only rotational symmetry, and serves as a macroscopic symbol of the famous conclusions of L. Pasteur concerning the "asymmetrical" molecule. In the crystal forms of quartz, actual right- and left-handed structures are visibly and clearly characterised, and the compensated racemic variety also exists; this is shown in certain twin formations in which right- and left-handed quartz are combined in regular fashion.[1]

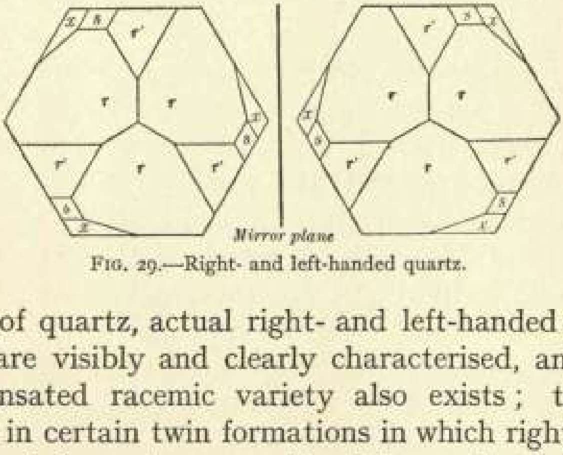


FIG. 29.—Right- and left-handed quartz.

In addition, the remarkable property possessed by most crystals of splitting along definite planes affords an indication of the arrangement of the particles; it may, of course, be assumed that the particles in the surface formed by a cleavage lie close to one another, each bound firmly to its neighbours. Perpendicular

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[1] This is illustrated by imagining the two forms of Fig. 29 displaced parallel into one another.

to the cleavage plane, as in a direction of weaker cohesion, greater distances prevail, and in consequence splitting along such planes is possible.

OUTLINES OF GENERAL CRYSTALLOGRAPHIC MORPHOLOGY

I. THE RELATIONS OF THE GROSS STRUCTURE

In the way indicated above, the study of crystal morphology arises as an introduction to the subject of stereochemistry of the solid state. It is, in this way, a part of chemistry. Every student of chemistry must, therefore, find himself immersed in a specialised subject at the outset. After a greatly changed cultivation of the crystallographic soil, much superfluous undergrowth of names and derivations having been rooted up and simple methods of development followed, the wanderer who picks his way carefully has no very special troubles to fear in this region ; indeed, it may be said that one is now able to go forth in this province, as in a well-tended garden, with artistic enjoyment.

As an example of such a guiding plan in the ornamentation of the inorganic world, so important in stereochemistry, the following scheme will be briefly developed.

The idea of deriving the multiplicity of crystallographic forms from five types all mutually connected, which may be called primitive forms, has already been brought forward by G. v. Tschermak, and followed in his teaching. The fundamental rules of crystallographic symmetry and, therefore, of crystal-structural types, are embodied in these primitive forms, for they are fundamental in the varied morphology of crystals, being exemplified by the so-called centre of symmetry, axes of symmetry, and symmetry planes. If the crystal structure possesses a centre of symmetry, to every boundary plane there belongs an equivalent parallel opposite surface, and thus lines through the centre of the crystal cut the external surface in two corresponding points. The symmetry axes indicate, in a certain sense, the rhythm in which similar structural particles grouped about a given direction repeat themselves in different positions; thus if, say, the axis is senary, as in a six-sided prism, then this will appear to an observer, after a rotation of 60° about the vertical, just as before. A symmetry plane divides a body into halves, which have the appearance of an object and its mirror image (Fig. 28, p. 26).

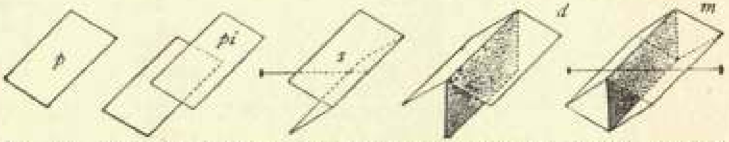


FIG. 30.—The five primitive forms of crystallography: pedion, pinacoid, sphenoid, doma, prisma.

The primitive form *p* (the pedion, Fig. 30) represents a surface standing alone, i.e. a form devoid of symmetry; *pi* (the pinacoid), with a surface and a similar parallel surface, is the embodiment of the principle of centre symmetry; *s* (the sphenoid), with one surface and another flap-like surface, represents the fundamental idea of rotation in binary rhythm; *d* (the doma) represents the principle of reflexion; and finally, *m* (the prisma), the combination $d + s$, $d + pi$, or $s + pi$, which all give the same *m*. From these five types, to some extent representative of five structural rules in the inorganic world, all the multiplicity of the remaining macro-stereochemistry may be derived by an application of the ideas of A. Schönflies as cases of rhythmical repetition of the primitive forms, according to the numbers 2, 3, 4, and 6, about a principal direction in the structure. Thus the ternary rhythm must appear in a whirl form and dominated by the octant (Fig. 31). It is fundamental that the rhythms may be developed in a simple (gyric) fashion, or by rotation and reflexion together (gyroidal) (Fig. 32). Nevertheless, this development is very convenient, as the combined procedure leads to only four new forms.

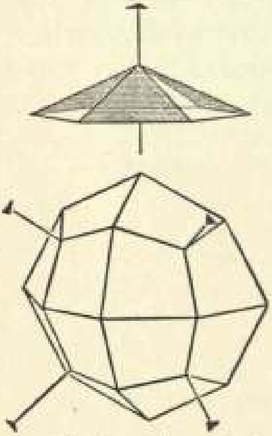


FIG. 31.—Simple and isometric (octant) whirl structure.

FIG. 32.—Gyric and gyroidal rhythms.

In the following table the thirty-two crystal classes are summarised as types of the crystallographic, and, therefore, stereochemical arrangements. These classes were known already in the time of J. Ch. F. Hessel (1831), and have all been discovered in crystalline materials, except in the case of $\underline{3p}$. They are to some extent the architectural styles in

TABLE OF THE THIRTY-TWO CRYSTAL CLASSES.

Structural Elements.	I. Gyric Development.					II. Gyroidal Development.	
	1. Pedial Element.	2. Pinacoidal Element.	3. Sphenoidal Element.	4. Domatic Element.	5. Prismatic Element.	1a. Pedial Element.	4a. Sphenoidal Element.
Primitive forms: Triclinic and monoclinic system . .	*p*	*pi*	*s*	*d*	*m*	—	—
Binary rhythm of the primitive forms: Rhombic system . .	$\boxed{2p}$	$\boxed{2pi}$	2*s*	2*d*	2*m*	—	—
Ternary rhythm of the primitive forms: Trigonal system . .	3*p*	3*pi*	3*s*	3*d*	3*m*	$\underline{3p}$	$\underline{3s}$
Tetrad rhythm of the primitive forms: Tetragonal system .	4*p*	4*pi*	4*s*	4*d*	4*m*	$\underline{4p}$	$\underline{4s}$
Senary rhythm of the primitive forms: Hexagonal system .	6*p*	6*pi*	6*s*	6*d*	6*m*	—	—
Ternary rhythm of the primitive forms with octants: Isometric system	*ip*	*ipi*	*is*	*id*	*im*	—	—

The rows are series of the same rhythm, the columns those of the same primitive forms. 2*p* and 2*pi*, being identical with *m* and *s*, are bracketed, and are only included in the table for the sake of completeness.

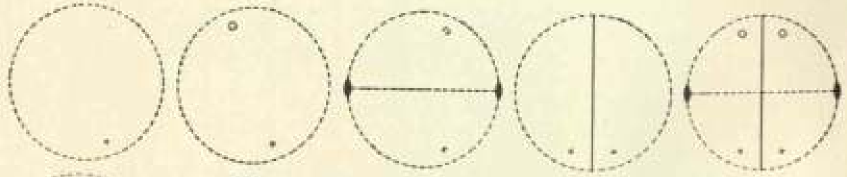
The symbols of the classes are to be read, for example, as three *p*, three *pi*, and so on; 3 bar *p*, 3 bar *s*, etc.: written out in full they are, say, for the ternary series, trigyric pedial, trigyric pinacoidal, trigyric sphenoidal, trigyric domatic, trigyric prismatic; sodium periodate, dolomite, quartz, tourmaline, calc-spar, are examples of these. The series is concluded with trigyroidal pedial (no example yet known) and trigyroidal sphenoidal (benitoite). For the isometric rhythm the development is characterised as isometric pedial, etc.

Further details in F. Rinne's "Einfuhrung in die Kristallographisch-optischen sowie röntgenographischen Untersuchungen," 4th edition, Leipsic; published by Dr. Jaenecke.

the crystal realm. A cursory examination of the table shows the simplicity of the relations running through it.

2. REPRODUCTION OF CRYSTALLOGRAPHIC FORMS IN PROJECTION

It is especially convenient in considering the matters treated above to turn from pictures of the crystallographic configurations in perspective and to symbolise the formal relations in projection. In Fig. 33 this is done for the primitive forms. To render the figure clear, it is noticed that an X in the diagram represents a surface in the upper portion of a crystal which has been cut in half by a horizontal plane; a circle represents an under surface. Such a "figurative point" in the centre of the projection denotes a surface parallel to the paper, whilst one on the circumference represents a plane perpendicular to the paper, meeting the circle in the point marked. Finally, the points between the centre and the circumference are symbols of surfaces placed obliquely.



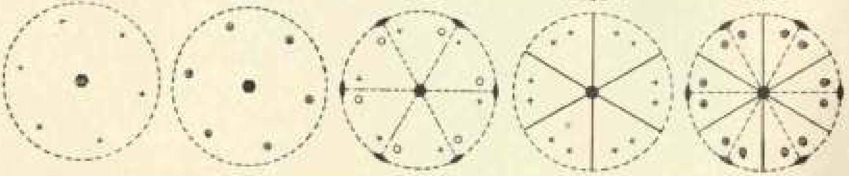


Fig. 33.—Projection diagrams of the five primitive forms of crystallography.
Fig. 34.—Projection diagrams of the senary rhythm of the primitive forms.

It is now easy to represent the effect of a rhythmic repetition of the five primitive forms in projection. In Fig. 34 this is done for a senary rhythm, using oblique surfaces as the general case. The result gives the five simple whirl elements of the hexagonal system. A development in accordance with the principle of rotation-with-reflexion gives nothing new in the hexagonal series. In a similar manner we obtain in the other systems general examples of the external crystallographic forms, and at the same time indications as to the arrangement of the particles in the fine-structure.

3. FINE-STRUCTURE RELATIONS OF GENERAL CRYSTALLOGRAPHIC MORPHOLOGY

For the purposes of leptology, this grouping in crystal classes is further subdivided into a large number of space groupings, thus completing the classification. As new variations of the symmetry elements, we have to consider the following: translation-with-rotation and translation-with-reflexion, that is to say, the resultant motions arising from rotation or reflexion, together with translation. The result in the former case is a screw form. Fig. 35*b* serves as an example of such a screw axis, and Fig. 35*d* shows a translation with reflexion.

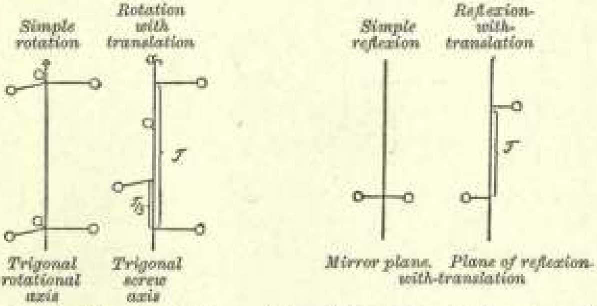


FIG. 35, *a-d*.—Simple rotation and translation-with-rotation (screw form). Simple reflexion and translation-with-reflexion.

For the rest, it is recognised as a result of the space-lattice principle, that for every crystal structure, considered from a stereochemical standpoint, all

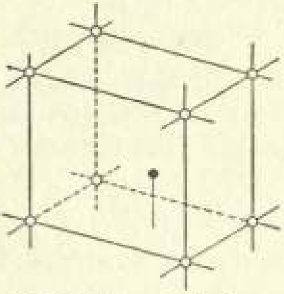


FIG. 36.—Asymmetric fine-structure.

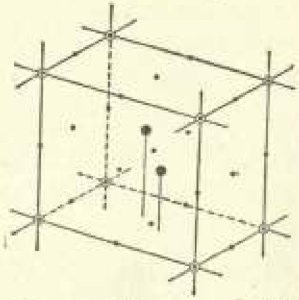


FIG. 37.—Fine-structure with symmetry centre.

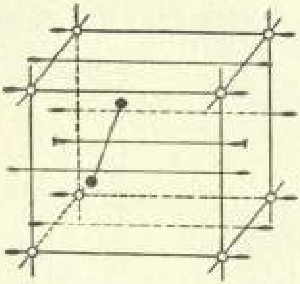


FIG. 38.—Fine-structure with binary arrangement.

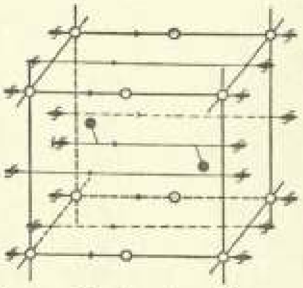


FIG. 39.—Fine-structure with arrangement on a binary screw axis.

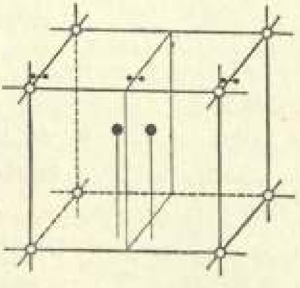


FIG. 40.—Fine-structure with reflexion.

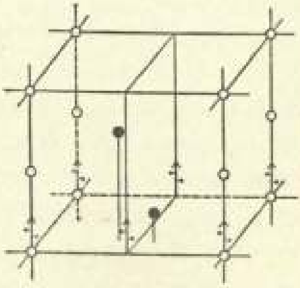


FIG. 41.—Fine-structure with translation-with-reflexion.

FIGS. 36-41.—Simple stereograms of crystallographic fine-structure.

the symmetry elements, and therefore all the fine-structural particles, occur in the crystal in periodic sequence, as Figs. 36-41 show for the simplest cases of crystal structure. In short, allowing for all the crystallographic possibilities, there are 230 types of crystallographic fine-structure, and consequently a similar number in the stereochemistry of the solid state. Every crystallographic substance is constituted according to one of these schemes of A. Schönflies and E. Fedorow, and its specific character in the material world is expressed in the absolute measure of the periodicity in the point system, and in the magnitude of its angles.

EXTENSION OF THE MANIFOLD OF CRYSTALLOGRAPHIC TYPES BY TWIN FORMATION

Reviewing the fine-structural relations, the thirty-two classes with their subdivisions into 230 space groupings present themselves as the embodiment of the principle of association. Each crystal unit is the model of a structural style containing certain elements of this aggregate. Taken together they constitute a complete system of forms based on Haüy's fundamental law (p. 8), a system to which mathematical thought has nothing to add.

It is thus a surprising thing to observe that nature in numberless cases pushes this principle of association still further, for she takes as unit the whole crystal and combines it in regular fashion with its like to give so-called twinnings. It was G. v. Tschermak again who pointed out the parallelism between form development from elements, such as the five primitive forms and this higher association into twins. If a certain crystal lacks a centre of symmetry, as, for example, the "hemimorphic succinic iodimide" shown in Fig. 42, this is occasionally remedied in nature by a regular growing together of two individuals. The complex (Fig. 43) is centre symmetrical. In the same way, twin formation with respect to a symmetry axis is accompanied by an increase in the symmetry. If, for example, a right-handed quartz (Fig. 44) exhibits the symmetry elements 3*s*, then its association, often occurring as an ingrowth with a left-handed quartz in a twinning, as in Fig. 46, is of the type 3*m*. Thus there is an increase in the symmetry from the sphenoidal *s* form to the prismatic *m* form (p. 31). On the other

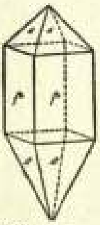


FIG. 42.—Hemimorphic crystal of succinic iodimide.

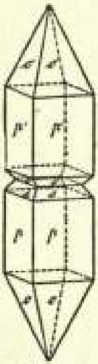


FIG. 43.—Centre symmetrical twin of succinic iodimide.

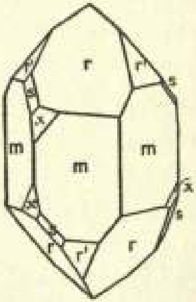


FIG. 44.—Right-handed quartz.

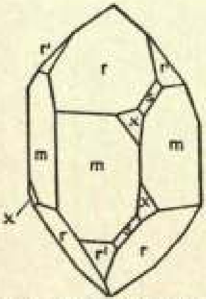


FIG. 45.—Left-handed quartz.

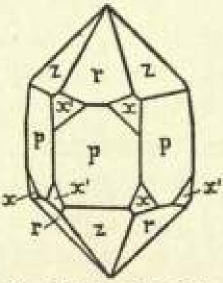


FIG. 46.—Right- and left-handed quartz, twinned.

hand, a regular twin formation of two right- or left-handed quartz crystals (Fig. 47) has the symmetry 6*s*. Such regular non-parallel combinations can be constructed by rotating one crystal with respect to the other about a fixed axis (in the example of Fig. 47, 60° about the whirl axis). A combination along a twinning plane *z*, after application of a rotation of 180° about the normal to *z*, acts similarly as illustrated by gypsum (Figs. 48 and 49).

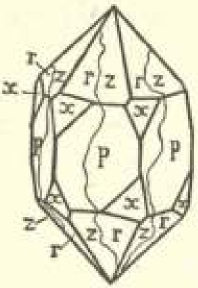


FIG. 47.—
Two left-handed quartz, twinned.

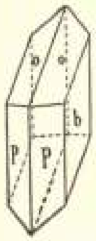


FIG. 48.—Gypsum.

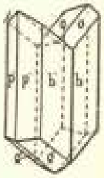


FIG. 49.—
Gypsum twinning.

The symmetry is thus augmented by a mirror plane, and the type 2*d* replaces that of *m*.

Such extraordinarily widespread phenomena in nature are certainly of considerable general significance. This consists primarily in the recognition that a visibly high symmetry may in reality represent an aggregation of parts of lower symmetry, even if in the limit the complexity is no longer recognisable by the eye owing to fineness of the parts. Actually there are many gradations of such mimesy from macroscopically definite twinnings (such as pseudo-hexagonal chrysoberyl) (Fig. 50) to the finest structures arising from "polysynthetic" repetition of very thin lamellæ, shown, for example, by microcline, the fineness of which verges on the sub-microscopic.

We may recognise, therefore, in twin formation an attempt towards higher symmetry than that possessed by the individual crystal; in addition, however, the relations also indicate that the twin grouping, in contrast to the ideal parallelism in the structure of a simple crystal, presents a less compact fitting-in of the particles with each other. The space-lattices of the parts of the twin do not pass continuously one into the other. In this respect it is of further interest that, according to the ideas of Ch. Friedel, fine-structural parallelopipeds, at least of higher orders, may be constructed which satisfy, or nearly so, the condition of parallelism. The diagram of Fig. 52 makes this clear.

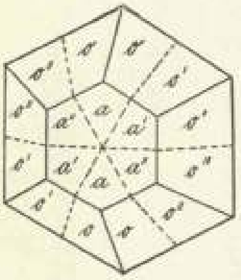


FIG. 50.—Chrysoberyl sextet as an example of mimesy

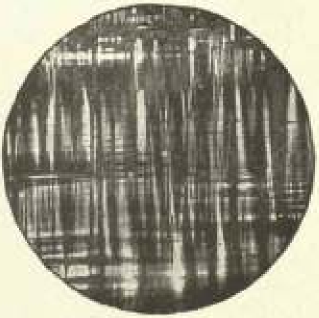


FIG. 51.—Fine twinning of microcline (micrograph)

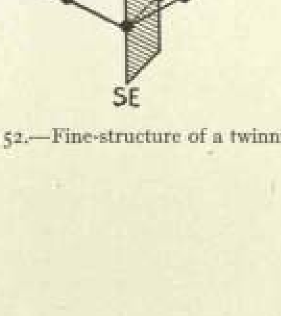
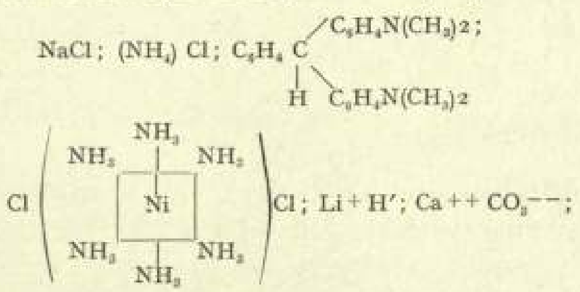


FIG. 52.—Fine-structure of a twinning

IV. FINE-STRUCTURAL UNITY OF MATTER

FINE-STRUCTURE OF AMORPHOUS BODIES COMPARED WITH THAT OF CRYSTALS

IT would be contrary to scientific principle if we were to leave the fine-structural relations of crystals, which have chiefly interested us up to now, without attempting to connect them up with general leptology which concerns the physicist and chemist, in their study of the numerous examples of amorphous bodies. Actually, crystals and amorphous bodies are very closely related regarding their fine-structure. The name of the latter class hardly accords with the facts of leptology. The ordinary chemical formulæ and ideas concerning the morphology of atoms of gases and liquids, indicate clearly a definite anisotropic structure. In this way, chemical formulæ, such as, for example,



$$NaCl;\ (NH_4)\,Cl;\ C_6H_5\,\underset{H}{\overset{|}{C}}\!\begin{array}{l}\nearrow C_6H_4N(CH_3)2;\\ \searrow C_6H_4N(CH_3)2\end{array}$$

$$Cl\left(\begin{array}{ccc} & NH_3 & \\ NH_3 & | & NH_3 \\ & Ni & \\ NH_3 & | & NH_3 \\ & NH_3 & \end{array}\right)Cl;\ Li^{+}H';\ Ca^{++}CO_3^{--};$$

and the diagrams of Fig. 53 represent fine-structural schemes. To F. M. Jaeger must be accorded the special merit of having first recognised and enlarged upon the symmetry relations of the individuals of amorphous bodies in his very fine work, "Lectures on the Principle of Symmetry" (1917). Figures such as 53, 54, and many others of atoms, ions, and molecules show, without further remark, a regularity in the form of the individual leptons, a regularity constantly referred to by chemist and physicist. Considerations of symmetry, whether it be total absence of symmetry, centre symmetry, rhythmic architecture in the sense of gyric or gyroidal repetition, or, finally, mirror symmetry, are of importance here as in crystals.

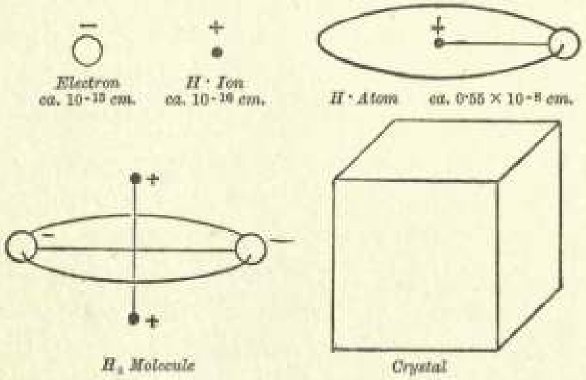


FIG. 53.—The leptonic series. Models of an electron, atom, ion, molecule, and a crystal.

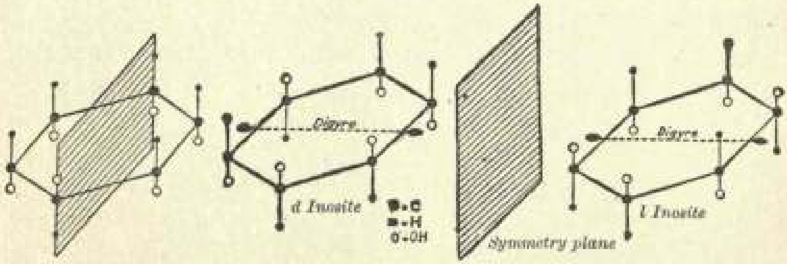


FIG. 54.—Examples of symmetrical molecules.

In fact, we may assert with P. Debye and P. Scherrer that, allowing for the difference of scale, as regards general structure there is no essential difference " between a crystal and a chemical molecule, for both have the characteristic property of containing atoms regularly arranged."

With respect to this intimate relationship, it may be added that between the leptonic forms of a liquid or gas from which crystals are separating and the crystals themselves there is a definite morphological connection. To each crystal type will belong certain characteristic preliminary forms occurring in crystallisation.

This fundamental and general relationship of the fine-structures of atoms, molecules, and crystals may also be applied to the arrangement of the negative electrons forming the external shell of the atom, which swarm of peripheral corpuscles gives to the atomic complex its " shape." We speak of the symmetry of atoms as of crystals, meaning by that the symmetry of the external electron arrangement. The tetrahedral form of a carbon atom, for example, is indicated by four electrons at the corner of a tetrahedron. Following A. Johnsen, we presuppose a minimum symmetry of the atom in crystallography, and this is determined by crystallographic symmetry relations. The minimum symmetry for a given kind of atom changes with the symmetry conditions prevailing at the place where the particle occurs in the fine-structure. The carbon atom of the diamond has to fulfil other symmetry relations than that of graphite. In consequence, the arrangement of the electrons in these two cases must be different. That this is so is shown distinctly by their different optical properties. Thus we may compare the transparency of the diamond, on the one hand, with the blackness of graphite, on the other. But even in the same crystal the electron arrangements of similar atoms may differ. In the diamond all the carbon atoms are identical; in graphite two varieties must be postulated to satisfy symmetry considerations. Recognising this, the mutual influence of different atoms and ions in the crystal is to be borne in mind, for their forms must depend on their neighbours for the time being. The action of a fluorine ion on the fine-structure of a neighbouring sodium ion is different from that of chlorine, bromine, or iodine ions, and these again are affected differently by the electron orbits of sodium potassium, rubidium, and caesium. Moreover, temperature itself must be recognised as a factor tending to determine the structure.

The electron arrangement in free atoms or molecules will not be essentially different from that in the crystal. Indeed, recently the physicists M. Born, H. Landé, and others, following crystallography, speak of cubic and other polyhedral atoms. The diagrams in Figs. 55-57 are drawn in accordance with this general idea. In particular, the known periodicity of the series of the elements with respect to the number eight, suggests as a probable distribution a surface-centred octahedral arrangement for elements with eight external electrons. By increasing the volume, that is, by adding further electron shells for the elements of higher atomic number, other stable arrangements, partly of a crystallographic nature, but approximating to an isotropic distribution, will arise; such configurations are treated in detail in a recent treatise by H. Tertsch.[1] Finally, the electron swarm becomes less stable as

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[1] Compare p. 84 and p. 181.

the charge on the nucleus is increased, so that the series of possible elements on our earth ends with uranium, a spontaneously disintegrating atom with ninety-two external electrons.

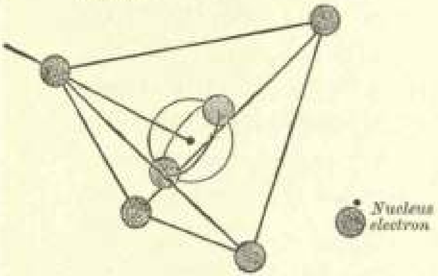

Fig. 55.

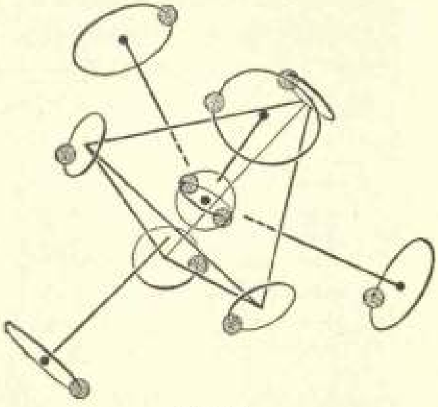

Fig. 56.

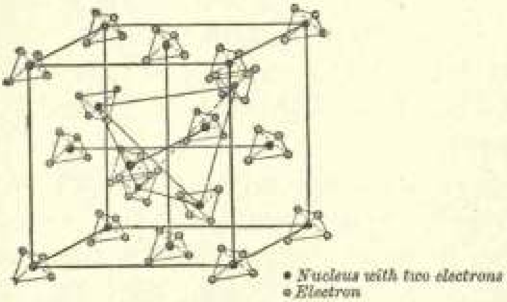

Fig. 57.

Figs. 55-57.—Schemes for electron groupings in atoms, molecules, and crystals. Examples: carbon atom, methane molecule, diamond.

PHYSICAL INVESTIGATIONS ON THE GENERAL FORMS OF ATOMS AND MOLECULES

Fitting in with our ideas on the analogy between crystals and individual leptons, a similar correspondence in the behaviour of crystalline and amorphous substances of the same chemical composition is shown in certain physical processes. We find that the curves obtained by Cl. Schaefer and M. Schubert for the reflexion of short ultra-red waves by quartz and opal completely correspond, a clear indication of the fine-structural similarity of the SiO_2 particles, in spite of the difference in the gross forms, quartz showing the characteristic space-lattice structure lacking in the opal. In their action on X-rays, too, amorphous and crystalline materials behave in much the same general fashion. An extremely fine crystal powder approximates for this purpose to the amorphous material with which the complete crystal is thus linked up through intermediate forms. According to Debye and Scherrer, the subdivision in soot actually extends to complexes of only thirty atoms of carbon; but these still give the normal X-ray effect of crystals.

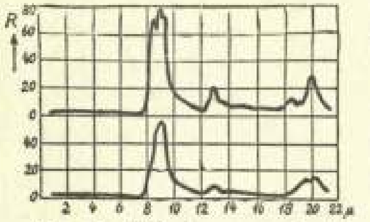

Fig. 58.—Reflexion curves in the ultra-red for quartz and opal. After Cl. Schaefer and M. Schubert.

With amorphous substances circular shadings round the point of impact of the primary ray are obtained, although, on account of the small number of components in the kinetic unit, the considerable internal heat motions, and the irregular state of aggregation[1] of the particles, only one or two weak and diffuse rings appear on the plate. It seems to me, however, that all this points to a definite regular form of the particle. Fig. 59 illustrates the production of such an effect, exaggerated for the sake of clearness, with the imaginary case of a molecule with cubic arrangements of its atoms.[2]

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[1] Also occasionally, as in glass, owing to the interaction of the different types of molecules.

[2] For readers interested in crystallography, diagrammatic derivations of the lines in the Debye-Scherrer diagram are shown in Fig. 59.

NOTE.—The conception of colloidal matter is not synonymous with that of amorphous substances. Its characteristic is a medley of particles of magnitude 10^{-6} to 10^{-7} cm., which thus lie between leptonic dimensions (about 10^{-8} cm.) and microscopic visbility (about 10^{-5} cm.); they may be either crystalline or amorphous. The colloidal solutions of gold and silver, for example, previously regarded as amorphous, show, according to P. Scherrer,

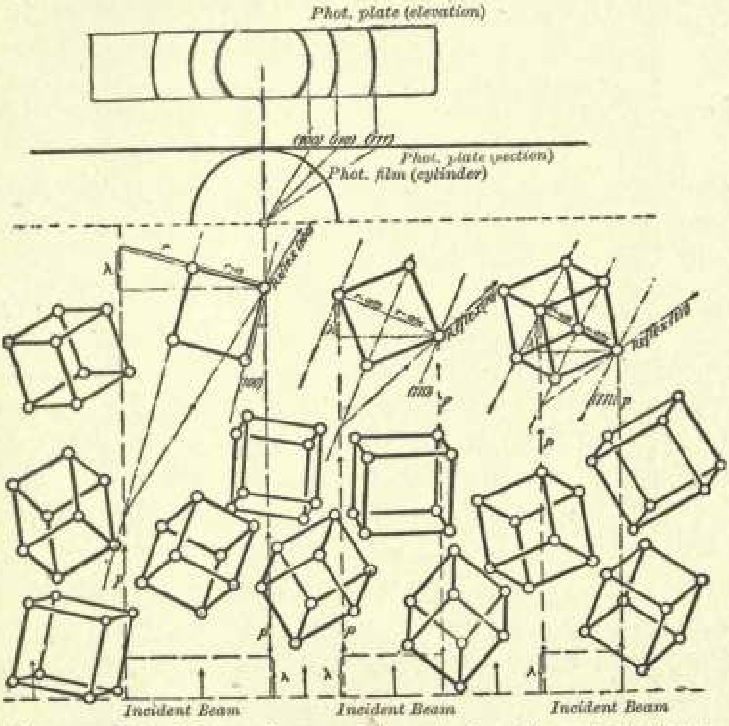

FIG. 59.—Debye-Scherrer diagram. Example of a cubic molecule shown schematically.

obtained from the principal structure planes in the imaginary cube molecule. These are obtained by applying the principle of reflexion, but it must be remembered that the fundamental phenomenon is one of diffraction.

the typical phenomena of crystalline materials (Fig. 60, upper diagram). Silica gel also gives a crystal effect, but at the same time acts an amorphous substance (Fig. 60, lower diagram). In this preparation we have to deal with an amorphous gel containing small SiO_2 crystals disseminated in it.

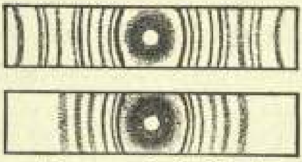

FIG. 60.—Debye-Scherrer diagrams of colloidal silver and silica gel. After P. Scherrer.

ATOMIC DOMAINS

Stereograms of crystals, such as that of Fig. 61, which shows the elementary cell of metallic sodium in representing the atoms as mere points, give no indications as to their solidarity.[1] It is possible, however, to endow such symbols of the crystal structure with a dynamical basis, and, in fact, this is done by describing about each atom a domain, to represent a portion of space which it claims for itself and keeps free from other atoms. Under the action of attractive and repulsive forces the atoms in the structure mutually maintain each other in an equilibrium arrangement, which is characterised in the close packing of these atom domains, which are to the first approximation spherical. The radius of the domain is given simply as half the least distance between the atoms in a stereogram similar, say, to Fig. 61. Thus Fig. 62 shows the domain picture for the sodium of the previous stereogram.

In this case the radius of the domain of each atom

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[1] In the scheme for diamond (p. 43) this is indicated.

amounts to $1{\cdot}86 \times 10^{-8}$ cm. Passing from one material to another as from sodium to sodium chloride (Fig. 63), thus comparing simple substances with compounds, we arrive finally at a table of magnitudes for the atomic domains, a table obtained by W. L. Bragg, who first carried out systematic experiments on these lines.

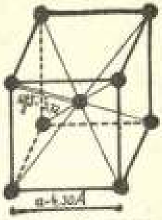


FIG. 61.—Stereogram of sodium crystal.

P. Niggli has given a similar scheme. Further applications in crystallography are due to G. Aminoff, and the author has also expressed his views on these very promising relations, both in his lectures and in occasional publications. Some new determinations may here be put before the reader for his guidance (compare also p. 107).

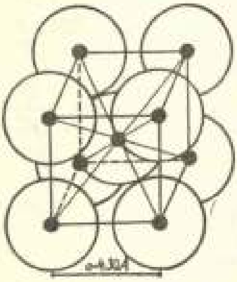


FIG. 62.—Atom domains in stereogram of sodium crystal.

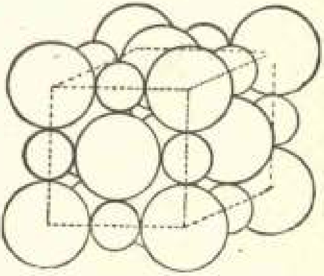


FIG. 63.—Atom domains in stereogram of rock-salt.

Diameters of crystallographic atom domains in 10^{-8} cm. units :—

Li^+	3·00	Mg^{++}	2·99	F^-	1·17	O	1·26
Na^+	3·51	Ca^{++}	3·51	Cl^-	2·12	S	2·00
K^+	4·15	Sr^{++}	3·96	Br^-	2·45	N	1·30
Rb^+	4·47	Ba^{++}	4·36	I^-	2·93	C	1·56
Cs^+	5·04						

That the atomic domain depends on the nature of the surrounding atoms and the electric charge, has already been emphasised by K. Fajans, H. Grimm, and W. L. Bragg. The alkali metals, for example, show somewhat larger values than their salt ions tabulated above. We have, in fact, Li, 3·02; Na, 3·72; K, 4·59; Rb, 4·94; Cs, 5·37.

The transference of these numbers obtained in the case of the crystal to the individual leptons, is a procedure in perfect accord with the views adopted in this book. In accordance with the considerations on p. 39 et seq., the chance of error is not so great as might at first appear. An investigation of this point is contained in the Figs. 64 and 65, and the values given agree very well with those arrived at from determinations of the mean free paths of the molecules.

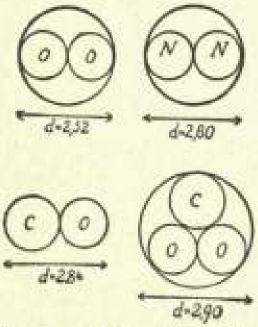


FIG. 64.—Molecular domains of O_2; N_2; CO; CO_2.

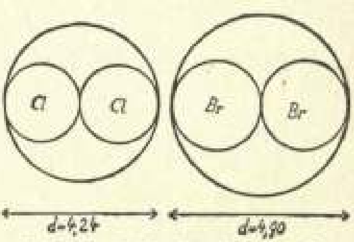


FIG. 65.—Molecular domains of Cl_2; Br_2.

Crystallographic Data.		Molecular Diameter.	
		Landolt and Börnstein's Tables.	Nernst. Theoretical Chemistry.
O_2	2·52 . 10^{-8} cm.	2·60 10^{-8} cm.	2·90 . 10^{-8} cm.
N_2	2·60 . 10^{-8} cm.	2·80 . 10^{-8} cm.	3·0 . 10^{-8} cm.
CO_2	2·90 . 10^{-8} cm.	2·9 . 10^{-8} cm.	2·9 . 10^{-8} cm.
Cl_2	4·24 . 10^{-8} cm.	4·8 . 10^{-8} cm	4·3 . 10^{-8} cm.

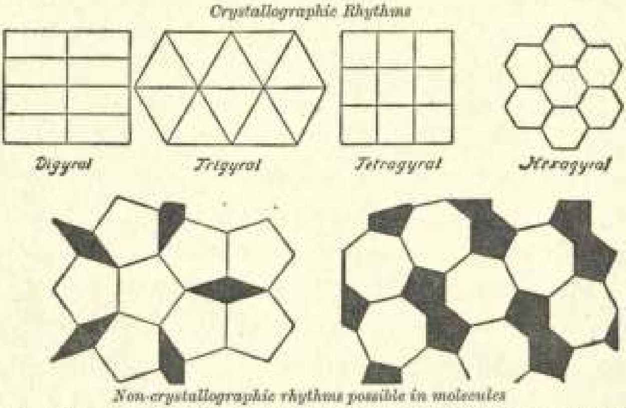
The mathematical treatment of the question leads to the most difficult branch of mathematics, the problem of several bodies. For a long time, however, approximations must suffice. Nevertheless, thanks to the efforts of M. Born, A. Landé, K. Fajans, F. Madelung, H. Thirring, and others, methods of approach to the end in view have been laid down, e.g. with respect to the attractive and repulsive action of the ions. The attraction here is put inversely as the square of the distance apart of the ion centres, whilst the potential of the repulsive forces (corresponding for the alkali halides to the compressibility of the crystal) involves a higher (5-9) power of the distance. This will naturally depend on the size and nature of the particles, and in view of the anisotropy of the sphere of action, may vary with direction.

Although the working out of exact mathematical theories of the fine-structure of matter must be left to the future, a glance at the spacial crystal schemes at once suggests the diagnosis and interpretation of many peculiar properties of substances.

DIFFERENCE BETWEEN THE STRUCTURE OF INDIVIDUAL LEPTONS AND CRYSTALS

The chief difference in the construction of crystalline bodies and the individuals of amorphous substances lies in the restriction of the rhythm. In the fine-structure of crystals, owing to the fact that each structural unit is joined to its neighbours, this rhythm exhibits a three-dimensional periodicity. Such space-lattice structure is clearly only possible when the repetition is according to the numbers 2, 3, 4, and 6, or with no repetition at all. Pentad, septad, and compound axes of higher period are here theoretically excluded, nor are they found in practice.

A boundary surface not containing rifts or gaps is known to be impossible with such polyhedra (Fig. 66)[1] We thus have here the essential principle in the restriction of the crystalline forms to the thirty-two classes of page 31, and thus to 230 space groupings.


Crystallographic Rhythms

Non-crystallographic rhythms possible in molecules

FIG. 66.—Diagrams showing crystallographic and two non-crystallographic rhythms (pentad and septad).

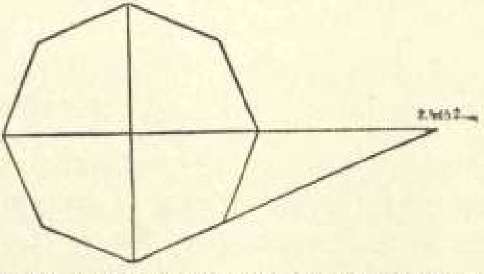


FIG. 67.—Irrational axial section for eight-fold rhythm.

Further, this fine-structural limitation is in agreement with Haüy's crystallographic law of simple rational axial sections. A crystal rhythm corresponding to the number 8 (Fig. 67), cannot arise, for such a

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[1] E. A. Wülfing has already pointed out the importance of this fact in crystallography.

regular octagon would give an axial section of 2·4142 . . . Similar relations hold good when repetition occurs according to any number other than 2, 3, 4, or 6, from which it also follows that of the "regular" polyhedra of mathematics, the cube, tetrahedron, octahedron, and icosahedron, only the first three are represented in the inorganic realm of nature. The Figs. 68, 70-72 should show the reader that the first three fall within the above restriction in the rhythmic arrangement of their surfaces, whilst the icosahedron, the non-crystallographic five-fold repetition of which is clearly shown in Fig. 72, does not. Such inadmissible rhythms are absent from the macroscopic crystal form, and also from the fine-structure. With regard to the latter, the Laue diagrams are unimpeachable witnesses (Fig. 73); in the structure of free atoms and molecules, both crystallographic and non-crystallographic rhythms may equally well occur.

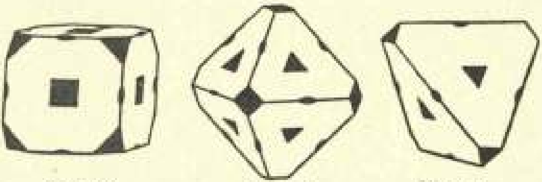

Fig. 68. Fig. 70. Fig. 71.

Figs. 68, 70, 71.—The mathematical regular polyhedra of crystallography.

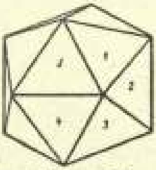

Fig. 72.—The non-crystallographic regular icosahedron.

Note.—Fig. 69, which appeared erroneously in the original, has been deleted.

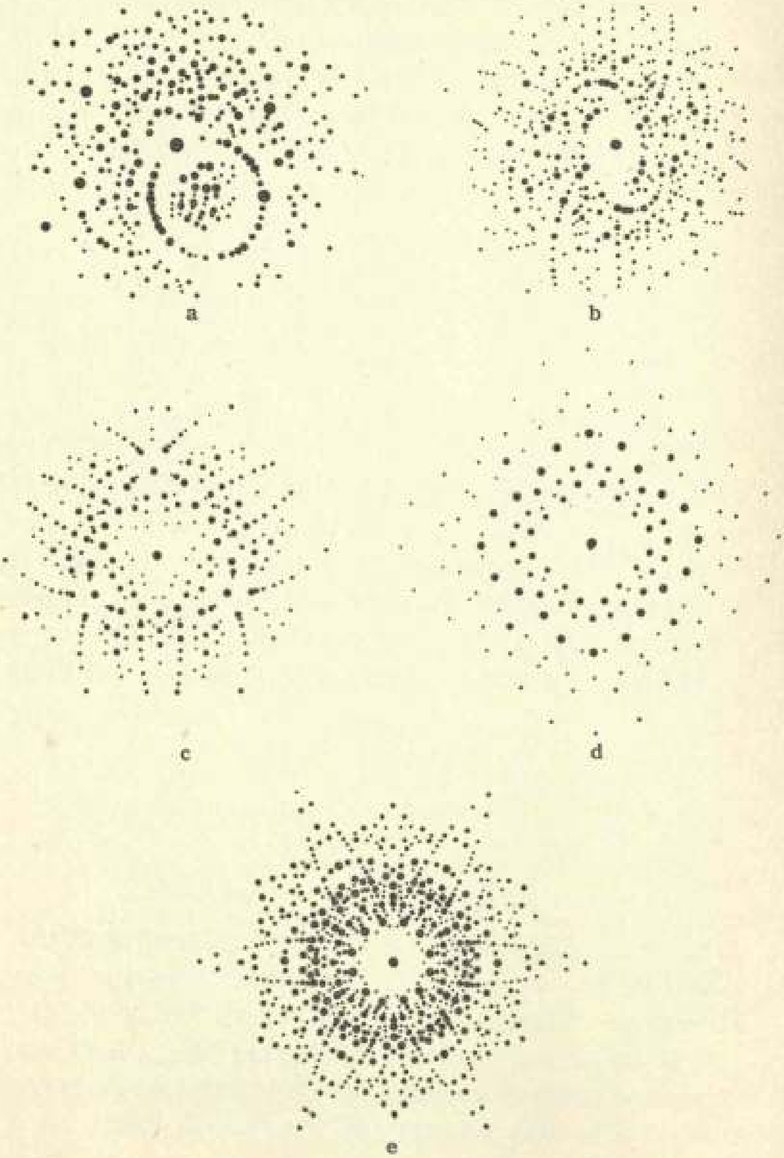

FIG. 73.—Laue diagrams with repetition according to the numbers 1, 2, 3, 4, and 6. After photographs by F. Rinne. a. Cyanite. b. Sanidine. c. Calc-spar. d. Rock-salt. e. Beryl.

DIAGRAMS

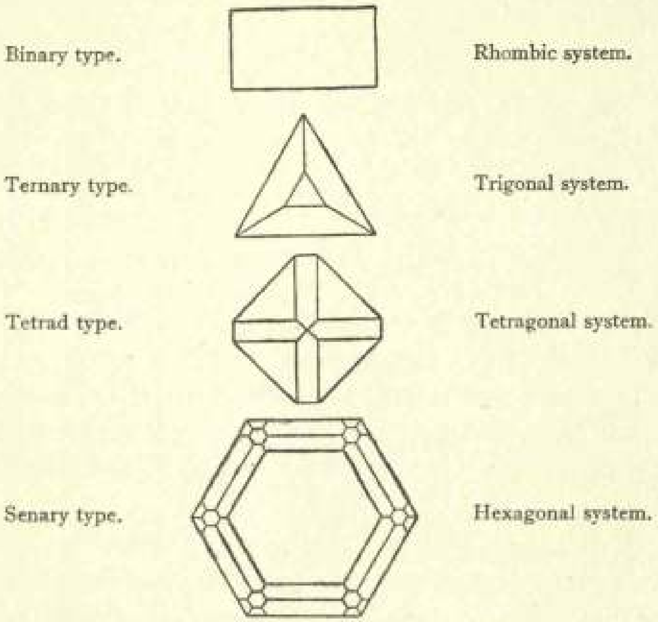

FIG. 74.—Whirl forms of the crystal types deduced from the primitive forms.

V. THE GENERAL CHARACTERISTICS OF THE FINE-STRUCTURE OF MATTER

FINE-STRUCTURAL CHARACTER OF CRYSTALS

IF, as we have emphasised, the difference in the architectural rhythms of the structures of individual leptons and crystals is merely a matter of detail, then the question arises as to what constitutes the prevailing characteristic in the fine-structure of all substances.

Taking crystals as types, we find that they exhibit very definitely two peculiar qualities—firstly, change of properties with direction (anisotropy); and, secondly, stability (isostasy).

A. CHANGE OF PROPERTIES WITH DIRECTION IN CRYSTALS

This anisotropy makes its appearance in the morphology of the crystal, in the regular arrangement of the external faces. Rock-salt, for example, may develop in a certain direction a surface, say, that of the cube; and this development repeats itself in a definite series of isolated directions, to which the edges and angles of the structure conform.

The diamond is provided with an octahedral form in a similar way. As to the fine-structure, Figs. 75-78 represent with remarkable clearness the various modes of formation of certain principal surfaces of the minerals, showing the anisotropy of the structure.

The change of physical properties with direction is very obvious in crystals showing cleavage. Thus for rock-salt there are three directions, perpendicular to the cube surfaces, in which the cohesion of the crystal is a minimum. The resistance to splitting in these directions is only one-third of that in the direction of the cube diagonal. The cleavage planes are, therefore, regularly oriented surfaces of maximum brittleness. In like manner, many crystals show particular planes of maximum plasticity. These are surfaces in which internal displacements may easily occur; with ice they arise as planes parallel to the surface of the ice floe. Hardness is also a directional property in crystalline materials. The resistance to disrupture, which shows itself as hardness, is often different in different directions of the crystal; thus it is a familiar fact to diamond workers that the cube surfaces of the gem are more difficult to prepare by polishing than the octahedron surfaces. Garnet, too, is harder on the cube surfaces than on the octahedron and rhombic dodecahedron, according to the researches of P. J. Holmquist on polishing. Even on the same surface of a crystal the hardness,

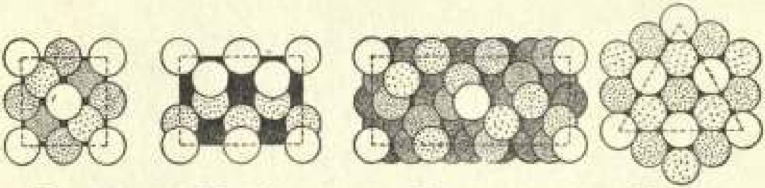

Fig. 75. Fig. 76. Fig. 77. Fig. 78.

Figs. 75-78.—Structure of the diamond parallel to surfaces of the cube, rhombic dodecahedron, pyramidal cube, and octahedron.

as measured by scratching, varies with the orientation of the scratch made by the test needle. Cyanite is a classical example of this.

Further, demonstrations of this change of properties with direction are given, often very strikingly, by optical tests. On passing ordinary daylight through the mineral cordierite such extremes as these arise in the absorption of light; a preparation in a certain direction appears dark blue; that in another direction, yellow; and in a third, grey. Moreover, the customary idea of constant wave length as a measure of the velocity of propagation of the light fails for all non-isometric crystals. For such substances the value of λ for a given colour changes with the direction of the light, and wave length curves can be drawn showing the variation diagrammatically.

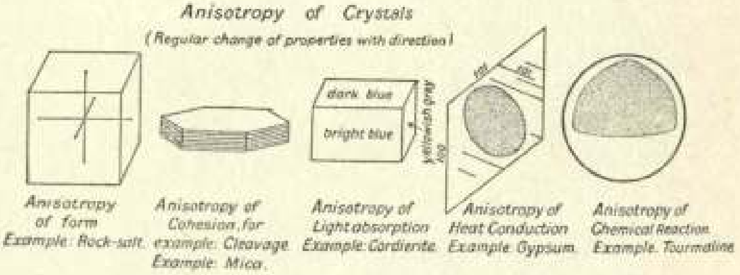

FIG. 79.—Demonstrations of the anisotropy of crystals.

Variation of thermal properties with direction may also, in many crystals, be very clearly demonstrated. Fig. 79*d* indicates the heat conduction in a cleaved plate of gypsum. A thin layer of wax has been deposited on the gypsum plate, and the preparation heated from a central point with a hot wire.

The wax is melted to various extents in different directions corresponding to the heat conduction in gypsum ; the perimeter of the figure formed by the melted wax is indicative of the heat conduction in the crystal beneath.

Even in chemical actions a definite change of properties of materials with direction is unmistakable. Thus, for calc-spar, varying intensity in the reaction $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$ is clearly shown by the different amounts of CO_2 liberated under the same conditions from the different faces of the mineral. Hence resistance of calc-spar to attack by hydrochloric acid varies with direction. The differences which arise are surprisingly large. According to O. Mügge, quartz is attacked by fluoric acid 150 times more easily in the direction of the whirl axis than in the direction perpendicular thereto.

It is of considerable significance that in crystalline materials " simple vectorial " directional differences can occur. The tetrahedron is a morphological example of this ; it lacks a centre of symmetry.

A chemical example is depicted in Fig. 79*e*. The diagram represents a tourmaline sphere which has been transformed by caustic potash to a bee-hive shaped body, a clear indication that the chemical reaction between the silicate and its corrodent occurs much more rapidly in the direction from below to above than from above to below.

It is, therefore, a characteristic of crystalline materials evidenced by numerous experiments of morphological, physical, and chemical nature that they exhibit different properties in different directions.

Corresponding to this the sphere of action of crystals is also anisotropic, as growth phenomena in particular show. A crystalline sphere grows to a body with edges, corners, and plane faces.

B. STABILITY OF CRYSTALS

Associated with the characteristic of anisotropy in the crystal is the second general property, internal equilibrium or isostasy; the whole constitution of the crystal as a stable form exemplifies this. A. Nold has especially taken this into account in his work on the crystal structure of the diamond. However, in the fine-structure of crystals the question is one of dynamical equilibrium, that is to say, kinetic stability or isodynamostasy.[1]

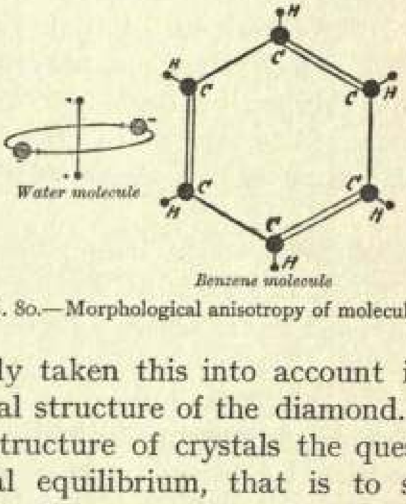

FIG. 80.—Morphological anisotropy of molecules.

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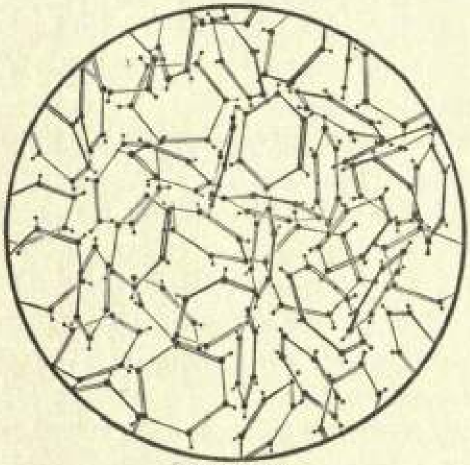
[1] As a parallel to this, there is the isostasy of geology, from which science the name isostasy is here borrowed. The earth, however, is not in isostatic, but in isodynamic equilibrium. Its rotation involves equatorial bulging, and as a result of this there arise fissures tending to prevent such an adjustment; these, as the boundaries of continents, and rifts within them, run from north-east to south-west, south-east to north-west, and meridionally.

FINE-STRUCTURAL CHARACTER OF GASES AND LIQUIDS

The general characteristics in the construction of the individual leptons (electrons, ions, atoms, and molecules) cannot be different. The graphical schemes and formulæ given for the structure of atoms and molecules indicate morphological anisotropy; but their morphological, as well as their chemical and physical anisotropy, will be entirely obscured by the irregular arrangement of the particles and will thus be transformed into an isotropy by averaging. Morphologically, this is illustrated by the spherical form of free gases (e.g. the earth's atmosphere) and in the drop shape of liquids. The general stereophysical conception of the electrons, atoms, and molecules as kinetic units at once indicates their isodynamostatic character.



Benzene drop

FIG. 81.—Pseudoisotropy of an aggregate of molecules (benzene drop).

GENERAL CHARACTER OF THE FINE-STRUCTURE OF MATTER

According to the above, the fine-structural arrangements of every substance represent anisotropic stability forms.

Their structure will be conditioned by attracting and repelling forces. The particular arrangement of the particles of an aggregate is always the result of a complex action of all its particles on one another; it is not characterised by some kind of linear or curvilinear force threads.

In addition, the aggregation units, whether atoms, ions, molecules, or crystals, also act on each other when in close proximity. There arises, besides the endoleptonic field of force effective in the individual structures, an interstitial field depending on the reciprocal relations of the component substances, and which, therefore, is not constant for each type of atom, but is a function of the nature and arrangement of the neighbouring ones. What is observed in chemical processes is a consequence of this interaction, whether it be a change in arrangement, association of previously separated similar or dissimilar particles to higher units, disruption or substitution, or whether the action be partly more physical or definitely chemical. The setting up of a physical field, a change of temperature in particular, or a change of pressure, may initiate similar processes or modify them. In other words, all physical and chemical actions of substances proceed in accordance with these ideas.

VI. THE SERIES OF TRANSFORMATIONS OF MATTER

GASES, LIQUIDS, LIQUID CRYSTALS, CRYSTALS

THE broadest survey of the general physical relations of fine-structural aggregates under the influence of attractive and repulsive forces anisotropically directed, is afforded by a consideration of the changes of state which all substances pass through when their physical conditions are altered. By changing the temperature of a substance, that is, by speeding-up or retarding the motions of its fine-structural particles, it is possible, as is well known, to pass the substance through a long series of metamorphoses extending through the gaseous, liquid, and solid crystalline states. Thus H_2O, for example, traverses the states, water vapour ⇄ liquid ⇄ ice, and on the basis of the mechanical theory of heat, we are in a position to form a very clear picture of these changes.

In the gaseous state there is very considerable leptonic unrest. With individual motions of the velocity of a bullet the particles speed hither and thither, although only travelling minute distances in straight paths; colliding, rebounding, thrusting aside, each molecule wins for itself a portion of space the size of which is the same for all gases. That the same number of material particles of any type take up the same space is the essence of Avogadro's

Hypothesis. J. Loschmidt (1865) was able, in furtherance of this hypothesis, to estimate the number of particles per c.c. At 0° C. and one atmosphere pressure there are 27·6 trillion; truly a dense population of space, although, however, it should again be emphasised that from particle to particle a space of average dimensions thirty to forty times the size of one particle must be assumed. The inter-connection of the individual atoms or molecules by force fields is therefore very slight in gases; the resistance to mechanical subdivision of masses of gas, in a certain sense the hardness, is correspondingly small. Moreover, the disperseness depends on the pressure in accordance with Mariotte's law, and on the temperature, an alteration of 1° C. involving a change in volume of $\frac{1}{273}$ for any gas whatever. A permanent arrangement of the particles, say about some instantaneous centre of their motion, is prevented by their rapid movement and diffuse distribution, for they roam about passing from one place to another by irregular diffusion.

In liquids, on account of the smaller distances of the particles, a field loosely binding the molecules is present, as well as the endoleptonic forces, and with this comes increased resistance of the mass to subdivision, as the viscosity indicates. Indeed, internal friction may often increase to considerable hardness, as, for example, in glass, which is to be regarded in a physical chemical sense as a "rigid liquid." Silica glass in its cohesion stands only a little way behind quartz. For all liquids, the hardness varies with the temperature. Warm water flows through a funnel much faster than cold, owing to there being a large diminution of the internal cohesion of the particles, while glass on heating approximates to an ordinary liquid.

In general, a permanent arrangement of the particles does not arise in liquids. The case is different for the so-called liquid crystals of O. Lehmann. There the molecules arrange themselves in the interstitial field of force more or less regularly oriented with respect to each other, very often with one direction parallel, so that the anisotropy inherent in each one is shown by the single optical axis (as in a crystal with a simple whirl axis). Three-dimensional periodicity of arrangement, however, is lacking in this microcosm. Thus Huckel, on investigating such substances with X-rays by the Debye-Scherrer method, did not obtain crystal diffraction patterns. On the contrary, there appeared only the indistinct interference ring shown by amorphous bodies.[1] These so-called liquid crystals are not then strictly crystals, but rather intermediate stages to true crystals, and as such " penecrystals," as one might call them, they are of very great interest in science. Their discovery and preparation by O. Lehmann and D. Vorländer, in particular, is one of the finest achievements of science.

Still further connections and transitional stages between the structures of individual leptons and typical crystals would possibly, if not probably, be established if large molecules containing many atoms, such as those of albumen and starch, with

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[1] In spite of this result, it would be of interest to investigate the effect of passing the rays perpendicular to the common direction of the molecules. Quite possibly interference diagrams would be obtained of the type shown by fibres and flakes, although less distinctly than for these substances.

numerous similar groups in their structure,[1] were capable of existing in space-lattice arrangement wholly or in part. They would then give a Debye-Scherrer crystal effect, contrasting, possibly only in the matter of degree, with ordinary molecules, which, owing to the small number of similar structural groups in the kinetic unit, do not furnish a space-lattice arrangement. Let us assign, in this

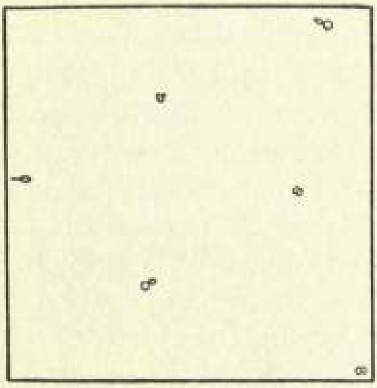

Fig. 82.

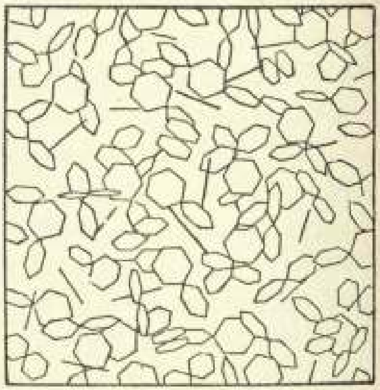

Fig. 83.

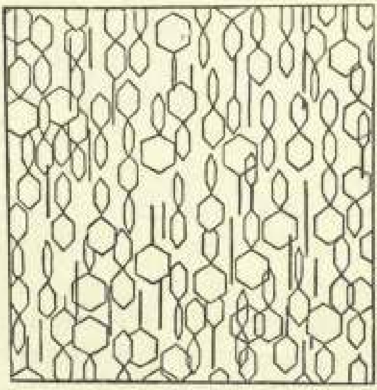

Fig. 84.

Figs. 82-84.—Schemes for the gaseous, normal fluid, and liquid crystal states.

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[1] Probably, too, atoms containing many electrons.

connection, at least eight equal valued particles to an elementary parallelopiped. Substances with formulæ such as $C_{450}H_{720}N_{116}S_6O_{243}$ (serum-albumen), $C_{758}H_{1203}N_{195}O_{218}FeS_3$ (Dog's Hæmoglobin), gliadin with thirty-eight molecular radicals of glutaminic acid, and similar complexes, should possess enough similar groups for crystalline structure in the molecule; aggregates of only about thirty atoms of carbon in graphite still show space-lattice character

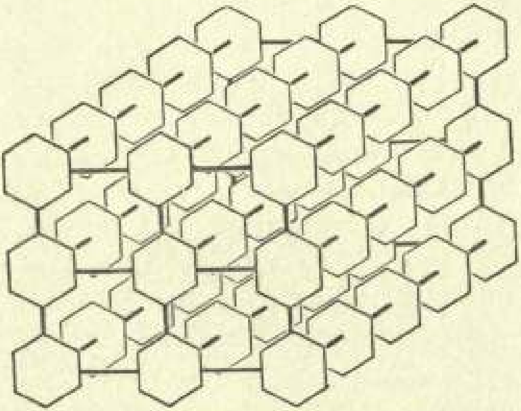

Fig. 85.—Scheme for the crystal state.

according to Debye and Scherrer, as has already been mentioned.

The results of the experiments of P. Scherrer, R. O. Hertzog, and W. Jancke on cotton, cellulose, starch, etc., for which the crystal effect with X-rays was observed, certainly deserve further consideration from the above point of view as being evidence for the fine-structural nature of "crystalline molecules."

On crystallisation the already anisotropic particles arrange themselves in regular fashion into a space-lattice; by this the formation of external surfaces in accordance with Haüy's Law (p. 8) is rendered possible. Thus, in the external ornamentation, we have a reliable criterion for the crystalline nature of a substance. A fine-structural medley of individual leptons gives under the uniform action of the surface forces, a spherical form to the lepton complex (Fig. 81, p. 59), a form, moreover, not foreign to crystalline materials, especially when very small masses are considered. Fig. 86, showing drop-shaped globulites, slightly curved longulites, pearl-like margarites, in strings, and hair-like trichites, gives some elegant examples from the mineral world. With larger crystallisations of benzophenone and ice, for example, R. Nacken has also obtained circular crystal forms by using special methods of cooling.

The great disperseness of gases is enormously diminished on crystallisation; in liquids, too, in general, the same thing occurs.[1] In this connection some figures for sodium and the diamond, as two extreme types, will be of interest to the reader.

Number of atoms per c.c.		Ratio.
1. Gas at boiling-point (820° C.)	$5{\cdot}5 \times 10^{18}$	3550
2. Liquid at boiling-point	$19{,}500 \times 10^{18}$	
3. Liquid at solidifying-point, 97·6° C.	$24{,}500 \times 10^{18}$	1·03
4. Crystal at solidifying-point	$25{,}000 \times 10^{18}$	

In solid sodium, with its body-centred space-lattice (only two atoms in the elementary cell) and its large *a*-value for the cube edge ($4{\cdot}3 \times 10^{-8}$ cm.), we are dealing with a soft metal. The condensation from gas to fluid is considerable; that for fluid to crystal, small.

With the hard, compact diamond (eight atoms in the elementary cell, $a = 3{\cdot}53 \times 10^{-8}$ cm.), a much

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[1] Exceptions to this, as in the case of H_2O, for example, are explained by assuming molecular variations in the liquid when the crystallisation point is reached.

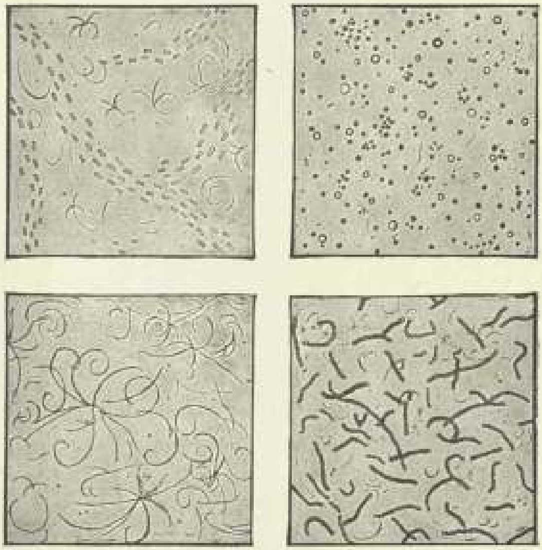

FIG. 86.—Globular and curvilinear crystals of microscopic dimensions

more extensive condensation occurs on crystallisation; 1 c.c. of this gem contains 180·000 trillion carbon atoms, compared with 1·3 trillion in carbon vapour at 5500° C. Naturally, with such close packing of the particles of matter, the cohesion between them becomes enormous.

A contraction of the substance in crystallisation until the external surfaces of the atoms touch is not, however, to be assumed, in view of the known possibilities of diffusion in the crystal. With change of temperature zeolites absorb and expel H_2O through their siliceous substance, liquids such as carbon disulphide can pass in and out of dehydrated chabasite, gold atoms penetrate lead to a perceptible extent in a short time, and irregular structures in isomorphous mixtures of metals or salts adjust themselves on tempering by wandering of the particles in the solid crystal. The atoms must, therefore, in these cases be "able to pass by one another." The conception of "close packing of spheres," so useful in crystallography, must not therefore be understood as an actual contiguity of the material atoms. As has already been stated on page 46, the matter here is one of a subdivision of space, dependent to some extent on the external conditions, into "spheres of influence" around the atoms.

In correspondence with these relations the kinematic conditions alter as the series of metamorphoses of matter is passed through. While the motion of the individual leptons in the ideal gas state of matter, neglecting collisions of the particles, is practically independent of the surroundings, this freedom of path is restricted in liquids by the reciprocal force fields, and the liberty of the structural units of crystals amounts merely to a tenth of the distance between the atoms. Lower temperatures naturally signify here a slowing down and limitation of the motion of the structural groups, and we may imagine that at very low temperatures the particles in a certain sense "freeze hard." But even at the absolute zero the energy of intra-atomic motion still remains; the frictionless agitation of the structural units of the atom determines the general constitution of matter, and is eternal.

The types of fine-structural state are therefore easily distinguished. Differences in the motion, in the distances apart, and in the mutual interaction of the particles, determine the constitution of these states under discussion, and thus nothing is more natural than that changes of state should modify the structure of the particles. If this does not occur to the extent of an actual change in the chemical character of the substance on transition from the gaseous to the fluid and solid states, the identity of the molecules in the different states of aggregation cannot, after what has been said, be admitted: the particles of gases and liquids are changed in passing through the series of metamorphoses of matter.[1]

Further, in the opinion of physical chemists, the state of affairs is complicated still more in the gaseous

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[1] In this connection the physical condition of a substance is occasionally indicated in the abbreviated symbol for its chemical nature as a printed formula. Just as the charges of the ions are expressed by $\cdot$ and $'$, or $+$ and $-$, the gaseous, liquid, amorphous, and solid crystalline states are denoted by the symbols $\uparrow$, $\frown$, $\cdot\ \cdot$, and $\frown\frown$ (the usual crystallographic sign) respectively. For example: $H\overset{\uparrow}{_2}O$, $\overparen{H_2O}$, $\overset{\frown\frown}{H_2O}$: and $\cdot SiO_2 \cdot$ for silica glass. In chemical equations, too, such as $\overset{\frown\frown}{MgCO_3} = \overparen{MgO} + \overset{\uparrow}{CO_2}$, the actual physical condition of the substances is shown immediately.

and fluid phases by equilibria between different types of molecule.

A. Smits follows up this idea in his theory of polymorphism, even to the extent of relating the process of crystallisation of substances without decomposition to an internal equilibrium between different types of molecule.

DISCONTINUITIES OF LOWER ORDER IN THE TRANSFORMATION SERIES. POLYMORPHISM. ENANTIOMORPHY.

Besides the reverse changes from the gaseous to the liquid state,[1] and from these to the crystalline, within each of these states (and also for liquid crystals) less drastic discontinuous transitions are possible. The relations of crystals whose greater capacity for changes of internal structure is obvious in their frequent polymorphism[2] are here again typical.

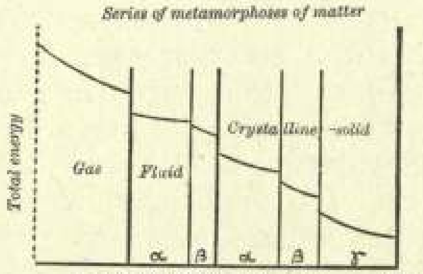

FIG. 87.—Subdivision of the series of metamorphoses.

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[1] A transition which can be accomplished continuously by application of a certain pressure and temperature.

[2] Termed allotropy for elements.

Examination characterises these crystal modifications as forms of the same substances in a chemical sense, which differ from each other in their energy content. In the fine-structure this is expressed as a variation in the arrangement of the component particles, that is, in the architecture ; the stabilities are different, and tend, therefore, to cause transformation of one modification into another. Transition occurs if the difference is so considerable that the internal resistance to structural change can be overcome.

This may be brought about by a correspondingly large change in the external conditions, generally the temperature or pressure, and sometimes both ; from among many cases of this we mention, as instructive examples, the abrupt change of borazite[1] and of α-quartz $\rightleftarrows$ β-quartz at 575° (Figs. 88 and 89), or the transitions of ice. According to a diagram worked out by G. Tammann, ice passes through five different forms with increase of pressure at $-30°$ C. Occasionally the catalytic influence of a chemical field, that is, the intimate proximity of a certain substance, brings about a transition which would not

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[1] The investigation of this mineral gives very elegant physical chemical demonstrations of fine-structure if a borazite plate is viewed between crossed nicols and its temperature raised. Owing to the considerable double refraction it transmits bright polarisation colours. On exceeding 265° the isotropy of the α-borazite spreads out from a point like a dark curtain over the previously radiant field, fluctuating with each small variation of temperature, and finally enveloping the whole in deep shadow. On cooling, the curtain rolls back and the structural particles are restored to their old rhombic equilibrium arrangement. In other cases change of modification is immediately evidenced optically by a colour change. Red mercuric iodide is a striking example of this. On heating above 126° it changes from its tetragonal equilibrium arrangement to a yellow rhombic form.

otherwise occur. H. E. Boeke and the author have shown that the iron sulphide of magnetic pyrites serves as an example of this; transformation only takes place in the presence of a little carbon or excess of iron.

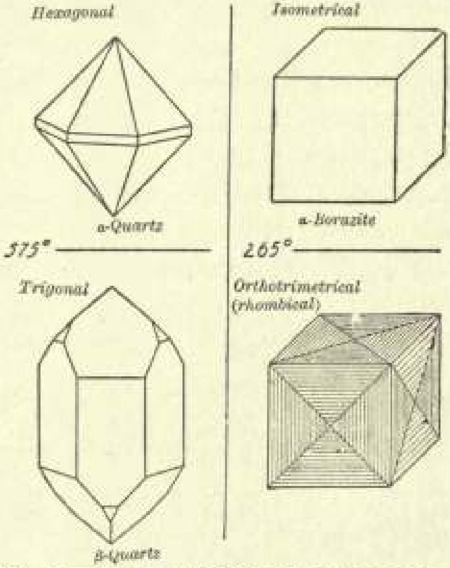


FIG. 88.—Homöomeric modification of quartz and borazite.

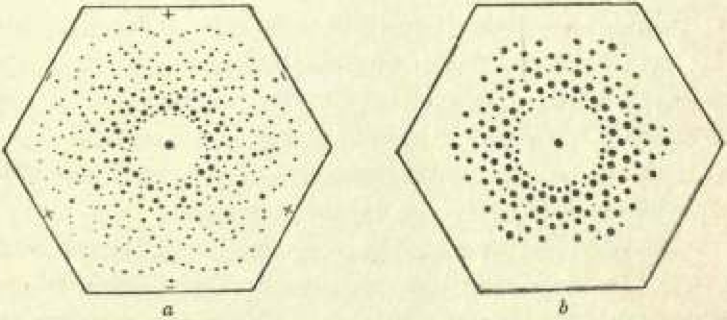


FIG. 89.—*a* and *b*. Laue diagrams of β-quartz and α-quartz. After F. Rinne.

After a change in the fine-structure a new equilibrium arrangement is in every case established, which need not, however, represent the most stable configuration under the existing circumstances, but, on the contrary, may be, in accordance with Ostwald's step-rule, that which in energy content is nearest the original state.

For polytype modifications such as those of carborundum, discovered by H. Baumhauer, H. Espig's experiments, carried out in my institute, have shown that equally large elementary cells contain the same number of molecules (24).

These modifications cannot differ, therefore, in specific weight; they will, nevertheless, require different amounts of energy to change their molecular motions, i.e. their specific heats are different. A change of one carborundum modification into another is not known. Such changes of structure are to be observed, however, in other cases, for generally the modifications are structures with definitely unequal stabilities, except at the transition point.

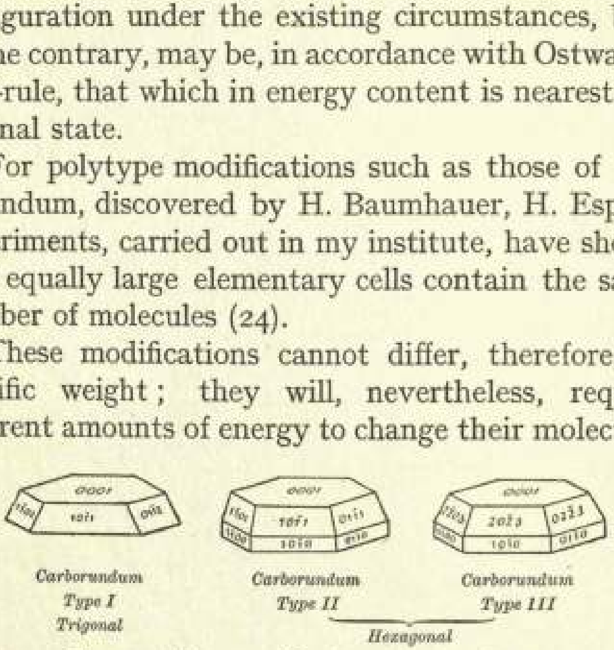
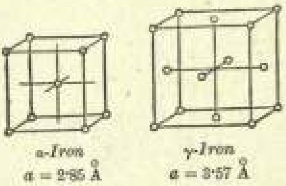


FIG. 90.—Polytype modifications of carborundum.

If the difference in the fine-structure is not too great the modifications are homöomeric, that is to say, transformable one into the other without breaking up the whole structure. This is the case for the quartz referred to, and also for borazite and leucite. With these minerals it is easy, by heating one modification above the limiting temperature to change it over into the other, and, on reversing the process, by lowering the temperature to return to the first modification as often as desired. The solidity of the crystal structure does not preclude exact experiment, and Laue diagrams give a picture of this "dance of the leptons" in the change from β- to α-quartz. In this case the ternary arrangement of the particles becomes, as though at some mysterious word of command, a senary arrangement, as Figs. 89*a* and *b* show, a truly wonderful glimpse of a fine-structural sanctuary of nature. A similar case arises with iron, and here the investigations of A. Westgren have disclosed the relations of the fine-structure. Four modifications of iron are known—α, β, γ, and δ irons. On heating to above 769° the α passes into the β variety; at 906° this gives the γ modification, and finally an increase of temperature to 1401° leaves the metal in the δ state; the transitions in every case are indicated by thermal changes.



α-Iron $a = 2{\cdot}85$ Å

γ-Iron $a = 3{\cdot}57$ Å

FIG. 91.—Stereograms of iron After A. Westgren.

The transformation $\alpha \rightleftarrows \beta$ is very clearly shown. Here at 769° lies the upper limit of the technically important property of ferromagnetism (capacity for intense magnetisation) possessed by the metal. In their fine-structure α and β irons are closely allied, differing, however, from the γ metal; Westgren was able to establish that the former have body-centred lattices, whilst that of γ-iron is surface-centred (Fig. 91). The transition from one variety of iron into another takes place quite smoothly. On the other hand, with carbon tetrabromide for example (Fig. 93), clearly marked fractures arise on slowly heating or cooling, and even more so in the transition from diamond to graphite, an example of allomerism which P. Debye and P. Scherrer have made classical.

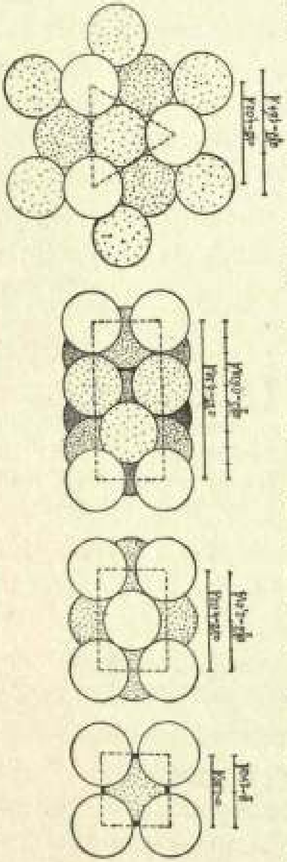


FIG. 92*a*.—Atom domains of α-iron.[1] Planes of the cube, rhombic dodecahedron, a pyramidal cube and the octahedron.

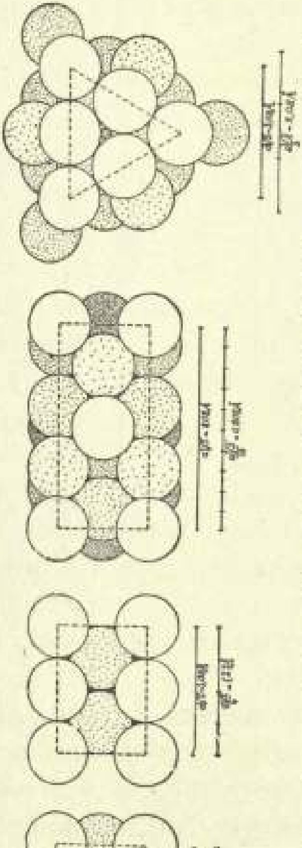


FIG. 92*b*.—Atom domains of γ-iron. Planes of the cube, rhombic dodecahedron, a pyramidal cube, and the octahedron.

In diamond the carbon particles are arranged in aliphatic tetrahedral grouping, but in graphite they are arranged in the aromatic ring form which is

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[1] The lower scales in Figs. 92*a* and *b* relate to depth distances.

a very different arrangement, and one requiring much more space from ring to ring. Graphite is in a certain sense an elongated diamond (Fig. 94).

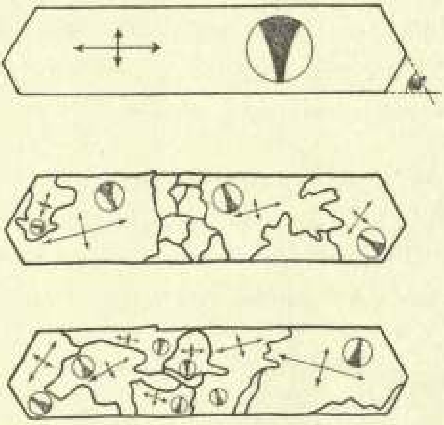

FIG. 93.—Change of modification of carbon tetrabromide, the external form remaining intact but showing internal mosaic formations.

The restoration of the atoms to the diamond arrangement has not yet been accomplished.

In conclusion, the remarkable enantiomorphy of crystals, as shown by quartz and cane sugar, for example, should also be mentioned.

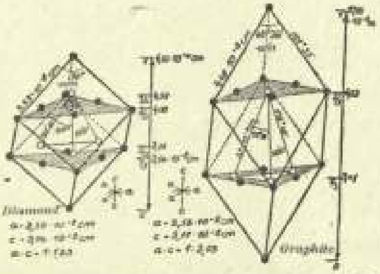

FIG. 94.—Allomeric modifications of carbon (diamond and graphite).

The two varieties which call for consideration are differentiated as right- and left-handed; as regards their macro- and micro-stereochemistry, each variety taken by itself is without mirror symmetry, but the two together are symmetrical one to the other, as the halves of the human body. Their stability to changes of external conditions is exactly the same. They are obtained mixed together indiscriminately, and are not convertible one into the other.

Clearly then the modifications of a crystalline material like the isomers of liquids and gases are chemically different substances, although, at the same time, the divergences in their material relations are, for the most part, not very large. In the case of carbon, however, they are not small (graphite is oxidisable to graphitic acid, diamond is not), nor with calcium carbonate are they inconsiderable (boiling with cobalt nitrate solution colours aragonite violet, but calc-spar blue); quartz, finally, scarcely shows them at all.

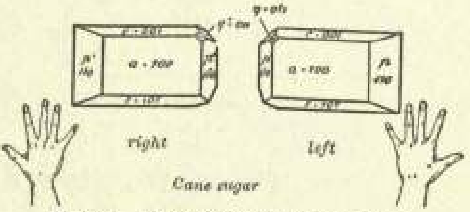

FIG. 95.—Enantiomorphy of cane sugar.

REVIEW AND UNIFIED CONCEPTION OF THE STATES OF MATTER

A survey of the whole series of metamorphoses from the gas to the last modification in the temperature scale presents a picture of discontinuous energy changes, and between these discontinuous changes steady variations within each state, which possibly represent energy exchanges in minute jumps. According to that idea, large energy quanta are composed of small quanta, which for the observed continuous changes follow each other in a steady series, whilst for the sudden discontinuous changes they rush over a steep fall. Structurally, in the former case one is concerned with fine leptonic jumps, in the latter with motions of larger leptonic complexes.

Regarding the fine-structural changes of substances in this way, we arrive at a unified conception of the states in which matter is presented to us. Starting from the absolute zero and continuing to the highest temperature obtainable, matter passes through a series in which the transition points (whether these be boundaries between the solid, crystalline, liquid, or gaseous states, or terminating points of sub-states within these) represent obstacles on a constantly rising road, which must be overcome by especially large expenditure of energy. The substance deviates more and more from the character it possesses by virtue of its own particular constitution. In ordinary experiments carried out at room temperature, that is, at about 290° absolute, we must in consequence assume considerable restrictive influences at work on the crystal, resulting in modifications of its proper constitution.[1] The investigation of matter at very low temperatures eliminates, as much as possible, the enormous influence of the surrounding circumstances on the primitive structure. Thus, of all the states of aggregation, the solid crystalline approximates most nearly to that of ideal matter.

[1] Of these, temperature is the most active; after that, pressure and chemical action are the most important.

VII. GENERAL TECTONIC ARRANGEMENTS IN THE FINE-STRUCTURE OF CRYSTALS

ANALYSIS OF STEREOCHEMICAL FORMULÆ

A CONSIDERATION of the results of fine-structural researches from a chemical standpoint suggests many questions of general importance.

First, it is an obvious conclusion that the suggested schemes express the analytical constitution of the substances they represent. It is, of course, necessary to argue correctly from the fine-structure. For example, the diagram for the stereochemical formula of fluor-spar CaF_2 (Fig. 96*a*) contains in the tectonic unit there depicted 14Ca and 8F atoms, leading apparently to the incorrect formula $Ca_{14}F_8$; but it must be remembered that each Ca at a corner of the figure is shared by eight cubes, since the fine-structure is repeated indefinitely, often on all sides. Consequently, each of these only represents an eighth of a Ca. Similarly, a Ca on a surface of the cube (as on a wall separating two cubes) must be counted as $\frac{1}{2}$Ca, whilst the 8F atoms in the inside of the figure must be reckoned in full. We have, therefore, $(8 \cdot \frac{1}{8} \cdot + 6 \cdot \frac{1}{2})$Ca and 8F, or Ca_4F_8 corresponding to the actual CaF_2. In the same way, the reader will easily decipher the stereogram of iron carbide Fe_3C, and the formula of ice H_2O (Figs. 96*b* and *c*).

If, according to this, a stoichiometrical balance for a portion of the crystalline body surrounded by others is recognised, it seems unmistakable that the crystal as a whole does not conform to the requirements of the law of simple multiple proportions, if its space-lattice structure extends to the external surfaces. In this case the particles lacking neighbours would not balance analytically, and there would be an excess of one kind. The edge of the elementary cell of fluor-spar (shown in Fig. 96*a*) is $5{\cdot}44 \times 10^{-8}$ cm. long. A cube of the mineral of $5{\cdot}44 \times 10^{-7}$ cm. side which is thus of colloidal dimensions would give, in accordance with the above scheme, the ratio Ca : F = 36·51 : 63·49, instead of the theoretical value 33·33 : 66·66. By increasing the size of the cube the deviation from the ideal ratio would gradually become smaller, and, finally, analytically indetectable. Since, however, it is unlikely that for crystals the law of simple multiple proportions does not hold good, there only remains the assumption that the regular space-lattice arrangement of the particles fails in the surface zone.

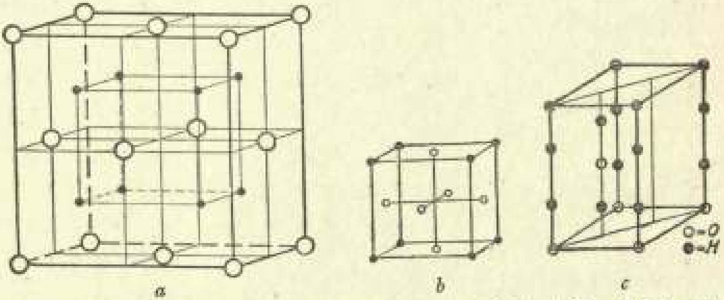

FIG. 96.—Stereochemical formulæ. *a*. Fluor-spar CaF$_2$. After W. H. and W. L. Bragg. *b*. Iron carbide Fe$_3$C. After A. Westgren. *c*. Ice H$_2$O. After G. Aminoff.

VALENCY

No less important chemically is the question as to how valency is exhibited in crystals. We may expect, therefore, that the study of the specially regular crystalline materials will lead to a better understanding of the controversial nature of valency. For gases and liquids the only rules of valency which have actually been experimentally confirmed are restricted mainly to the specification of how many atoms have found a place round another atom under definite chemical and physical conditions. With regard to the fine-structure, it is of interest to note that, in substances with simple valency, it is rare that more than eight atoms are united to one of another (as the series FNa; F_2Mg; F_3Al; F_4Si; F_5P; F_6S; – ; F_8Os shows), and that these combining numbers for a given atom depend on the temperature, i.e. on the motion of the particles. Both of these are clearly structural characteristics permitting of obvious explanation.

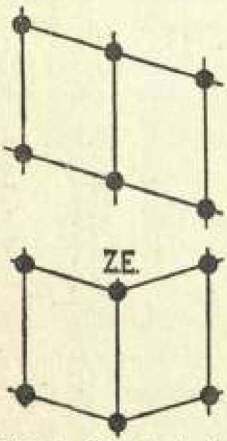

FIG. 97.—Net of a simple crystal and its twin form.

As to the spatial arrangement of the particles, no definite result is arrived at in terms of valency, although it appears quite natural in CH_4 for us to place the 4H satellites round the central carbon atom in similar positions on the corners or sides of a tetrahedron (compare Fig. 56, p. 43). In particular, it is entirely a formal characterisation if valency or co-ordination bonds are represented as single directed lines of force between the atoms and molecules. In

Fig. 97 it is clearly seen that such bonds between similar atoms at the common surface of a twin have different directions from those in the simple crystal. We must, however, note that such tensors have only the character of pedagogical simplification, and not that of reality, just as the customary representation of chemical formulæ on paper is, to a certain extent, merely a simplified projection of very complicated spacial arrangements. The "structural chemical" mode of representation in a plane, and the drawing in of directed bonds, are but symbolisations, superficial and linear respectively. Plane arrangements of the atoms or of their centres of motion are not, of course, excluded; for benzene, in fact, such an arrangement is very probable. In this example we have a limiting case in which matter is practically reduced to a plane. A methylation of benzene leads at once to a definitely three-dimensional molecular structure.[1] In general terms, the constellation of the particles must be thought of as a complex action of the anisotropic fields of force, gradually weakening, which always surround the particles. As is well known, especially in inorganic chemistry, we cannot get on without introducing some spacial co-ordination action besides valency; A. Werner has discussed this very ingeniously. Organic chemistry, owing to the special nature of the nucleus of all its compounds, carbon, for which the valency and co-ordination

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[1] This does not lessen the great value in teaching the notions of directed singular valency and co-ordination forces, and their representation as lines in plane formulæ. It is an indication of the considerable practical utility of this handy method of representation that such a formulation of the certainly very complicated interaction of the oscillating particles generally guides us safely through the innumerable phenomena of chemistry.

numbers are the same, might easily attempt to dispense with such conceptions.

In contrast to these uncertainties in the case of amorphous materials, X-ray experiments on crystals have disclosed not only how many particles at any time surround one atom, but, in addition, details as to the spacial arrangement of the centres of the particles in terms of centimetre co-ordinates. Thus it is known definitely that, in the case of diamond, each C atom is placed at the centre of a tetrahedron, at the corners of which are four others, each $1{\cdot}53 \times 10^{-8}$ cm. from the centre; in rock-salt each Na atom is surrounded at a distance of $2{\cdot}81 \times 10^{-8}$ cm. by 6 Cl atoms on the normals to the surface of a cube, and each Cl similarly by 6 Na's.[1] In addition, spacial representation of the atomic domains gives us a clear insight into the dynamical relations; in Fig. 98 this is done for sodium chloride.

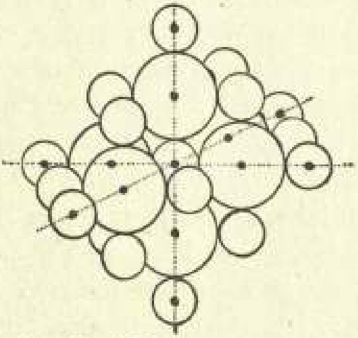

FIG. 98.—Axial arrangement of the atom domains in rock-salt.

All the other rules of valency lead us here to somewhat insecure ground. It is true that in crystal stereochemical figures connecting links may be looked upon as valency tensors, and it is in this way seen that in the diamond the tetravalency of carbon is clearly shown graphically. In other cases, a valency distribution is symbolised, as for rock-salt in $\frac{1}{6}$ values, and in similar ways for other substances. It must not be forgotten, however, that the methods

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[1] See also Fig. 96, p. 79, and Fig. 24*d*, p. 22.

discussed above are only graphical aids, and merely summarise diagrammatically the field of force.

In this connection it must be ascertained whether any further knowledge of valency relations is available from a consideration of the crystallographic evidence of a definite "form" for the structural particles: and here we are helped by ideas of H. J. van't Hoff, who assumed that it is the definite form of the atoms which involves directional maxima in the tendency to aggregate. These maxima therefore determine the fine-structural distribution possible, and therefore the valency.

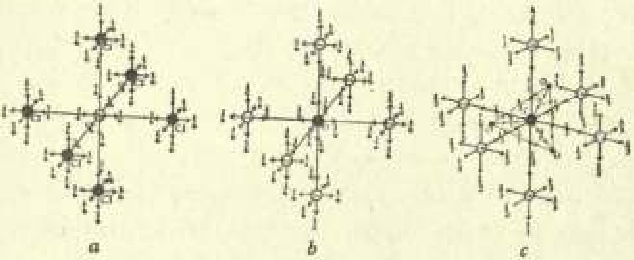

FIG. 99.—Valency schemes for *a* and *b* Rock-salt; *c*, calc-spar.

Thus a carbon atom, owing to the tetrahedral arrangement of its external electrons, presents a specially stable distribution for four hydrogen atoms at the corners of a tetrahedron rotated with respect to the carbon tetrahedron, so that the H atoms lie over its four faces (Fig. 56, p. 43). The normal quadrivalency of carbon arises then primarily as the result of a stable arrangement in the field of force, and kinetic relations are therefore of importance here.

This anisotropy in the shape of the atom will exist also in the atomic domain, concerning which reference is made on page 46; in these domains, however, the corners and edges will be rounded off.

A zero valency arises if a stability already high permits of no further additions. The relations of substances possessing the character of rare gases may, following the ideas of Bohr, W. Kossel, and in particular H. Tertsch, be regarded in this way. After filling an electron zone with 8, again 8, then 18 (= 6 + 12), again 18, and finally 32 (= 24 + 8) electrons corresponding to the periods in the system of the elements,[1] a shield so stable from outside influence is constructed that a fine-structural deformation and chemical change is rendered difficult to a high degree. Thus zero valency is obtained in each case. Figs. 100-103 represent these stable electronic arrangements diagrammatically in crystallographic form. Helium (with two negative electrons) has probably pinacoidal stability (Fig. 30, p. 29).[2] The other numbers, 8, 18 = 6 + 12, 32 = 8 + 24, are in accordance with the crystallographic motives of the cube (six surfaces, eight corners), the rhombic dodecahedron (twelve surfaces over the edges of the cube), and the pyramidal cube (twenty-four surfaces over the six of the cube).

In the construction of molecules analogous cases are not improbable. That tetrahedral grouping, as

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[1] 1 H, 2 **He**; 1 Li, 2 Be, 3 B, 4 C, 5 N, 6 O, 7 F, 8 **Ne**; 1 Na, 2 Mg, 3 Al, 4 Si, 5 P, 6 S, 7 Cl, 8 **Ar**; 1 K, 2 Ca, 3 Sc, 4 Ti, 5 V, 6 Cr, 7 Mn, 8 Fe, 9 Co, 10 Ni, 11 Cu, 12 Zn, 13 Ga, 14 Ge, 15 As, 16 Se, 17 Br, 18 **Kr**; 1 Rb, 2 Sr, 3 Y, 4 Zr, 5 Nb, 6 Mo, 7-8 Ru, 9 Rh, 10 Pd, 11 Ag, 12 Cd, 13 In, 14 Sn, 15 Sb, 16 Te, 17 J, 18 **X**; 1 Cs, 2 Ba, 3-19 the rare earths, 20 W, 21-22 Os, 23 Ir, 24 Pt, 25 Au, 26 Hg, 27 Tl, 28 Pb, 29 Bi, 30 Po, 31-32 **Em**; 1-2 Ra, 3 Ac, 4 Th, 5 Br, 6 U.

[2] The total electrons in the negative shell may probably be arranged for the rare gases in the following way: He 2; Neon 2 + 8; Ar 2 + 8 + 8; Kr 2 + 8 + 6 + 12 + 8; X = 2 + 8 + 6 + 12 + 6 + 12 + 8; Em = 2 + 8 + 8 + 6 + 12 + 6 + 12 + 24 + 8.

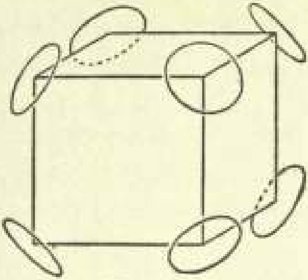

FIG. 100.

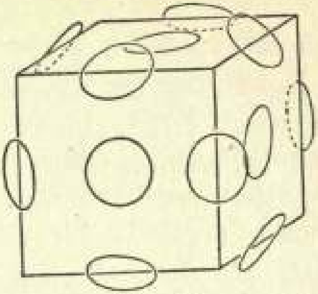

FIG. 101.

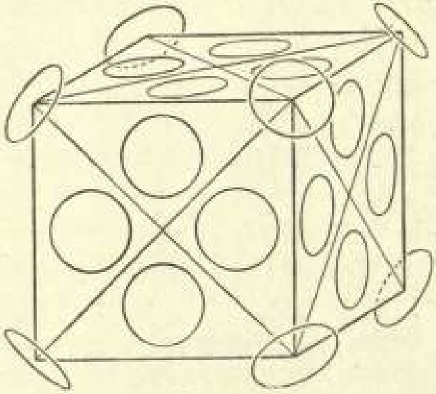

FIG. 102.

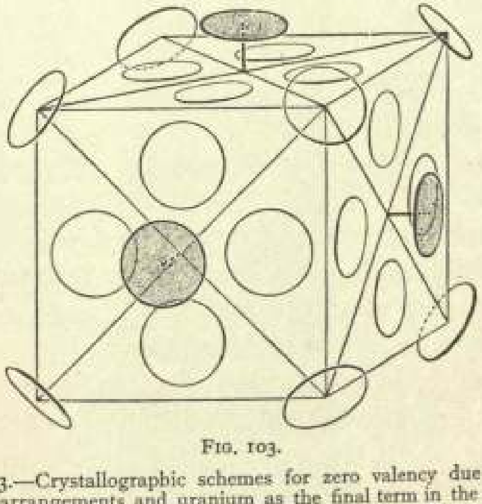

FIG. 103.

FIGS. 100-103.—Crystallographic schemes for zero valency due to perstable electron arrangements and uranium as the final term in the atom series. Rare gases: Shell with 8 electrons for neon and argon; shell with 6 + 12 = 18 electrons for krypton and xenon; shell with 24 + 8 = 32 electrons for emanium; uranium as the final member of the electron aggregates.

is to be assumed for CH_4, with its great regularity, favours to a certain extent chemical stability is shown definitely by the properties of methane.

To substances which require only small variations in their external electron shells to attain the external structural balance of a rare gas, we must, on the other hand, readily assign high chemical affinity. The left and right-hand neighbours of the rare gases in the systems of the elements are of this type; the alkalies and halogens. Their tendency to combine one with the other is great, and according to W. Kossel, this is brought about through the loss of an electron by the alkali and by a gain of one by the halogen.

The following small table of the names and numbers of electrons in the atoms renders this clear:[1]

Halogens.	Rare Gases.	Alkalies.
1 Hydrogen.	2 Helium.	3 Lithium.
9 Fluorine.	10 Neon.	11 Sodium.
17 Chlorine.	18 Argon.	19 Potassium.
35 Bromine.	36 Krypton	37 Rubidium.
53 Iodine.	54 Xenon.	55 Caesium.

In a similar manner it will be readily assumed that molecules, too, with the great internal tension which must arise if the stability is not fully established, tend to like transformations.

Moreover, in connection with these assumptions as to the mode of action of valency, the occasionally

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[1] In view of the analogy between Li H and the halides, H is included in this comparison.

observable changes of valency in changes of crystal modification, i.e. in stereochemical structural rearrangements, should be noticed. In the diamond the quadrivalency of carbon is expressed as four equally large maxima in the arrangement. In graphite structure, on the other hand, it is seen that a 4 × 1 is differentiated into a 3 + 1 valency. This change in the form of the field of force is, to some extent, the first step towards a diminution of valency; it forms an intermediate stage to a tri- or divalency of carbon. Since it may well be assumed that, in the process of changing from diamond to graphite, a variation of atomic form by rearrangement of the electrons takes place (which the optical differences of clear diamond and black graphite, besides considerations of crystallographic symmetry, indicate), then it is quite obvious that a change in the shape of the atoms goes hand in hand with a change in their method of arrangement. The idea that morphological changes themselves occur under the influence of alterations in the material surroundings, and of alterations of temperature affecting the internal motions, harmonises in the best possible way with the experimental result that the valency of the substance may depend on the kind of matter with which it is in valency connection, and also on the temperature.

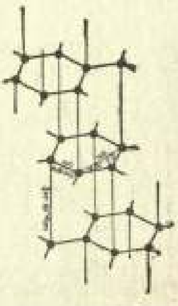


FIG. 104.—Valency scheme for graphite.

MOLECULES IN THE CRYSTAL STRUCTURE

It will appear of great importance to the chemist in dealing with these crystallographic stereochemical formulæ to investigate the positions of the molecules which come under his consideration in the chemistry of gases and liquids. Occasionally it happens that the molecular scheme appears in the elementary cell, as, for instance, those in Fig. 24, page 22. That has, however, as little foundation as the representation of the macroscopic crystal as a molecular unit; for we are concerned in both cases with more or less arbitrary sections from the fine-structure. For zinc sulphide, Fig. 105 might just as well be proposed as Fig. 106, both of them are consistent with the ratio Zn : S = 1 : 1. It appears from this that the discussion of the appropriate architectural relations must be attempted in some other way.

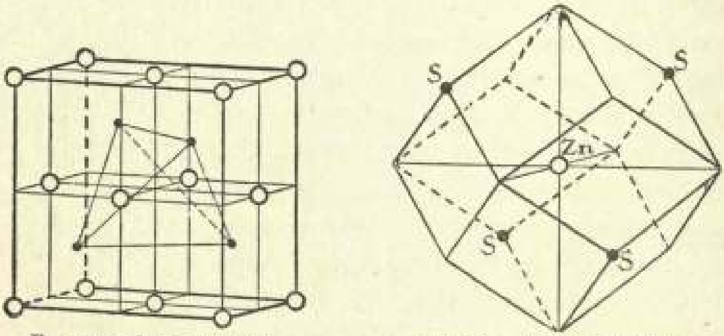


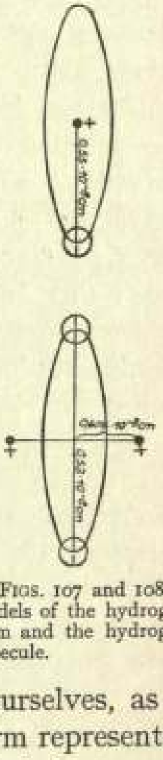
FIG. 105.—A cube section.

FIG. 106.—A rhombic dodecahedral section.

Stereochemical formula for zinc-blende ZnS.

In particular, it must be remembered that the chemical properties of a substance are characterised above all in the organisation of its general architecture. As we study an example of architectural art, such as a cathedral, not only as an architectural unit, but recognising its morphological subdivision, so it is an important chemical problem to investigate crystals in the same way. The customary method of writing formulæ as Hg, Cl', $\mathrm{Na}^{\cdot}\,\mathrm{Cl}'$, $(\mathrm{NH}_4)^{\cdot}\,\mathrm{Cl}'$, $\mathrm{Ca}^{\cdot\cdot}\,\mathrm{CO}'_3{}'$, $\mathrm{NH(CH_3)_3I}$, $\mathrm{C_6H_4\,(COOH)\,(NH_2)}$ accords with this. In such symbols the chemical individuality is emphasised, as well as the appropriate tectonic organisation, as exhibited in reactions. Hence special efforts must be made to find out the inner groupings in the architecture of crystals.

On the other hand, however, it must be added that the kinetic units in the erection of higher chemical complexes, as in the aggregation of atoms to molecules, and so to crystal units, may become indistinguishable in the fine-structure, or may even be dissolved altogether. This is the case, for example, in the formation of a molecule of H_2 from its atoms. It cannot be ascertained in the scheme shown which of the two electrons belonged, originally, to a given nucleus. The earlier individualities are in such extreme cases completely destroyed.



Figs. 107 and 108.—Models of the hydrogen atom and the hydrogen molecule.

Therefore, we are not to restrict ourselves, as a matter of course, to a rigorously uniform representation of the fine-structure of the crystal, but must expect numerous gradations in view of the great abundance of chemical conditions which exist in it. Naturally, in formal mathematical representation, an arrangement in an atomic space-lattice is always possible by joining up the similar and similarly situated atoms into a lattice unit. This procedure, however, invests the crystal structure with practically no physical chemical properties. The presentation of a purely atomistic structure of the crystal, or its comprehensive characterisation with co-ordination bonds, is obviously too general.

Considering the results already obtained in crystal leptology with a view to a physical chemical interpretation, the desired organisation into radicals is, in fact, often definitely shown in the architecture. The Braggs, as originators of fine-structural schemes, have pointed out the dumbbell-like connection of the two sulphur atoms in iron pyrites, and, in somewhat greater detail, P. Niggli has expressed the opinion that the representation of the complete crystal as a purely atomistic space-lattice complex certainly may always be carried out formally, but that many interconnections between certain atoms forming structural groups (as P. Niggli called them) stand out clearly on a merely architectural consideration of the schemes. These structural groups I have designated geometrical radicals or leptyles in adaptation to chemical ideas. Finally, groups of a molecular nature are occasionally unmistakable in the crystal arrangement. Such leptyles occur in iron pyrites with its doublet S_2, in calc-spar with the ion CO_3, and in rutile and anatase with the molecular TiO_2 complex. A fine example of leptyle grouping has been investigated by Dickinson ("Journal of the American Chemical Society," vol. xliv., 1922, p. 287). Moreover, for organic substances with ring formation, such a fine-structural grouping must be assumed according to P. v. Groth, who formerly brought into prominence the atomistic crystal structure. As regards cyclic chains of atoms so fundamental chemically, which can with certainty be attributed to the molecules of benzene, naphthalene, and other organic substances, it is more than probable that these chains persist in crystallisation. Crystallised organic compounds will often be molecular

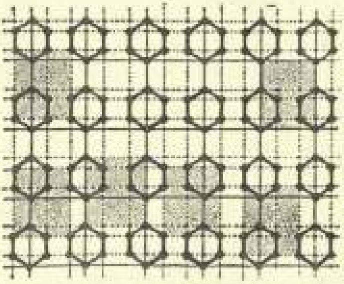


FIG. 109.—Physical chemical system of molecules split up geometrically into six different space-lattices.

aggregates loosely knit into space-lattices. This conception W. H. Bragg has taken as fundamental in his present researches on organic compounds.

In the same connection considerations of cleavage can be brought forward. According to E. Schiebold,

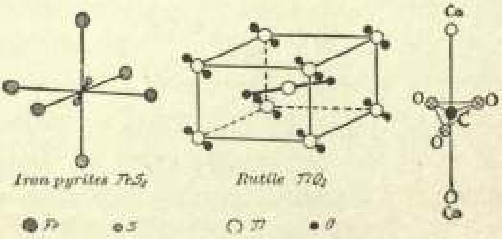


FIG. 110.—The leptyles S_2 in Iron pyrites FeS_2, TiO_2 in rutile, CO_3 in calc-spar.

such planes are to be regarded as plane rifts in the fine-structure, as it is accepted that these surfaces of separation do not cut through any strong chemical bond. With graphite this is clearly shown, as cleavage along the principal plane in the fine-structure separates out to some extent packs of ring radicals with their 3 + 1 valency by cutting through the extenuated connecting links. According to A. Johnsen, twin cleavage with separate motion of the structural groups Ca and CO_3 demonstrates this same relation. We are concerned here with a very remarkable property of calcspar which, on the application of a lateral pressure, permits portions of the whole structure to slide to a position symmetrical with the stationary part (Fig. 112).

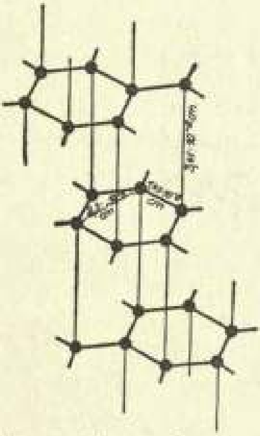


Fig. 111.—Structural groups in graphite.

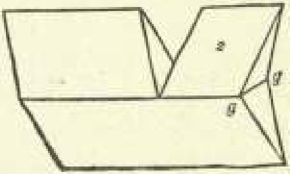


Fig. 112.—Twin gliding of calcspar.

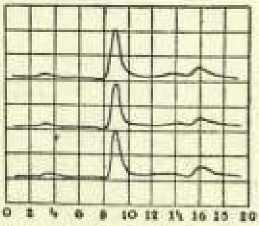


Fig. 113.—Analogous selective reflexion in the ultra-red of the hydrated sulphates of Mg – K, Co – K, Zn – K. After Cl. Schaefer and M. Schubert.

In this so-called simple displacement or twin slipping, the Ca atoms on one side, the CO_3 complexes of the fine-structure on the other, shift apart each as a complete whole.

The researches of Cl. Schaefer on the reflexion of ultra-red radiation by crystalline salts and the constant effect, there observed, of the groups NO_3, SO_4, SeO_4, CrO_4, and H_2O, also illustrate the idea under discussion, as occasionally in these cases definite radicals can be separated out partly by chemical treatment of the crystal structure.

In short, there is no lack of well-supported opinions that the crystal lattices are organised to a varying degree in natural complexes, more or less simple, up to the molecular type. With this in view, A. Reis has classified crystal lattices from a chemical standpoint, and has emphasised, following the lead of W. Nernst, F. Haber, M. Born, and others, the special nature of salts as ionic structures.

Thus neutral atom lattices, atom ion lattices, neutral and charged radical lattices, as well as molecular lattices, are to be differentiated, to which series I should like to add one more, the mixed lattice. Calc-spar $Ca \cdot CO_3$, and zeolites such as heulandite,[1] are examples of mixed lattices. The H_2O contained in the latter mineral is set so loosely in the fine-structure that it evaporates from the crystal on the temperature being raised, until an equilibrium content is reached. On lowering the temperature the H_2O is again taken up from the surroundings without the remaining structural complex being damaged or in any way broken up, as is shown by the Laue diagrams. That indicates great structural independence of the water particles. They are

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[1] Indeed, fundamentally all lattices with isotopic substances (p. 185) have already a mixed character. The isotopes of a given atomic variety, say, Cl_{35}, Cl_{37}, and Cl_{39}, are, of course, to be thought of as separated in space and replaceable one by another (compare Fig. 119, p. 98).

to be considered as regularly arranged structural particles only loosely coupled to the silicate space-lattice.

Complete kinetic units in the sense of individual leptons in ideal gases are themselves quite ineffective in the isodynamostasy of the whole; for the leptyles, however, this naturally is not so. Like all structural particles, they occur in the crystal in complex structural connexion with those above and below. The kinetic unit for crystalline materials is the whole crystal. In this sense it replaces as a new compound the individual molecule of gases and liquids. Within the crystal, affinity tensors, in the sense of valency theory, pass in and out from one structural particle to another throughout the whole structure; the crystal is in this respect a leptoblast. With reference to the cohesion prevailing through the whole system, P. Pfeiffer has made the relations clear in the designation "molecular linkage."

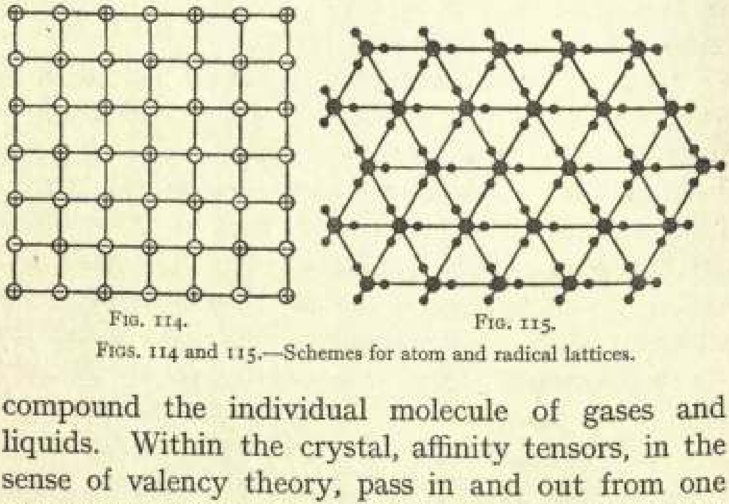
FIG. 114. FIG. 115.

FIGS. 114 and 115.—Schemes for atom and radical lattices.

The cohesion of the structural groups arising as a result of force fields, in general, very strong, prevents the disrupture which is possible for liquids and gases on the application of mechanical force. This cohesion enables a crystalline material more or less to withstand fracture, and renders crystals, in consequence, correspondingly hard materials.

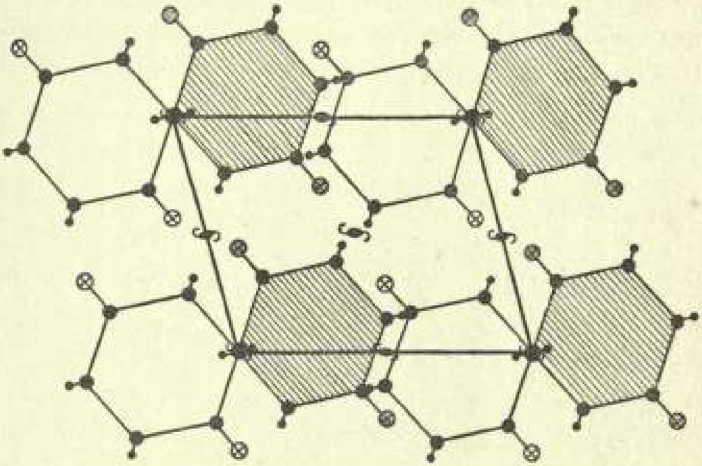

FIG. 116.—Scheme for the molecular lattice of an aromatic compound $C_6H_4X_2p$ (compare also Fig. 85, p. 65, and Fig. 109, p. 91).

The chemical facts alone indicate how the inner structure is organised in general, yet surprising results sometimes arise. This is shown by a research in my institute by Lotte Berndt on olivine, to which is ascribed the formula of an orthosilicate

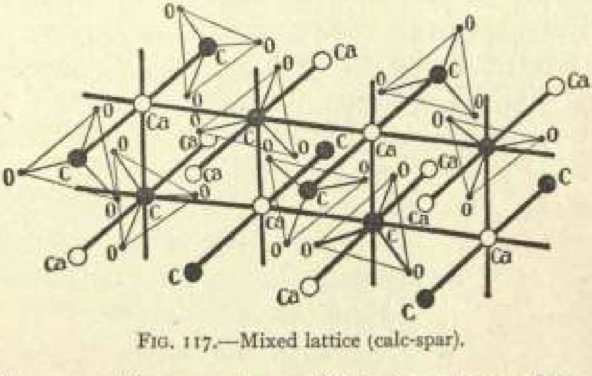

FIG. 117.—Mixed lattice (calc-spar).

$Mg_2(SiO_4)$. According to these experiments a corresponding organisation into the structural groups of Mg and SiO_4 leptyles (charged) is to be expected. The symmetry of the space grouping proves, however, that SiO_4 leptyles do not arise in the fine-structure. On the contrary, the atoms in the olivine must be separated into MgO- and SiO_2-groups. Presumably this will be shown by reflexion experiments in the ultra-red, page 92. More comprehensive experiments on silica salts, as to their nature as ortho-, meta-, or polysilicates, would be of the greatest interest in crystal stereochemistry.

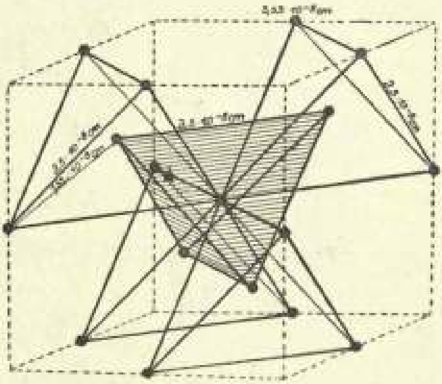

FIG. 118.—Leptoblastic structure for diamond.

VIII. ASSOCIATION OF THE FINE-STRUCTURAL PARTICLES IN MIXED CRYSTALS AND OUT-GROWTHS ON CRYSTALS

TRANSITIONS BETWEEN CHEMICAL COMBINATION AND PHYSICAL MIXTURE. MIXED CRYSTALS

IT is an especially interesting point to note in dealing with the structure of crystals that they permit, to a greater or less extent, indiscriminate heterogeneity of their constituents without injury to their stability. Such is the case for isomorphous mixtures. We find here certain atoms or groups of atoms replaced by others in the fine-structure of the crystals. It is certain that crystals with isotopic constituents (p. 185) must be reckoned as isomorphous mixtures. In NaCl crystals, for example, three kinds of chlorine atoms are to be assumed, Cl_{35} (i.e. with the atomic weight 35), Cl_{37}, and perhaps Cl_{39}. Although these atomic sub-types have different masses they do not differ chemically. Such isotopic mixed crystals represent the ideal case of isomorphous substitution.[1] In addition, in the interchanges of isomorphous mixed crystals, we are concerned with substituents quite analogous chemically; in the mixtures NaCl and NaBr, $Ba(NO_3)_2$ and $Pb(NO_3)_2$, KCl and K(CN), for example, the Cl and

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[1] Owing to the uniform intermixture of the chlorine isotopes on the earth, one has presumably in rock-salt always 77 per cent. Cl_{35}, and 23 per cent. Cl_{37}, with traces of Cl_{39}. Theoretically, however, any arbitrary mixture is possible.

Br, Ba and Pb atoms respectively displace each other in the fine-structure. This interchange may also occur with chemical radicals such as NH_4, which replaces K, or CN, which is interchangeable, with Br. Similarly, the groups SO_4, SeO_4, CrO_4, and the members of many other series may be substituted one for another.

With such complex space-lattices, it is not uncommon for optical anomalies[1] (or in the isometric system double refraction in the place of the isotropy possessed by the pure components) to indicate, according to G. Tammann, unequal apportionment of the substituents. For barium lead nitrate the abnormal phenomena disappear with time, even at ordinary temperatures or on heating; they are not found, therefore, in mixtures which, like pyrop in eruptive rocks, crystallised at higher temperature.

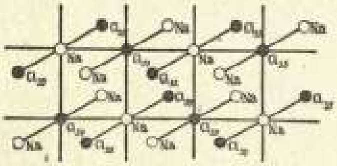

Fig. 119.—Scheme for the isomorphous mixture of $NaCl_{35}$, $NaCl_{37}$, $NaCl_{39}$.

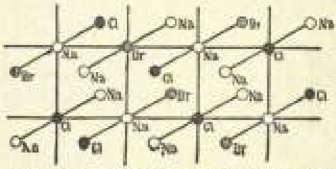

Fig. 120.—Scheme for the isomorphous mixture of NaCl and NaBr.

PHYSICAL CHEMICAL SIGNIFICANCE OF THE MIXED CRYSTAL

As regards the X-ray effect, the fine-structural heterogeneity in question is not evidenced experimentally in diffraction, which is an indication that in isomorphous mixtures the substitution is, as assumed above, complete. If in mixed crystals there existed intergrowing layers of first one and then the other

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[1] R. Erauns has given from the results of very many actual observations an excellent summary of these anomalies.

substance, such as very thin sheets of KBr and KCl growing together to give the mixed crystal (KBr and KCl), then each component would naturally give its own interference pattern in the Debye-Scherrer diagram. This, however, is not the case. On the other hand, Hadding found such double patterns for NaK felspar, showing that here one has a sub-microscopic mechanical mixture of the two felspar varieties, and not a simple interchange of sodium and potassium ions.

How are we, therefore, to think of this newly implanted portion of the fine-structure in combination with the whole? These matters lead to the consideration of a fundamental question in chemistry, namely, the relation between chemical compound and physical mixture.

If the existence of mutual coupling by the action of forces effective only very near the atom is to be emphasised, then isomorphous mixtures must come under the headings of chemical compounds. All atoms in a mixed crystal stand certainly in definite chemical connexion one with another. Moreover, no reliable line of demarcation between compounds and mixtures can be laid down in passing from one pure crystal through the series of mixtures to the other pure substance. In the unmixed calcium carbonate of calc-spar, for example, a chemical compound in every sense exists. If now a manganese atom occupies one of the numerous corresponding places not occupied by a calcium atom, then certainly the constitution of the whole as a chemical compound is not abruptly destroyed. Thus, by repeated substitution of atom for atom by correspondingly small quanta in the crystal, one may pass right to the other end of the series $CaCO_3 - MnCO_3$.

It is impossible to draw a line between chemical combination and mixture. The case of alteration in the structure of zeolithic isomorphous mixtures will be similarly judged. In these silicates more and more Ca, for example, can be replaced by Na_2 if a solution of NaCl is allowed to act on a crystal containing calcium. In accordance with the laws of mass action, a crystallographic chemical change in the structure takes place, which presents in its various stages a complete series of isomorphous mixtures from the Ca to the Na_2 mineral. In consequence, the structural parts must be in chemical combination with one another.

Although then isomorphous mixtures in the regular chemical coupling of their structural parts suggest chemical compounds, still on the other hand they do not accord with the second characteristic of such compounds. As H. Kopp has already emphasized, the distinguishing feature of a chemical compound is constancy of atomic proportions, in spite of very great variation of the original conditions.

Typical molar mixtures, the constitution of which follows change of the external conditions in a continuous fashion, show the opposite effect. Evidently this is the case for isomorphous mixtures. If, for example, the KBr content of a mixed solution of KBr and KCl be steadily increased, the composition of the mixed crystals (K(Cl, Br)) separating varies continuously in correspondence.

Meanwhile we recognize immediately, in these isomorphous mixtures, that the difference in question is bridged over in the fact that the continuous variations of their chemical constitution are actually at the same time discontinuous. It is only because of the atomistic, and therefore analytically very small, discontinuous changes in that large leptonic unit, the crystal, that practical continuity obtains. In this it will be readily assumed that those intermediate stages, for which the substituents stand in simple stoichiometrical ratio to one another, and for which a uniformity of distribution in the space-lattice is to be anticipated, will stand out somewhat from the others in, say, their optical or chemical properties. The researches of G. Tammann on isomorphous mixtures point to this conclusion.

We may venture to conjecture that for these ratios the linkages in the force field are strengthened.

Mixed crystals then have a specially important physico-chemical interest, owing to their explicit character as intermediate stages between chemical compounds and physical mixtures.

The inner meaning of this is that chemical and physical methods of association are not so essentially different as has been assumed for some time in chemistry.

Not uncommonly, a claim for the sharpest separation of the two conceptions is made. Many, especially old chemists and physicists, have, however, signified their acceptance of the same conception as is arrived at here. Of these may be named H. Boerhave, C. L. Berthollet, J. B. Biot, J. C. Poggendorff, H. Kopp, Guldberg, and Waage, D. Mendeléef, H. J. van't Hoff, and many others, and as W. Nernst, the master of modern chemistry, expresses it shortly in his text-book of theoretical chemistry, "the differences between physical mixture and chemical combination are really matters of degree, and we find in nature all gradations between the two."

OUTGROWTHS WITH SUBSTANCES NOT ISOMORPHOUS

This being so, these ideas may be extended even further to include the observed outgrowths according to definite laws which occur for various substances, e.g. rutile (TiO_2) and hæmatite (Fe_2O_3), or potassium iodide and the complicated silicate, mica. When the particles are near in a leptonic sense, physico-chemical reciprocal actions come into play which may lead to coupling up. It is convenient following F. Grandjean to speak of a "champ moléculaire de contact." As is known, crystallising potassium iodide deposits on mica regularly oriented with respect to its mica substratum, and, moreover, in crystals showing octahedron surfaces, in contrast to the cubic form of freely formed individual crystals.

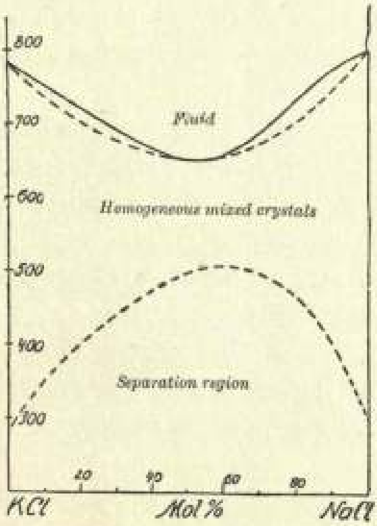

FIG. 121.—Crystallisation of NaCl and KCl from the molten state and separating out of the crystal mixture.

Apart from these macroscopic compounds, a series of phenomena may be obtained in macroscopic and microscopic experiments, which extend the idea of the formation of oriented crystallographic aggregates from the colloidal state down to the greatest dispersivity, i.e. to molecules.

Thus chemical and physical modes of coupling of the particles converge in their essentials to the same thing. Strong and weak linkages are connected by intermediate cases, which can, even in the same substance, be followed through as gradations from the one extreme of chemical combination to the other of evident indifference. Certainly, in this generally important connection the frequent occurrence of a variation of the isomorphous miscibility with temperature is worthy of notice. NaCl and KCl, for example, at high temperatures, as they are obtained by crystallisation from the molten state, occur in the space lattice in arbitrary proportions, Na, K and Cl particles being then linked up in some regular fashion. On lowering the temperature this power of coupling up internally, possessed by the NaCl-KCl crystal fine-structure decreases steadily. The mixture separates out, and finally NaCl and KCl particles lie in contact with, but independently of, each other in a physical mixture.[1] The reciprocal action is not, however, entirely extinct at lower temperatures. On a freshly cleaved substratum of rock-salt a concentrated KCl solution deposits small cubic sylvine

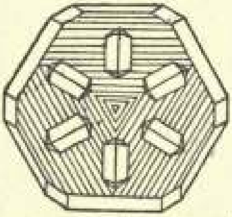

FIG. 122.—Regular outgrowth of rutile on iron glance.

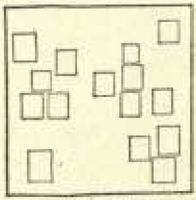

FIG. 123.—Parallel outgrowth of KCl and NaCl.

As crystallographic evidence of the weakening force field, and as symbolic forms of adsorption compounds (p. 130).

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[1] In Fig. 121 these relations are set out in a diagram for which we are indebted to the studies of Kurnakow, Shemtschushny, and Nacken. A. Smits gives also the complete system

$$KCl - NaCl - H_2O.$$

crystals in parallel orientation to the substratum, which is a definite indication that an actual chemical field is set up between the KCl and NaCl, under the influence of which the KCl particles arrange themselves parallel to the NaCl space-lattice. In the reverse case, also, NaCl will deposit on sylvine oriented parallel to the KCl space-lattice.

In view of these examples, an important role must certainly be ascribed to temperature in determining the capacity of aggregation in solution of the molecules.

IX. MORPHOTROPY

HISTORICAL

THE particular type of fine-structural constellation in the molecule or crystal, depends naturally, in the first place, on the nature of the components. It is, therefore, of great interest to compare in this respect various substances with each other, and the most likely method of attack appears to be by chemical substitution.

On these lines P. v. Groth has founded the science of morphotropy. By comparing crystalline forms, he succeeded in showing how the replacement of H by (OH), NO_2, NH_2, CH_3, Cl, in benzene (C_6H_6) manifests itself in changes of corresponding angles, and ultimately of the symmetry. It became possible to determine the morphological value of atoms and radicals, and by multiplying examples to lay down general rules in this respect.

Isomorphism, with its interchanges of allied substances, say of potassium by rubidium in the sulphate, presents itself here as isomorphotropy. Subsequently, as the result of work by W. Muthmann and F. Becke in particular, it was possible to interpret these morphological values with respect to definite physico-chemical masses such as the mol. The axial ratio $a : b : c$, with a different unit of length $b = 1$, for every crystal, was now replaced by the cm. values of the " topic axes," so that absolute comparison could be carried out. Further, the axial lengths of the elementary cell can be employed as cell axes, and, finally, those of molecular and atomic regions as leptonic axes ; this is actually done in a table which follows. The morphotropic variations of the fine-structure have been termed by A. Johnsen, topotropy.

A brief statement such as the following gives a general idea of these important relations.

STEREOCHEMICAL AXES

Using the Loschmidt number $N = 6{\cdot}06 \times 10^{23}$ as the estimated number of molecules in the mol (gram molecule)[1] of any substance, it is possible to calculate the number of molecules in any other mass, and further, by a knowledge of the density) mass in grams per c.c.), the number in an arbitrary unit of space. Of these space units the elementary cell (a term due to P. v. Groth) interests us in fine-structure work ; the reader is already acquainted with it in Fig. 24, page 22. Its dimensions are determined by X-ray methods. The number and also the weight of the molecules belonging to it can be easily calculated theoretically.

The known cell volume, and the number *n* of molecules composing it, give immediately the portion of space appertaining to each of the *n* molecules of the cell.[2]

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[1] By this is meant the number representing the molecular weight in grams of the substance. For NaCl the components Na and Cl of atomic weights 23·0 and 35·46 respectively, it amounts to 23 + 35·46 = 58·46.

[2] The weight of a mol G_M is connected with the volume of a mol V_M and the density S by the equation $G_M = V_M S$. The mol axes are obtained in cm. by a simple calculation. In crystallo-

Nothing now stands in the way of numerical comparisons of the fine-structure of crystallographic and chemically similar substances.

As an example of such an investigation, the table for the closely related isometric salts of KCl, KBr, and KI is here given. Sodium chloride, NaCl, and the cyanide, KCN, are also included. In structure, all these are of the sodium chloride type (p. 22).

Formula.	Specific Weight at 20°.	Mol.			Cell (cube.)			Molecular Domain.			Number of Molecules in the Cell.
		Volume C. Cm.	Weight g.	Cube Axes *a* Cm.	Volume 10^{-24} C. Cm.	Weight 10^{-24} g.	Axes *a* 10^{-8} Cm.	Volume 10^{-24} C. Cm.	Weight 10^{-24} g.	Axes 10^{-8} Cm.	
KCl	1·990	37·64	74·56	3·346	247·72	492·96	6·280	61·93	123·24	3·956	4
KBr	2·756	43·19	119·02	3·508	285·52	786·92	6·585	71·38	196·73	4·148	4
KI	3·134	52·97	166·02	3·756	350·24	1097·64	7·049	87·56	274·41	4·441	4
KCN	1·546	42·13	65·11	3·480	279·73	432·30	6·54	66·93	108·08	4·117	4
NaCl	2·173	26·90	58·46	2·996	177·58	386·52	5·628	44·47	96·63	3·543	4

In the series KCl, KBr, KI, with the same cation K^+ and varying anion, the continuously increasing appropriation of space by the compounds, both as regards volume and axial lengths, is very definitely indicated, as is also the fine-structural equivalence of the group (CN) and the bromine ion. Sodium and potassium show their morphological action in a similar way.

MORPHOTROPIC CONSTRUCTIONS

Making use of the results for "atomic domains" (p. 46), fine-structures can often be predicted with

graphy they are termed "topic axes" by F. Becke and W. Muthmann. Denoting the Loschmidt number by N, we have $\frac{V_M}{N} = V_L$ (V_L = leptonic volume, i.e. volume of one molecule), and placing N molecules in the cell Z, $V_Z = n \, . \, V_L$.

surprisingly close approximation to the actual measurements. In a certain sense the spherical domains lie at hand as bricks to be built up in a definite structural scheme. To take an example, the number $d_{Ca} = 3{\cdot}51$ obtained as a mean from various calcium compounds, and the value $d_1 = 1{\cdot}26$ from MgO lead to the cubic elementary cell constructed in the NaCl type, of CaO with an edge, $a = 3{\cdot}51 + 1{\cdot}26 = 4{\cdot}77 \times 10^{-8}$ cm.; X-ray value $= 4{\cdot}8 \times 10^{-8}$ cm.

Further, let us suppose that we are dealing with the still unknown fine-structure of rubidium chloride. The NaCl type is here to be expected with an elementary cell of side $6{\cdot}59 \times 10^{-8}$ cm. corresponding to the assumptions $d_{Rb} = 4{\cdot}47 + d_{Cl} = 2{\cdot}12 \times 10^{-8}$ cm., which will be approximately true.

The simple relation holding for the atomic domains of allied substances makes it possible to investigate, either graphically or mathematically, new types of atoms with regard to their atomic domains. In this way the series $Mg^{++} = 2{\cdot}99$; $Ca^{++} = 3{\cdot}51$; $Sr^{++} = 3{\cdot}96$; $Ba^{++} = 4{\cdot}36$ leads to the radium ion $Ra^{++} = 4{\cdot}90$. Taking the domain diameter of $O^{--} = 1{\cdot}26$, we arrive at the elementary cell of radium oxide $Ra^{++}O^{--}$, built in the NaCl pattern with presumably a cube edge of length $6{\cdot}16 \times 10^{-8}$ cm.

Even more complicated constructions may be carried out giving satisfactory agreement with X-ray and goniometric investigations.

In this connection the trigonal crystalline salt CsCl . ICl may serve as an example. In Fig. 124 the spherical atom domains of the elements named are piled up one on the other in close packing. Their dimensions ($\frac{1}{2}d_{Cs} = 2{\cdot}52 + d_{Cl} = 2{\cdot}12 + d_I = 2{\cdot}93$

$+ d_{Cl} = 2{\cdot}12 + \frac{1}{2}d_{Cs} = 2{\cdot}52$) give the result 12·21 $\times 10^{-8}$ cm. X-ray research leads to the same number 12·2, certainly a good, if somewhat fortuitous agreement, as regards accuracy. If with this close packing of spheres two material axial lines are constructed, the Cs ions touching those of Cl and I, the arrangement shown in Fig. 124 is obtained with an angle $\epsilon = 39^\circ\ 44'$, which corresponds to an angle $41^\circ\ 57'$ in the goniometric measurements of the crystal. We might well rest content with this satisfactory agreement, but the fact is of crystallographic interest that a very small elongation of the caesium domain in this trigonal, and therefore geometric rotational structure, gives the angle $\epsilon = 42^\circ$, which the crystal actually exhibits according to goniometric observations. Fig. 125 illustrates this point.

In Fig. 126 NaF . HF, as an example morphotropic to CsCl . ICl, is similarly constructed. Here also it is easy, by a slight alteration of the hydrogen, to build up a crystal form of the compound verified almost exactly by X-ray researches.

Finally, reversing the argument, it appears possible also to test a substance of known molecular volume with respect to its structural type. The case of the caesium salts CsCl, CsBr, CsI, may here serve as an example. Their molecular volumes (molecular weight divided by specific weight) are, according to a table in P. Groth's "Chemischer Kristallographie," 41·80, 47·40, 56·85 respectively. If these molecular volumes are calculated for a body-centred elementary cell, the results come with convincing approximation, for CsCl = 42·56, CsBr = 48·72, CsI = 58·70, indicating the existence of this type of structure, while a construction in the NaCl scheme gives the widely deviating values 55·28, 63·28, 76·25.

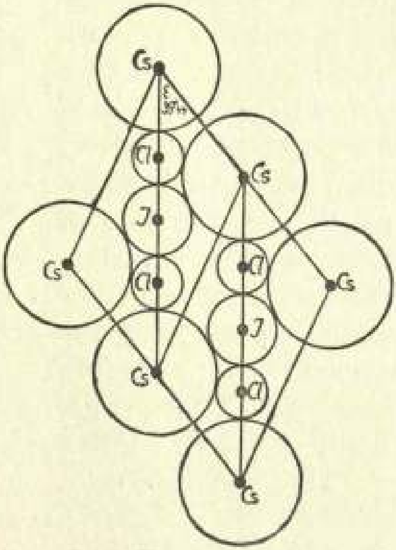


Fig. 124.—
Construction of trigonal CsCl . ICl
from spherical atom domains.

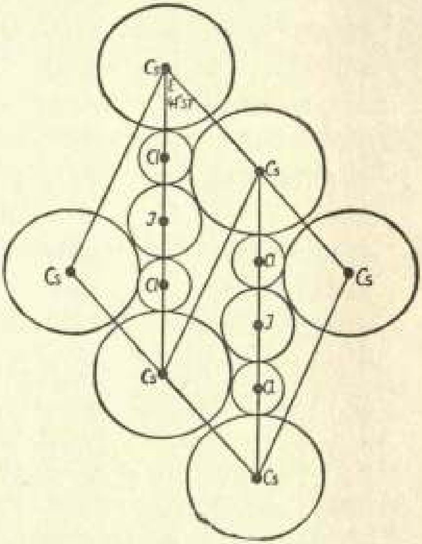
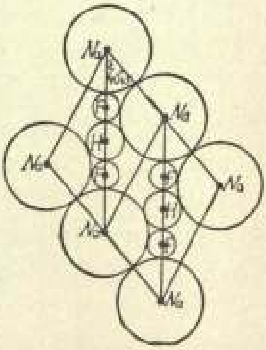


Fig. 125.—
Construction of trigonal CsCl . ICl
using rotational ellipsoids for Cs.

Fig. 126.—Construction of NaF . HF
from atom domains.



Moreover, recent X-ray experiments of Davey have shown that the former assumption is correct.

Strictly, it must be supposed, according to K. Fajans and H. Grimm, that the space dominated by an ion, say K^+, will be affected by its particular neighbours, e.g. F^-, Cl^-, Br^-, or I^-. Thus for no constituent in a compound is the atomic domain always exactly the same.[1] For the most part, however, the relations are comparatively simple, inasmuch as it is possible, according to W. Biltz, F. A. Henglein, and E. Schiebold, to obtain graphically definite linear connections between the magnitudes concerned (p. 184). In short, we are on a very promising road leading to a knowledge of the activities of the particles in the crystal microcosm, and consequently to the prediction of the properties of crystals.

EXAMPLES OF FINE-STRUCTURAL MORPHOTROPY FROM THE MINERAL WORLD

For the formulation of general laws every material is of the same value. At the same time, for those interested in natural science, there is a special attraction in investigating the constitution and the laws of association of the substances which make up the structural material of the earth. Moreover, the frequently large size of such crystals is a favourable factor in the investigation; without the naturally occurring forms of quartz and calc-spar fundamental physical and chemical phenomena, such as double refraction, circular polarisation, etc., would certainly not have been discovered so soon.

In the study of fine-structure, rock-salt, zincblende, lead-glance, calc-spar, magnetite, and several

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[1] Hydrogen appears to be particularly sensitive in this respect. G. Aminoff estimated from the crystal structure of $Mn(OH)_2$ and ice $r_H = 1{\cdot}15 \times 10^{-8}$ cm. and $1{\cdot}12 + 10^{-8}$ cm. respectively. Vegard obtained for NH_4Cl and NH_4Br, $0{\cdot}83$ and $0{\cdot}84 \times 10^{-8}$ cm. respectively, whilst, again, NH_4I and another modification of NH_4Br gave $r_H = 1{\cdot}12$, or $0{\cdot}99 \times 10^{-8}$ cm.

more substances, have served for investigations which have become classical, whilst there remain in the collections of the mineralogist many likely materials for fine-structural investigation, such as quartz, the felspars, mica, augite, hornblende, gypsum and anhydrite, apatite, cinnabar, and numerous other mineralogical forms besides.

With a view to adding to these examples from the mineral world, particularly in a morphological connection, I proposed to one of my students, Herr M. Mechling, that he should undertake, under the direction of my assistant, E. Schiebold, and myself, a study of cobaltite, CoAsS, so that the results might be applied in a topotropical connection with reference to iron pyrites FeSS.

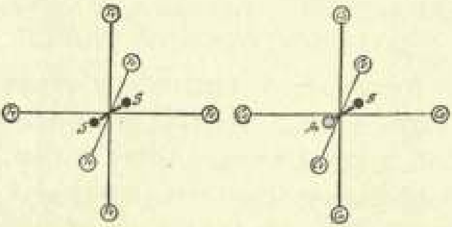

FIG. 127.—Topotropy for FeS_2 (iron pyrites) and CoAsS (cobaltite).

The structure scheme for iron pyrites, according to investigations of W. H. Bragg and W. L. Bragg, is shown in Fig. 127: Fe at the corners and on the surface centres of the elementary cube containing four molecules, and of side $5{\cdot}40 \times 10^{-8}$ cm.; S_2 as a double atom placed centre symmetrically on the ternary axis. Considered topotropically, Co appears in the place of Fe, and an As appears for one S of the doublet in this equilibrium system, deforming it and giving rise to another stable arrangement. It is found that the length of the cube side is only very slightly changed, namely, from 5·40 to 5·66 × 10^{-8} cm., the remaining S is displaced from its position on the body diagonal of the cube, and, at the same time, the substituted As does not take the position of the displaced S atom. The centre symmetry is lost on account of the leptonic inequality of As and S in the new arrangement of the atoms. Cobaltite structure belongs not to the pinacoidal group, as does iron pyrites, but to the pedial group. All mirror symmetry in the fine-structure has vanished.[1]

For the unusually numerous isomorphous mixtures in the mineral world it is further possible not only to compare topotropically the extreme substances of the sequence of mixtures, but also to follow out the process of change, step by step, in the series. With this in view, Lotte Berndt, under the direction of Dr. Schiebold and myself, has worked on a particular case. The mineral investigated was olivine. The elementary structural cell of this Mg_2SiO_4 substance (so-called forsterite) is a rectangular parallelopiped. It is of considerable interest to see how this elementary cell changes when iron atoms are introduced for one part of the Mg in Mg_2SiO_4, by which process a so-called isomorphous mixture $(Mg, Fe)_2SiO_4$ (chrysolite) is obtained, and resulting, finally, in Fe_2SiO_4. The topotropic effect is brought out in the following table:[2]

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[1] According to later research on etch figures by H. Schneiderhöhn, there occurs for cobaltite a rhombic transformation modification with very fine twinned lamellæ. The consequent mimetic isometric structure gives rise in the Laue diagram to an effect of correspondingly high symmetry.

[2] In this a_z, b_z, c_z denote the edge lengths of the elementary cell.

	a_2	b_2	c_2 in 10^{-8} cm.
Forsterite Mg_2SiO_4	4·74	10·19	5·97
Chrysolite $(Mg, Fe)_2SiO_4$ with about 7 per cent. FeO	4·84	10·40	6·10
Fayalite Fe_2SiO_4	4·99	10·89	6·31

It is indeed a triumph of physics that, thanks to X-rays, the absolute values of such small displacements in the microcosm can be measured.

X. ISOTYPY

CRYSTAL SYSTEMS, CRYSTAL CLASSES, CRYSTAL FORMS AS STABILITY TYPES

THE fine-structure of atoms, molecules, and crystals may justly be compared with the astronomical megacosm. In both cases the question is one of statico-dynamical stability systems. It is immediately obvious, then, that as certain structural arrangements recur in star systems, so also types arise in minute structure.

In the visible crystal world such isotypes are given in the crystal systems (syngonies) and crystal classes.

The groupings in the table of page 31 must, in this way, be thought of as stability schemes, and it is probable that they could be calculated as a consequence of attracting and repelling forces. In this way new light is thrown on the crystallographic ideas stated at the beginning of this book, for there we had to deal with cases of isodynamostasy on a large scale. Further, the considerations may be extended to the specific goniometric ratios within the subdivisions. With this in

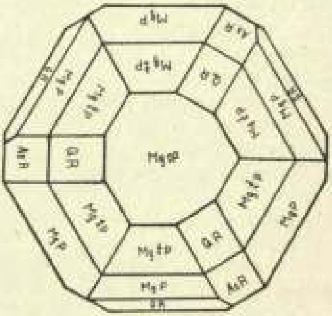

FIG. 128.—Isotypic form grouping.

view I have noticed the remarkable analogy in the crystal forms of very different substances, especially those of simple chemical constitution, such as the elements, oxides, sulphides, halides, etc., in which certain architectural characteristics are repeated. For these the stability form of the complete isometric system is required; for trigonal substances the arsenic, quartz, and graphite type, as well as that of hexagonal magnesium. These crystallographic form groups stand in close morphological relation, as the plan in Fig. 128, page 115, indicates diagrammatically.[1]

FINE-STRUCTURE GROUPS AS STABILITY TYPES

Furthermore, by means of X-ray investigation of crystals, there is an opportunity of examining the case of isotypy with reference to the fine-structure. In

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[1] As examples of special isotypy the following hexagonal substances (magnesium type) are tabulated :—

	a : c	End surface : pyramidal
Magnesium, Mg	1 : 1·6391	62° 9′
Beryllium, Be	1 : 1·5802	61° 17′
Cadmium, Cd	1 : 1·6554	62° 23′
Irodosmine, (Ir, Os)	1 : 1·6288	62° 0′
Zinc oxide, ZnO	1 : 1·6219	61° 54′
Beryllium oxide, BeO	1 : 1·6305	62° 2′
Wurtzite, ZnS	1 : 1·6006	61° 35′
Greenockite, CdS	1 : 1·6218	61° 54′
Magnetic pyrites, FeS	1 : 1·6502	62° 19′
Covellite, CuS	1 : 1·5888	61° 24′
Arsenic-nickel, NiAs	1 : 1·6389	62° 9′
Antimony-nickel, NiSb	1 : 1·7220	63° 18′
Silver iodide, AgI	1 : 1·6392	62° 9′
Ice, H_2O	1 : 1·617	61° 50′
Tridymite, SiO_2	1 : 1·6530	62° 21′
Cadmium iodide, CdI_2	1 : 1·5940	61° 29′
Lead iodide, PbI_2	1 : 1·6758	62° 40′
Carborundum, CSi	1 : 1·6324	62° 3′
Copper glance (pseudo-hexagonal), Cu_2S	1 : 1·6707	62° 36′
Chrysoberyl (pseudo-hexagonal) $BeOAl_2O_3$	1 : 1·6231	61° 55′

fact, the correctness of the idea becomes more and more obvious, for certain structural schemes occur in remarkable abundance, and in peculiarly close architectural relation to one another. For the examples mentioned up to now, the case of a surface-centred elementary cell with its tetrahedral placing of the atoms in the form of the isometric type for elements and simple compounds, occurs very frequently indeed. This corresponds to a very stable style of structure, which still stands out prominently on trigonal deformation. On closer consideration of the elementary cells (Fig. 129 and 24, p. 22), the pre-eminent importance of the tetrahedral grouping will be easily recognised as parts of the sections there depicted, not only for diamond and zinc-blende, for example, but also for copper, rock-salt, fluor-spar, and in the deformed calc-spar. In Fig. 130 tetrahedral types of structure are reproduced to show their special character.

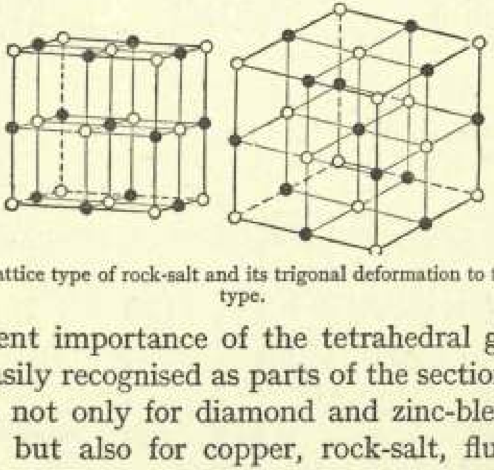

FIG. 129.—Lattice type of rock-salt and its trigonal deformation to the calc-spar type.

In view of the isotypic agreement in the stability of the isometric diamond and zinc-blende fine-structure, it was of great interest to see if this equilibrium form transmits itself to any extent to the hexagonal type, a form I have ascribed to magnesium, and to which carborundum consisting of C and Si also belongs. The attractive problem of investigating the fine-structure of this carbide by means of the delicate and yet so powerful agency of X-rays was undertaken and carried out with great success by H. Espig, under the direction of Dr. E. Schiebold and myself, on type II. of carborundum.

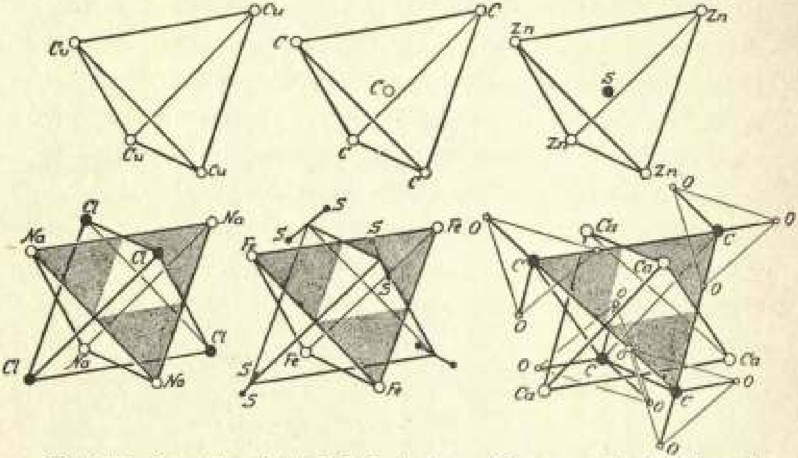

FIG. 130.—Examples of tetrahedral structure: Copper, rock-salt, diamond, zinc-blende, iron pyrites, calc-spar.

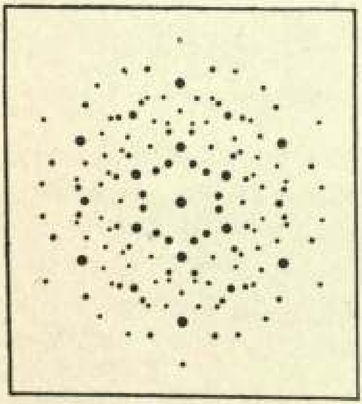

FIG. 131.

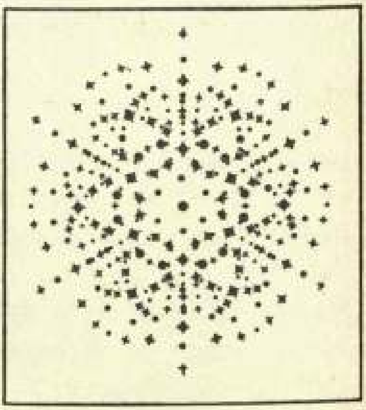

FIG. 132.

FIGS. 131 and 132.—Family relationship between the Laue diagrams of a diamond twinning (plate parallel to the octahedral surface) and of carborundum (plate parallel to the end surface).

I had already earlier pointed out, in a comparison of the Laue diagrams of diamond and silicon carbide, the great resemblance of these spectral symbols of the fine-structure; this is brought out well enough in Figs. 131 and 132. As the crosses in the figure for carborundum show, it contains all the reflexions of the diamond. The detailed X-ray study of H. Espig very clearly indicated the correctness of the assumption of a structural affinity. The tetrahedral diamond structure is involved to some extent as a component of carborundum. Its carbon atoms constitute goniometrically a form nearly identical

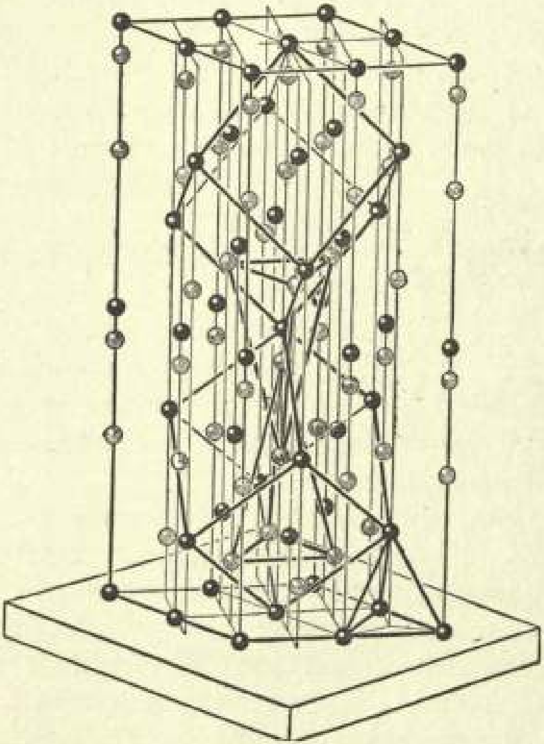

FIG 133.—Fine-structure of modification II. of carborundum. C, dark; Si, light circles.

with those of diamond. In this way, one of the two (for the diamond, equal valued) carbon families is reproduced here, the Si atoms of the carborundum replacing the second tetrahedral group of the diamond. Here, however, an important change in configuration occurs, in that this type of atom is arranged not in tetrahedra, but in slender trigonal pyramids, which are set with the apex of one in the body of another. Moreover, the rearrangement of the C and Si stars in this complicated heaven is also shown in the variation of the side length of the carbon tetrahedron; it amounts in the diamond to $2{\cdot}5 \times 10^{-8}$, and in carborundum to $3{\cdot}1 \times 10^{-8}$ cm. Thus both the diamond and carborundum belong, crystallographically, to a special type, and it is now definitely recognised that they are in consequence intimately connected fine-structurally.

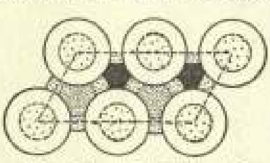

FIG. 134.—Tetrahedral fine-structure of hexagonal zinc oxide. Large atom domain (d = 2·64)Zn, small, (*d* = 1·26)O.

The same thing applies to hexagonal zinc oxide, which W. L. Bragg has investigated. According to him its oxygen atoms form everywhere the middle points of tetrahedra whose corners are occupied by zinc atoms. Hexagonal zinc oxide stands, therefore, in close relation to isometric zinc sulphide, and also to the diamond.[1] According to G. Aminoff, an analogous case in connection with isotypy arises for $Mg(OH)_2$ and H_2O. In its formal fine-structure, $Mg(OH)_2$ can be regarded as $H_2O \,.\, OH_2$ structure, for which one H_2 has been replaced by a magnesium atom and spacial condensation has occurred.

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[1] Isometric ZnS shows in its Zn and S tetrahedral groups the two tetahedra of the diamond (compare Fig. 24*d* and 24*e*, p. 22).

XI. CRYSTAL GROWTH AND SOLUTION

THE conception of the crystal as the stability form of attractive and repulsive anisotropic forces, involves the assertion of its reaction to external physical or chemical changes in order to accommodate itself to the new conditions.

In this sense we may consider the extensibility and compressibility of crystalline materials, and many other physical properties, under the influence of temperature or pressure change. The capacity of crystals to react to their surroundings stands out as specially obvious in the easily observable phenomena of growth and solution. These may therefore be briefly considered here.

PURE CRYSTAL GROWTH

Every crystal has grown from a tiny nucleus, and in this process of enlargement by addition of successive shells of parallel placed particles, the anisotropic character of the substance is very clearly shown. In this way we get, in general, not a sphere, but a faceted body, indicating that the nucleus grows with different velocities along different directions, in the form of a growth pyramid; the crystal is thereby divided up genetically, as F. Becke first emphasised. Directions of similar growth recur at intervals.

According to the fundamental work of A. Johnsen, which was extended by R. Gross and others, the curve of growth velocity, which is obtained by drawing proportional vectors from some fixed point in accordance with this growth anisotropy of the crystal, shows maxima and minima, and, moreover, very sharp gradients. Null or infinite extremes do not occur. Normal to the minima directions, the large crystal surfaces naturally unfold

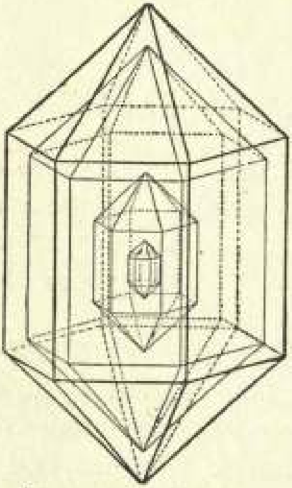
FIG. 135.—Growth by deposition of successive shells (example of quartz).

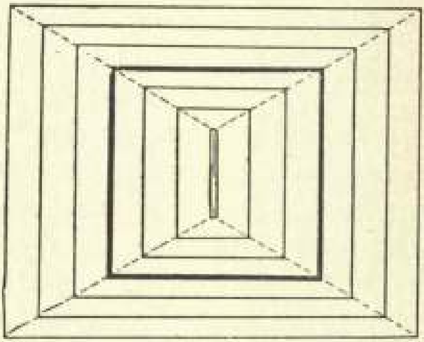
FIG. 136.—Growth pyramids.

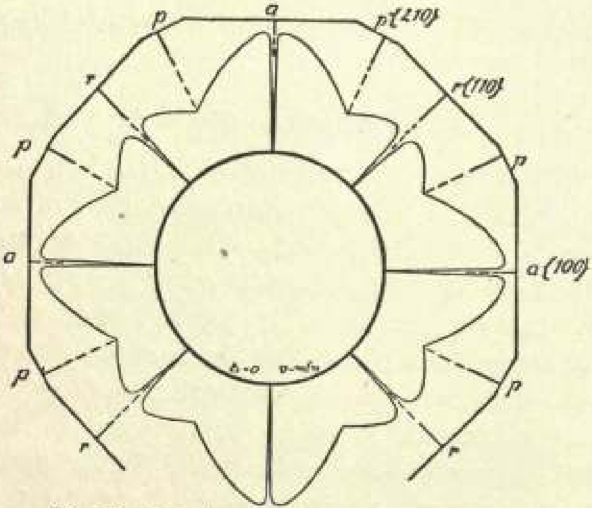

FIG. 137.—Intensity curve for the growth of rock-salt.

themselves, since these remain near the origin. To them is to be ascribed a lower surface energy compared with the faster-growing surfaces.

F. Haber, F. Paneth, P. Niggli, and others have represented the outer zone of the crystal as unsaturated with respect to valency. It attempts, therefore, to reach equilibrium by addition of new particles. Harmony with the outside is not attained, for a new surface is there, and the growth still continues.

P. Niggli made a considerable

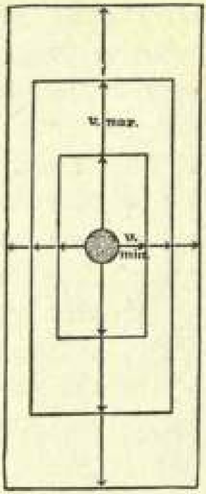

FIG. 138.—Anisotropy of growth.

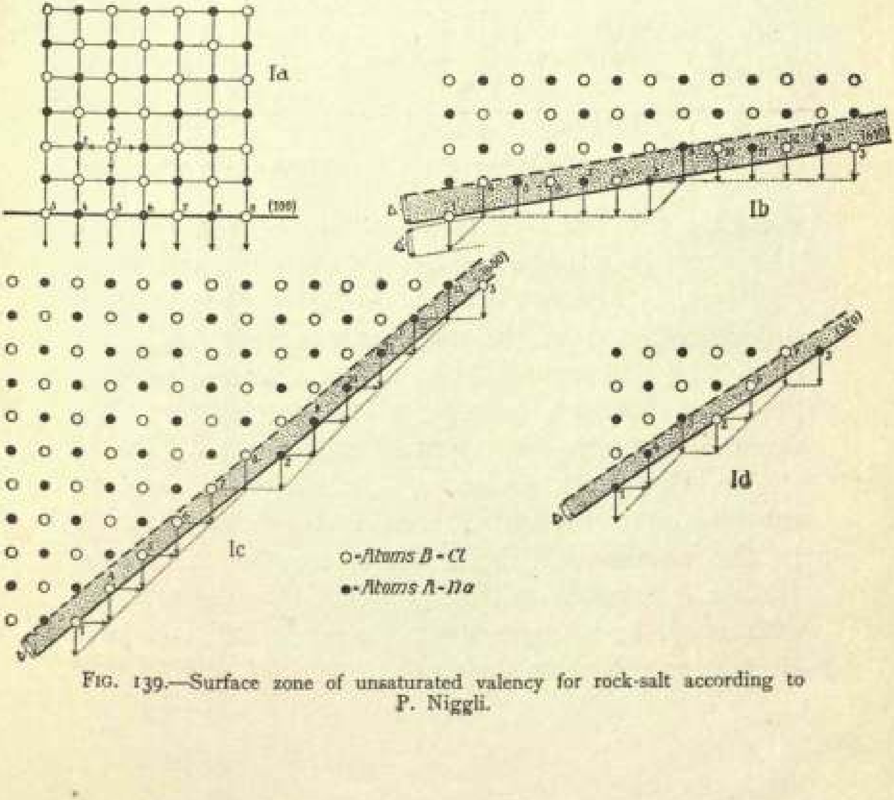

FIG. 139.—Surface zone of unsaturated valency for rock-salt according to P. Niggli.

advance in this matter when he assumed the growth velocity proportional to the thickness $\triangle$ of the assumed unsaturated crystal layer, a magnitude different for different surfaces. In this way he arrived at theoretical growth intensity curves, which, with lead-glance and rock-salt (Fig. 139), for example, agree very well with our ideas derived from the morphology of these minerals.

Valeton has developed some very illuminating views on the growth of crystals, with special reference to the structure of rock-salt from sodium and chlorine ions. The deposition of new particles depends, he says, on the fine-structural nature of the surface. The chess-board aggregation in the cube planes of positive Na and negative Cl atoms is very clearly differentiated from the uniform octahedral surfaces containing either sodium or chlorine (Figs. 140-142. See also Fig. 27, p. 26). The former are less favourable to the retention of an impinging ion of the solution than the latter. An ion which is to be retained on a cube surface must strike almost exactly in the middle of a field, whilst for the octahedral surface it depends on the sign of the ion, there being, on the whole, a 50 per cent. chance. The cube will therefore grow more slowly than the octahedron, and

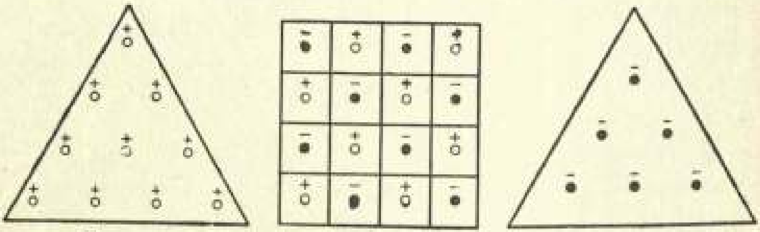

Fig. 140. Fig. 141. Fig. 142.

Figs. 140-142.—Ion groupings on the cube and octahedron surfaces of rock-salt. After Valeton.

will, in consequence, predominate in rock-salt. An important point to be noticed in this connection is that whilst with the Niggli idea cube the octahedron and rhombic dodecahedron surfaces do not differ in the thickness of their unsaturated zones (zero in each

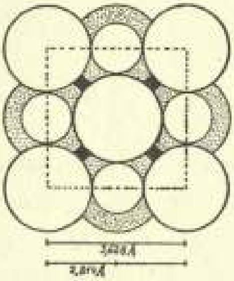

FIG. 143.

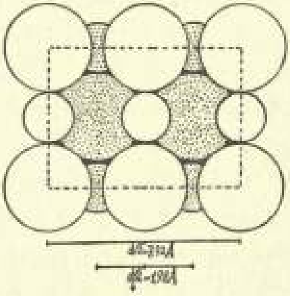

FIG. 144.

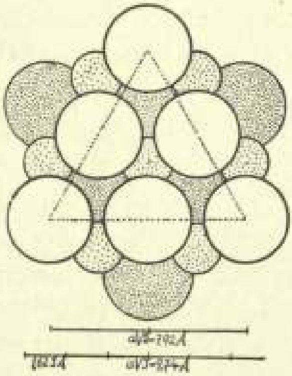

FIG. 145*a*.

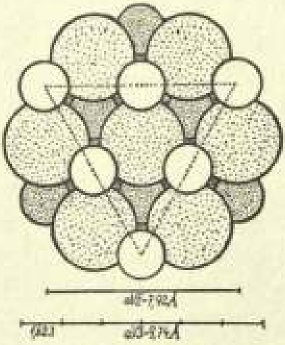

FIG. 145*b*.

FIGS. 143-145.—Surface structure of the cube, rhombic dodecahedron and octahedron surfaces of rock-salt, indicating the arrangement of the atom domains. (The second scale relates to depth distances.)

case), on Valeton's views there arises the possibility of growth differences for these surfaces. In this respect the great dissimilarity of the surfaces may be indicated in greater detail by Figs. 143-145. These show fine-structural aspects of such surfaces, indicating not merely the external plane but also the region beneath by representation of the atomic domains. The action of the attractive forces, which presumably are capable of making their influence felt over several periods of the fine-structure from the inside, outwards, will for a cube surface be screened off by packs of only two layers by the covering of the atomic domains.[1] Matters are otherwise for the octahedron, or even for the pyramidal cube surfaces, as Figs. 144 and 145 demonstrate.

Certainly these fine-structural differences with respect to the region below the surface, together with the net density (as the measure of the number of particles belonging to the layer), are of immediate significance as obvious explanations of the variation of growth with direction in the crystal. Further, it must be remembered in all these considerations that in crystal growth we are concerned with the action of a complicated chemical field between the crystal and its surroundings, otherwise there would be no possibility of explaining the great influence on the crystallisation of the other things present in the solution, which can give to sodium chloride, in one case, the form of a cube; and in another case, that of an octahedron or a pyramidal cube (Fig. 146).[2]

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[1] Here, as in other cases as for diamond (p. 55), and still to a considerable extent in zinc-blende, canals as penetrating rifts in the structure persist in these constructions which traverse the crystal in certain directions, forming a check pattern. Their significance, taken together, as a porosity of the crystal, remains to be investigated in another place.

[2] We might assume for this that the surface of the crystal is chemically compensated by a special arrangement of the particles there, and under the influence of the solution immediately rearranges itself (compare p. 79).

In consequence, such additions to the solution must possess the power of altering the factors conditioning growth velocity at the crystal surfaces. For example, the growth normal to the octahedron surface may be retarded, and this external form imparted to the crystal. Such, more or less, effective protection of the surface will be explained by the adsorption of the other substance present in solution, an explanation proposed by R. Marc. Experiment very definitely supports his hypothesis of a retardation of growth by adsorbed substances. With calcium sulphate, for example, on addition of merely a trace of a certain dye, which is absorbed by the crystal, we get, in contrast to the well-formed crystals obtained from pure solution, an irregular mass of thin sheets. When the crystal surface is saturated adsorptively it loses the power of acting as a nucleus. Such crystals may be shaken up in supersaturated solution for days without disturbing the supersaturation.

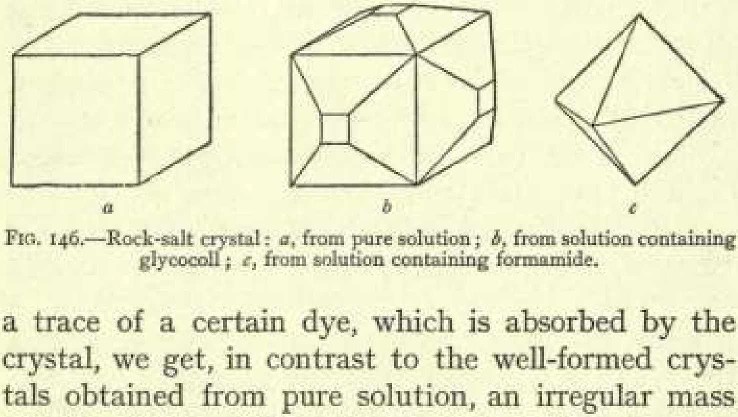

FIG. 146.—Rock-salt crystal: *a*, from pure solution; *b*, from solution containing glycocoll; *c*, from solution containing formamide.

The particular form of a crystal constitutes a morphological symbol of the equilibrium of the balanced force fields which arise between its own substance and the materials around.

MIXED CRYSTAL GROWTH

For the analytical chemist crystallisation and crystal growth have a special importance. Crystallisation is for him a process of molecular selection, inasmuch as one kind of matter separates cleanly in crystal nuclei, on which more of the same substance is then deposited. This process brings to mind in a general way the ability of organisms in an abundance of material, say, of a solution, to apply it to the growth of a certain one.

Of considerable general interest in physical chemistry, and of significance to the analytical chemist, is a circumstance which may diminish the value of crystallisation as a means of purification. If, in the chemical field between crystal and solution, besides the substance chemically identical with the crystal, there exist also others, which, although different, are chemically analogous to it, as, for example, besides the chloride of potassium, those of Rb or (NH_4), then interchange of atoms or radicals may occur.

This has been known as an experimental fact since the researches of J. N. Fuchs and F. E. Mitscherlich, and later, in the light of space-lattice theory, has become very clearly understood, finestructurally.[1] The case here is one of the growth of isomorphous mixtures (p. 97). Moreover, different mixtures, or the pure extremes of substances so related, are able to build themselves up into layers. A splendid example of this is shown in Fig. 148 for zonal tourmaline.

The inclusion of such alternative structural units in the growth can naturally only take place in so far

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[1] See Fig. 147.

as the stability of the whole is not imperilled. Often that is not at all the case for extensive isomorphous mixtures as for felspar, olivine, and other minerals. In other cases, warpings of the form or optical anomalies point to discordance in the structure of such heterogeneous lattices. There exists also a certain danger with respect to the architectural cohesion, that on change of the temperature the alternating particles may lose more and more their structural equivalence by the swinging round of their electrons, i.e. by change of form. A pair of substances such as Na and K is simply incapable of this alternating incorporation in the growth, unless the atomic structures are first in a similar condition. This leptonic isomorphism depends on the physico-chemical factors, temperature, and pressure, as well as on the action of the surrounding material, these being the effective influences on the fine-structure. In this respect the marked change in the miscibility with temperature of NaCl and KCl already mentioned on page 103, is of interest.

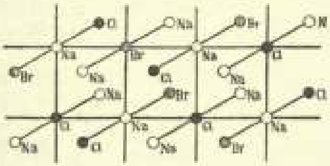

FIG. 147.—Isomorphous alternation of Cl and Br in the space-lattice.

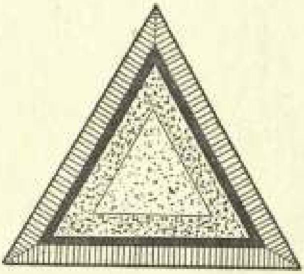

FIG. 148.—Isomorphous stratification Example: tourmaline.

Especially worthy of note in these phenomena of regular incorporation in mixed growth are those cases in which occasionally a substance quite foreign is incorporated. Many minerals bound together macroscopically in regular fashion, such as cyanite, staurolite, rutile, and iron-glance exhibit the relationship (Fig. 122, p. 103). For very small dimensions of the definitely oriented guest material, and for more extensive growth of the surrounding host, a kind of colloidal solid solution with regular packing of the substances, but without any stoichiometrical ratio one to another, is arrived at as, for example, in "adsorption compounds," "occlusion," and the like.

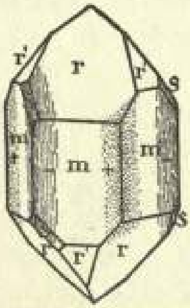

FIG. 149.—Demonstration of electric forces by the deposition of sulphur and red lead on quartz.

As to the forces of cohesion between the crystal particles and such foreign bodies, no deviation will be made from the hypothesis of electrical coupling. This hypothesis has continually increasing support, as, for instance, in connection with the flocculation of colloidal substances. There again it is possible to employ crystals as types with actual visual observation. Electrically bound charges may, in fact, be immediately observed for pyro-electric crystals like quartz, which on change of temperature becomes electrified positively and negatively respectively on its alternate column edges (Fig. 149). To show the distribution of the oppositely charged regions in such cases, A. Kundt employs a mixture of sulphur and red lead which has become electrified by being blown out of a suitable sprinkling apparatus. The positive red lead sticks to the negative parts of the crystal, coating them red, the negative sulphur deposits on the positive regions, which consequently appear yellow. In this way an adsorption coupling of crystallographic nature can be immediately detected for quartz.

COLLECTIVE CRYSTALLISATION

It is further of great physico-chemical interest that forces tending to form aggregates exist not only between crystal and solution, but also between crystal and crystal. In fact, it is certainly one of the most remarkable phenomena of the crystal world that in spite of the rigidity of the material there is this tendency to collect together to larger individuals, i.e. the space-lattices of neighbouring crystals tend to set themselves parallel and to link up ; this process, which I have studied in various cases, I have termed "collective crystallisation," which indicates its nature. The effect is, in view of the coalescence of small particles to form large ones, a "coarsening of the grain." The process may be demonstrated in a few minutes by heating up cast steel. Every chemist is acquainted with it in the much-used platinum crucible, and the technical lighting workman, in fine tungsten filaments, the innumerable small crystal individuals of which, on glowing, are turned round into single crystals which may be a metre in length. Tungsten trioxide also is convenient for showing the phenomena, and calc-spar too, if care is taken that in the intense heating the CO_2 is not allowed to escape, as is the case if the experiment is carried out in a carbonic acid bomb. The marmorisation of dense limestone in contact and regional metamorphosis is also a case of this collective crystallisation.[1]

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[1] What happened here was a transformation of ordinary dense limestone into marble by molten masses, perhaps of granite type,

In such cases of closely packed, new-grown structures (as Figs. 150*b* and 151*b* show), the individuals hinder each other in the production of regular crystallographic forms. If, on the other hand, they

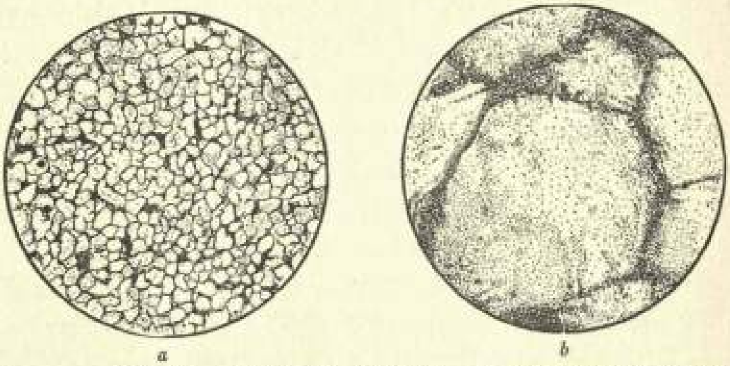

Fig. 150.—Collective crystallisation for iron: *a*, Martin steel; *b*, the same Martin steel glowed in the furnace.

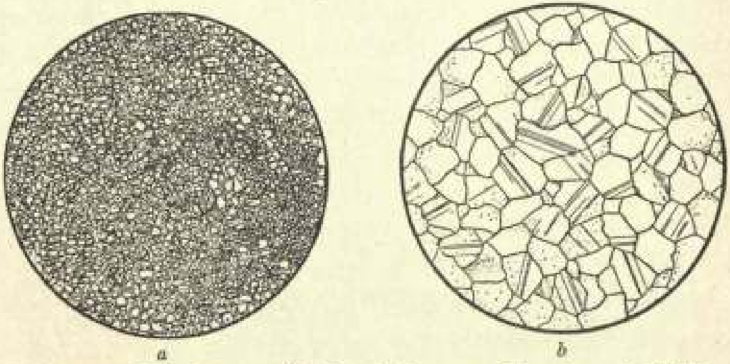

Fig. 151.—Collective crystallisation of calc-spar: *a*, limestone; *b*, marble.

which, arising from the depths of the earth, stuck fast in the stony crust, and then, by reactive action of the gases and liquids liberated, and the high temperature, extensively transformed the matter around. Here, at the "regions of contact," collective crystallisation played a great part, and, in addition, many substances finely disseminated in the original material became associated into large crystals of, perhaps, graphite, andalusite, augite, garnet, etc., so that here again collective crystallisation was effective.

swim around freely in a liquid, association by collective crystallisation, with new development of crystal surfaces, can proceed. This is the case for the highly interesting combination of contiguous ammonium oleate crystals described by O. Lehmann. Elongated pyramidal individuals coalesce to a structural unit more or less definitely crystallographic in contour, or, at least, to a group of crystals with their principal axes parallel (Fig. 152). Moreover, it may probably be assumed that in every crystallisation, to begin with, numerous sub-microscopic crystals arise which form by aggregation visible crystal nuclei in the above manner.

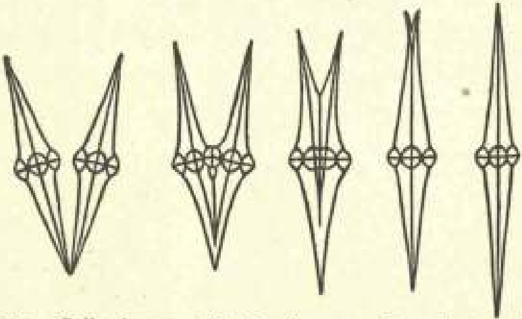

FIG. 152.—Collective crystallisation for ammonium oleate. After O. Lehmann.

CRYSTAL SOLUTION

Corresponding to many of the observations on crystal growth, a knowledge of crystal solution has lately been developed to a very gratifying extent. The observations here indicate that the principles of the phenomena are closely connected. It appears of use in dealing with the solution of crystals, as in the discussions on their growth, to employ the very clear picturisation of the atomic domain stereograms. In this way we see immediately, as the examples of Figs. 143-5, page 125, show, the anisotropy which occurs both in solution and growth. It becomes clear that the displacement of the surface, by the attack of the solvent on the crystal structure, takes place with varying rapidity, depending on the direction of attack. Research definitely corroborates this statement, to which the pretty phenomena of etch figures bear immediate witness. These are formed in large numbers, and mostly of microscopic dimensions, on crystal surfaces attacked by a solvent, and represent, in the form of cavities or eminences with regular edge and surface boundaries the symmetry of the crystal faces on which they occur (Fig. 153*a*). On examining all the results so obtained, the structural style of the whole crystal body becomes evident. With the reflexion goniometer corresponding light figures may be measured (Fig. 153*b*). In both figures the binary character of the surface is brought out. Good examples of solution anisotropy are very neatly shown by plates cut into circles, an example of which is shown in Fig. 154. It represents an initially circular plate of gypsum, which on immersion in water has changed to a pointed figure of elliptic periphery, owing to the anisotropy of the solution velocity. The relations of polished crystal bodies of

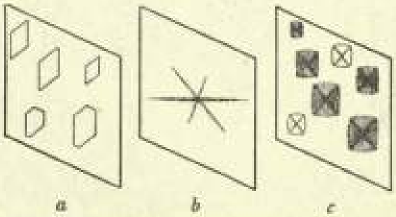

FIG. 153, *a*, *b*, *c*.—Etch figures and the corresponding light figures on a side surface of gypsum, together with figures for the same mineral dehydrated.

regular, and in particular, cubic form, or of crystal spheres, are known in even greater detail. Growth and solution velocity mutually correspond, the representative vectors rising and falling together. The directions of rapid growth are those of rapid solution, and vice versa. During the solution of a crystal a struggle takes place between the anisotropic velocities of solution. The surfaces, which quickly approach to the mid-point of the crystal, and which are those having large solution velocities in the direction of their normals, will gain more and more area, suppressing the slower ones which will probably be present at the start, and will finally form the boundary planes of the residual body. The scheme of Fig. 155 depicts such a final form for anhydrite. In the same connexion several figures from a research of W. Schnorr on rock-salt may be mentioned. Specimens of the mineral which are initially cubic (Fig. 156) assume the forms shown in Figs. 157, 158, 159, 160, when immersed in an unsaturated solution of sodium chloride containing urea. At first there

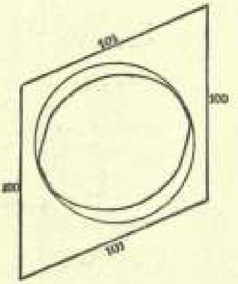

FIG. 154.—Anisotropy of crystal solution. Example: Initially circular plate of gypsum in dissolution.

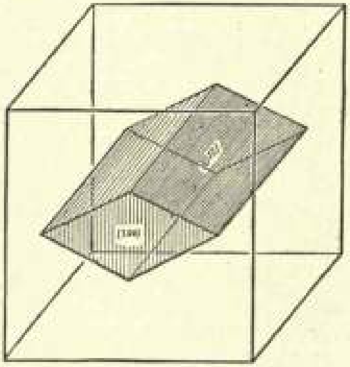

FIG. 155.—Reproduction of a permanently conformal solution form. Example: Anhydrite in sulphuric acid.

are formed, on the cube edges, surfaces of the pyramidal cube, which suppress the original form, but are then suppressed by those of the icositetrahedron. The icositetrahedron so produced is quite unaltered in shape on further solution. A stability form as the expression of the equilibrium attained is arrived at in this way. Under constant conditions, during solution, as also during growth, the velocity of displacement of a surface is found to be always the same.

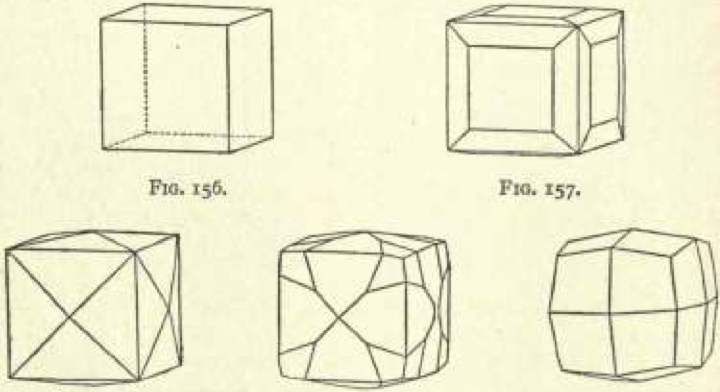

Fig. 156. Fig. 157.

Fig. 158. Fig. 159. Fig. 160.

Figs. 156-160.—Solution process for a rock-salt cube in an unsaturated solution of sodium chloride containing urea. After W. Schnorr.

An analogy between growth and solution also arises in this way, since, in both cases, the question is one of definite reciprocal action between crystal and its environment, depending on the nature of the other substances present, i.e. on the chemical field. The morphological action of an anisotropic solution depends not only on the crystal but also on the particular solvent. This may be very clearly shown for anhydrite, which W. Burckhardt has investigated on this point at my suggestion. According to whether sulphuric acid, nitric acid, water, or salt solution was employed, different solution forms were obtained from a cubic cleave of the rhombic mineral (Fig. 161).

The symmetry of the solution body is naturally the same in all states of its formation and for every solvent. It is identical with that of the growth figure. From the phenomena of solution the particular class of the thirty-two crystal classes to which a substance belongs may be determined.

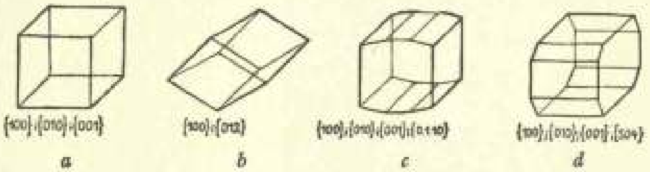

FIG. 161.—Variation of the solution form for different solvents. Example: Anhydrite. *a*, Tri-pinacoidal initial cleave; *b*, solution in sulphuric acid; *c*, in nitric acid or water; *d*, in salt solution.

SUMMARY OF CRYSTAL GROWTH AND SOLUTION

In a general survey of the processes of crystal growth and solution it must be considered that the question is, broadly, one of the displacement of the boundary between solid crystalline and liquid (in certain cases, gaseous) masses which are exerting forces on each other in opposite directions. In growth the attractive forces of the crystal preponderate; in solution those of the surrounding matter are greatest. The external surface is correspondingly displaced. All circumstances which diminish the electrical connection of the crystal particles act in the direction of solution, and vice versa. Water, with its high dielectric constant, and consequent extensive diminution of the electric attraction, brings many crystals to destruction.

Such crystals dissolve as soon as the conditions of temperature, i.e. of the motion of the particles, and the modifying influence of other substances in the solution, permit a displacement of the surface inwards as the result of the opposing forces acting in this direction. For insoluble substances the internal cohesion preponderates over physico-chemical forces, tending to break up the structure.

XII. CHEMICAL ACTIONS ON CRYSTALS

ANISOTROPY OF CHEMICAL ACTIONS ON CRYSTALS

ALTHOUGH the phenomena of growth, solution and chemical action are dealt with separately, no fundamental contrast in the processes is implied. On the contrary, they are very closely related. Thus the reaction $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$ for calc-spar manifests its regular anisotropy not only in pretty microscopic etch figures (and also light figures) (Fig. 162), but also in the varying amounts of CO_2 developed in unit time on the morphologically different surfaces. The same thing applies for the reaction body. Fig. 163 gives a beautiful example of this. Fig. 164 depicts such a case indicating the variation with change of the corrosive agent employed; it refers to the decomposition of a tourmaline by caustic potash and hydrofluoric acid, which was recently studied in my institute by Lotte Kulazewski. The reactions with the silico-borate in question are especially interesting, as, owing to the trigyric domatic character of the mineral, they proceed vectorially (differently in the upper and lower halves of the tourmaline sphere), as a comparison of the diagrams Figs. 164*a* and *b* and *c* and *d* indicates. Figs. 164*a* and *c* represent the

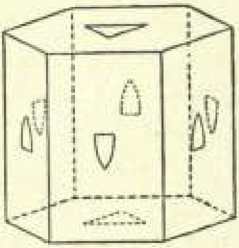

FIG. 162.—Etch figures on a calc-spar crystal.

upper, Figs. *b* and *d* the lower hemispheres with respect to the light reflexion of the reaction body; both hemispheres are depicted up to beyond the equator. On allowing the reaction to proceed further, the vectorial character of the chemical process is realised morphologically with extraordinary effect, in that the sphere becomes more and more flattened on one side, and finally is transformed into a dome-shaped body, which has already been illustrated in Fig. 79*e*, page 56. In cases of centre symmetrical structure the chemical action is tensorial, i.e. equal in any one direction, and the corresponding opposite direction.

ANISOTROPIC CHEMICAL REACTIONS OF MOLECULES

For individual molecules in gases or liquids the morphological principle of chemical reaction cannot differ from that for crystals. Indeed, the fundamental conception of the stereochemistry of chemical reactions, such as the localisation of the replacement of one or more hydrogen atoms in the benzene molecule by Cl, NH_2, CH_3, or other radicals,[1] corresponds to this assertion. The process of chemical action, according to this, is always definitely anisotropic, and the action for molecules only differs from that for crystals in the suppression of a restricting rhythm in the structure, and consequently in the chemical relations. A centre or mirror symmetrical arrangement, or a "plurality" of places liable to attack may naturally, however, play a rôle in chemical operations with molecules, inasmuch as completely similar topical relations (such as the two (NH_4) groups

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[1] For the mechanics of such processes, compare page 158.

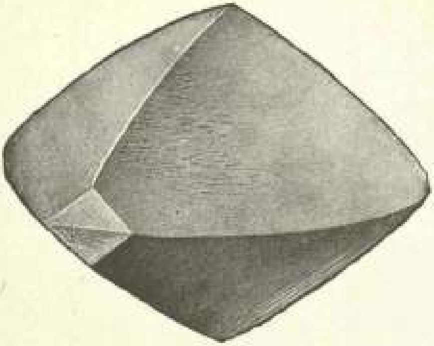

FIG. 163.—Reaction body of a sphere of topaz after treatment with caustic potash. *After M. Eichler*

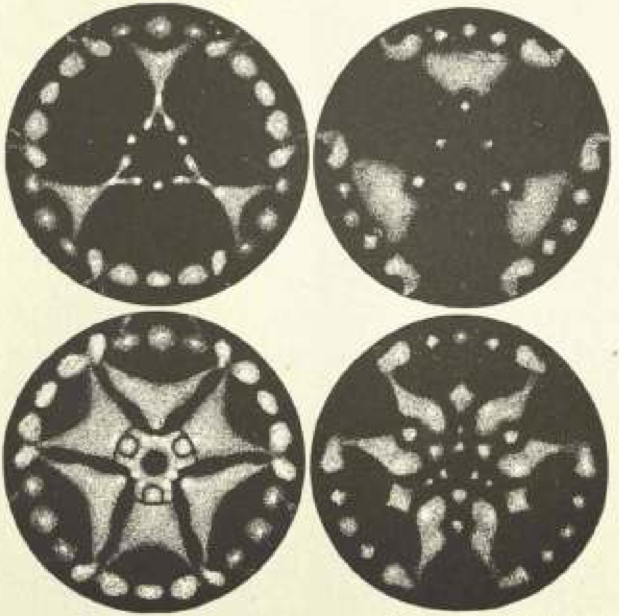

FIG. 164.—Reaction anisotropy with ternary rhythm obtained by treating a tourmaline sphere with 1 (left-hand figure), caustic potash ; *a*, top surface ; *b*, under surface. 2 (right-hand figure). hydrofluoric acid ; *c*, top surface ; *d*, under surface of the sphere. (Vectorial anisotropy of chemical reaction.) *After Ch. Kulaszewski*

in $(NH_4)_2\ CO_3$ molecule) may show in similar reactions their equal fine-structural and equal chemical rank in the complex.

STRUCTURAL RIGIDITY OF ELECTRONS, ATOMS, MOLECULES AND CRYSTALS

According to the above, an estimate of the chemical nature of substances and of their changes turns on the investigation of fine-structure and its variations. This can only be carried out completely by reference to the stages in the graduated series which extends from the simplest form of matter, from electrons to atoms and molecules, and finally to crystals.

With respect to the possibility of initiation of chemical reaction and its continuance, the general structural rigidity of the particles is the question of prime importance, inasmuch as the resistance to chemical change is dependent on this factor. As the particular circumstances vary considerably, we are interested here in the general state of affairs, that is, whether, for the purpose of the present consideration, the graduated series from electron to crystal is arranged in accordance with the structural rigidity. An examination of the series from the lowest to the highest member indicates unmistakably an increasing fine-structural complication, and parallel with this, a decrease in the rigidity of the various types.

The architecture of the electron has remained up to now imperturbable. Such forms are, we may say, fortresses still untaken.

Practically the same thing holds for the atom as for the electron, as far as the central portion, the nucleus is concerned. A variation of this inner structure, the main mass of the atomic system, is only possible by enormous expenditure of energy. As we know, Rutherford has managed to cause disintegration of nitrogen atoms $\overset{14}{\mathrm{N}}$ into $2\overset{1}{\mathrm{H}}^{+}$ and $3\overset{4}{\mathrm{He}}^{++}$ by powerful bombardment with He^{++} particles. Only one out of every 100,000 shots resulted in an actual collision. Although, therefore, the nucleus of the atom is not indivisible, it is a structure extremely difficult to split up.

For the outer shell the case is otherwise. As regards this external zone, the atomic system does not, in point of fact, accord with its name. On the contrary, the atom shell is quite easy to split up, and is thus "eutomic." Since the acceptance of Sv. v. Arrhenius' conception of ions, and following that, the fine-structural explanation of their formation, as a splitting off of electrons from the outer sphere or an insertion of the same, the matter has become one of easily effected superficial variations. The idea of structural variations in the atom is made use of when light emission and absorption are explained as the transposition of an electron from one stable path to another, with consequent loss or gain of energy quanta. In such cases quite small quantities of energy render possible very real changes in the outer sphere of the atom.

It would be superfluous here to go into details concerning the disruption and aggregation of molecules and their transformation by substitution; this is, in fact, the main topic of chemistry. The inconceivable abundance of these phenomena shows how such changes can take place, with varying energy exchanges, which, in general, occur with relatively greater facility than in a physical field (e.g. by a rise of temperature or through the action of matter).

Passing through the structural series to the final and most complicated forms, namely, crystals, which are specially considered here, the relations point in the same direction of readier variation in the architecture. With crystals it is quite usual for the structure to collapse on application of physical or chemical influences, and for the matter to assume a lower structural type. For instance, in the action of HCl on calc-spar, the space-lattice complex of the latter is broken up with the formation of free molecules, $CaCl_2$, H_2O, and CO_2.

CRYSTALLOGRAPHIC CHEMICAL CHANGES IN THE STRUCTURE. UNDERMINING AND RECONSTRUCTION

In less frequent cases, however, chemical changes occur in crystalline materials without destruction of the crystal structure, i.e. with preservation of the high crystalline status of the substance. We are then concerned with a particularly important case of the so-called topochemical reactions of V. Kohlschütter, that is, with a structural undermining. Further, it is occasionally possible to reverse the process or to substitute something else for the substance removed, and thus to transform the crystal structure without at the same time destroying the crystalline character of the material. But naturally, these are extreme cases which are linked up by intermediate examples of more or less drastic disturbance with the other extreme of complete destruction of the crystalline form during chemical reaction.

It is profitable to compare a process of ideal crystallographic chemical undermining with the partial destruction of a framework structure from which the filling between the beams has been removed. On account of this, the structure becomes less compact without, however, collapsing, and the principal structural lines are still maintained. The simile may be readily extended to a reconstruction. The beams, although remaining in position, may, in the partial disruption, be damaged to some extent by splitting and transverse fracture, and as structural particles in an undermining or reconstruction may become displaced, the stability of the whole may be impaired and finally lost.

In the light of space-lattice theory, it may be assumed for the ideal case of undermining that from a point system such as the one of Fig. 9, page 10, one space-lattice is removed without the remainder collapsing, although it may be deformed to a new equilibrium arrangement. In reconstruction compensation is made for the removed lattice. We must, however, expect many gradations of the above, while still more complicated rearrangements and dismemberments even to the dissolution of the molecule, may occur.

The structural residue which remains after glowing the natural fluorine-containing cerium didymium lanthanum calcium carbonate (so-called parisite) is, according to G. Aminoff, surprisingly well preserved, so that it responds tolerably well to the searching test of the Laue diagram. Figs. 165-166 give a diagrammatic representation of this interesting case.

A more or less extensive dehydration may be effected for minerals of the zeolite group without the destruction of the crystal form. It is known that

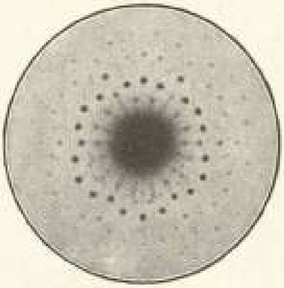

FIG. 165.

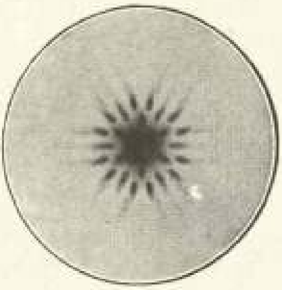

FIG. 166.

FIGS. 165, 166.—Laue diagrams of parisite (synchysite) and metaparisite
After G. Aminoff

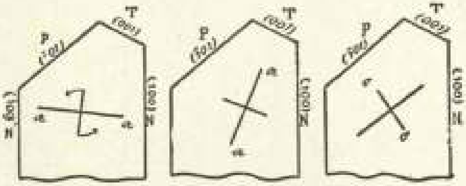

FIG. 167.—Optics of heulandite and metaheulandite

in heulandite, for example, the loss of water takes place practically continuously, and that sometimes an equilibrium between the hydrosilicate and its surroundings is established. Interesting parallel phenomena to this are the optical relations of the mineral. Like the hands on a clock, the extinction directions move round indicating the water content of the substance. Here then is a good opportunity to study a chemical equilibrium by an optical method (e.g. by polarised light). Observations by O. Weigel and K. H. Scheumann confirm quantitatively that there is, in fact, a very exact parallelism between the chemical composition and the optics of the material, for their variations accord precisely. The crystalline nature of heulandite remains undisturbed for this variation to and fro of the chemical composition, at least as regards the first stages of dehydration, as is proved by the Laue diagrams. The continuation of the process leads to more drastic deformations. In the removal of water from this zeolite, so long as about three mols remain, we are concerned, not with a process very vital to the architectural stability, but rather with the removal of a constituent which is only loosely, although regularly coupled to the silicate space-lattice. This is in complete agreement with the view that heulandite is morphologically closely allied to its felspar anhydride. The diagrams of Fig. 170 show the marked analogy in the appropriate angle relations. The magnitudes of the axial ratios indicate the same thing; but, in addition, the morphological influence of the H_2O becomes apparent in the length of the "*b*" axis.

In this particular we find a considerable mor-

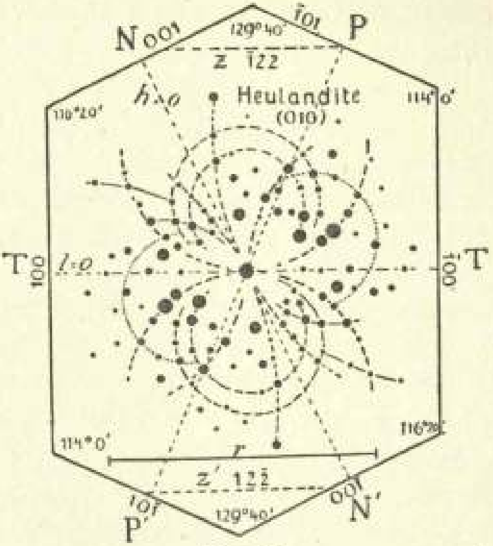

Fig. 168.

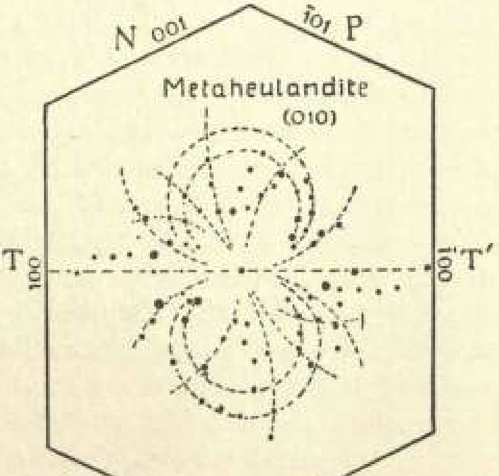

Fig. 169.

Figs. 168 and 169.—Laue diagrams of heulandite and metaheulandite.

phological difference in the structures of felspar and heulandite :—

Sanidine . $a:b:c = 1:1{\cdot}5:0{\cdot}8$; $\beta = 64°$.
Heulandite . $a:b:c = 1:2{\cdot}0:0{\cdot}8$; $\beta = 64°$.

Among zeolites scolecite is of very great interest. Its change into metascolecite leads, just as in a change of modification, to an actual transformation of the silicate structure, indicating that here the water content is certainly of fundamental importance to the whole. Although we may use the methods of ordinary and X-ray optics, which prove the persistence of a space-lattice arrangement in metascolecite, the phenomena may also be conveniently demonstrated pyroelectrically. With reference to Fig. 172, I found, in fact, that on dehydration of scolecite the front and side surfaces become interchanged as regards the symmetry relations. I found a case of structural undermining of exceptional chemical simplicity in brucite, the natural trigonal $Mg(OH)_2$. At about 400° expulsion of the water begins, which wanders out from the point system

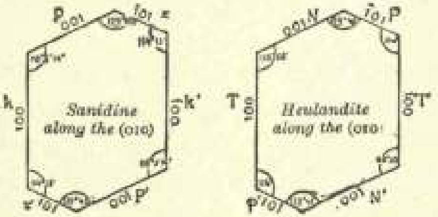

FIG. 170.—Comparison of sanidine and heulandite.

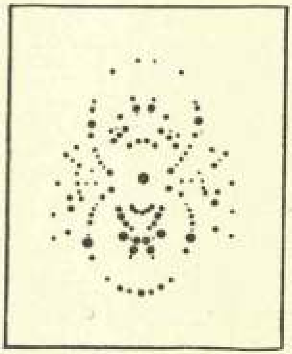

FIG. 171.—Laue diagram of metascolecite.

by diffusion and evaporates from the crystal to the outside, the effect increasing with increasing temperature, till finally MgO as a pseudomorph of $Mg(OH)_2$ is left. A comparison shows that the crystal optics of a trigonal body, although weakened, still remain with reversal of the double refraction, the directions of the optical axes being unchanged (Fig. 173). The more sensitive X-ray tests show, on the other hand, that the change has not occurred without deformation. While brucite gives a Laue diagram of mere points, I found for MgO, obtained from brucite, a star-like X-ray figure (Fig. 174-5), a fact also mentioned by G. Aminoff. It indicates regular bending such as can be produced with the same effect on mica, rock-salt, and other substances. In addition, inner variations of the structure occur

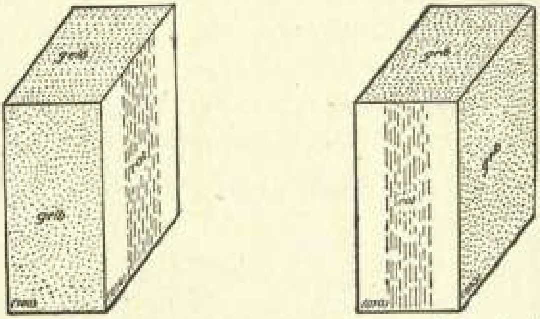

FIG. 172.—Pyroelectric effect for scolecite and metascolecite (sprinkled with sulphur and red lead).

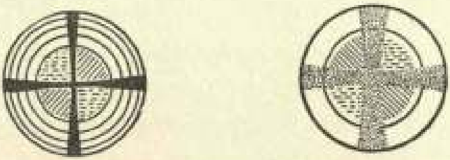

FIG. 173.—Optics of brucite (MgO . H_2O) and metabrucite (MgO).

on the expulsion of the H_2O. The high temperature appropriate to the undermining is favourable to this. O. Pauli informs me that he actually obtained with glowed metabrucite the Debye-Scherrer diagram of periclase, that is, of the isometric form of MgO, which according to him and Gerlach is given on heating magnesite, $MgCO_3$, to a red heat.

Such phenomena are transitional to those for which very drastic rearrangements in the fine-structure occur in the topochemical reaction of dehydration, as in the change of gypsum $CaSO_4 2H_2O$ to the so-called subhydrate $CaSO_4 \frac{1}{2} H_2O$, and then to the anhydride $CaSO_4$. The constitutional difference between anhydrous and dihydrol calcium sulphate is at once indicated by the macrostereochemistry of the crystal form. Gypsum is monoclinic, while anhydrite is rhombic, which is quite a different type of structure (Figs. 176-177).

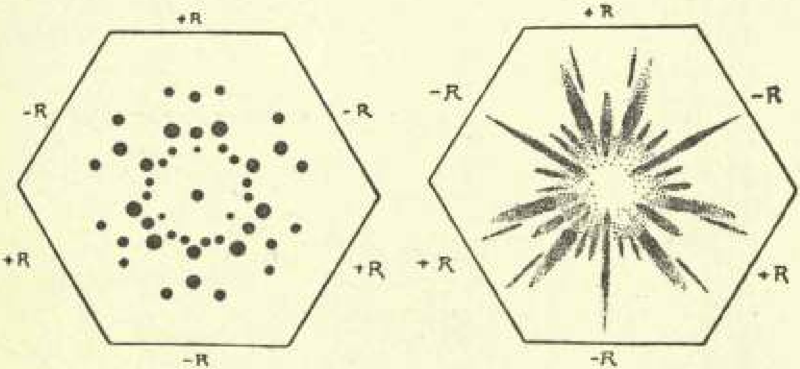

Fig. 174.

Fig. 175.

Figs. 174-175.—Laue diagrams of brucite and metabrucite. (X-ray star figure.)

This variation in the function of water in crystal structure is also shown in physical chemical diagrams, such as are depicted in Fig. 178. In hydrated barium chloride the H_2O is an essential fine-structural constituent. On heating the crystal it is expelled in quanta (to some extent in large fine-structural, and

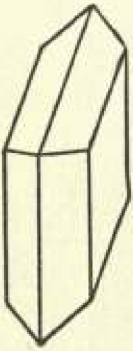

Fig. 176.

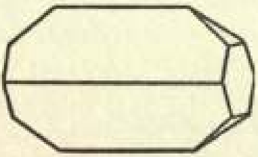

Fig. 177.

Figs. 176, 177.—Gypsum ($CaSo_42H_2O$) and anhydrite ($CaSo_4$).

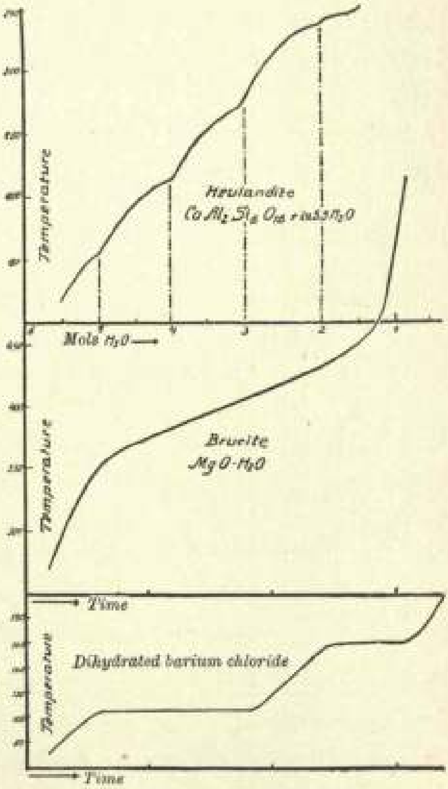

Fig. 178.—Diagrams for the dehydration of heulandite (after O. Weigel), brucite (after O. Westphal), and hydrated barium chloride.

thus chemical, aggregates) at "boiling points" corresponding to the bends in the curve of Fig. 178. Brucite shows one segment corresponding to evaporation, and the researches of O. Weigel and K. H. Scheumann indicate that for heulandite the curve is, at least to begin with, nearly a straight ascending line, which, according to O. Weigel, is of interest in that it shows singular points for the simple stoichiometrical ratios of silicate and water. At these positions evaporation is checked by momentary strengthening of the bonds between water and silicate.

The undermining of crystals may, however, take place to an extent much greater than is represented by the removal of a relatively small part of the constituents which water usually represents. The calcium aluminium hydrosilicate $CaOAl_2O36SiO_2c$. 5·5 aq. of heulandite, for example, may be reduced fine-structurally to SiO_2. The entire filling of basic constituents is then removed, the result being just as though the skeleton of some silicious plant had been prepared by burning the organic wrapping. The relict of the zeolite so obtained still shows (especially after glowing, probably under the influence of collective crystallisation) definite optical agreement with the original substance, the hard rigid pseudomorph of which it represents. If, starting from desmine zeolite, all the basic constituents are simultaneously withdrawn with hydrochloric acid, a SiO_2 optically analogous to the original desmine is obtained. Thus the same chemical substance SiO_2 appears here to have a

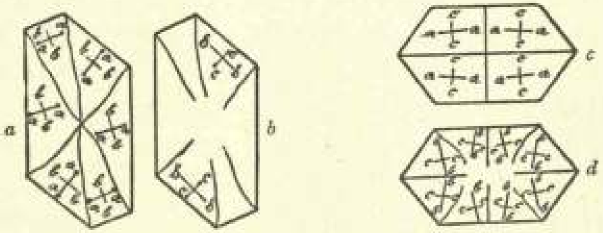

FIG. 179.—*a-b*—Form and optics of heulandite and its silicon dioxide; *c-d*—form and optics of desmine and its silicon dioxide.

varying structure depending on its previous history; in the one case it is a heulandite, in the other a desmine residue.

We may experiment in the same way with dark mica (biotite) and break it down to a very soft SiO_2 in flakes, similar to biotite, which, as SiO_2-metabiotite, is similar optically to mica. The X-ray experiments show, however, that in such extensive undermining of the structure considerable disturbances in a leptonic sense have occurred. X-ray diagrams are no longer obtainable for the residual silica of the zeolites and mica. This is also the case for so-called koenenite a $3MgO . Al_2O_3 . 2MgCl_2 . 6H_2O$, which may be reduced to Al_2O_3, in very soft flakes corresponding to the form of the original crystal. Doubtless, in such cases, there occurs extensive devastation of the inner architecture within the external frame of the structure, which still stands. Using ordinary light, this view is not supported to the same extent as with the sensitive X-rays, which fail to give regular reflexion because of the increased agitation of the atoms in the structure, following the rise in temperature.[1] Moreover, weak double refraction may accompany needle, flake, or prism structure. In other cases, however, the weakening of the structure makes itself, ultimately, macroscopically evident. For scolecite and olivine, for example, one obtains as a residue of the chemical action a silica gel no longer coherent. The loosening of the structure has then

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[1] A roughness of the surface reduces the reflexion of ordinary light. The work of E. Wagner shows that in the same way the capacity to reflect X-rays is diminished by the deviation from planeness which arises in the planes of the space-lattice, owing to the increased motion of the particles following a rise in temperature.

become so great that a spontaneous disintegration ensues. Here then is an interesting series of substances which in their general construction and fine-structure form bridges between crystalline, amorphous solid, and, finally, on the attainment of the greatest dispersion, fluid materials.

A crystallographic reconstruction corresponding to a substitution in molecular chemistry may be easily effected for zeolites, either by replacing water or by exchanging, more or less extensively, the Ca for Na by the action of a Na-salt solution. When water has been removed, other substances, such as carbon bisulphide, alcohol, etc., may also be introduced. In every case the crystalline nature remains intact and specific optical characteristics are unchanged.

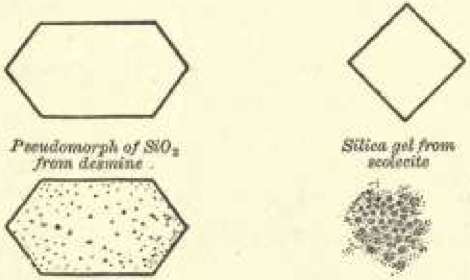

FIG. 180.—(Left-hand figure): Desmine and its silicon dioxide. (Right-hand figure): Scolecite and its silicon dioxide.

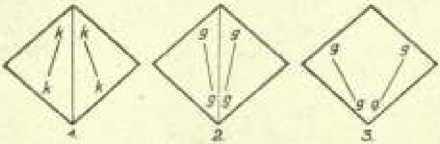

FIG. 181.—Reconstruction of chabasite: 1, chabasite; 2, metachabasite with carbon disulphide: 3, metachabasite with ethyl alcohol.

That substances so very different from H_2O chemically, occur as substituents in the space-lattice must, however, not be assumed. Here also such ideal cases will be passed over as stratifications of the type of macroscopic intergrowths as are found so often in minerals; a similar arrangement may occur in fine-structural dimensions. It appears to me that the oxidation of graphite to graphitic acid is of this type, the latter substance showing optical properties (uniaxial) which graphite would show if it were transparent.

RESISTANCE TO MECHANICAL DISRUPTION AND CHEMICAL ATTACK

We are led from the foregoing to the view that, in chemico-anatomical preparation and substitution processes[1] (as have been mentioned above in a series of examples), there exists a correspondence with reactions, especially those of undermining and reconstruction of molecules, with which the chemist is concerned, and which, particularly in organic chemistry, he has so much under control. The resistances, too,

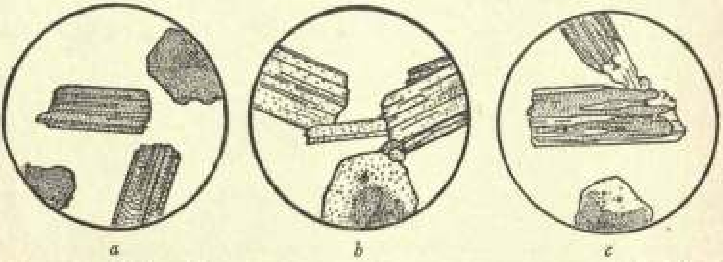

FIG. 182.—Undermining during bleaching (bauerite process) and chlorite reconstruction of biotite: *a*, biotite, fresh; *b*, in bleaching; *c*, in chlorite process.

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[1] These may be increased by turning to processes in nature. The well-known bleaching (bauerite process) and very extensive chloritisation of dark mica are examples (Fig. 182).

which occasionally oppose the transformation he wishes to effect, have their counterparts in crystalline fine-structure. Leptonically considered, close-built arrangements in which the neighbouring particles to some extent screen one another, tend to oppose chemical just as they oppose mechanical attack. This is shown, for example, in the strong chemical resistance of the leptonically close-built, hard diamond, contrasting with the oxidation of the more loosely-built graphite. In the same way, zeolites such as desmine and heulandite, with structures much extended by the large water content, are attacked by acids very much more readily than are their anhydrous analogues, the felspars, which are specifically heavier and harder.

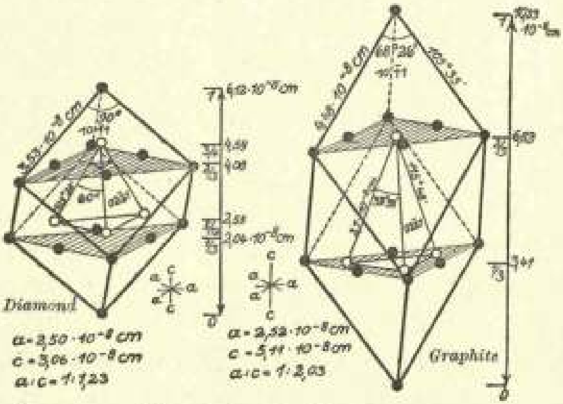

FIG. 183.—Stereograms of the closely packed, hard, chemically resistive diamond, and the loosely built, soft, chemically more easily attackable graphite.

We thus have a noteworthy connection between the mechanical hardness, especially as resistance to fracture, and the chemical reactivity of crystals. It is certainly not merely by chance that gems such as diamond, ruby, zirconia, tourmaline, topaz, rock-crystal, etc., are chemically and mechanically strong. For these close atom packing must be assumed, but even then we shall not be surprised if very close atom arrangements go parallel with great softness of the material. This is the case for graphite (Fig. 183). The structural form indicates at once the origin of the very easy mechanical disrupture. It is due to the weak connections between the densely packed planes. Testing the hardness by scratching separates to some extent the rigidly built, but loosely coupled, planes. The softness of many organic compounds suggests a corresponding structure. In such compounds molecules more or less rigidly constructed internally will be only loosely linked up to one another.

With chemical series it appears quite understandable from the fine-structural standpoint that forms specially stable compared with their neighbours should periodically arise.

This is, indeed, a striking feature of the natural series of the atoms, in which the rare gases are singled out as terms with very stable electron distributions (p. 85), and which oppose, apparently with effect, great resistance to chemical change. Their next neighbours, the alkalies and halogens, on the other hand, exhibit the greatest readiness to react chemically. We may add to these cases of periodically recurring resistance the above-mentioned breaks in the process of dehydration of zeolites, although here the effect is much less marked. At a point of simple molecular ratio between silicate and water increased resistance is offered to the separation of the components. The " lag points " studied by G. Tammann in the structural changes of mixed crystals (such as gold-silver, gold-copper, silver chloride-sodium chloride, etc.), in connection with the old metallurgical method of gold and silver separation by "quartation," are to be judged similarly, assuming enhanced fine-structural stability and consequent increased chemical resistance. According to G. Tammann, these points occur for especially simple distributions of the atom varieties, as for molar fractions $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, etc., of the resistive component, which acts as a protective substance for the second component, which is, chemically, more easily attacked,

XIII. AN ATTEMPT TO FORM SOME IDEA OF THE COURSE OF CHEMICAL REACTIONS FROM OBSERVATIONS ON CRYSTALS

AS our knowledge of the structure of atoms and molecules, as well as of their fine-structural variations in material physical fields, is still in its infancy, efforts to form some idea of the mechanics of chemical reaction have, quite naturally, a merely tentative character. In order to get at the matter it will be advantageous to advance into this unknown region from various sides. We are thus justified, in the present undertaking, which treats the question from a crystallographic standpoint, in anticipating that the best-ordered materials are here, as in other cases, likely to give us useful suggestions.

CHEMICAL SYMMETRY ACTIONS

The space-lattice constitution of the crystal must serve as the fundamental conception in this work. In its particular fine-structural symmetry and special tectonic nature are characterised the physico-chemical connections of the particles.

As a result of this, for every particular case we find at once certain indications as to the mechanics of the chemical processes in the bodies concerned, and a basis for generalisation is obtained. Since, for example, $CaCO_3$ of calc-spar, which is constructed from $Ca^{\cdot\cdot}$ and $CO'_3{}'$ ions in a ternary rhythm (Fig. 117, p. 95), undergoes, on heating, the well-known reaction of splitting into CaO and CO_2, it must be assumed for the fine mechanics of this process that, on account of the increased heat motions, first the geometrico-chemical radical CO_3, as a ring of three O's about a centre carbon, becomes loosened in the fine-structure. With increasing temperature these radicals, together with the calcium atoms, which are free moving groups in the material field, undergo a separation into CO_2 and O, which links up with Ca to form CaO.

According to this, the loosening of the particles in the fine-structure is always to be regarded from the standpoint of symmetry action. Those particles of the structure, coupled together by rhythm or reflexion, participate simultaneously in the process, and since such coupling thus occurs throughout the entire crystal many million times, the process appears to us in analytical chemistry as a discontinuous change, possibly in a series of steps, if the new arrangement contains the departing component again in definite symmetry disposition, as is the case, for example, in the ignition of gypsum to the subhydrate. A practically steady variation can have its origin in complicated re-groupings of the point system, closely following on one another.

For non-crystalline substances such as gases and liquids the relations in the molecule cannot, as regards main principles, be thought of in any other way. Crystal regularity is, indeed, only a special case of fine-structural arrangement. The four H's of an individual CH_4 molecule are, in this sense, coupled up in a symmetry arrangement just as the three O's in the CO_3 radical calc-spar. They must participate simultaneously in action as markers of the equal valued corners of the tetrahedral molecule, so long as this symmetry persists.

PRE-CHEMICAL PROCESSES AND DISCONTINUOUS REACTIONS. MASS ACTION AND CATALYSTS. HEAT AS A CATALYST.

In following up the above observations, a very important point must be discussed. Since it actually happens that in the chemical field, i.e. in the reciprocal action of several types of molecule, one only of the four H's of the CH_4 molecule may participate in chemical action (say $CH_4 + Cl_2 = CH_3Cl + HCl$), then on the basis of the symmetry action set forth above, it is necessary to assume that the four H's of CH_4, before the completion of the chemical reaction, that is, in a pre-chemical process, will be differentiated by the fine-structural prominence of one of their number. The tetrahedral placing of the four H's must have become changed under the reciprocal anisotropic influence of neighbouring molecules CH_4 and Cl_2 in such a way that one of the four has obtained a singular position in the fine-structure, the other three remaining equivalent. The four H's, instead of representing the corners of a tetrahedron, mark out those of a trigonal pyramid (Fig. 184). The hydrogen at the apex is in a certain sense connected to the remainder of the molecule by very weak threads. It is these which naturally give way first when the mutual change of form of the deforming interacting molecules exceeds a certain measure of tension. Substitution in this stereochemical body occurs localised at the hydrogen atom, which has become particularised in the fine-structure, and a new stable arrangement is set up. When, in the case of more complicated substances, splitting occurs, depending, of course, on the appropriate molecular structure, the process is directly comparable with the rupture of the internal connections of crystals during cleavage which cuts through the weaker bonds. In aliphatic compounds C – C couplings are, according to Wollers, weak arrangements; for aromatic compounds separation occurs more readily between C and H.

The law of mass action is, in the above sense, the expression of the fact that numerous deformation forces keep the fine-structural displacement constantly directed towards one side.

In addition, the analogous role of catalysts in the fine-structure becomes evident. The tension necessarily preceding chemical action may well be increased by the presence of a third type of molecule. The action may, in some cases, be initiated by such a third party. In the actual chemical transformation the auxiliary substance does not participate, and, in consequence, suffers no loss: it can officiate in innumerable cases, one after the other, in the molecular swarm, and in so doing produces a great effect, although present in very small quantity. Thus such material catalytic factors function pre-chemically. The substances concerned represent catalysts as they deform the fine-structure. If it be desired to include the preparatory tension process in the chemical action, there is no formal objection. Physical and chemical processes merge into one. I think the observations of J. Stark and myself are pertinent in this connection.

Raising the temperature, as the acceleration of the internal fine-structural motions, can be similarly considered as catalytic. It is understood that in this case, weak bonds between structural groups will give way sooner than they would at lower temperatures; they are, we may say, pulled about at the higher temperature. If, for example, in $NaCl \cdot 2H_2O$, the water molecules, which do not concern the monovalency of Na and Cl, and are but loosely held by co-ordination bonds, the thermal oscillation of the particles is considerably increased, the weak binding forces will be overcome first. Water is suddenly liberated in cases where the molecules are dissimilarly attacked, as for $BaCl_2 \cdot 2H_2O$, in two stages, one after the other (at 105° and 162°; see Fig. 178, p. 150); sometimes in even more, as for $CuSO_4 \cdot 5H_2O$. When the tension becomes sufficiently large under the influence of the rise in temperature, "valency tensors" also break apart such as those between the ions Ca and CO_3 during lime-burning and in other similar cases of chemical decomposition.

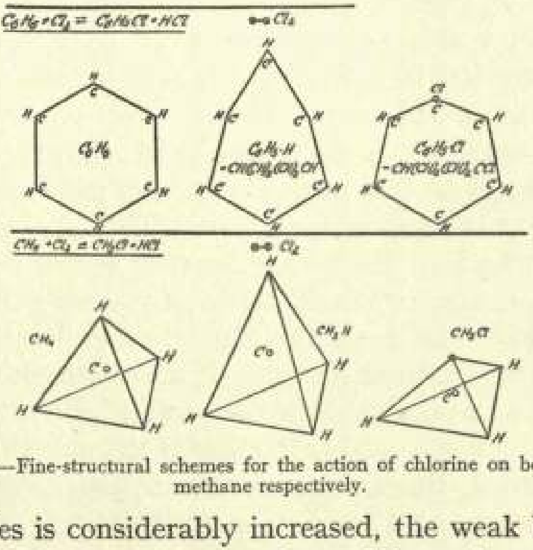

FIG. 184.—Fine-structural schemes for the action of chlorine on benzene and methane respectively.

To illustrate these points the schemes of Fig. 184 are shown, which refer to methane and benzene as typical cases. The final structure there derived for C_6H_5Cl appears to me to agree completely with the diagram already published by J. Stark in his excellent book, "Die Elektrizität im chemischen Atom," a happy case of the agreement of results derived from different standpoints.

It was also of interest to me, on looking through the literature, to learn from a hint by E. Färber in "Naturwissenschaften," that, in the deliberations of the older chemical generation, representation of a weakening of the bond in the molecule before the occurrence of the chemical reaction occasionally played a role. This is seen in the assertion of A. Kekule, who says that "during the approach of the molecules the connections of the atoms in the same are already weakened, for one part of the chemical affinity is bound by the atoms of the other molecule until finally the previously united atoms entirely lose their interconnection and the newly formed molecules separate."

One ventures to extend the scheme in the above to the assumption of a pre-chemical molecular deformation.

CRYSTALLOGRAPHIC INDICATORS OF CHEMICAL PROCESSES

Since the physical, chemical, and crystallographic considerations agree, as they do, we are now in the position to corroborate, to some extent at least, the assumption of preliminary structural changes in crystallographic experiments. In particular, observation of the conditions for certain crystallisations lead once more to the postulation of molecular fore-forms in solution from which crystals are separating, an assumption which has already been mentioned on page 41. While, for example, $CaCO_3$ salt separates out from a pure calcium carbonate solution in trigonal form of the 3m class as calc-spar, experiment shows that the addition of magnesium sulphate to the solution causes the formation of a stereo-chemically different variety, digonal aragonite of the 2m group. Thus one or other modification of $CaCO_3$ must certainly be predetermined by molecular pre-forms in the solution.[1] A still more varied example of this has been investigated by O. Pauli in my institute; his experiment deals with acid phenyl acridonium sulphate, which appears in different modifications according to the proportions of water, sulphuric acid, and alcohol in the solution. Figs. 186

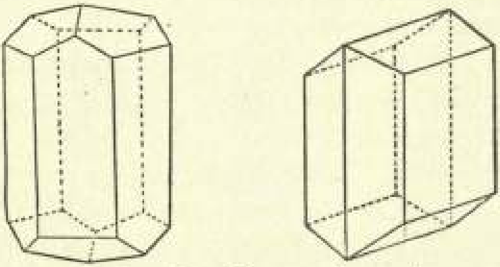

FIG. 185.—Calc-spar and aragonite.

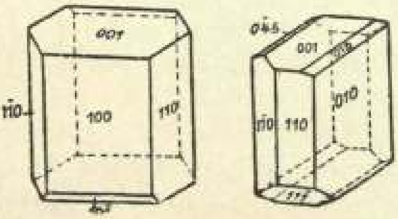

FIG. 186.—Monoclinic and triclinic modifications of acid phenyl acridonium sulphate.

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[1] Probably as $CaCO_3$ or $CaOCO_2$, possibly as a loose compound with $MgSO_4$.

and 187 give diagrammatically the appropriate[1] conditions.

For the most part, then, we are supported in the conclusion that chemical reactions do not occur abruptly, but after preliminary actions, in cases which permit a leisurely although indirect observation of the changes of state by means of physical indicators. Occasionally that is the case for changes of crystallographic modifications, which are not, indeed, merely physical, but also chemical actions (p. 70). For the investigation of the general course of the fine-structural processes inside the substance, optical methods may be used as in the elegant studies of A. Hantzsch and his pupils, where absorption phenomena in the ultra-violet were employed as

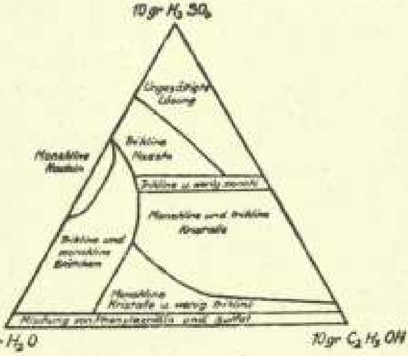

FIG. 187.—Crystallization diagram for acid phenyl acridonium sulphate.

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[1] Different molecular pre-forms of crystallisation will arise if at higher temperatures, or with certain other substances in the solution, salts poor in water crystallise out. The same holds good if at low temperatures, or in the presence of other substances, salts rich in water are formed. The diagrams of van't Hoff and D'Ans, in particular, furnish classical examples of this.

indicators of chemical processes. For the stereochemical changes to be determined here, investigation of the refractive index is helpful. In this particular I have studied exactly, with R. Kolb,

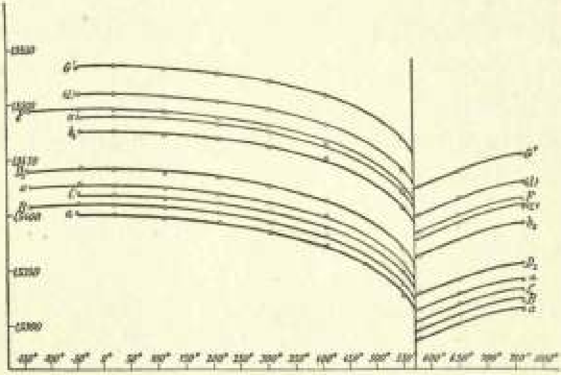


FIG. 188.—Curves of the refractive indices ω of β and α quartz for various kinds of light.

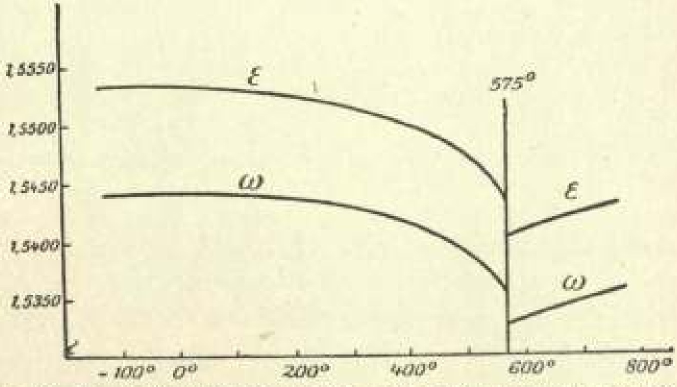


FIG. 189.—Curves of the refractive indices ω and ε of β and α quartz for sodium light characterising the variation of the double refraction.

such a physico-chemical process for quartz, which, on exceeding 575°, changes from the trigonal β into the hexagonal α state ($3s \rightleftarrows 6s$) (Fig. 88, p. 71), as the Laue diagrams show in very neat fashion (Fig. 89, p. 71). With respect to the refractive indices, Figs. 188 and 189 explain fully. It is clearly seen for the case in question, $\beta \rightarrow \alpha$ quartz, that on nearing 575° the gradient of the curves is much increased, and at the temperature named exhibits a discontinuous drop. This line must be regarded as a definite indication that the process 3s → 6s quartz is led up to by a gradually developing tension in the structure; this increases as a pre-chemical action until the sudden rearrangement by a discontinuous change in the fine-structure.

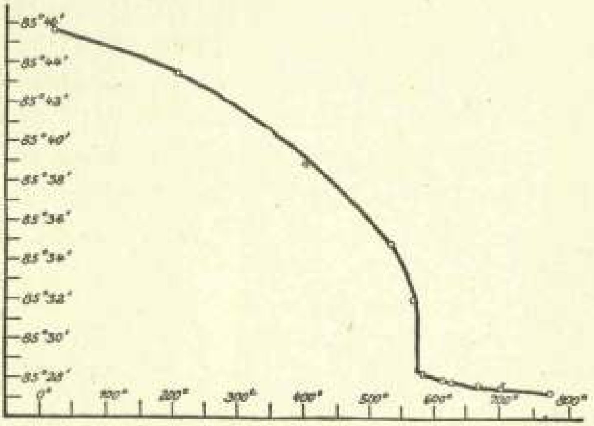


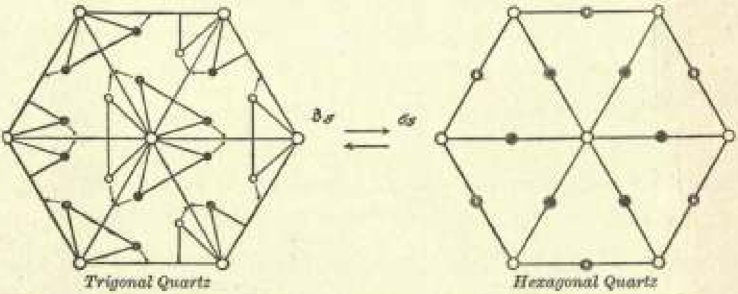
FIG. 190.—Curve of the angle variation of β and α quartz.

FIG. 191.—Curve of the angle variation of β leucite.

Similar conclusions to those obtained above follow from the observations which I carried out in collaboration with R. Kolb on quartz with respect to its morphological variation on transformation (Fig. 190). F. E. Wright obtained similar results for the same mineral.

The thermo-goniometrical researches of R. Grossman made, under the direction of P. Niggli and myself, on borazite and leucite (Fig. 191), show analogous results.

Although the fine-structural relations of quartz are not determined experimentally, still, by resorting to the representations of J. Beckenkamp, and especially by following the discussions of P. Niggli, it is possible to make a provisional diagram for the transition of the quartz modifications. In Figs. 192 and 193 such a scheme is depicted. The arrows in the diagram of the screw trigyric structure indicate



FIGS. 192 and 193.—Fine-structural diagram symbolising the transition $3s \rightleftarrows 6s$ of the quartz modifications.

the tendency of the O particles in the Si  $\mathrm{Si}\begin{smallmatrix}\diagup\mathrm{O}\\ |\\ \diagdown\mathrm{O}\end{smallmatrix}$ triangle to set themselves in the screw hexagonal arrangement, a tendency which steadily becomes more effective as the temperature rises; finally, the sudden rupture of the tension which has increased to the limit gives the β form.

Thus crystallographic considerations support the assumption that one can, in ideal schematic fashion, represent a chemical transformation as the action of a physical or chemical field of such a character that the change in the chemical structure is led up to by a state of fine-structural strain and deformation;

this becomes increasingly pronounced, and finally leading, by a sudden adjustment, to the new stable system.

Many gradations of the relation may, of course, arise. In particular, owing to great resistance, the period of strain may be more or less diminished so that the discontinuous chemical action then occurs almost or entirely without this intermediary state. On the other hand, a pre-chemical deformation may become very much extended, so that the discontinuous change is correspondingly lessened or absent altogether. The transition of modification, from aragonite to calc-spar by heat, points to this. With a view to learning more about the change, I suggested to K. Wünscher a thermo-goniometrical and thermo-optical research. It was shown that angle and refractive index variations, on heating the mineral to 325°, are a function of the temperature, increasing and decreasing with it. For higher temperatures, however, the tension process in connection with the transformation of aragonite into calc-spar occurs to some extent in spontaneous glidings, for at constant temperature the form and optical properties of the mineral vary, the variations being more rapid the higher the temperature taken. Finally, the substance completes the transition of one into the other modification by a sudden adjustment.

XIV. ANALOGY OF THE MORPHOLOGICAL ACTION OF PHYSICAL AND CHEMICAL FIELDS ON CRYSTALS

IT is of considerable interest to compare the easily observable homogeneous deformations of the crystal structure which occur under the influence of heat, with variations of crystallographic form in the chemical field.

THERMAL INFLUENCES ON THE CRYSTAL FORM

The action of temperature change on the morphology of the crystal becomes apparent, as is well known, in explicit formal symmetry actions, the general type of which is most easily studied for spheres. Such forms remain, for uniform rise of temperature, isoradial if they are composed of isometric substances. The sphere remains for temperature variations as such intact. The change is restricted to an alteration of the radius. Crystallographic ternary, tetrad, or senary substances, on the other hand, show transformation of the initial form to a rotation ellipsoid, the axes of rotation coinciding with the crystallographic main-axes. Spheres of rhombic, monoclinic, and triclinic substances finally give rise to triaxial ellipsoids, the principal directions of which are arranged in accordance with the symmetry (Figs. 194-196).

Although the morphological reaction to change in the heat motion of the particles appears usually simple, the complicated interlacing of fine-structural force fields is shown here in the occasional contraction and not extension, with increase of temperature. It may, in fact, happen that for anisotropic substances, in certain directions, dilatation occurs, and in others contraction. For cuprite it happens that with rise of temperature in the region below − 4·3°, isoradial contraction takes place. On heating trigonal calc-spar it expands along the rotation axis, at

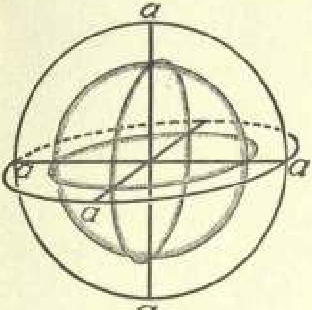


Fig. 194.

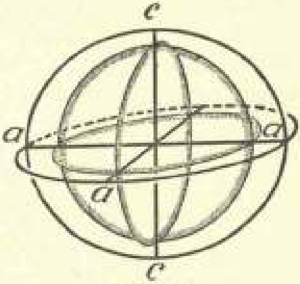


Fig. 195.

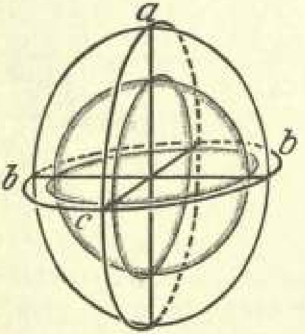


Fig. 196.

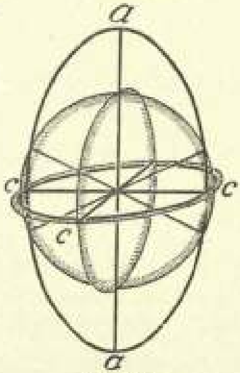


Fig. 197.

Figs. 194-196.—Schemes for the homogereous deformation of isometric, uniaxial and trimetric crystals on heating (initial sphere shaded).

Fig. 197.—Scheme for the homogeneous deformation of a calc-spar sphere on heating. Coefficient of expansion in the direction $a = 0{\cdot}0_4 2621$, $c = -0{\cdot}0_4 0540$ in the intermediate direction shown $= 0$ (initial sphere shaded).

the same time contracting in all directions perpendicular thereto. As a result, radii of the initial sphere, inclined at 65° 49·5′ to the principal axis, will not be altered in length by temperature change (Fig. 197).

Hexagonal silver iodide has, on the other hand, a negative expansion coefficient along the crystallographic vertical ($\alpha_c = -0{\cdot}0_4 0397$) ; in the horizontal direction it expands on heating ($\alpha_a = 0{\cdot}0_4 065$). The cubic coefficient $\alpha_c + 2\alpha_a$ is $= -0{\cdot}0_4 0267$. The volume of the salt is therefore reduced by rise of temperature.

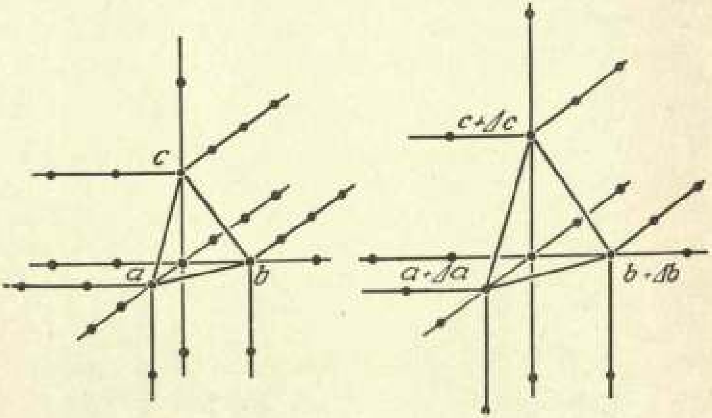


Fig. 198. Fig. 199.

Figs. 198 and 199.—Schemes for fine-structural variation in the physical field. Preservation of the indices and zone relations.

From a fine-structural aspect such relations may readily be understood in the symbolical representation, as an alteration of the distance between the centres of heat motion corresponding to the visible change of form. The Figs. 198 and 199 above show this with the necessary diagrammatic exaggeration.

In these figures one recognises as the ruling conditions the preservation of the symmetry, of the parallel edges (the zone relations), and of the indices which, in the triangular surface shown retain their unit values 1*a* : 1*b* : 1*c*. Angles and axial ratios alter within the limits of the prevailing symmetry.

The extension coefficients, the order of which has already been given in the special case of Fig. 197 give us an idea of the absolute value of the variations. They are usually very small. For example, in the elementary cube of rock-salt (Fig. 24*b*, p. 22),

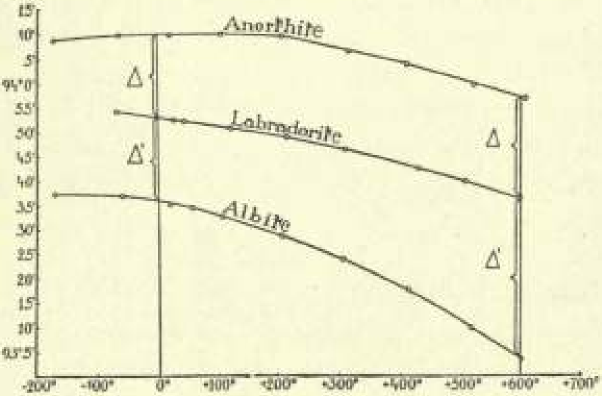


FIG. 200.—Variation of the cleavage angle of the plagioclases, albite, labradorite, and anorthite.

the side length increases merely from 5·63 × 10⁻⁸ cm. at 0° to 5·77 × 10⁻⁸ cm. at 500°. The angular deformations of anisotropic substances known since the time of Mitscherlich (1799-1863) are correspondingly small.

To extend his studies on calc-spar I investigated the angle variations of the rhombohedral cleavage form of this mineral over the extensive temperature interval from – 165° C. to 596° C., i.e. for 761°. I found a change of angle of about 1° 9′ 20″, i.e. about 9·1′ to each 100° on an almost linear graph. Usually the thermo-morphological reaction is even smaller. For quartz I measured a change of the rhombohedron angle of only 14·0′ for 553° (20° – 573°), i.e. not 3′ per 100° C.

Of course, in such variations of form sometimes there arise very complicated fine-structural processes, which may be inferred from appropriate diagrams. Although the curve obtained in the example of calc-spar rises almost linearly, in other cases well-marked curvature is shown as for quartz, already referred to (Fig. 190), and the plagioclases. In Fig. 200 the second curve, which relates to an isomorphous mixture of albite and anorthite, termed labradorite, also deviates from the arithmetic mean of the other two, showing that the angle and the accompanying fine-structural variations in such cases are not simply additive.

CHEMICAL INFLUENCES ON THE CRYSTAL FORM

The analogous inquiry as to the morphological action of a chemical field on the fine-structure fails in general owing to the impossibility of magnifying the effect sufficiently for observation. If, for example, a crystal of calc-spar is suspended in water, then a deformation of the crystal is certainly to be assumed, but cannot be rendered visible experimentally. In contrast to the thermal action, the influence of the chemical field is restricted in the above case to the surface. It can make itself felt in the peripheral processes of growth and solution of the crystal, but not markedly in transformation of the structure. Moreover, a simultaneous action throughout the whole body of the crystal, i.e. permeation of the liquid to all parts, would be necessary to correspond to the effect of heat. For some crystals that is actually brought about, as for those of albumen. Indeed, the process exceeds in definiteness all expectations. Albumen crystals take up water either from the surrounding liquid or from an atmosphere containing water vapour. In this case, then, the particles of the space-lattice are surrounded with water molecules. In the reciprocal anisotropic action between the crystal structural groups and the water particles regularly arranged about them, an unusually large deformation of the crystal makes its appearance, the crystallographic symmetry remaining unaltered.

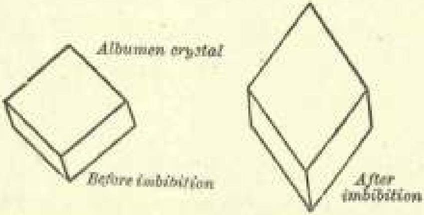


Fig. 201.—Homogeneous deformation of a crystal of albumen by imbibition.

The isometric albumen crystals swell up, remaining trigonal, with anisotropic variation of the angles. According to A. F. W. Schimper, to whom chiefly we are indebted for the appropriate observations, the plane polar-angle of trigonal albumen (obtained from Brazil nuts) changes from 60½° to 39½°, and thus by a very large amount. Fig. 201 shows diagrammatically a similar case of extensive deformation for the cubic rhombohedra of albumen occurring in solanine. These are drawn out to a very definitely acute-angled form, the plane polar angle of which amounts now to 68° instead of 90½°. It is especially interesting that for albumen from Brazil nuts, perpendicular to the ternary axis no observable swelling occurs, whilst the linear measure of the enlargement in the axial direction is very considerable.

The optics of albumen crystals deformed by swelling in water show a regular variation, as is also the case for those expanded thermally. Isotropic crystals remain, with variations of the refractive index, isotropic; double refracting forms alter the magnitude of this property. All return again on evaporation of the water to their original states.[1] According to this, the morphological actions of thermal and chemical fields in crystals are exactly similar, probably an indication that the thermal process also is to be regarded from a chemical standpoint, and, as a bombardment of the structural particles by electrons, is analogous to chemical action.

COMPARISON OF THE THERMAL AND CHEMICAL INFLUENCES ON THE CRYSTAL FORM

A comparison of the fine-structural effects following temperature variation, on the one hand, and under the influence of the chemical field, on the other, may best be carried out with respect to isomorphous substances. In this connection the following table (p. 177) will be of interest. It indicates the relatively large effect of a chemical substitution of Cl by Br or I in the potassium halides compared with that of a temperature change of about 500°. The molar cell and molecular domains (p. 107) relate to cube forms.

For KCl, then, the effect on the external form, measured by the axes of the molecular domain for a rise of temperature of about 500°, is to that produced

---

[1] Acids apparently break up the structure.

KCl.	Mol Domain.		Cell Domain.		Molecular Region.	
	Volume C. cm.	Axes Cm.	Volume 10^{-24} C. cm.	Axes 10^{-8} Cm.	Volume 10^{-24} C. Cm.	Axes 10^{-8} Cm.
20° 500°	37·64 40·19	3·346 3·425	247·72 265·72	6·280 6·429	61·93 66·43	3·956 4·050
	2·55	0·079	18·00	0·149	4·50	0·094
20° KCl KBr	37·64 43·19	3·346 3·508	247·72 285·52	6·280 6·585	61·93 71·38	3·956 4·148
	5·55	0·162	37·80	0·305	9·45	0·192
KBr KI	43·19 52·97	3·508 3·756	285·52 350·24	6·585 7·049	71·38 87·56	4·148 4·441
	9·78	0·248	64·72	0·464	16·18	0·293
KCl KI	37·64 52·97	3·346 3·756	247·72 350·24	6·280 7·049	61·93 87·56	3·956 4·441
	15·33	0·410	102·52	0·769	25·63	0·485

by a substitution of Br or I for Cl as 1 : 2·04 : 5·16. Naturally, the greater the change of temperature the larger will be the consequent variations, within the limits of one modification. In Fig. 200 of the felspars (p. 173), it is recognised how closely in such cases thermal and chemical effects can resemble each other.

The phenomena in question possess further a special interest, in that the action of a rise of temperature in the crystal and the loosening effect of a permeating substance are gradations in the process of melting and solution, that is, in the process of "rendering amorphous." Considered in connection with the series of metamorphoses (p. 69), which substances pass through on raising the temperature, continuous thermal homogeneous deformations figure as preliminaries to the abrupt collapse of the space-lattice arrangement, a process which generally runs parallel with the external phenomenon of melting, i.e. of "flowing apart." Under the influence of increased fine-structural agitation the crystal form is completely broken up, in accordance with Lindemann's views, if the vibrations of the particles about their positions of rest become commensurable with their distance apart, and so lead to their collision. The domains of the fine-structural groups merge together, and the forces binding the lattice are overcome by the disruptive action of the heat motions, the crystal form is destroyed and scattered into irregularly placed new kinetic units. In this sense the fine-structural deformation which precedes the sudden change appears analogous to the pre-chemical processes referred to previously (p. 160). The albumen crystals during imbibition strive in an exactly similar way to become amorphous. It is of great interest, and also characteristic, that the structure can be linearly extended before dissolution to such a large extent, often by several times its original length. Even with extensive dilatation the interleptylic fields of force give rise to some cohesive action. That must be ascribed to a regular incorporation of the water particles, which arrange themselves analogously to the H_2O in zeolites, and acting as a chemical cement bring about the observed cohesion. The water is present, however, in much greater quantity than in zeolites. Finally, there occurs separation into irregularly arranged particles, as may be observed very neatly, according to A. F. W. Schimper, in small crystals of albumen from the seeds of the castor oil plant. These, being cubic, swell isoradially in dilute sulphuric acid to three or four times their original diameter, and then immediately go into solution. To what extent, in structures of so many atoms the space-lattice arrangement is lost on transition to the colloidal, and finally to the molecularly, disperse state, further X-ray studies must show (compare p. 65).

XV. CRYSTAL PHYSIOLOGY AND THE CLASSIFICATION OF ATOMS

THE STANDARDS AND PHYSIOLOGY OF THE CLASSIFICATION

SCIENTIFIC classification, as a concise characterisation of the peculiarities and relations of the objects investigated, is of considerable importance. Its development must move parallel with the advance of knowledge, conforming to the broader purpose of ensuring simple and natural methods in our deliberations. In these times of radical changes in our ideas of the nature of matter, the systematic co-ordination of the results of investigations merits careful attention. The importance of the classification as the characterisation of the fine-structural particles and their family relationships is supported in a gratifying fashion by independent lines of thought from many directions. Our ideas of the constitution of atoms as neutral and ionised forms, both of normal weight and as isotopes, together with the conception of the element, play the leading role here. It appears to me not inappropriate in these questions also to emphasise the close connection of the various states which runs through the fine-structural series, electrons, atoms, ions, molecules, and crystals. The crystal, the highest and especially regular member of the series, easily observable in its external form and physical conditions, enables the general idea of the principles of classification to be readily grasped. In particular, it is clearly seen that considerable physiological breadth of property is to be ascribed to a leptonic unit. The appearance of a rigid regular form and of an inner homogeneity, say for ruby, is an illusion. A change of temperature changes the volume of the crystal, and in the case mentioned its form also. Optical tests of the refraction, double refraction, and absorption show that this crystalline form can experience changes in its inner constitution which are to be traced back, finally, to reversible rearrangements of the fine-structure.

X-ray data testify that, in correspondence with this general conclusion, the motion of the fine-structural particles is highly variable. Even analytical differences, as in the case of isomorphous mixtures, with its powerful influence on the optical absorption and the specific gravity, or the entrance and exit of water which occurs for zeolites, can arise without prejudicing the idea that we still are dealing with the same kind of crystal whose physiology alone changes within certain limits. In systematic classification the type retains its place, despite these variations. It seems to me that the transfer of such views to the classification of leptonic forms leads to a simple and natural formulation.

ELECTRONS, ATOMS, AND MOLECULES

The fundamental constitution of all things lies hidden in the electron as the elementary quantum of electricity and the primary constituent of matter;[1]

---

[1] If they have not to relinquish this rank to the archons as vortex pairs as suggested by O. Wiener.

electrons are therefore of the first importance. Their division into e^+ and e^- is, however, of so great systematic simplicity that it has, up to the present, sufficed.

The case is very different for the atoms, the classification of which has developed into a special study. Their general characteristic in the manifold of forms lies in the presence of a nucleus within the structural unit.

The highest grade of individual leptonic structures is represented by the molecule. Its special feature is that of a combination of atoms to a new unit, thus the presence of more than one nucleus in the kinetic unit.

Everything else in fine-structural phenomena, as they are presented in the gaseous, liquid, and crystalline states in quite inexhaustible abundance, comes under the head of modes of aggregation of the electronic, atomic, or molecular fine-structural forms. The force of the classification lies in the atomistic structural gradations.

ATOM TYPES

Reviewing, therefore, the scientific facts relating to the atomic units, there is now no further doubt that these units must be arranged in the order of their atomic numbers (corresponding to the X-ray spectra, p. 20). This is done in the following table (p. 183). In each case the atomic weight is subjoined thus, A.W., as it is not essential to the classification.

The terms of this series will, in accordance with scientific requirements, be designated atom types, and for the further systematic subdivision of these the expression atom sub-types is introduced. The table indicates the special property of atom types —the atomic number which, in accordance with the nuclear charge, fixes the position in the series from H to Ur. The characteristic of an atom is,

Atomic Number.	Name.	Symbol.	A.W.	Atomic Number.	Name.	Symbol.	A.W.
1	Hydrogen	H	1·008	47	Silver	Ag	107·88
2	Helium	He	4·00	48	Cadmium	Cd	112·4
3	Lithium	Li	6·94	49	Indium	In	114·8
4	Beryllium	Be	9·1	50	Tin	Sn	118·7
5	Boron	B	11·0	51	Antimony	Sb	120·2
6	Carbon	C	12·0	52	Tellurium	Te	127·5
7	Nitrogen	N	14·01	53	Iodine	I	126·92
8	Oxygen	O	16·00	54	Xenon	X	130·2
9	Fluorine	F	19·0	55	Caesium	Cs	132·81
10	Neon	Ne	20·2	56	Barium	Ba	137·37
11	Sodium	Na	23·00	57	Lanthanum	La	139·0
12	Magnesium	Mg	24·32	58	Cerium	Ce	140·25
13	Aluminium	Al	27·1	59	Praesodymium	Pr	140·9
14	Silicon	Si	28·3	60	Neodymium	Nd	144·3
15	Phosphorous	P	31·04	61	——	—	—
16	Sulphur	S	32·06	62	Samarium	Sm	150·4
17	Chlorine	Cl	35·46	63	Europium	Eu	152·0
18	Argon	Ar	39·88	64	Gadolinium	Gd	157·3
19	Potassium	K	39·10	65	Terbium	Td	159·2
20	Calcium	Ca	40·07	66	Dysprosium	Dy	162·5
21	Scandium	Sc	45·1	67	Holmium	Ho	163·5
22	Titanium	Ti	48·1	68	Erbium	Er	167·7
23	Vanadium	V	51·0	69	Thullium I.	Tu I	168·5
24	Chromium	Cr	52·0	70	Ytterbium	Yb	173·5
25	Manganese	Mn	54·93	71	Lutetium	Lu	175·0
26	Iron	Fe	55·84	72	Hafnium	Hf	—
27	Cobalt	Co	58·97	73	Tantalum	Ta	181·5
28	Nickel	Ni	58·68	74	Tungsten	W	184·0
29	Copper	Cu	63·57	75	——	—	—
30	Zinc	Zn	65·37	76	Osmium	Os	190·9
31	Gallium	Ga	69·9	77	Iridium	Ir	193·1
32	Germanium	Ge	72·5	78	Platinum	Pt	195·2
33	Arsenic	As	74·96	79	Gold	Au	197·2
34	Selenium	Se	79·2	80	Mercury	Hg	200·6
35	Bromine	Br	79·92	81	Thallium	Tl	204·0
36	Krypton	Kr	82·92	82	Lead	Pb	207·20
37	Rubidium	Rb	84·45	83	Bismuth	Bi	209·0
38	Strontium	Sr	87·63	84	Polonium	Po	210
39	Yttrium	Y	88·7	85	——	—	—
40	Zirconium	Zr	90·6	86	Emanium	Em	222
41	Niobium	Nb	93·5	87	——	—	—
42	Molydenum	Mo	96·0	88	Radium	Ra	225·97
43	——	—	—	89	Actinium	Ac	226
44	Ruthenium	Ru	101·7	90	Thorium	Th	232·15
45	Rhodium	Rh	102·9	91	Protactinium	Pa	230
46	Palladium	Pd	106·7	92	Uranium	Ur	238·2

therefore, its numbered place in the atomic series; briefly, its monotopy.

No term of the series can be dispensed with; each one fulfils the task of representing a necessary number in a sequence.

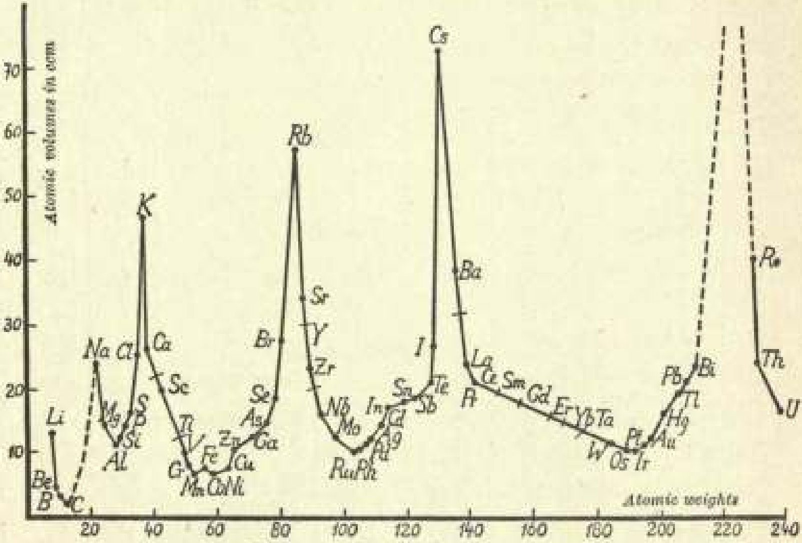


Fig. 202.—Graph of atomic volumes.

The periodic table of L. Meyer and D. J. Mendeleeff accomplishes in the familiar way a grouping of the atom types. The curve obtained for the atomic volumes (Fig. 202) serves the same purpose. With

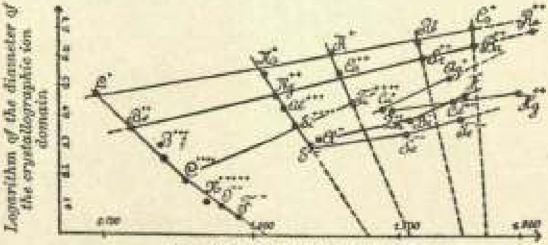


Fig. 203.—Graph showing series of atoms. After E. Schiebold.

reference to our ideas on crystallographic atomic domains, it appears of interest to indicate here a graphical arrangement of important atomic groups obtained by E. Schiebold. This is arrived at by taking the logarithms of both atomic number and the diameter of the atomic domain; the groups are signified by the arrangement of the points in the diagram which are often linear in series.

ATOM SUB-TYPES

The monotopy of the atom types is quite compatible with physiological differences which do not interfere with the constancy of the nuclear charge which is characteristic and equal to the atomic number. In this way atomic sub-types may possibly arise in the series of monotopes, characterised by fine-structural differences either in the region of the satellite electrons or in the nucleus.

We may therefore assume within the atomic types the following atomic sub-types. Differences in the outer electron shell differentiate neutral atoms from atom ions, which in turn separate into cations or plus atoms and anions or minus atoms. Owing to the extreme lightness of the electrons, the theoretical changes of weight arising from omission of a few negative particles from the outer shell, or by their entrance, are inconsiderable; neutral atoms are, with their corresponding + or − ions, practically isobaric. For other atomic sub-types a difference of the mass content, actually in the central nucleus (without change of its charge), of so extensive a nature occurs that a difference of atomic weight is observable. This is the case for isotopes, so termed in K. Fajan's fundamental papers on the subject. The members of such a group are, therefore, heterobaric.

ELEMENTS

Another criterion in classification is obtained from our conception of the element. Its characteristic is that its constitution consists entirely of monotopic atoms; thus elements are possible containing either only one atom sub-type or several different varieties. F. Paneth expresses this very neatly by differentiating between pure elements and mixed elements. The former contain only one atom sub-type, the latter more than one.

NORMAL MIXTURE AND SEPARATION OF ISOTOPES

Of primary importance in analytical chemistry is the remarkable fact that for elements containing heterobaric components a normal mixture is invariably found. For chlorine, with isotopes of mass 35, 37, and 39, the ordinary atomic weight 35·46 is always shown (whether the chlorine is extracted from eruptive minerals or deposited sediment, whether it is of terrestrial or meteoric origin), a circumstance which reminds us, at least formally, of the equilibrium phenomena of eutectics. Thus ordinary $Br_{79\cdot92}$ is $0\cdot46\ Br_{81} + 0\cdot54\ Br_{79}$; $Cl_{35\cdot46} = 0\cdot23\ Cl_{37} + 0\cdot77\ Cl_{35}$ (neglecting the small amount of Cl_{39}); $Si_{28\cdot3} = 0\cdot30\ Si_{29} + 0\cdot70\ Si_{28}$; $Ar_{39\cdot88} = 0\cdot97\ Ar_{40} + 0\cdot03\ Ar_{36}$, etc.

The mixed isotopic constitution of many of the atom types also enables us to understand why, in the Mendeléeff system, there occur occasionally deviations from the arrangement in order of atomic weight. For atoms of nearly the same weight it may easily happen that this admixture displaces an atom type from the natural sequence to a false position, as is the case for argon. If the lighter component (Ar_{36}) were present in somewhat greater proportion than is the case in the normal argon mixture ($Ar_{39\cdot88} = 0{\cdot}97\ Ar_{40} + $ only $0{\cdot}03\ Ar_{36}$), the rare gas would immediately assume its correct place in the Mendeléeff system before potassium (A.W. 39·10).

A partition of the isotopes by arrangement in separate positions in the fine-structure occurs in every crystallisation of a substance containing such atomic mixtures (compare Fig. 119, p. 98). As is well known, a separation of the components to a detectable extent has been accomplished in the researches of F. W. Aston who continued the work of Goldstein, W. Wien, J. J. Thomson, and others. By the different deviations of the ions in electrostatic and magnetic fields, Aston separated and identified the individual isotopes, one of the finest results of general scientific endeavour in the direction of a unified concept of matter as the aggregation of a primary constituent. The integral atomic weights of the iostopes point to this. Here the anomaly of hydrogen, with its non-integral atomic weight 1·008 compared with oxygen = 16, is not yet explained, but it now merely spurs us on completely to establish this otherwise predominant concept by further experimental work and study.

CONCLUSION

In reviewing all the various experiments and arguments dealt with above, which in the present early stages of fine-structural investigation naturally more often pass in a mere mention than lead to definite results, it is recognised that crystals are actually in many respects typical of the general conception of the constitution of matter. In their macroscopic form and their physico-chemical relations are reflected, not only the fine-structure and the physics and chemistry of their own particular microcosm, but also of matter in general. With their three-dimensional regularity and easy accessibility to direct observation, they are specially suited to serve as the starting point in the investigation of laws universally valid. In this way crystallography stimulates the physicist, chemist, and natural philosopher, as it itself, on the other hand, has gratefully received so much help from these great sister sciences.

In such common endeavour the sowing of the fine-structural soil cannot fail to germinate vigorously and, on progressive cultivation, to develop into a rich harvest. I hope that this present exposition will serve as a small contribution to the great work.

Readers wishing to acquire a more detailed knowledge of crystal science, are referred to the following series of works on the subject :—

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[Several of the older books given in the original are omitted and some English works have been included in the list.—Translator's Note.]

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