HISTORY
OF
PHYSICS

by MAX VON LAUE

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Physics of Crystals

THE SCIENCE of crystals belong exclusively to modern times. The regular forms of many diamonds and also the smooth faces of other crystals must undoubtedly have attracted attention from the remotest times. However, the apparent lack of regularity in the variation of their size and form most assuredly was the reason that no laws concerning crystals were discovered. In ancient times, the study of minerals, etc., did not advance beyond a purely casual state, and besides it was intertwined with mythology and superstitions about the magic power of gem stones.

A little book by Johannes Kepler, published in 1611, stands quite alone. The mere contemplation of the "hexagonal snow," which gave the book its title, led this gifted man to ideas of symmetry and even to imagining that snow is built up of densely packed spheres. Trains of thought such as he employed in 1596 in his "Prodromus" for the derivation of a law for the radii of the planetary orbits can be discerned in his geometrical discussions. This law was quickly found not to hold, but the viewpoint that the world is the work of a spirit who rejoices in simple mathematical relationships led Kepler here along a correct path. However, this pamphlet, which was composed half in jest, made no impression even on the few who read it.

It was quite an accomplishment, when in 1669 Niels Stenson (Nikolaus Steno, 1638-1687), found that the angles between similar pairs of faces of quartz are always the same no matter how they may be developed. He found this same constancy in several other crystalline materials. The name "rock crystal" (for quartz) gradually came to be applied in shortened form to all solids with well-developed natural features. In this same year, Erasmus Berthelsen (Bartholinus, 1625-1698) noted that Iceland spar (calcite) exhibits double refraction of light, a fact which Huygens explained in 1678 by means of the wave theory (Chapter IV). In 1688 Domenico Guglielminis (1655-1710) extended the law of the angular constancy to several varieties of crystalline salts. However, little progress was made for a whole century. The great strides made by the rest of physics did not touch crystallography, because the physicists seldom saw well-developed crystals, and the mineralogists who, of course, had plenty of such specimens were interested primarily in other problems. The difficult art of growing artificial crystals was not systematically developed until the twentieth century.

An exception is provided in the discovery of pyroelectricity in tourmaline, which, after a long period of misunderstanding, was recognized in 1758 by Franz Ulrich Theodor Äpinus as due to an electrical charge of the surfaces resulting from a temperature change.

Not until 1772 did another important work on crystal forms appear. In this, Jean Baptiste Rome de l'Isle (1736-1790) extended the law of the constancy of the plane angles to many other crystals. These angles, i.e., the position of the faces with respect to each other, are, as has been known since that time, the truly characteristic feature of each variety of crystal, whereas the size of the faces is greatly dependent on the conditions prevailing during the growth of the crystal.

With this law as a basis, geometrical crystallography was developed through tedious individual study and by no means without occasional excursions along wrong paths. However, the epoch-making studies of Christian Samuel Weiss (1780-1856), the investigations by his pupil Franz Ernst Neumann, the first physicist of note who also dealt with crystallography, and also the researches of Friedrich Mohs (1773-1839) and Karl Friedrich Naumann (1797-1873), and finally (1839) those of William Hallowes Miller (1801-1880) led to the "law of rational indices." This law states that the position of each crystal face can be characterized in terms of three moderately large whole numbers, their "indices," if previously three crystal axes are known together with one axial length on each. These investigators also attempted to divide crystals into systems. However, a complete systematization, the geometric demonstration on the basis of the rationality law that there are 32 crystal classes and no more, did not come until the end of that period, namely in 1830, when this advance was accomplished by Johann Friedrich Christian Hessel (1796-1872). Even his work was overlooked for decades, so that this systematization, though in a more elegant form, was set up anew in 1867 by Axel Gadolin (1828-1939), who was unaware of his predecessor. The goal of geometric crystallography was thus reached.

At first, the crystal classes were differentiated by the symmetries with respect to the positions of the boundary planes. The development of this knowledge was paralleled by a recognition that these same symmetries are decisive for the events which take place within the crystal, such as the propagation of light and elasticity. Calcite, in which double refraction was first observed, has only one optically prominent axis. Biaxiality was discovered in mica by Jean Baptiste Biot in 1812; David Brewster (1781-1868) confirmed this finding in topaz and other crystals in 1813, and in 1818 lengthened the list of double refracting materials to more than 100. The eminent astronomer, John Frederick William Herschel, supplemented this knowledge, for instance, by employing monochromatic light. But it was not until 1833 that the connection with the geometric symmetry of the position of the faces received its fundamentally correct formulation by Franz Neumann, who also referred the Fresnel crystal optics back to the elastic theory of light. This same great investigator created the theory of crystal elasticity, and his pupil, Woldemar Voigt, followed in his footsteps. The latter's *Textbook of Crystal Physics* (1910) is still the inexhaustible source of information concerning all physical questions about crystals. In it, for instance, there can be found the theory of pyroelectricity, which was given by Lord Kelvin in 1878, and likewise that of piezoelectricity, discovered in 1881 by Pierre Curie.

Today, however, the essence of the crystalline state is not seen in any of these properties, but in the arrangement of the atoms to produce space lattices, i.e., to form configurations with strict periodicity in three directions. All the properties just mentioned can easily be understood as consequences of this idea. The space lattice theory has a long history. The packing of spheres, of which Kepler wrote in 1611, were space lattices in fact, though he did not coin this idea. The much occupied Robert Hooke (1635-1703) in his *Micrographia* (1665) stated, as is true so frequently in other fields, a correct idea of crystal structure, without giving any basis for his belief and without developing the idea. In 1690 Huygens, in his "Traité de la lumière" (Chapter IV) on the basis of the cleavage of calcite, assumed a space lattice composed of minute ellipsoidal particles. Because of this same characteristic, Tobern Bergmann (1735-1784) in 1773, and, in a more general manner (1782 and later), René Just Haüy (1743-1822) conceived the crystal as akin to a masonry structure, constructed from the tiny parallelepipedal building stones, which likewise exhibits threefold periodicity. The first scientist, however, to combine the newly created concept of the chemical atom with this idea and to assume that space lattices are made up of chemical atoms was the physicist Ludwig August Seeber. With profound physical insight, he went even beyond this purely geometrical assumption, in that he definitely viewed the interatomic distances as being determined by the forces acting between the atoms and he related elasticity and thermal expansion to this postulate. He published his ideas in 1824, i.e., 32 years prior to the entry of atomistics into modern physics in the form of the kinetic theory of gases. But perhaps it was precisely for this reason that his feat, for it was a feat, fell into oblivion. Matters were not improved even when in 1831 the great Karl Friedrich Gauss, in discussing a mathematical book, pointed out the problems posed by Seeber's idea of the "parallelepipedal arrangement of points in space." Seeber's work was not disinterred until 1879 when Sohncke (see below) brought it back to light. The mathematics of the space lattice, which characterizes every such lattice, not by its content of physical structures, but purely through its congruence operations, developed entirely independent of Seeber's work.

Thus, in 1835 and 1836, Moritz Ludwig Frankenheim (1801-1869) put the question: Do the geometrically possible varieties of space lattices conform to the symmetries established in the case of crystals? Even before his second study, namely 1850, Auguste Bravais (1811-1863) derived the 14 space lattices, which bear his name, and which can be formed purely by *translations* of a point (without recourse to other congruence operations). These purely geometric-group theory attacks were extended in 1879 by Leonard Sohncke (1842-1897) who added certain other congruence operations and thus arrived at 65 different space groups. The complete solution of the mathematical problem, the setting up and enumeration of *all* the theoretically possible space groupings, is due, however, to the crystallographer Jevgraph Stepanowitsch von Federow (1853-1919) and the mathematician Artur Schoenflies (1853-1928). Independently, and by quite different methods, they both arrived in 1891 at 230 space groups.

At first, these studies had no effect on physics because no physical phenomenon required the acceptance of the space lattice hypothesis. Among the few physicists who were at all interested in crystallography, some adopted the opposite view, that in crystals, as elsewhere in matter, the molecular centers of gravity were distributed irregularly and that only the parallel placing of preferred directions in the molecules produced anisotropy. Neither was there much discussion of the hypothesis in mineralogy. Paul von Groth (1843-1927) alone upheld the Sohncke tradition in his teaching at Munich. The triumph of this hypothesis came in 1912 through the experiments of W. Friedrich and Paul Knipping who, by means of X rays, demonstrated the interference phenomena occasioned by the space lattice of the crystal, a finding which verified the prediction of M. von Laue. Because of their short wavelength, these waves are able to reveal optically the interatomic distances, whereas these elude radiations of longer wavelengths, such as light. These experiments also furnished the first decisive proof of the wave nature of X rays, which up to then had been denied by some eminent scientists because of the particularly striking quanta phenomena shown by them (Chapter XIV). The theory of this interference phenomenon, which Laue suggested in his first paper and which was verified quantitatively, is an easy generalization of the theory given by Schwerd (Chapter IV) in 1835 for optical gratings. The finding was doubted by some but not for long because the few sharp interference maxima of X rays are too suggestive of optical grating spectra. Though only an approximation, time has proved the theory to be an astoundingly close approximation. Here the wave theory of X rays and the atomic theory of crystals come together, one of those surprising events to which physics owes its powers of conviction.

This theory permits a comparison of the wavelength with the three period lengths of the space lattice. Since at first it was possible to state no more than their order of magnitude, an absolute determination of the wavelength was impossible. The difficulty lay in the ignorance of the atomic structure; it was not known how many atoms resided in the individual space lattice. At this point, in 1913 William Henry Bragg (1862-1942) and his son William Lawrence Bragg brought aid in the form of an hypothesis that had been set up in 1898 by William Barlow (1845-1934) concerning the structure of rock salt, NaCl. Once again, the idea of the densest spherical packing plays a part here. The Braggs confirmed this structure by means of the intensities of the interference maxima, and thus obtained an absolute measure for the lattice constant, and thereupon they could determine the wavelengths of the X rays in absolute terms, i.e., in centimeters. With this aid, they were also enabled to make absolute determinations of the lattice constants of other crystals. Usually these lie between 10^{-8} and 10^{-7} centimeter; however, considerably larger values are found for complicated organic compounds. In 1923 A. H. Compton observed the diffraction of X rays by artificial gratings, but his measurements added nothing to the earlier determinations of wavelengths except a very considerable increase in accuracy.

Measurement of the wavelength created X-ray spectroscopy. In 1908 C. G. Barkla and C. A. Sadler distinguished, by means of their different absorbabilities, the characteristic K, L, M • • • radiations of the chemical elements. Since 1913, initially through studies by the Braggs and H. G. J. Moseley (1887-1915), these radiations have been resolved into series of sharp spectral lines, whose wavelengths, independent of the chemical binding, exhibit simple relationships to the position in the periodic system. These radiations attained great importance with regard to atomistics (Chapters X and XIV) and besides led to the discovery (1923) of hafnium by G. von Hevesy and of rhenium (1925) by W. Noddack, J. Tacke, and Otto Berg (1874-1939.) The study of crystal structures, in which L. A. Seeber's idea finds its brilliant confirmation, has become a distinctly important branch of physics. The number of organic and inorganic crystals for which the atomic positions can now be accurately stated is in the thousands. Included are such complicated structures as those of the various silicates, the earliest being garnet, which was studied in 1925 by G. Menzer. Many metals, such as aluminum, silver, and copper, have been found to conform to the densest spherical packing, a verification of the thought published in 1611 by Kepler. A röntgenographic Fourier analysis of the electron density, proceeding from the establishment of the atomic centers, may serve also to give considerable information about the electron distribution in these and other not too complicated structures. This was known to W. H. Bragg in 1915.

X-rays have now also revealed the wide distribution of the crystalline condition. Of course, well-developed large crystals are relatively scarce; a "microcrystalline" structure of microscopic or still smaller crystallites in thorough confusion is met far oftener. This idea of crystallinity is an old one with respect to metals. However, the fact that wood, textile, muscle, and nerve fibers are likewise microcrystalline is new. In truth, the crystalline state is the normal condition of solids; only a few substances, the glasses in particular, are exceptions to this rule. Hence the entire atomic theory of solids, for instance the quantum theory of electrical conduction, emanates from the space lattice.

Space lattices performed a special mission after the establishment of wave mechanics (Chapter IV). In 1925 W. Elsasser deduced from L. de Broglie's theory that beams of electrons passing through crystals must show interference phenomena just as X-rays do. This expectation was verified in 1927 by experiments carried out by C. J. Davidson and L. H. Germer on one hand and by G. P. Thomson on the other. They thus furnished directly evident proof for this revolutionary theory and at the same time they strengthened it quantitatively by measuring the wavelengths of these rays. Corresponding results were obtained for helium and hydrogen atomic radiations of lesser energy (hundredths of electron volts) by Otto Stern (1929) and Th. Johnson (1931), likewise with the aid of crystals. In these cases, however, only the surfaces are active, since these rays do not penetrate solids. In contrast, space lattice effects have been revealed with neutrons just as plainly as with X-rays ever since American scientists have had access to the powerful sources of neutrons provided by the uranium piles (Chapter XI).

It should be pointed out that X-rays and electron interferences can be applied also to the determination of the form and size of simple gas molecules. This was demonstrated by P. Debye in 1915 with X-rays and by H. Mark and R. Wierl (1903-1932) with beams of electrons. These researches have furnished the distances between the atomic nuclei for many diatomic molecules, such as nitrogen, oxygen, and fluorine; they lie between 1×10^{-8} and 3×10^{-8} centimeter. It is known that the molecule of carbon dioxide is linear, whereas that of water is angular and so on. The molecule of carbon tetrachloride, CCl_4, has been measured especially well; the chlorine atoms form an equilateral tetrahedron, whose center is occupied by the carbon atom. The stereochemical concepts announced by J. H. van't Hoff in 1874 are thus completely substantiated.

The original theory of space lattice interferences presents, as was stated above, only an approximation which suffices in practically all instances for X-rays, but frequently fails for electrons. Its extension into a more exact "dynamic" theory for X-rays was furnished in various forms in 1914 by C. G. Darwin and in 1917 by P. P. Ewald, who, with its aid, were able to explain the deviations of the precision measurements made by W. Stenström (1919) from the earlier theory. The dynamic theory received its final form in 1931 at the hands of M. von Laue; its union with wave mechanics was accomplished in 1935 by M. Kohler. The corresponding advance for electrons had been made as early as 1928 by H. Bethe.

The dynamic theory, in contrast to its predecessor, describes also the waves in the interior of the crystal. Consequently, it is essential to the understanding of the interference effects, discovered in 1935 by W. Kossel, in the emission of monochromatic X-rays by crystals, in which the radiation sources accordingly reside in the space lattice itself. This radiation exhibits characteristic sharp maxima or minima of intensity in directions which are determined by interference conditions.

The original theory was likewise incomplete in so far as it completely disregarded the thermal motion of the atoms, even though the latter, in comparison with the three periods of the space lattice, are certainly not inconsiderable at room temperature and above. P. Debye in 1914 demonstrated that this factor had no influence on the position and sharpness of the interference maxima, but it does decrease their intensity. His theory has subsequently been tested by others. It was verified by W. L. Bragg and his associates through extensive series of measurements (1926-1933).