THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 19 MARCH, 1934 No. 3

A CENTURY OF PROGRESS IN CRYSTALLOGRAPHY*

HERBERT P. WHITLOCK, *American Museum of Natural History.*

Reviewing the history of the modern sciences it appears to us remarkable that in so many instances the person of one individual assembles the scattered observations and deductions of his predecessors, unifies and crystallizes the thought of his epoch and gives to his special branch of learning that impetus which kindling at the fire of his genius, lights his successors along the way to modern scientific attainment. In this way we speak of Newton as the father of mechanical physics; of Cuvier as the originator of comparative zoology, and of Linnaeus as the founder of biological classification.

A name that stands out conspicuously in the period of scientific renaissance included in the seventeenth and eighteenth centuries is that of René Just Haüy, creator of the science of crystallography, and one of the most profound analytical thinkers of this age of intellectual giants.

It has been said that Abbé Haüy obtained his first insight into the realm of natural science through the study of botany and that the symmetries of plant life paved the way in his mind to those more intricate and beautiful symmetries of crystallization which were to render his name renowned. Happening to attend a lecture on mineralogy given by Daubenton at the Muséum d'Histoire Naturelle his interest was aroused in the forms assumed by crystallized minerals.

This new world of inorganic shapes, complex and yet regular, impressed Haüy, fresh from the contemplation of the geometrical symmetry of the forms of plant life, with an apparent lack of orderly arrangement where his scientific instinct assured him that order must exist. How, he reasoned, can the same stone, the same salt, reveal itself in cubes, in prisms, in points without changing its composition to the extent of a single atom, while the roses have

* Presidential address presented at the fourteenth annual meeting of *The Mineralogical Society of America*, Chicago, Illinois, December 29, 1933.

always the same petals, the acorn the same curve, and the cedar the same height and the same development. In the midst of these speculations the Abbé Haüy had his attention directed to the internal structure of crystals when, by a happy accident, a six-sided prismatic crystal of calcite was broken in his presence into rhombohedral fragments. He rightly conceived these cleavage fragments to be essential to the crystal structure of calcite, and upon them, by a system of diminishing rows, *déscroissements*, of small rhombohedrons, he found that he could build up most of the solids that comprise the familiar crystal forms of calcite. From this significant observation it was but a step to the idea of developing the "primitive form" from the cleavage fragments of other mineral species, and of these to construct by diminishing layers of crystal particles, each layer having a definite relation to the preceding one, the complex modified crystal combinations that constitute what we now know as crystal habit.

The law of symmetry as announced by Haüy in 1815 may be justly stated to have founded crystallography upon a mathematical, which is equivalent to saying upon a rational, basis. As stated by him this law is as follows: It consists in this, that any one method of decrement (*décroissement*) is repeated on all these parts of the nucleus of which the resemblance is such, that one can be substituted for the other by changing the position of this nucleus with respect to the eye, without it (the nucleus) ceasing to be presented in the same aspect.[1]

So epochal was the presentation of this *natural geometry*, that there will appear to any one who will consult the literature of mineralogy in the latter half of the eighteenth and the first half of the nineteenth centuries, a well marked line of distinction between the old and the new, between those who wrote before Haüy published his famous "Essai" and those who succeeded him and profited by his teachings.

There now succeeded in the development of crystallographic science an era of observation in the field of mathematical crystallography. Armed with instruments of steadily increasing refinement and precision the crystallographers of the period between 1820 and 1920 toiled unceasingly at the collection of measurements of the angles between the faces of crystals, and at the consequent identification of "forms" characteristic of the many hundreds of

[1] Memoire sur une loi de Cristallisation.

mineral species subjected to this study. It soon became evident to these workers that the more accurately an angle between certain planes present on a crystal of a definite compound were measured, the closer would the resulting measurement approach to the theoretical value of that angle as calculated by the methods of spherical trigonometry.

The science of crystallography took on a certain resemblance to that of astronomy in that observation checked closely with calculation. As the astronomer is enabled to turn his telescope to a predetermined spot in the heavens and predict with certainty that at a fixed time in hours, minutes and seconds a definite star will be seen at that *exact* point, so the worker in the field of crystallography is enabled to predict that at some angle, accurately calculated in degrees and minutes, the reflected image of a certain crystal face will appear in the exact center of the field of vision of his instrument. Nor does the resemblance altogether stop at this point, for crystallographers soon adopted from astronomy the methods of spherical projection by which they were enabled to represent diagrammatically the crystal faces occurring on a crystal and the symmetrical grouping of them, much as stars are represented on celestial spheres and star maps. So crystallography developed into an exact science, beautiful and supremely satisfying in its coincidences and subtly but compellingly suggestive of some far reaching cause extending back of all of this marvelous order and symmetry. It was inevitable that scientists of this period, impressed with the mathematical exactitude with which the faces constituting the outward semblance of a crystal were disposed in symmetrical grouping, should seek for an explanation of this exactitude in the inner structure of that crystal. And, as the science of physics grew apace, it was equally inevitable that investigators of the middle nineteenth century should direct their attention to the physical properties of crystals as a possible key to ultimate crystal structure. This field proved a very fertile one. Crystal optics showed that light traversing a crystalline fragment reacted in accordance with the symmetry expressed by the disposition of the faces in a completely formed crystal of the substance composing the fragment. Similar results attended the investigation of the transmission of heat and electricity, and finally it was found that weak solvents, properly applied to the smooth faces of crystals would excavate minute pits whose shapes were dependent on the way the particles of matter that composed those crystals were arranged with respect to one another. All of this led step by step but with inevitable finality to the assumption of theoretical groupings of particles (space lattices, molecular networks), which taken together explained all of the variations of crystal symmetry. Thus from many points of view was the fundamental discovery of the Abbé Haüy checked, elaborated and rationalized.

It would be difficult to exaggerate the skill and insight displayed by the scientists of the early years of this formative period. Armed with instruments and apparatus which would be rejected as inadequate by many a high school student of today, they made up for this inadequacy by a manual skill in the handling of these appliances which, in very many instances, cause their results to stand against the assaults of modern students armed with modern instruments. Let us call to mind a few of the notable men in the field of science known as mathematical crystallography.

William Hyde Wollaston introduced the reflecting goniometer in 1809, thus rendering possible a far more accurate determination of the interfacial angles of crystals than was possible with the contact type of instrument previously in use.

Professor Christian Samuel Weiss of Berlin in 1815 developed a purely geometrical mode of treatment for crystals, and discarding the "mechanical presentation" of Haüy, referred the planes existing on them to certain fundamental lines or axes meeting in the center. Weiss's real contribution to his science was the defining of the isometric, tetragonal, orthorhombic and hexagonal systems.

Professor Frederich Mohs of Freiberg in 1822 added the monoclinic and triclinic system and brought the Weiss geometrical point of view in accord with Haüy's conception of decreased rows of units.

George Amadeus Carl Friedrich Naumann, pupil and successor to Mohs, in 1829 invented the system of crystal symbols that bears his name, and that for sixty years was a standard mode of expressing crystal forms.

The most important work among the early followers of Haüy was done by Professor William H. Miller of Cambridge University, who in 1839 deduced a still simpler and more workable system of crystal symbols, and by projecting the faces of a crystal upon the surface of a circumscribed sphere by means of radii normal to these faces, evolved the great principle of zonal relations in crystallography.

Among workers of the early years of the last century, a name that well deserves mention is that of A. Lévy, an enthusiastic and productive crystallographer, whose three volumes with atlas on the material on the famous Heuland Collection is a classic. Lévy also elaborated Haüy's conception of primitive forms into a system of crystal nomenclature that is still in use among French authors. Another famous name is that of James Dwight Dana, greatest of American mineralogists and crystallographers.

Turning now to what we may designate as the constructive phase of crystallographic research in the nineteenth century, we encounter a group of men who, from the laborious work of the mathematical crystallographers strove to formulate arrangements of the ultimate structural units of crystals that would account for the symmetry displayed, both internally and externally, by these bodies. Although a network of molecular points was conceived by Seeber in 1824, this period may be said to begin with the work of M. L. Frankenheim of Breslau, who eliminated from the problem of the structures assumed by the ultimate particles in space the consideration of the shape of the molecules. In thus breaking free from the hampering restrictions of Haüy's "molecules integrantes" Frankenheim limited his studies to the consideration of possible theoretical networks of points, and in 1842 announced that 15 different symmetrical continuous arrangements were possible.

Auguste Bravais of Paris in 1848 showed that the space lattices of Frankenheim were mathematically logical and reduced their number to 14 by proving two to be identical. So important was this advance that we now ascribe the 14 space lattices in which points may be distributed regularly in space to Bravais, and designate them as the "Bravais space lattices." Although the 14 space lattices of Bravais embraced the general symmetry of the six crystal systems, still they did by no means account for certain groups of crystals in every system, such as those with hemihedral or hemimorphic symmetry.

Meanwhile J. F. C. Hessel, an obscure crystallographic investigator of Leipzig, studying possible types of symmetry in solids bounded by plane faces, found that 32 such types included all geometrical forms that conform to Haüy's law of rational indices. Thus came into being the theoretical 32 classes of crystal, few of which had been observed in Hessel's time, but many of which he foretold the existence. Although the actual originator of the 32 groups, Hessel remained practically unknown for over 60 years, and the independent work of A. Gadolin, published in St. Petersburg in 1869 duplicated his investigations and carried forward the truth as he sought to propagate it.

Leonhart Sohncke of Leipzig, in 1879 showed how, by substituting for the single points of Bravais space-lattices, groups of similarly oriented points, it was possible to arrange points in space not alone in 14 but 65 typical ways. Most of the point systems of Sohncke are founded on the 14 lattices of Bravais but involve interpenetration of two or more lattices as well as certain movements of translation and rotation. With the 65 point systems of Sohncke much of the symmetry involved in the 32 groups, into which crystals had been divided, was explained in theory; there were however, certain groups of hemimorphic crystals showing dissimilar modifying planes on the two ends of a principal symmetry axis, and enantiomorphous crystals, of which the symmetry relation between corresponding pairs is such that they are described as right-handed and left-handed individuals, both of which categories were unexplainable by any of the point systems of Sohncke.

The culminating step in the coordination of theoretical particle grouping with actual morphological development in crystals was the result of independent discovery by E. von Fedorov, of St. Petersburg. A. Schoenflies, of Leipzig and W. Barlow, of London, who during the years 1890 to 1894 elaborated the Sohncke point systems, by the introduction of the principle of mirror-image symmetry, and added 165 possible particle groupings in space to the 65 previously recognized. All of these 230 point systems conform in symmetry to one of the 32 groups which are themselves exhaustive of all types of crystal development.

The field was now cleared for the last logical sequence in the series of discoveries that linked Haüy's broken calcite crystal to the full knowledge that we now possess regarding the intimate structure of crystallized bodies. Theoretically the chain of reasoning was complete, through the molecular space lattices of Bravais to the atomic point systems of Sohncke, von Fedorov, Schoenflies and Barlow, we knew that these three dimensional patterns must represent the relative positions of atoms in space, but we had no tangible evidence that such groupings of atoms actually existed.

It remained for physical science to shed light upon this problem, and the initial discovery was made in the year 1912 by Dr. von

Laue a physicist of Munich. Special study of the character of the x-rays had led research workers in the field of physics to suspect that the wave length of these vibrations closely approached in their almost infinitely small dimension the distances between successive layers of atoms in a crystal solid. von Laue conceived the idea of using the atomic structure of a crystal (copper vitriol was used in the first experiment) as a diffraction grating for x-rays. By passing a pencil of x-rays *through* a specially oriented crystal plate, von Laue obtained a spectrum diagram consisting of dark spots upon a photographic plate.

The symmetrical disposition of these slightly oval spots constituted a figure conforming to the atomic arrangement presented in the direction of the incident ray. Thus we have at last depicted in terms as it were of the atoms themselves, a plan of the structure erected within the crystal by its constituent atoms, a diffraction pattern. The credit for placing the x-ray investigation of crystal structure upon a *quantitative* basis, with respect to the relative and the actual distances between atoms in three dimensional patterns, is due to Sir William H. Bragg, and his son Professor William L. Bragg, who in 1915 applied to this problem the idea of "reflection" of the x-ray waves from definitely oriented planes traversing the atomic aggregate. In this way x-ray spectra were obtained which furnished data for analyses of crystal structure. As stated by the elder Bragg in the introductory chapter of *X-rays and Crystal Structure*, instead of guessing the internal arrangement of the atoms from the outward form assumed by the crystal, we find ourselves able to measure the actual distances from atom to atom, and to draw a diagram as if we were making a plan of a building. The science of crystallography has emerged into a new era of unrelated observational data as a result of its equipment with a new tool, the x-ray. Research is now being assiduously urged forward in the field of crystal structure in many laboratories on both sides of the Atlantic by physicists and crystallographers using either some form of the x-ray spectrometer, as devised by Sir William H. Bragg, or a still later type of apparatus that employs small amounts of crystallized material in the form of powder, instead of well developed, specially oriented crystals.

Already the literature in reviews under the heading *X-ray and Crystal Structure*, is not only important but exceedingly voluminous, and those of us who can remember back to the "goniometer pushing" period of research are forceably reminded of the issues of the old *Zeitschrift für Krystallographic* in the 90's when the mathematical crystallography phase of investigation held sway. And incidentally with the passing away of this former era, there has largely vanished from our midst the type of crystallographic draftsman whose beautifully executed work embellished the plates of these old issues of the *Zeitschrift*. I do not say that we are no longer capable of producing such crystal drawings, but I do affirm that we are losing the knack of making them, just as we can no longer manipulate a hand goniometer with the delicacy and skill of our forebears.

So much for what has happened and is happening in this ancient and honorable science. Now let us indulge ourselves in some speculation as to the character of its next phase of advancement. I venture to predict that the future holds out to us a period, the culminating one, in which the assiduously collected data of mathematical crystallographic research linked with the data now being collected in the crystal structure investigations, will lead to the solving of many far reaching problems to which we have not as yet the keys. To cite only two of these, there is the practically untouched mystery of the relation of crystal habit to crystal genesis, a problem of which I am convinced the answer lies in the study of already collected data, rather than in synthetic laboratory reproduction of conditions. There is also the still unsolved question of the influence of chemical composition on crystal system, a question so intimately bound up with the structure of the atom that it would seem as though we must first solve the physical riddle before we come to the crystallographic one.

But above all, fellow students of crystallography, let us bear in mind that the path to attainment is hard and the rewards are few. Ours must be essentially science for science's sake, and in our devotion to the tasks that lie before us in the years to come, and in our search for truth let us remember those wonderful words of Sir William H. Bragg:— In Science there is no religion, but it is the act of religion.