

Crystallography

By Ralph W. G. Wyckoff

FOR MANY YEARS I have been interested in why a science of crystallography came into being with the form and at the time it did, what its relation is to other physical sciences and what the future is liable to hold for it. When this lecture was first decided on I planned to make of it a more or less comprehensive lecture on the history of crystallography—one is needed. But I am not going to do this mainly because I have recently had to make certain unexpected major decisions that have consumed the time that would have been needed to document so serious a talk. There is, however, point to even some rambling comments on the growth of crystallography; we are already too inclined to take our subject for granted and to forget that little more than a generation ago the study of crystals was something carried out in very few universities and then usually in a bare attic room whose sole equipment consisted of a few pearwood models and some mineral specimens removed for the afternoon from the neighboring mineralogical museum. Crystallography was generally considered a useful adjunct to the blowpipe as a way of identifying minerals, but not much more. The discovery that practically all solids, rather than only a few curiosities of nature, are crystalline made this obscurity a thing of the past and demonstrated that a concern with crystalline order must provide the nucleus for an expanding science of solid bodies.

It is just as true in science as in other things that the present is merely the point of transition between a known past and an unknown future. We cannot talk with genuine understanding about crystallography, or any other branch of science, without considering how it has assumed its present form and what it may be expected to become in consequence of the momentum gained through its growth thus far and through its interaction with other growing fields of human knowledge. As a generation in which all sorts of things are happening faster than we can properly absorb and understand them, we have a profound ignorance and even apathy about the past, and we rather dangerously fail to realize how deeply what we are and what we do in the present are determined by the past that has formed us. It would, I feel sure, be of great profit to most of us to wonder, as deeply as we are able, how we have come

to devote a major part of our lives to being crystallographers. In many cases, I am sure, it is not chance; it certainly is not that it brings wealth and power, and it is not that our subject is intrinsically more fascinating than numerous other facets of nature. It can only be that there are properties of crystals which exercise a profound attraction upon our minds. Many of us will find that it is a special feeling for order, and for symmetry in order, that thus works a sort of magic on us.

Natural science is at bottom the search for order among the phenomena that impress themselves on our human senses; and our subject is the pursuit of that order in the (solid) state of matter which exhibits orderliness of position to the greatest extent. Nowadays we tend to think of science as having a sort of self-evolving quality—of having a growth that is determined mainly by the material facilities at hand for pursuing questions that recent observations have drawn to our attentions. These opportunistic factors are important but they are not dominant in determining the long-range growth of science. Overweighing the facilities we have for investigating nature is the question of what we are really seeking to learn from nature, and this question of the fundamental character and purpose of our inquiry is something that is rooted partly in history and partly in the basic attitudes towards life of the times in which we live. For us, as individuals, it is inextricably bound up with our conscious goals in life. And this average human goal, this basic attitude whose conscious realization and satisfaction makes the difference between the sense of success or failure in life, this conscious direction of the individual life has not remained constant during the past and we must hope will not become frozen into any single, uniform pattern in the future. It is the form taken by this central motive in life which has determined the societies of the past; it was its shift for many individuals which has brought natural science as we know it into being during the past 400 years; and it is a rapid further change in this human quest which has so profoundly unsettled the society in which we now find ourselves. This is certainly not the occasion to expound notions about the central human aim and its transformations, but I do want to emphasize that science, including our branch of it, has

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evolved as a partial expression of this basic human quest. Only in the measure that we see and comprehend this, each for himself, do we commence to gain a real understanding of the lives we ourselves are living.

FROM THE OUTSET man has sought knowledge of nature for two contrasting reasons: (1) idealistically, to provide a framework upon which to build an "understanding" of the world and to add meaning to his existence in it, and (2) practically, to utilize nature for his own ends. Both are legitimate, and indeed should be complementary. As far as the outlook of even the cultured people of an era is concerned, the idea that man can dominate and control any important aspect of nature is a very modern one—to both the classical and medieval world, man was the dependent child of nature. And as long as this attitude endured nature was something to be propitiated, not something to be investigated and ultimately controlled through dissection and purposive experiment. It is this attitude that explains why, though there was plenty of experimentation in the ancient world, it commonly ended in passive observation endlessly repeated. We are now so accustomed to working through the medium of the consciously arranged experiment designed in advance to tell us something specific about an aspect of nature that it is hard to realize how novel is this attitude. But it was only at the time of the Renaissance that it came to animate the minds of a sufficient number of men, and it is this new, consciously active and aggressive orientation of the human intellect towards the outer world of nature that has brought about modern science with its cataclysmic impact on the whole scheme of human life. This comparative coming-of-age of the intellect, this step in the maturation of the human psyche, has brought its obvious rewards, but there are also developing dangers of which we are only commencing to be adequately aware. Those of us who have growing children know how inevitably the period of passive and dependent childhood is followed by an aggressively assertive adolescence which is blind to everything except that which it somehow fancies it knows. We are now in the adolescence of the human intellect, with all its attendant dangers and all its magnificent promises for a more adult future—

provided that in our present willfulness we do not destroy that future. It is this immature arrogance of the intellect that was so largely responsible for the grossly materialistic phase of human thought from which there are signs we are emerging; but there are still plenty of intellectuals who are sure that their present vision encompasses the knowable.

We should not forget that modern science was initiated by men whose approach to the unknown can only be described as reverential; and it is a warning of present danger that it is becoming increasingly difficult to maintain that unrestricted preoccupation with and devotion to the truly unknown which is at the root of all significant extensions of our knowledge of nature. This cannot be maintained in the absence of a proper respect for what we do not yet know any more than it can prosper in a mental climate that values knowledge only for the uses, in terms of material wealth and power, that can be made of it. In an immediate future full of uncertainties one of the most momentous is whether pure science is itself going to founder for one or the other of these reasons in the very midst of the so-called scientific age.

The form which natural science has taken is determined in the first place by the questions we ask about nature. They are today, as they always have been, questions of the greatest simplicity. What we can know about the outside world is determined by the impact it makes on our senses, and of course nowadays on the instruments invented to extend the range and the sensitivity of our sense perceptions. Our primary concern has therefore been with what objects *do* in affecting our senses; and physics grew up in response to this concern. In the first place it was a study of motion and of light. Somewhat more sophisticated than the question of how matter acts is the almost equally elementary one of what it *is*. From ancient times man has speculated interminably about this, but knowledge has come only through the experimental study of how different kinds of matter interact. Chemistry, as the study of what matter is, followed physics, as the study of what it does. But there are two aspects of any inquiry into what an object is: one, involving its form, is morphology; the other, dealing with its substance, is the

chemistry just mentioned. Our subject, crystallography, is in the original sense that branch of morphology which is concerned with the outer form of inanimate objects having shapes expressive of internal order. For this reason, as well as because the single crystals that so clearly express this order are after all a very minor component among solids, it was inevitable that their careful study was not one of the first things to be taken up by a developing physical science. Crystallography, as the weaker sister of chemistry, is inevitably one of the last of the physical sciences to take shape.

Our subject has two roots in the distant past; its idealistic one is in geometry, the practical one is concerned with minerals as crystals. From earliest times geometrical figures have been, both in their own right and as visual representations of the simplest numerical relationships, symbols of deep psychological and religious significance; they are in that sense the most primitive statements of that faith in, and concern with, order in nature which is at the core of all natural science. It is very hard for us, in our present cultural environment, to reconstruct for ourselves the meaning these geometrical forms had for earlier peoples. We can read about it in the thought of certain ancient philosophers—Pythagoras is the one most familiar to us; and some of us, perhaps those in whom these earlier patterns of thought persist, can recapture through childhood memories the true magical meaning these symbols then held for us. I do not intend to go into these very real, though unscientific, matters but I want to point out that these notions reappear in more elaborate form in the attraction which the "perfect" solids held for the ancients, in the medieval ideas that led Dürer to give conspicuous place to a polyhedron in his *Melancholia* and perhaps most strikingly of all in Kepler's well-known representation of the solar system through a series of concentric regular solids. None of the speculations centering around these geometrical figures was or became scientific in the sense of being an inquiry into the make-up of the outside world; what they have to tell us is rather something about the human mind.

THERE ARE MANY RECORDS from the past about single crystals as minerals, especially those that are important as jewels. But as far as I know the beginnings of what we would look on as a scientific approach to crystals are to be found here and there in records of the seventeenth century. Thus Steno dealt with quartz inclusions, diamonds, and other minerals as examples of solids which have been formed in nature subsequent to the creation, and he speculated that they had in fact grown in much the same way that one can obtain salt and alum crystals. This is one of the beginnings of an attempt to reconstruct the history of the earth through observation rather than through pure speculation. Boyle and especially Hooke were doing similar things and working with much the same crystals, though Boyle seems to have been especially interested in minerals and their possible origins. Hooke speculated as to how such orderly growth could take place

and explained it by imagining that his crystals were indeed a stacking of spherical particles, a process which he illustrated with lead shot. And thus the idea of close packing was first applied to crystals almost exactly 300 years ago.

Calcite, as Iceland spar, was another crystal that attracted much attention in these early days. There are records of all sorts of observations made on it by Bartholinus; among these were crude measurements suggesting constancy in interfacial angles. His observations of its double refraction were taken up, extended, and "explained" by picturing this crystal too as a stacking of particles that were spheroidal rather than spherical.

Much more attention seems to have been given to crystals in the eighteenth century but it was only towards its end that order began to emerge from the observations that were made. At first the existence of polymorphs and of drastically different habits for the same substance fostered ideas that form was more or less accidental and not characteristic of a crystalline species. At this time too, quaint and anthropomorphic ideas persisted concerning the vital character of crystal growth and the ability of a salt to induce crystallization in other materials through a sort of "fertilization." From the standpoint of such notions, it was not hard to look on diamond for instance as a form of alum, achieved by a sort of biological union of diverse elements. Evidently the first step towards an ordered description of crystals was the demonstration that irrespective of gross appearance, all crystals of a substance (if not polymorphic) have the same symmetry properties. The name of Romé de l'Isle is associated with this. The great formulation of descriptive crystallography was, however, the work of Haüy, who died as recently as 1822. I do not need to outline to this group his contributions or the essential role that cleavage played in their formulation. The geometrical theories which culminated later in the century in the theory of space groups are the direct outgrowths of Haüy's ideas combined with the realization that atoms were the chemically indivisible building units of crystals, as of all other forms of matter. It is equally unnecessary for me to trace for you the evolution, from these ideas and in response to their incompleteness, of the space lattices of Frankenheim and of Bravais, of the simple space groups of Sohncke and of the complete theories of Schoenflies, Barlow, and Federow. What I want to do is rather to talk about the revolutionary expansion in crystallography that followed the discovery of X-ray diffraction and to trace what seem to me to be main currents in the subsequent evolution of the subject.

The Laue experiment, whose 40th anniversary we are this year celebrating, developed from problems which had little to do with crystals. It arose, of course, from an attempt to establish the true nature of X-rays which had not been settled in the years since Roentgen discovered them. Both Professors von Laue and Ewald talked about some of the circumstances that led up to the successful effort to diffract X-rays with crystals at the time of our Cambridge meeting four years ago; we

should, I believe, exert all necessary pressure on Professor Ewald to talk to us about it in more detail. He, more than anybody else, is able to provide in permanent form an essential record of the mental climate that helped bring this experiment into being.

Both crystal structure and X-ray spectroscopy began with the experiments of the Braggs that followed immediately on the heels of the success of Laue, Friedrich, and Knipping. Their initial work was so immediate and great a success very largely because of the happy choices made of structures for the alkali halides, calcite, and other crystals they worked with. It is interesting to note how these models were pictures of the packing of spherical "atoms" that harked back through the British crystallographers to the ideas of Huyghens and of Hooke. These successful guesses, which in hindsight is what they really were, combined with the simplified thinking that was introduced by the inspired reflection analogy of W. L. Bragg, gave the use of X-rays a headlong start in unraveling the atomic arrangements in more complicated crystals.

These beginnings of crystal analysis were timely in relation to a steadily growing general interest in the solid state of matter. The atomic hypothesis itself, and most of the early information gained about atoms and later about molecules, arose from the study of gases. In the latter part of the last century and the early years of this, an equally thoroughgoing preoccupation with solutions, especially those involving ions, replaced this initial concern with gases. The physical chemistry of forty or fifty years ago had only three chapters: (1) a historical one dealing with gases; (2) its main substance—solutions of ionic compounds; and (3) a smattering of thermodynamics and a hodgepodge of miscellaneous observations which went under the title of colloid chemistry. But the study of solutions was beginning to be a field of diminishing returns and this combined with our ignorance of solids made an increasing preoccupation with them inevitable once successful methods for their study appeared. This preoccupation has been steadily growing during the last thirty years.

On the whole, however, it was not determinations of the structure of a few simple single crystals which gave the study of solids a new value in the eyes of science in general. Rather it was the realization, surprising to most people at the time, that arose from the demonstration by powder methods that nearly all solids are crystalline. It is hard, even for those of us who were brought up at the time, to realize how insignificant a role the crystalline state played in the thought of physical scientists before the Laue experiment.

As crystal analysts we must try to see our subject in its proper relation to this growing science of solids, for we are not its only link with the past. The essential business of this science is of course to correlate, as far as possible, the physical properties of solids with what we can learn about their composition and structure. During the second half of the last century, at about the same time that crystal geometry was being perfected into the theory of space groups, various attempts

were made to relate superficial crystal geometry with the physical properties of crystals. Voigt's *Lehrbuch der Kristallphysik* is the integrated expression of this "classical" theory of solids. Such a theory became obviously inadequate as soon as atomic positions could be established, but the solid state physics that is now growing up can be thought of as a restatement of Voigt in atomic terms and it may ultimately take this form. In any event such a physics of solids must be the real goal of all our studies, and determinations of crystal structure must be looked on as an essential, but only preliminary, step in the building of this physics. If we fail to realize the position of crystal analysis in this larger scheme, we shall inevitably be left behind as the subject grows and we shall, more or less by default, leave its evolution to others. There is still plenty to be done in our own specialty but we would do well to keep our broader goal in mind and gradually to become oriented towards its realization.

I do not now, however, intend to review this solid state physics or the contributions of crystal structure to its growth. Instead I want to discuss briefly what seems to me to have been the principal steps in the development of crystal analysis and to mention indications from this past concerning directions of growth in the immediate future.

CRYSTAL ANALYSIS has developed thus far through the realization and solution of a very few questions. What have these been? As I suggested a moment ago the first structure determinations were really inspired guesses about atomic arrangements which proved to be compatible with a very limited number of more or less qualitative experimental data. They were thus in the nature of possible, rather than necessarily correct, atomic arrangements. This caused some of us to wonder if there was any way of increasing the probability of their correctness by devising procedures that would deduce structures. Such a procedure necessarily involved a statement of all possibilities and then a selection among them using the available data. It was here, of course, that the theory of space groups became essential. The resulting ability to consider all possible structures for a crystal had a number of consequences, some good and some others definitely restrictive. The advantages are obvious. On the other hand it led to a concentration upon simple crystals of high enough symmetry so that the attainable, rather qualitative, data could discriminate among the several possibilities that space group theory listed. This was not too serious in the early days and it led to successful analyses of many simple structures which we could then consider known with a high degree of certainty. Such knowledge was valuable both in its own right and as a firm basis upon which to build a more quantitative knowledge of the laws of X-ray reflection. These results with simple crystals did demonstrate that most of their atoms were in positions required by exact conformity to symmetry theory. The orderliness in atomic arrangement was indeed so great that some of us came

to think of natural crystals as such geometrically perfect atomic arrangements. And this was a mistake, for the perfect crystal is a rarity; experience has now amply demonstrated that we only understand the structure of a crystal if we not only know what the ideal structure would be but also how the real specimens depart from the state of geometrically perfect order. As time goes on this study of the departures from perfect order in crystals is becoming more and more important. I want to come back to it again in a few minutes.

It was inevitable that if crystal structure was to develop and broaden, some way must be found to deal with more complex crystals and with those of lower symmetry. The Braggs' introduction of Fourier methods of analysis is what made this possible. For their essence and intrinsic worth lies in a substitution of all the data for a selected few as criteria for choosing the right structure. Not only did these methods assure that the available data would contribute to a choice of atomic positions but they encouraged the accumulation of all attainable data since for all but the simplest structures both the accuracy and the certainty of the determination are enhanced as the data increase.

Though Fourier methods are the heart of this extension of crystal analysis from simple structures having two or three variables to those now engaging successful attention though they have a hundred or more, these methods are not in themselves a panacea. For their successful application they need supplementary information and are the more powerful as more information is available. For example they have not displaced the earlier applications of space group theory results. Likewise their introduction into crystal analysis has, as we all know, led to highly profitable extensions of the methods themselves. This was initiated by Patterson's development of the squared function and its interpretation in terms of interatomic distances; it is being continued by current research into methods for ascertaining the signs of Fourier terms, as begun by Harker and Kasper, by investigation of the so-called implication functions and by inquiries into the value of functions higher than the square. And, of course, there are many practical as well as theoretical supplements: for example, through working with isomorphous compounds to help fix signs, and through corrections for incompleteness of Fourier series. To this practical category also belong aids to calculation, like Bragg's fly's eye, Pepinsky's X-RAC, and the several procedures using commercial calculating machines which, by the time they save, have revolutionized our notions of the kinds of problems that can successfully be undertaken.

There is another chapter of our knowledge gained through the study of simple crystals which forms an integral part of our present day equipment for analyzing very complicated structures, and that is a knowledge of reasonable interatomic distances. A concern with the significance of the atomic separations that are the outcome of a complete crystal analysis has agitated crystal analysts from the very outset. I am not going to review the subject of atomic radii, as deduced from

experiment or as calculated on semitheoretical grounds. Nor shall I more than recall to your minds the profitable use that has been made of the idea of packed ions of fixed sizes, as for instance, by the Bragg school in the analysis of silicates. But I would like to remind you that our present knowledge of what atomic separations to expect in a crystal, routinely applied by every crystal analyst, is an invaluable inheritance from the earlier work with simple crystals. If I were giving a comprehensive account of our present day methods of crystal analysis I should have to point out the impressive developments that have taken place in our experimental methods of handling crystals and measuring their numerous reflections—it is a very far cry, indeed, from the beautiful apparatus we now can buy to the lead-covered wooden boxes that were the basis for our apparatus thirty years ago.

And now I think it is time to ask what really are some of the problems that are agitating us at the moment and into what they are liable to grow. In the beginning it was so remarkable and unexpected a thing that we should be able to ascertain where the atoms were in any crystal that we were quite content to work with those substances that seemed most likely to give convincing results. These results with simple crystals did two things: as I have already said they instilled in us a better understanding of the depth to which order extends in the natural world; and they gave that wider understanding of the value of studying solids that has since supplied the facilities required for our expanding subject. This value is so generally accepted now that most of the younger of you can scarcely realize how new is this attitude; but it is worth recalling the few institutions that were willing twenty-five years ago to support any work in crystal structure, and that in spite of the very modest requirements we then had in the matter of apparatus.

Most early applications of crystal structure methods were in the field of inorganic substances. Now a concern with the more complicated molecules of organic chemistry has overshadowed many of these earlier fields of interest. In fact the current preoccupation with organic structures, and especially with the information about organic molecules that it furnishes, tends to make many look on our subject as a tool of organic chemistry. Even among some crystal analysts this has gone to the point where so much attention is given to describing the molecule of the crystal being studied that it is hard to find in the published paper just what the structure as a whole turned out to be. Beyond doubt this study of the structure of organic molecules is at the moment a most fruitful aspect of crystal analysis; but equally beyond doubt this absorption in organic molecular structure is only a phase of our subject; its true and somewhat more subordinate place will be found as time goes on.

LEAVING ASIDE the everpresent problem of how to fortify methods of analysis, it seems to me that the major question we now have to face is: how

deeply into nature does order in particle arrangement extend? The existence of molecular "rotation" in some simple aliphatic compounds showed beyond debate that order does not necessarily extend to the positions of all atoms in a crystal. Since then, incomplete order of many sorts has been found, ranging from limited oscillations about an axis to the seeming complete lack of atomic order that prevails, for instance, in the hexagonal cyclopentane recently described by Fankuchen and his co-workers. Other kinds of incomplete order which we have come to recognize occur in alloys, with or without mechanical working, and in the deficit structures encountered even among simple inorganic crystals. But certainly one of the most important problems concerning incomplete order is that involving the more complicated organic crystals. It is at the heart of the protein problem. Thus far the shortest recorded spacing for a complex organic crystal has seemed to depend on its molecular weight. Thus from vitamin B₁₂ with a molecular weight of slightly more than 1000 the shortest observed spacing is around 1 Å, while the thousands of reflections from hemoglobin exceed 2 Å. If it turns out that crystals with these large molecules cannot be made to give shorter reflections, it will be hard to avoid the conclusion that the atoms in their molecules need not fill very exactly the positions in space defined by their gross symmetry. If they are such "atomically sloppy" structures, this fact presents a definite restriction on what can be accomplished by studying them with X-rays. We may determine the over-all distribution of matter within their molecules, in terms of the "globs" that Harker is talking about, but we really may not be able to settle the shape of the polypeptide chain linkages in proteins by our methods. The contrasting approaches now being taken to this question, as exemplified by Astbury, by Perutz and Bragg, and by Pauling and Corey on the one hand, and by Harker, on the other, are important both for their bearing on the future use of X-ray methods in this field and as illustrations of the two approaches we make to nature. What I will call here the Harker approach is the direct appeal to nature and to our observation of it; it is in essence inductive and synthetic. Its answer has a high measure of certainty but is rarely as complete as we might wish. The contrasting approach, illustrated by the Astbury, et al., attack on the protein problem, sets up a detailed solution and then sees whether or not it is compatible with the experimental data. The answers we get in this way are necessarily as complete as our assumptions, but they are not necessarily convincing. Usually there is need for both approaches to nature and sometimes the one, sometimes the other, is the more fruitful. For the problem of protein structure, a detailed answer down to the level of atomic positions (including a definition of the shape of the peptide linkage) can have real meaning only if the data can select among all reasonable solutions at this level of detail—and this we do not yet know. In every growing science there is some measure of rivalry between these inductive and deductive approaches, and there is greatest

progress when they can both be used. Though both should be cultivated together, each of us tends to prefer one or the other: which it depends primarily on our psychological make-ups. Some of us would rather be absolutely certain of a few things and are content to leave the rest for the present unknown or in doubt; others are genuinely so upset by the existence of this shadowland of knowledge that they prefer a complete picture of it all, even if there is no certainty that any of this complete picture is true.

Beyond doubt the answer we get to the question of how deeply order in particle arrangement extends into complex organic crystals will have a profound influence on the direction and emphasis to be given crystal analysis in the years immediately ahead. But there are other factors too that will influence this future. Dominating these is the role that we elect to play in the evolving science of solids. I do not know in what other directions our subject should evolve but a few things are clear. For one thing increasing attention is sure to be given to the departures from perfect crystalline order to which reference has already been made. Another is a renewal of interest in the varied phenomena of crystal growth as presaged by the theoretical work of Frank and the observations that are beginning to be made with the electron microscope. Many alloys have atomic arrangements so complex that they have hitherto been too difficult for satisfactory analysis; as knowledge of their structures increases it undoubtedly will greatly enhance our understanding of metals and their alloys. I cannot stop without drawing your attention to the possibilities for new knowledge that lie in the examination of solids in which there is subcrystalline order in particle arrangement. Such solids, of the greatest importance to the living state, are built up by indefinitely long filamentous molecules. These molecules are grouped in bundles, sheets, and fabrics which by their arrangements determine the characteristic properties of the solids. Something about this order can be gained from low angle X-ray measurements but far more can be learned with the electron microscope.

If the world remains stable enough so that research can flourish, if most of the energies of science and scientists are not swallowed up in the invention and perfection of more and more complex and brutal agents of human destruction, if the spirit of free inquiry into the secrets of nature which has created the great and rewarding body of natural science over the last three hundred years is not wiped out by the widespread assault now being made on the functioning of the individual human mind, we may expect that the study of solids will be for the immediate future in the forefront of our steadily widening, as well as deepening, penetration into the secrets of nature. And it is our duty as scientists not only to add something to the sum total of the knowledge we have received from our predecessors, but to use whatever intelligence we have, and wisdom we may have acquired, to preserve that spirit of individual free-inquiry which is the foundation for all of man's growth.