

## X-RAY ANALYSIS AND THE STRUCTURE OF MATTER\*

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WHEN the new methods of X-ray analysis were first introduced a quarter of a century ago, there was naturally no clear realization of the extent and character of the fields of research in which they would eventually be employed. Certain applications were found for them at once, but the years have brought wide and unexpected developments. Some of these are gathering themselves together, and, in conjunction with other methods of physics and chemistry, begin to form what might well be called a new branch of science.

In the early phase of the X-ray crystal studies, the object of interest was the perfect crystal; in the later phase, attention is directed towards the departures from perfection, which turn out to be of the greatest interest and importance.

## EARLY WORK ON CRYSTAL STRUCTURE

It will be remembered that the method of analysis of the structure of matter by means of X-rays was based upon a suggestion made by Dr. M. von Laue. If the atoms in a crystal were in regular array, the passage of ether waves through the crystal should be accompanied by diffraction effects, provided that the lengths of the waves were of the same order of magnitude as the spacings of the atoms. In the case of the ether waves emitted by an X-ray bulb—if indeed the X-rays were ether waves, of which there was some doubt at the time—there were reasons to suppose that the wave-lengths were of the magnitude required. The experiment was made, and was successful.

The diffraction effects provided means whereby the crystalline arrangements could be calculated. The researches of the first few years of X-ray analysis were therefore concerned with the character of the crystalline arrangement in a number of the simpler cases. As confidence grew and skill increased, more difficult structures were attacked, and indeed it has been very surprising to find what complicated structures can be unravelled. One helpful circumstance has been the existence of families of substances, since the progressive differences in the members of a family give rise to corresponding changes in the diffraction patterns. Thus, for example, the large family of silicates was examined and the connexions between composition and diffraction effects, and

again between the latter and structure, were observed and compared. Certain simplicities and uniformities then appeared, and it became possible to put in order a mass of details which had not previously appeared to have any relation with each other.

It was not long before the results in this field of research became so numerous that books of no small size were required to contain them. In thousands of cases, the dimensions of the unit cell of the crystal were determined, and at least the space group or character of the arrangement of the atoms within the cell. In a number of these cases the exact relative positions of the atoms could be found, though this additional task has often been formidable. Work of this kind continues, and rightly so, to be the occupation of many investigators. All such work belongs to the first phase to which I have referred.

## IMPERFECTIONS OF CRYSTALS

The application of the X-ray methods has for some time been entering on a second phase. It now deals with a natural phenomenon differing entirely from that which was the first to be examined. The earlier work was concerned with the arrangement of the atoms in a perfect crystal, that is to say, a body in which the mutual forces are balanced, and the arrangement is complete. Thermal movements may still be there, but the average dispositions of the atoms are settled, and are uniform throughout the body of the crystal.

It is doubtful whether there is such a thing as a perfect crystal large enough to be handled; perhaps the crystals of diamond and graphite are nearest to perfection. In almost all cases there are deviations from complete uniformity. A crystal that has every appearance of being perfect may consist of an assemblage of minute crystallites, more nearly perfect individually but lacking uniformity of orientation to a greater or less degree. Other bodies that do not appear to be crystalline at all may consist of crystallites oriented so irregularly that the bodies seem to be isotropic. The crystallites may vary in size as well as in relative orientation. Two or more crystal forms may be present in the same body, so mixed together that only the X-ray methods can make any attempt to disentangle them. Sometimes one

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greater lattice overrides in a more or less regular fashion a smaller lattice, as a pattern of ploughed fields may override a pattern of furrows. Also a lattice may be distorted by strain. In a substance in the liquid state there may be associations and partial arrangements sufficient to show X-ray diffraction.

Moreover, arrangements and dimensions may vary with time, both in solids and liquids; some forms or extents of arrangement may even disappear, new forms may appear at the expense of the old. Perfection of crystalline arrangement is a goal which is never achieved. In fact the processes of the world are based upon such deviations from perfection, and their continuous modification. If all arrangements of atoms were complete, there would be nothing left but stagnation and the peace of death.

It will be seen, therefore, that a new field of research of extraordinary interest is being opened up. It is in this field that the physicist and chemist, and indeed scientists of every persuasion, must look for explanation of many of the properties of their materials, such as their relations to magnetism and electricity, thermal conductivity, tensile strength, various surface effects and so on; and also the time changes in these properties, such as the creep to which the engineer has to give so much attention. Properties such as these have been called by Orowan and others the 'sensitive' properties, since they depend on the particular state of a body, which state in turn depends largely on the conditions of the new field of which I am speaking. The biologist finds interest in it, because the life processes seem to involve the relations between large aggregates, molecules or assemblages of molecules, with one another or with media in which they are imbedded. Somewhere in this field life and matter are first found in association.

It may seem unreasonable to expect help in the resolution of such complications from the X-ray diffraction effects. It is to be remembered, however, that the X-ray photographs are very rich in information. The gratings are three-dimensional and may be examined from a variety of aspects; each photograph or spectrometer record is a two-dimensional diagram of positions and intensities of diffracted spots. A light spectrum of the ordinary kind is uni-dimensional only. The photographs vary in definition, being less easy to read as they deal with more complicated cases; but the technique is rapidly improving.

#### MOSAIC EFFECT

The earliest of these phenomena of the larger field was the so-called mosaic effect. A crystal of

rocksalt, for example, is a mass of small crystals, each of which approaches to regularity far more completely than the whole. The separate crystallites are not in perfect alignment with each other. Hence arose one of the perplexities of the early days. It was extraordinary to find that the less perfect crystal reflected the X-rays in greater intensity than the more perfect, and that the reflections from the face of a crystal—quartz, for example—might be increased if the surface was roughened. The puzzle is solved if we remember that, as Darwin and others pointed out, one crystallite may screen another. If the orientations of the two are exactly the same, and they are set at the proper angle for reflecting the incident X-rays, the first crystallite will partly absorb the rays in producing its own reflection and the lower will not have its full opportunity. But if, as is usual, the crystal is moved through small angles about the above setting so as to give every crystallite its chance—provided that the X-rays can penetrate the crystal so far as to reach it—and if the second is in the right orientation for reflection when the first is not, then the incident rays get through the first and are reflected by the second; the integration of all effects therefore gives a larger total when the crystallites are not parallel.

This mosaic character is very common, even in crystals of the purest material. There are indications, as remarked by Goetz and others, that in some cases at least it is the state of greater equilibrium. Thus W. A. Wood shows that crystals of copper and other metals of extreme purity are reduced by cold working to crystallites in more or less complete disarray. The substances do not then return to their former state, though they can be taken some way towards it by moderate heating. To restore them to their original state it would be necessary to begin over again from the melt. A similar effect was shown by Ewald to occur in the case of rocksalt. It may also be significant that of the two forms of diamond examined by Robertson and Fox, that which is the more transparent to infra-red and ultra-violet, and may therefore be taken to be in greater internal equilibrium, is also the one in which there is some mosaic character.

If this form of disintegration of a larger crystal into crystallites is really due to the release of energy, it might be expected to proceed until the process was complete and the substance became amorphous. Wood shows that it does not proceed indefinitely and that the copper crystallites have an average linear dimension of about 700 Å.; for silver the figure is 800, for nickel 1200, and so on. The disintegration ceases at a certain point. The metals were of extreme purity. Unless it appears



that the mere trace of impurity governs the effect, it must be supposed that the disposition to form aggregates of definite magnitude is present in the copper atoms themselves.

The presence of crystallites of a definite pattern, their dimensions, their preference for any particular orientation in relation to the body which contains them and their proportional amounts are all determined by the X-ray photographs. It is to be remembered that the diffraction spectra of a compound of different crystallites do not modify or disturb each other's evidence. The data on which calculations are based are the forms and intensities of the spots and lines in the X-ray photographs. The calculations are often difficult and lengthy because so many factors have to be taken into consideration; in fact there is plenty of evidence, and the most troublesome part of the business is its interpretation.

#### APPLICATIONS TO METALS AND TO LARGE MOLECULES

It will be readily understood that such measurements as these can be of great assistance in the study of metals. It is possible to examine in a new and most effective way the phase diagrams of the metallurgist, and the various effects of composition, temperature and time, and this not only for binary alloys but also for ternary and still more complicated mixtures. With these powers in hand, and with the remarkable accuracy of the modern X-ray spectrometer, which can show minute changes of form due to temperature or an admixture of foreign atoms, and can show also any variations in the extent of order and disorder in the atomic arrangements, it is not surprising that theoretical metallurgy has acquired a new life and that practical metallurgy begins to gain thereby.

Since the X-ray methods can do so much to discover the composition of molecules, even very large molecules such as the phthalocyanines (Robertson) or the sterols (Bernal, Crowfoot and others), and also to determine the arrangement of the molecules in crystalline aggregates, and yet further to find any preferred orientations that there may be, the methods can be fitly used for the examination of fibrous materials. In cotton, silk, rubber and many other substances there are long-chain molecules which are linked together into crystallites having preferred orientations along the length of the fibre. So also nerve, muscle, horn and such-like contain proteins and keratins in fibrous forms. It is even possible, as Bernal has shown, to find some details of the composition, structure and arrangement of immense molecules such as those of a virus. Very interesting papers

on these subjects have been communicated to the Royal Society, some of them during the present year.

It is to be observed that the extension of the X-ray methods to these larger scale problems is greatly facilitated by extrapolation from simpler observations. In the case of organic substances, the modes of assemblage into characteristic combinations of atoms, such as the association of carbon atoms in the benzene ring, are governed by rules which are so closely followed in the simpler cases that they can be assumed to hold in the more complicated. These rules relate to the distance from atom to atom in various cases, and the mutual orientations of atoms. In this way very important suggestions have been made in respect to the construction of the more difficult assemblages.

It is to be remembered, of course, that there are other physical methods of observation which contribute to the understanding of the complex substances of Nature, which are all the more efficient now that the X-ray methods are able to make their characteristic contribution. First of all comes chemical science, the power of which is so obvious and well known that I need not do more than refer to it. Optical properties have been found to be extremely useful. So also the magnetic properties are found to be closely related to structure. Thus, for example, the disposition of a molecule containing benzene rings can often be predicted from diamagnetic measurements.

The sum total of these powers, some new, some old, all reinforcing each other in a common advance, is so great that, as I have already said, a new field of inquiry of first-rate importance has been well entered. That which the eye can see is one thing; that which the microscope reveals is another. Far beyond any vision is the individual atom and the atomic nucleus, of which so much has been discovered in recent years. But a vast range of magnitudes lying approximately between 10 and 10,000 Å. has never been accessible to the direct attack which the ranges on either side of it have experienced. Within this range lie all the processes which are concerned in the building of living substances, animal and plant, and in the changes of growth and decay. In this range lie also elements that are the origin of the properties of our materials, alloys, glasses, fibrous substances of all kinds, and here take place transformations which change these properties, some of them especially rapidly when urged by heat, some so slowly that centuries must pass before they become visible or effective. The recent advance into this new field is only the preliminary to what is sure to follow. We have before us an inquiry of supreme interest.