

The Grain-like Structure of Solids*

By Sir William Bragg, O.M., K.B.E., P.R.S.

A CURSORY glance over the research work described in the scientific publications of to-day shows that remarkable interest is concentrated on magnitudes which are too small to be examined in detail under the microscope and too large to be studied conveniently by X-ray methods. Such magnitudes are to be found in all lines of research, medical, industrial, and purely scientific. Their behaviour presents numerous problems of great interest, and also of considerable difficulty. Solutions are of pressing importance, because the want of knowledge is in all cases a hindrance to progress. When in the course of our work we arrive at these magnitudes we realize that we are facing a key position.

The microscope makes it possible to detect objects as small as a few hundred angströms in diameter, but it is far from revealing the details of objects so small as this. There are other optical methods of detecting such magnitudes. Thus Langmuir has recently shown how the polarization effects of films no more than a few dozen angströms thick can be made visible: but again this method does not supply a means of examining detail.

The X-rays in a sense go too far. Their wavelengths are such that the crystalline arrangement of atoms and molecules can be measured with very great accuracy, but their field of view is too narrow to take in the details of larger structures. Thus there is a gap in the means of inquiry, and it is remarkable how consistently the particular deficiency has inconvenient results.

Magnitudes of this order occur, for example, in the metallurgical field. Their importance is more obvious now that the structures of metals and their alloys are better known. The X-ray methods determine with accuracy the details of the crystal structure of iron and its alloys, but such information is insufficient for a prediction of the behaviour of a specimen of steel. As Smekal has observed, there are certain properties which are clearly connected with structure; and are 'insensitive' to any treatments to which the steel has been submitted in its previous history. But there are other properties, to be described as 'sensitive', which can be modified profoundly by treatment, such as tensile strength, plasticity and hardness, as well as electrical and magnetic properties, and these are most important qualities in practice.

Long ago the microscope showed the metal to be an assemblage of grains; and the conditions of the assemblage are clearly connected with the 'sensitive' properties. But the exact details of the connexion are difficult to investigate because they fall within the region in which direct illumination fails.

Metallurgical theory hovers continually over the idea that a metal or an alloy contains minute groups of atoms, or is even a compound of such groups, which may be called crystallites, since the arrangement of the atoms within each one is perfectly regular. The X-ray diffraction is regular, and the lines of a 'powder diagram' are clear and sharp. Thus Gough and Wood in their examination of the fatigue of metals due to the cyclic repetition—sometimes to millions of times—of an imposed stress, found that the visible grains gradually broke up to an extent which in any one experiment depended on the magnitude of the stress. Fracture in any one region occurred when the break up into crystallites was complete. It did not imply the disruption of atom from atom, resulting in complete disarray, but merely a separation into minute crystals the magnitudes of which were arranged more or less closely about some average. This was shown by the form of the X-ray photograph. A definite stage had been reached in the break up of the material. The existence of such an average would imply that the dimensions of the crystallite are in some way referable to numerical relations between the form or dimensions of the atoms of the metal: analogous to, but far more complicated than, the formation of the benzene ring of definite form and size from atoms of carbon each of which has tetrahedral qualities.

The discussion as to the specific existence, nature and effect of crystallites has been conducted with great eagerness; very much research on the mosaic structure of crystals in general has been undertaken, and several interesting theories have been put forward. At first, theories were suggested which would have provided a super lattice, consisting of a regular arrangement of crystallites, even in the case of a pure metal. But this suggestion could not be maintained, as it evolved a second linear dimension out of a first. Buerger has suggested that the grain-like structure of a metal is due to conditions of growth, various crystalline processes meeting and joining together in irregular

* From the presidential address to the Royal Society, delivered on November 30.

fashion during the formation of the whole mass. This, however, would lead to a casual formation which does not seem to be in accord with metallurgical experiment. G. I. Taylor's ingenious theory of the hardening of a metal by working requires the existence of crystallites of some form. The whole question is still obscure, yet it is extremely important because the properties of metals and alloys depend to a large extent on the grain-like structure which they possess. Whether so-called 'crystallites' are formed under some law governing their size or are merely accidental assemblages, they are a centre of interest in the examination of metallic properties.

Similar conditions prevail in other cases where the behaviour of materials is under consideration. In April of this year the International Association for the Testing of Materials met in London. The work of the conference was closely connected with pure scientific research, depending on results already obtained and suggesting numerous opportunities for the increase of knowledge. It was remarkable that in the case of one material after another the discussion directed attention to the importance of grain-like structure, and showed that the 'grain', if I may extend the word widely from its general use in metallurgy, was the object of attack. Thus in the vast variety of fibrous materials, the fibre corresponds to the metal grain, and its study is quite as interesting and important. In all colloidal problems the condition and properties of the minute particle are fundamental. In materials derived from living organisms, the cell and its parts are the centre of interest; and of course somewhere in the region of which I am speaking are the outposts of life itself. Even in dielectrics and lubricants, the groupings of atoms and molecules determine the general behaviour.

Moreover, a very considerable change in the use of materials for construction has come about in recent years in consequence of the fact that the gradual changes due to time have become really important. The so-called 'creep' of materials is now one of the chief pre-occupations of the engineer. Its new importance is due to two causes. In the first place, the development of machinery has necessitated more perfect fitting, and less allowance for clearance than was at one time the case, as for example in modern turbines and internal combustion engines. In such fine adjustments a creep of one part in a thousand is a very serious matter. In the second place, the working temperatures have been greatly increased, and creep is thereby encouraged. There is no doubt that in any specimen but a perfect crystal slow changes take place continuously. At every moment molecules are being helped over the barriers which have

kept them from positions of greater equilibrium. In this way new crystallizations are set up, or older crystallizations extended. Strain may encourage transfer from one position to another. One might almost say that every portion of a solid is a liquid for a certain fraction of its time, and that the atoms in that portion are capable of a movement which is restricted and guided by the stabilizing action of their surroundings.

The laws which govern these movements are very complicated, and detailed knowledge is scanty though badly wanted. Thus, for example, Dr. Bailey, a pioneer in these matters, finds that the addition of 1 per cent chromium to a 0.5 per cent molybdenum steel increases its initial resistance to creep below a certain temperature and lessens it above. It is probable that the addition of chromium atoms locks the grain structure so long as they stay where they are: but heat facilitates their moving, all the more readily because the complicated alloy has the looser structure. Once they have moved, the material would be better without them. But such a rough explanation would be well set aside for a detailed knowledge of the processes involved. Here are very interesting problems of physics and chemistry.

The careful examination of a visible cellulose fibre shows, it is said by some, that it is built up of lesser fibres, fibrillæ or fibrils which again consist of ellipsoidal objects of dimensions roughly 1.5μ and 1.1μ . Each such object may contain many millions of cellulose chains, but very little is known of the structure of the contents or of the sheath that encloses them and seems to be the source of their characteristic influence. Chemical analysis and X-ray examination give a satisfactory picture of the cellulose chain-like molecule, and some information also of the details of the molecular assemblages. But information is wanted respecting the larger groups and the fibril formation on which the fibre properties obviously depend. If the fibre belongs to a living organism, change with time may be synonymous with growth. If the fibre is an element of some material in use, it is still subject to change which may seriously affect its quality.

Change may be external or internal. The slow rearrangements of recrystallization or devitrification are due to internal forces: but surface changes due to reactions with surrounding atoms such as corrosion or hydration may also affect behaviour. Naturally such surface changes are the more important the smaller the particle of the substance, as the colloid chemist points out. Thus, for example, it is a much discussed question as to how clay holds the water that is associated with it. The X-ray analysis supplies a very reasonable picture of the clay crystal; the positions of the

atoms of oxygen, silicon, aluminium, magnesium, iron and the rest are known with considerable accuracy. But the remarkable properties of clay are dependent on the behaviour of the larger flake-like assemblages of colloidal dimensions, which lie between the direct observation of the X-ray methods and those of the microscope.

In dielectrics the slow changes of time bring about rearrangements, hastened by the electrical tensions to which the material is subjected. The electrical forces look for the weakest point for a break-through, just as a stress discovers the weakest point of a chain or any member of a structure. Changes are therefore important. One would wish that a structure was like the "Deacon's shay", which was so designed that every part was as strong as every other so that when the shay came to its end, it became a heap of dust upon the road. Unfortunately, that is not the case with any material in use: and whatever its structure an equal balancing is apt to be destroyed by changes in its grain-like condition.

Perhaps the structure of the huge protein molecules may suggest a way of closing the gap in our knowledge and our means of inquiry. It is a very striking fact that their magnitudes tend definitely to group themselves about certain values, which, moreover, are simply related to one another. They are not mere groups of atoms thrown together without design. Their definite formation implies obedience to rules which must be in force at the beginning of the assembling, and are in force until an unavoidable result is reached. This would mean, as indeed a vast number of observations already imply, that the junction of carbon atoms is

governed by strict geometrical laws of distance and orientation. It has indeed been pointed out by Dr. Wrinch and others that the long chains consisting of two carbons and one nitrogen in regular succession can be formed, under the guidance of the rules mentioned, into space-enclosing sheets presenting an external appearance of linked hexagons, and the number of sizes to which these assemblages can attain is limited. Possibly we have here an example of a form of procedure from the groupings of a few atoms to the larger assemblages of thousands, the process depending on a certain obedience to laws of building which have been shown to hold in the simpler case. We are encouraged to hope that this may be so, by the unexpected strictness and definiteness of the building rules in the cases which fall within the scope of the X-ray methods.

The constitution of the solid body is being examined now as it has never been possible to examine it before. We are not surprised that it is found to possess a grain-like structure, or that this structure is of first-rate importance. It is not only of interest from the purely scientific point of view, but also it turns out to be of fundamental importance to all the constructive work of industry and to all the examinations of living constructions within the domain of biology. In the effort to know its details and to understand their significance a host of interesting scientific inquiries make their appearance, so that industry and science more than ever play into each other's hands. It is certainly to be expected that from these tempting labours there will result much improvement of natural knowledge.

Progress in the Transport and Storage of Foodstuffs

THE work of the Food Investigation Board is carried out in the interests of the general body of consumers in Great Britain and is directed to reducing waste and improving the variety and quality of foodstuffs generally available by the application of scientific knowledge to the problems of storage and transport. The annual report of the Board*, besides describing the Board's activities, includes, in the report of the Director of Food Investigation, a concise statement of the progress of the investigations carried out during the year under review, many of which have not yet reached the stage at which full publication of the results

is feasible. The keynote of the Board's activities in 1936 was its co-operation with other bodies interested in similar problems of food preservation in different parts of the world. The British Commonwealth Scientific Conference met during September 1936, and the members visited the various experimental stations maintained by the Board, namely, the Low Temperature Research Station at Cambridge, the Torry Research Station at Aberdeen, and the Ditton Laboratory at East Malling in Kent. The seventh International Congress of Refrigeration was held at The Hague in June 1936 and was attended by several members of the Department of Scientific and Industrial Research. A number of visits abroad were paid by members of the Food Investigation staff: thus

* Report of the Food Investigation Board for the Year 1936: Department of Scientific and Industrial Research. Pp. 235 + v. (London: H.M. Stationery Office, 1937.) 3s. 6d. net.