

An Aspect
of Order in
the Physical
World

An Inaugural Lecture

GIVEN IN THE UNIVERSITY COLLEGE OF
RHODESIA AND NYASALAND

E. L. Yates

OXFORD UNIVERSITY PRESS

AN ASPECT OF ORDER IN THE PHYSICAL WORLD

*An Inaugural Lecture
given in the University College of
Rhodesia and Nyasaland*

by

E. L. YATES
Professor of Physics

LONDON
OXFORD UNIVERSITY PRESS

1961

Oxford University Press, Amen House, London E.C.4

GLASGOW NEW YORK TORONTO MELBOURNE WELLINGTON
BOMBAY CALCUTTA MADRAS KARACHI KUALA LUMPUR
CAPE TOWN IBADAN NAIROBI ACCRA

© *University College of Rhodesia and Nyasaland 1961*

*Distributed in Central Africa
solely by Messrs. Kingstons Ltd.
on behalf of the University College of
Rhodesia and Nyasaland*

PRINTED IN GREAT BRITAIN

AN ASPECT OF ORDER IN THE PHYSICAL WORLD

PHYSICS is a fundamental science. The purpose of this Inaugural Lecture is to substantiate this statement in one small respect in which I am particularly interested. In case I am accused of arguing from the particular to the general, let me hasten to say right at the beginning that the claim of physics to be a fundamental science is not new and is supported by much more evidence than I can bring in one lecture. I am not producing a thesis, nor a library of theses; this is a single lecture, so I hope I may be forgiven for selecting only a small aspect of physical science in which I have a direct and personal interest—after all, I have been invited to give a lecture to inaugurate the chair which I am honoured to occupy, so this lecture is very much a personal matter.

SCIENTIFIC METHOD

It is not necessary to dwell at length on the basic methods of the scientist. The technique of observation, hypothesis, experimentation, examination, generalization, synthesis, and prediction; a process, or series of processes, which is commonly understood as the scientific method, is displayed in the physical sciences more clearly than in any other branch of human activity. Nothing in this lecture conflicts with the application of the scientific method, although we are considering only a small part of physical science. I will go further. I claim that the information that I wish to lay before you tonight has been obtained directly and unequivocally by the strict application of the scientific

method. It is a continual source of wonder and delight to me that the philosophical and speculative nature of modern physics is the direct consequence of the application of what is commonly considered a rational and mechanistic application of the cold logic of the scientific method. That this description of the scientific method is neither final nor complete is generally agreed; nevertheless it has been from an attempt to apply strictly the scientific method that the inadequacy of a rational mechanistic view of the physical world has been demonstrated. While it has been argued that the physical world is mechanistic and it is the scientist who, in his interpretation of his observations, imposes a philosophy of his own on the physical events he observes, few physicists today would attempt to draw a clear line of demarcation between the observer and the events being observed. 'Subjective decisions are inseparably mixed with objective observations . . . we have lost confidence in the possibility of separating knowledge from decision, we are aware of being at every moment spectators and actors in the drama of life', says Max Born in his Guthrie Lecture [1]. Physics is not only fundamental in the use of the scientific method, but the study of the physical world has also led to fundamental conclusions.

THE SOLID STATE

In recent years the solid state has received a great deal of attention from physicists. The study of the solid state is essentially the study of the fundamental problem of interaction between the elementary particles of matter, the atoms, when they are packed close together. During the last century the properties of gases were studied in considerable detail. The simpler structure of a gas lends itself more easily to mathematical description than the more

complex structure of a solid. The relatively wide separation of the molecules of a gas simplifies greatly the theoretical treatment of its properties. In the case of a solid, the closeness of approach of the constituent atoms necessitates the use of more difficult mathematical treatment, and factors which may be neglected in the case of a gas can no longer be ignored when the gas is compressed and cooled through the liquid state to the solid state. The discovery of tools, such as X-rays, has also enabled us to discover the inner constitution of solid matter and to study the arrangement of the atoms which make up the bulk material.

The outer crust of the earth on which we live is solid. A very large variety of natural solids is found, but the proportion of silica is as high as that of any other single mineral in the rocks of the earth's crust. If a large crystal of silica or quartz is examined, clearly defined faces are seen as the crystal is rotated. The crystalline form shown by the regular arrangement of the faces is common to nearly all the solids with which we are familiar. Very few truly amorphous solids exist, and, with the increasing application of improved techniques, a degree of crystallinity is being discovered where none was previously thought to occur. The characteristic features of a crystalline solid are the regularity of its outward form, its remarkable symmetry, and, as we shall try to show in this lecture, the inner ordered arrangement of its constituent atoms.

SNOW CRYSTALS

Snow crystals grow under ideal conditions. On the minute ice nucleus, condensation takes place. The water molecule adheres to the cold nucleus in certain well-defined positions relative to the other water molecules present. The snow crystal, so formed, descends slowly to

earth, growing by the addition of water molecules until the developed snow crystal, when examined under the microscope, exhibits supreme beauty and amazing symmetry [2]. Snow crystals occur in many different shapes and by no means all are perfect, but all exhibit the well-known symmetry properties of the crystalline state. Furthermore, if a good snow crystal showing sixfold symmetry is examined carefully under the microscope, it is found that a curved line, or even a dot, on one of the six arms is repeated on each of the other five in an identical position. A growth on the fern-like arms is identical on each arm, the hexagonal symmetry is complete. An explanation of this remarkable symmetry and why one arm informs each of the other five of its additional growth is not yet established. Professor Tolansky has suggested that the growth of the snow crystal is an example of a 'resonance' phenomenon [3].

THE DIAMOND

Let us turn from the soft transient snow to the hard brilliant diamond. There is no need to emphasize the beautiful symmetry of the diamond crystal. Although the jeweller has polished faces of his own choice, he could not obtain the brilliant crystal, which every young woman wishes to wear in her engagement ring, were it not for the regularity of the atomic arrangement of the carbon atoms of which the diamond is composed. Contrary to popular belief diamonds are the commonest of all gem stones. Part of the high price goes in the high cost of extraction, for the diamonds are thinly distributed. Five tons of ore must be raised, crushed, and sorted to extract the weight of a single carat.

When examined under a high-power microscope, practi-

cally all octahedral diamonds exhibit a striking distribution of triangular pits on their faces. These pits are a growth phenomenon. Such pits are called trigons and can appear in very great profusion. At times they are easily recorded, but sometimes they are small and extremely shallow, often a mere few crystal spaces in depth. These trigons are, almost invariably, regularly rectilinear and are strictly orientated, with the vertex pointing to a crystal edge.

Diamond, being merely crystallized carbon, burns away very slowly to carbon dioxide if heated in an oxidizing atmosphere, as was established even by Lavoisier. A very careful study of this oxidation process has recently been carried out by Professor Tolansky and has yielded much interesting information [4]. When heated in an oxidizing atmosphere, at about 500° C., very small triangular etch pits appear on octahedral faces. These resemble growth trigons, but are oppositely orientated. Etching by this method, on cleavage faces of diamonds, reveals striking crystallographically orientated arrays of etched pits which throw light on the internal structure of the diamond. More intensive etching can lead to a curious 'block' pattern, on a microscale.

The external symmetry, displayed by our two illustrations of the snow crystal and the diamond, is characteristic of all crystals, and, as I have already stated, most of the solid matter to be found in nature is crystalline in structure. The special etching technique and the microscope have enabled a picture of the internal structure of the crystal, similar in design to the external features, to be revealed. However, we have available a more expert tool with which to examine the internal constitution of crystals. This tool is X-rays. The use of X-rays enables the crystallographer to 'see' inside the crystal and to determine the

regular arrangement of the atoms or groups of atoms of which the crystal is composed. When X-rays are used to examine the internal structure of the diamond crystal, for example, we find that the atoms of carbon are arranged in

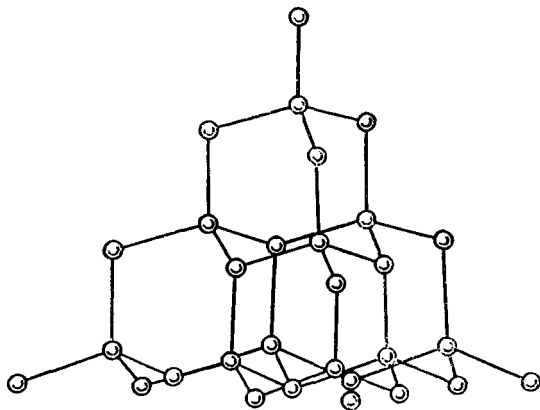


FIG. 1. The diamond structure.

a symmetrical manner; each atom is situated at the centroid of a regular tetrahedron. Each carbon atom is symmetrically surrounded by four nearest neighbours.

THE STRUCTURE OF METALS AND ALLOYS

One of the simplest cases to study is that of a pure metal. When the atomic arrangement of the iron crystal is examined it is found that the atoms arrange themselves in regular rows in cubic formation such that, if one unit only is imagined, the atoms are found one at each corner and one at the centre of a cube. In the case of nickel the atoms are arranged at the corners of a cube with additional atoms at the mid-points of each of the six faces of the cube. Iron is said to have a body-centred cubic structure and nickel a face-centred cubic structure. Many other metals crystallize

in similar forms although some, notably zinc, exhibit the close-packed hexagonal structure.

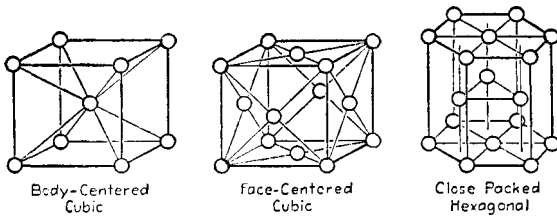


FIG. 2. The principal metallic structures.

It is worth noting that both the face-centred cubic and the close-packed hexagonal structures may be reached by the close packing of equal spheres in layers. There are two ways of arranging equivalent spheres to minimize the interstitial volume. One way leads to a structure with cubic symmetry which is the face-centred cubic structure; the other has hexagonal close-packed structure. Spheres may be arranged in a single close-packed layer by placing each sphere in contact with six neighbours. A second similar layer may be packed on top of this by placing each sphere in contact with three spheres of the bottom layer. A third layer can be added in two ways. In the cubic structure the spheres in the third layer are placed over gaps in the first layer which were not used when the second layer was added. In the hexagonal structure the spheres in the third layer are placed directly over the spheres of the first layer.

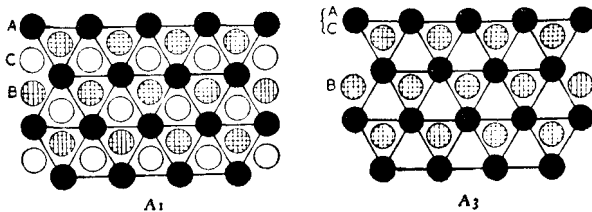


FIG. 3. Illustrating the close packing of regular spheres in the face-centred cubic structure (A_1) and the close-packed hexagonal structure (A_3).

Models may also be used to illustrate the two possible arrangements of close-packed equal spheres [5]. It is worth pointing out that the close-packed arrangement of atoms is very common among the elements. Of sixty-eight solid elements, thirty-seven of them crystallize in either the face-centred cubic or the hexagonal close-packed form at normal temperatures. A further twelve crystallize in the body-centred cubic form, while only three adopt the diamond-like structure. In addition, at least two of the body-centred cubic elements, sodium and lithium, transform to hexagonal close-packed or to face-centred cubic structures at low temperatures. When it is realized that if hard spheres are arranged in either the face-centred cubic or the hexagonal close-packed structures they occupy nearly three-quarters of the available volume, it is immediately apparent that nature prefers the constituent atoms of its stable elements to 'bind' closely together. If the spheres were thrown in at random, they would occupy at least 15 per cent. more volume than if they were close-packed in either the cubic or hexagonal arrangements.

THE SUPERLATTICE

In the preceding paragraph it is stated that nickel normally crystallizes in the face-centred cubic form. In the iron-nickel alloy system the nickel-rich alloys also adopt the face-centred cubic structure. The iron-nickel alloy system is an example of a substitutional alloy in which atoms of nickel are replaced by atoms of iron, with an expansion but without a change in structure of the basic nickel lattice.

Consider the simple case of three times as many nickel atoms as iron atoms, that is FeNi_3 . A number of different arrangements are possible, but two cases only may be con-

sidered now. In the first case the nickel and iron atoms are situated at random in the crystal lattice. It remains face-centred cubic for there is no reason to suppose that the random distribution of the iron atoms distorts the lattice beyond the stage at which the majority of the nickel atoms are unable to maintain their initial positions. The expansion of the lattice from 3.5171\AA . units for pure nickel to 3.5544\AA . units for the alloy shows that the addition of the iron atoms increases the distance apart of the nickel atoms [6]. However, it is still a close-packed cubic lattice. The sizes of the nickel and iron atoms are similar, and, if it is assumed that they are spherical in shape, it is possible to make a model of wooden spheres to illustrate the disordered alloy crystal.

When this alloy is heated at 495°C . for a long time, or cooled very slowly through the temperature range 500°C . to 490°C . over many hours, an ordered structure appears [7]. The heat energy supplied is used by the iron atoms to change places with certain nickel atoms until, if perfection could be reached, a completely ordered face-centred cubic structure would be obtained. The model shows this clearly. The wooden spheres are still close-packed, but one row in any layer contains alternate black and white spheres, while the next row contains all white spheres, and so on across the layer. It is seen that each iron atom is surrounded by twelve nickel neighbours, six in one plane, all touching each other round the central iron atom, three above in three of the spaces between the spheres, and three below in the other three spaces. No closer packing is possible. Furthermore, the energy of such a system is a minimum. This is important, for the equilibrium position of any physical system is defined when the potential energy has a stationary value. In this case the energy in the ordered

state is less than in the disordered state and so the ordered crystal lattice represents an equilibrium or preferred state. The iron and nickel atoms arrange themselves in such a way that, in equilibrium, they form an ordered lattice; each iron atom is surrounded by twelve nickel atoms and no more symmetrical arrangement is possible in the case of close-packed spheres. These ordered structures, or superlattices, have been observed in a number of alloys. For example, it is known that in binary alloys there are more than thirty different alloy systems in which an ordered structure has been observed; there may very well be more. The phenomenon is not unique to the iron-nickel system; I chose the iron-nickel system as an illustration of the general phenomenon partly because of my personal interest in it. For various reasons the study of other alloy systems, for example, copper-gold, is much simpler than the iron-nickel system, and in this case, considerably more work has been done on it. But the iron-nickel binary alloy system has many interesting features in other directions and these make the more difficult system worth investigating. The electronic structures of copper and gold atoms are simpler than the electronic structures of iron and nickel atoms. The influence of the unsaturated '3d' level and full '4s' level on the binding energy of the iron and nickel atoms in the iron-nickel alloy profoundly affects the properties of the alloy.

In the copper-gold system three compositions of the alloy have been found to give an ordered structure or superlattice, AuCu_3 , AuCu , and Au_3Cu , that is, at compositions of 25 per cent. atoms of gold to 75 per cent. atoms of copper, equal numbers, and 25 per cent. atoms of copper to 75 per cent. atoms of gold, respectively. In this alloy the structure is again face-centred cubic. Both copper and gold are face-centred cubic structures. If gold atoms are

added to the copper lattice, when the composition AuCu_3 is reached a superlattice occurs. The gold atoms arrange themselves in lattice positions similar to those of the iron atoms in the case of the iron-nickel alloy, FeNi_3 . In the ordered structure, the gold atoms arrange themselves at the corners of the cube completely surrounded by twelve copper atoms. In the disordered structure, each gold atom has, on the average, three gold out of the twelve atoms surrounding it.

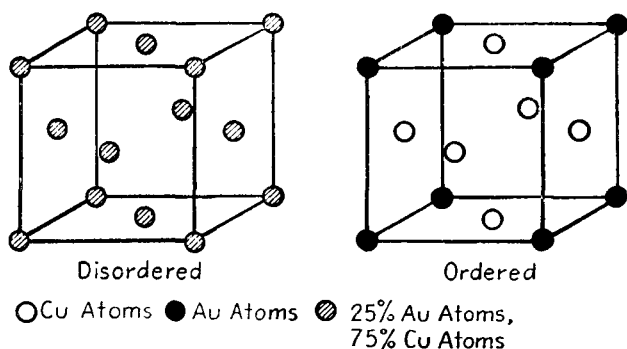


FIG. 4. The structure of the alloy AuCu_3 .

If now more gold is added to the copper, when the composition AuCu is reached, namely equal numbers of copper and gold atoms, a face-centred cubic structure in the ordered state is no longer obtained. Two ordered arrangements are possible. One is a body-centred cubic structure, in which 'black' atoms are situated at the corners of the cube and 'white' atoms at the centre of the cube. This occurs in a number of ordered structures, but not in copper-gold. In copper-gold the structure becomes tetragonal; it is no longer cubic. The structure may be imagined to consist of planes alternately containing only gold atoms and only copper atoms. Each atom now has eight nearest

neighbours of the opposite kind in adjacent planes, and four of the same kind in its own plane, at a slightly greater distance apart. It is still a face-centred structure but the 'height' of the unit cell is less than the 'width'.

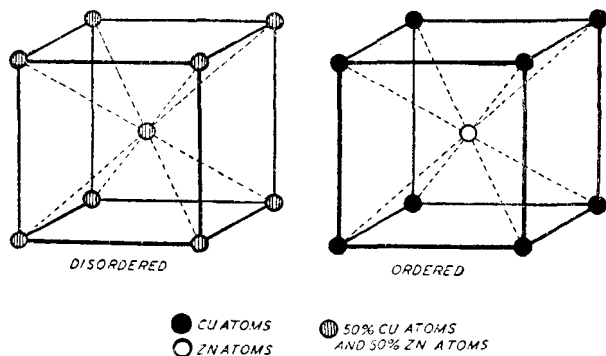


FIG. 5. The body-centred cubic structure of a binary alloy containing equal numbers of atoms of each constituent (brass).

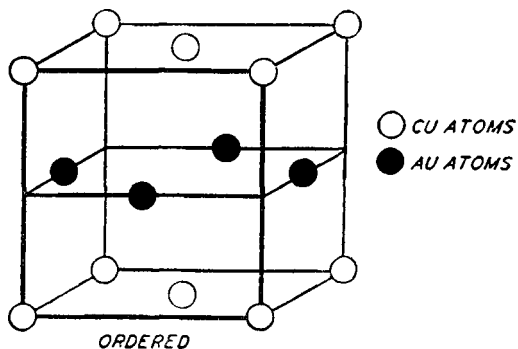


FIG. 6. The face-centred tetragonal structure of the superlattice AuCu.

In the disordered structure the lattice is face-centred cubic, for each atom has on the average six like and six unlike neighbours. When more gold is added to the copper-gold alloy until the percentage composition of 75 atomic per cent. gold, 25 atomic per cent. copper is reached, namely

Au_3Cu , the structure is again face-centred cubic and is a superlattice very similar to AuCu_3 except, of course, that the positions of the copper and gold atoms are interchanged.

Now let us return to the iron-nickel alloy system. We have seen that at the composition FeNi_3 , in which there are three nickel atoms to every iron atom, a superlattice or ordered structure is obtained, under rather difficult conditions. When more iron atoms are added to this alloy, the ordered structure is not maintained. However, when the composition of equal numbers of iron and nickel atoms is reached, namely 50 atomic per cent., we have some evidence that a superlattice or an ordered structure is developing, but much more work needs to be done before we can be certain of this [7]. It would be interesting to discover whether the superlattice at 50 atomic per cent. iron-nickel alloy is a tetragonal structure similar to the copper-gold alloy, or whether it is body-centred cubic. Evidence so far suggests that the structure is not appreciably changed from the face-centred cubic which exists in the disordered state; in other words it may very well be a tetragonal structure.

I would, however, like to point out that we may still obtain a face-centred cubic structure by imagining the crystals to be subject to a series of 'stacking faults'. Stacking faults are well known in alloy structures. Let us suppose that we have a face-centred cubic structure. Layers of atoms, which we may distinguish by *A*, *B*, and *C*, are arranged in order, as we have explained before. The continuation of the structure throughout the whole metal would be *ABCABCABC*, but it is always possible, under certain conditions, to obtain a structure something like *ABCACABC*. This is still predominantly a face-centred structure, but faults have developed in it. To return to our model with the black and white spheres, the FeNi_3

structure can be illustrated by arranging a series of close-packed layers containing alternate black and white spheres in the first layer, all white in the second layer, black and white in the third, and so on. Clearly, if a superlattice Fe_3Ni exists, and there may be reasons for supposing that it does, then it could be formed, or be illustrated, by alternate layers of close-packed spheres containing alternate black and white spheres, but the second row would be all black, the third black and white, and so on. This model is similar in arrangement to the model of FeNi_3 , except that the white and black spheres have been interchanged.

On the assumption that the sizes of the black and white spheres are the same, an ordered face-centred cubic arrangement can be built up on a pattern of equal numbers of black and white, all white, equal, all black, equal, and so on. The regions over which the FeNi_3 and Fe_3Ni compositions extend may be considerably broader than a few atomic layers. If these regions are reasonably equal, the overall composition will be FeNi . When the sizes of the black and white spheres are not the same, the structure will not be as regular as this, but it is easy to see that it will consist of two superlattices, one FeNi_3 and the other Fe_3Ni , arranged in one structure with what might be called 'stacking faults' between them. Such a structure would show diffuse scattering of an X-ray beam; it would also show considerable broadening of X-ray diffraction lines. These have been observed, but interpretation will certainly not be as simple as I have suggested [8].

There is an alternative possibility which is worth considering. Many simple ionic compounds crystallize in a face-centred cubic structure similar to that of sodium chloride. This consists of two interlocking face-centred cubic structures, one of sodium ions and the other of chlorine ions.

Each sodium ion has six nearest neighbours of chlorine ions, and twelve next nearest neighbours of sodium ions. The same arrangement applies, in reverse, to each chlorine ion.

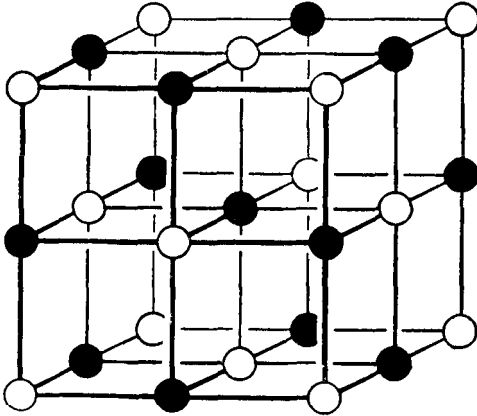


FIG. 7. The sodium chloride structure.

- Sodium.
- Chlorine.

The existence of an intermetallic compound of composition AB , having such a simple structure as that typified by sodium chloride, has not been reported. It is conceivable that the ordered alloy $FeNi$ adopts this structure. This remote possibility immediately raises the question of the nature of the binding forces between the iron and nickel atoms. Iron and nickel belong to the transition series of elements, and, as has been mentioned earlier, they share a common electronic structure, with filled 's' levels but with vacancies in their 'd' levels. Chemically they would be considered to have zero valency. While under normal terminology the binding forces would not be considered as ionic; nevertheless, the effect of the vacancies in the 'd' levels cannot be ignored, and if the ordered structure of $FeNi$ proves to be of the ionic type similar to sodium

chloride an interesting avenue of research is revealed. The 'sharing' of electrons in the 'd' levels might explain some of the peculiar physical properties of iron-nickel alloys in the neighbourhood of the composition represented by FeNi. For example, such alloys exhibit anomalous magnetic properties, abnormally low coefficients of thermal expansion, and they are very sensitive to cold work.

SHORT-RANGE ORDER

In the previous discussion we have seen how it is possible to obtain an ordered structure over limited regions. Each region may be perfectly ordered in itself, but along the borders of the ordered regions, where one region impinges on another, a disordered or random composition occurs. This phenomenon is known as 'short-range order'. It is now believed to be much more common than was thought at one time. The alloy FeNi₃ reaches a high degree of order when annealed at 495° C. for a long time. There is reason to believe that this is a long-range ordering process. The ordered arrangement of the iron and nickel atoms persists throughout a considerable body of the alloy. At temperatures greater than 500° C. the long-range order breaks up into domains of short-range order, and short-range order may exist at higher temperatures than is possible for long-range order. The disordered phase may contain a considerable number of ordered domains separated by regions of disorder. In the ordered phase these regions of disorder are reduced; in perfect order they would be absent. It is doubtful if any alloy can be obtained in the perfectly ordered state, except perhaps at the zero of temperature. At high temperatures the atomic vibrations are too vigorous to allow of an ordered structure except over very limited regions. At intermediate temperatures, and under suitable

conditions, the regions of short-range order may grow until a state approximating to long-range order is reached.

LIQUIDS

The concepts of short-range order and long-range order have an interesting application for understanding the characteristic difference between a solid and a liquid. In a liquid there is very definite short-range order but no long-range order, while in a solid we have long-range order as well as short-range order. The positions of two atoms in a crystal, however distant from each other, are exactly correlated; whereas, in a liquid, there is no correlation whatever between distant molecules. There is, however, a definite order of neighbouring molecules with respect to their distances apart as well as to the number of molecules surrounding a given one. The absence of long-range order may be taken to be one of the remarkable characteristics of a liquid in comparison with a solid.

PLASTIC SOLIDS

It may be suggested that in demonstrating the ordered arrangement of the atoms in a solid I have ignored a range of solids such as glass and plastic materials. However, it has been shown that the atoms of glass are linked by forces essentially the same as in crystals [9]. Over large ranges of temperature the atoms are oscillating about definite equilibrium positions. As in crystals, extended three-dimensional networks are formed. The principal difference between a crystal network and a glass network is the presence of symmetry and periodicity in the former and the absence of symmetry and periodicity in the latter. However, when glass is old it devitrifies. When glass has devitrified it has reverted to the crystalline state in which the atoms are

regularly arranged; a state of long-range order has occurred. This crystallization is readily observed in panes of old glass. In glass at normal temperatures the attainment of equilibrium is a very slow process.

Fibrous substances, such as wood, cotton, wool, asbestos, are at least partly crystalline, for their X-ray diffraction patterns show that they possess some periodicity of structure, although the crystallites of which they are composed may be very small in one or more directions, and they may contain disordered material between the crystallites. Rubber-like solids are of an intermediate type. They are amorphous when unstretched, but they become crystalline when stretched. The change is reversible. In certain 'plastic' fibres, in which the properties are due to long chain-like molecules, and in which the cohesive forces are strong enough to maintain a limited local order but insufficient to prevent flexibility and extension, the crystalline state is increased irreversibly by stretching. Nylon is an example of this type of fibre.

DISLOCATIONS

Perhaps I have painted a rather idealized picture in which nature prefers an ordered arrangement to a state of disorder. The study of the physical world is an exciting enterprise at all times, and no small contributions to the adventure are the deviations from the idealized models. The purpose of this lecture was not to discuss the deviations, but I would be untrue to my task if I were to ignore them and to pretend they do not exist. Nevertheless I believe that they do in fact represent deviations from a pattern; the exceptions which prove the rule. There is one type of deviation from the ordered structure, the dislocation, which is itself a verification of the underlying order in the structure of the metal or other crystal. In recent years the

mechanism of crystal growth has received considerable attention, and in the interpretation of the remarkably fascinating observations made on growing crystals, the dislocation in the lattice plays a major part.

Dislocations in the metal can be set up in a number of ways. The existence of dislocations and the movement of a dislocation through a lattice can be demonstrated by moving a layer of spheres over the underlayer, or by means of the bubble raft [10]. When the dislocation reaches the face of the crystal it leaves a step. It is on these steps that crystal growth takes place. Direct evidence has been obtained of the mechanism of crystal growth, and it is a further illustration of the ordered arrangement of the crystal constituents [11].

CONCLUSION

I started this lecture by saying that my intention was to illustrate the claim of physics to be a fundamental science. I have drawn your attention to the study of the solid state which leads to the conclusion that nature prefers an ordered arrangement to a disordered one. I could have chosen a very different branch of physics were I familiar with it. I could have shown that, just as we have been looking at the arrangement of sub-microscopic atoms, so we could have seen that the same hypotheses which serve as the laws of physics in the laboratory also serve in the vast distances of astronomical space. There is revealed a unity which transcends the diversity of data. There is revealed an order and consistency which it is difficult to believe is simply imposed by man's subjective desire for beauty and tidiness. We are led to the conclusion, perhaps in spite of ourselves, that the universe in which we live is characterized by an ordered unity and faithfulness, without which the study



This work is licensed under a
Creative Commons
Attribution – NonCommercial - NoDerivs 3.0 License.

To view a copy of the license please see:
<http://creativecommons.org/licenses/by-nc-nd/3.0/>

This is a download from the BLDS Digital Library on OpenDocs
<http://opendocs.ids.ac.uk/opendocs/>