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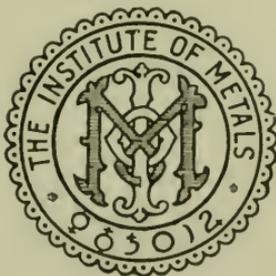
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1916 MAY LECTURE.*

**X-RAYS AND CRYSTAL STRUCTURE, WITH
SPECIAL REFERENCE TO CERTAIN
METALS.**

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IT will be my endeavour this evening to describe to you the new method of analyzing the structure of materials which are crystalline. It depends upon the use of X-rays, and I must therefore tell you something of those properties of the X-rays which are concerned, and afterwards give you an account of a few applications of the method and of the results obtained.

When successful, the new method results in the determination of the exact relative position of the atoms of which a crystal is composed. It has not as yet been applied to any but the simpler forms of crystals. It is a new science and must learn to walk before it tries to run. As progress is made more and more complex forms will no doubt be resolved. As experimenters in a new field we require practice, and moreover, we are not yet fully acquainted with the proper interpretation of many of the new facts which we observe. As time goes on, experience both in experiments and in interpretation will give us ever greater and greater command of the methods of the new research.

Let us begin then by a description of some of the more pertinent properties of X-rays.

They constitute, as we are aware, a form of radiation in which energy travels through space in straight lines. The rays are detected either by their action on a photographic plate or by the phosphorescence which they can produce on suitable screens, or by a certain curious effect upon a gas through which they pass. They are able, as we say, to ionize that gas; this means that some

* Delivered May 4, 1916, in the Hall of the Institution of Electrical Engineers, London.

of the atoms or molecules of the gas are affected by X-rays, the result being that each atom affected loses an electron which, in general, attaches itself to some other neighbouring atom. This has an electric consequence—the atom which has lost the electron is positively charged, that which has gained it is negatively charged. When electric force is applied the positive may be driven one way, the negative the other, and either can be swept as a charge into an electroscope or other instrument for measuring electrical quantity.

As a rule we use the last of these three methods in laboratory work with X-rays, and in particular, with the work I am about to describe. We cannot see X-rays, and the apparatus built to detect the ionizing effect constitutes an artificial eye specially designed for X-ray vision.

We have been in the habit of measuring the effects of X-rays by one or other of these means ever since their discovery twenty years ago, but while we have become familiar with the treatment of the rays, we have long been in doubt as to their nature. Many of the properties of the rays seem to indicate that they consist of streams of small energy-carrying centres of some sort. Others again are more in agreement with the hypothesis that they are, like light, a form of wave motion in the ether, and that the study of X-rays is but one chapter of the greater study of light. This is in spite of the fact that X-rays cannot be reflected or refracted as light can.

It is one of the results of the new method that fresh light is thrown upon the nature of X-rays. We find that they are as much a wave motion as light is, but there is a difference of degree, because the waves of light are perhaps one fifty-thousandth of an inch long, while the waves of X-radiation are ten thousand times shorter.

My immediate object is, in fact, to show you how certain X-ray effects are exactly analogous to certain effects of light, only that they are worked on a ten thousand times finer scale.

There is one optical effect familiar to all of us which is the basis of all that I have to say: that, when light is reflected from a very thin film, such as the wall of a soap-bubble or the thin sheet of oil that spreads over a pool of water into which tar or oil is dropped, brilliant colours of the spectrum are displayed by

the reflecting beam. Newton investigated this effect long ago.

The explanation of the phenomenon is not at all difficult.* Imagine a train of waves to be incident upon one surface of the soap film. A certain reflection of these waves takes place at the first surface, but some of the light goes on into the film and arrives at the second surface, where it is again divided. Following only that part which is reflected we find another division taking place when it once more meets the upper surface, and finally a certain portion emerges again from the film on the same side as that on which the first ray fell. Thus we have two reflected beams and, indeed, more, because the beam within the film will, so to speak, ricochet from side to side sending out a certain reflected beam into the open every time it strikes the upper surface.

The question is—what do all these reflected beams amount to when they are put together? Now comes a fundamental theoretical point: the reflected ray that emerges after having twice crossed the film has covered a little more ground than the reflected ray which has never entered the film at all. Suppose that it had just got one wave-length behind, such an effect would never be noticed, because the two waves would still run together, crest to crest and hollow to hollow. But if the loss was half a wave-length or a wave-length and a half or two wave-lengths and a half, and so on, the two reflected waves would be absolutely out of step, and, according to the well-known optical effect, they would destroy one another, and there would in fact be no reflection at all.

The lag of one wave behind the other measured in wave-lengths depends upon three things—the length of the wave, the thickness of the film, and the angle of incidence.

When the right relation holds between these quantities the reflected waves all conspire together and the reflection is good; when it does not the reflection is so much the worse. The explanation of the colour of the soap bubble, or any thin film of the kind, is now easy.

When white light, containing all wave-lengths and colours, falls upon the film it will depend upon the thickness of the film and the angle of incidence what wave-lengths will most be

* For a fuller description of this point see *X-Rays and Crystal Structure*, by W. H. Bragg and W. L. Bragg, p. 16. G. Bell & Sons.

reflected ; some colours will be, as it were, selected for reflection and others will not. If the angle is changed or if the film grows thinner the colour alters.

Now let us carry this one stage further. Suppose there are not simply two reflecting surfaces as in the case of the film, but a large number one behind the other. Such cases do occur in nature though with far less frequency, one of the best known instances being that of the crystals of chlorate of potash. When this crystal grows it has a peculiar habit of appearing in two forms, one the twin of the other. The crystals are naturally formed in thin wafers, and these consist of thousands of strata alternately formed of the two kinds. For some unknown reason the strata are very even, and as regards any one crystal are all alike in thickness. When a ray of light enters such a crystal it finds a reflecting surface at every boundary separating the two kinds, and the reflected beam which emerges is made up of the thousands of minor pencils which have come from the multitude of reflected surfaces. If the relation of which we have already spoken is exactly fulfilled, the various reflected pencils will have lost, in respect to the original, one, two, three or more complete wave-lengths. All will naturally join together and the reflection as a whole is good.

But in this case, if the relation is not exactly fulfilled the falling away in the intensity of the reflection is not gradual, as when there were only two surfaces, but is very abrupt and complete.

The crystals of chlorate of potash will pick up from incident white light falling at a certain angle, only an extremely narrow range of wave-length, and it is this that gives the brilliant colour. The colour of opals is due to the same cause.

Lord Rayleigh explained this action at the Royal Institution long ago. It is not nearly so well known as the simpler phenomenon of the single film.

It is to this effect that we find the parallel in the case of X-rays. That there should be such a parallel demands that the spacing of the reflecting planes should bear the same sort of numerical relation to the wave-length of the X-ray that the thickness of these chlorate of potash strata bears to the wave-length of light. The two quantities should, in each case, be of somewhat the same order.

Where are we to find the structure in which there are reflecting layers ten thousand times closer together than the twinning layers of the crystal we have been considering? That these actually exist in nature has been shown to us mainly by two men. The first of these was von Laue, Professor of Zurich, who pointed out that the regular distances between atom and atom in the crystal might be expected to do for X-rays what the same sort of arrangement on a grosser scale does for light; as for example in the colours of mother-of-pearl, or insects' wings, or the regular diffraction grating of the laboratory. The second was my son, who pointed out that the regularity of arrangement of the atoms in a crystal made it possible to think of them as all arranged in layers, that these layers could be looked on as reflecting surfaces, and that the same argument could then be applied as in the already known analogous case of light.

That a layer of atoms can be looked upon as a reflecting surface may seem strange. We are apt to think that reflecting surfaces must be continuous, but it is not so—a row of palings can, for example, reflect sound and give an echo.

We are now brought to the last stage of the explanation of the new method. Let us suppose we have a beam of X-rays of given wave-length, and that we allow this beam to fall upon the natural face of a crystal. The regularity of crystal structure obliges us to suppose that the natural crystal face contains a layer of atoms and that behind these are other parallel and exactly similar layers equally spaced one behind another. All taken together, they form the crystal itself.

Suppose the beam of X-rays is incident upon this set of layers at a certain angle. If the relation between wave-length, spacing, and angle, of which we have already spoken, is satisfied, there will be a reflection; if not there will be none. It is a very precise phenomenon indeed. The angle of incidence must be set to a very few minutes of arc if the reflection is to take place. We may turn the crystal round, gradually letting X-rays play on its face the whole time, and there will be no reflection until we arrive at the exact angle; then it flashes out and we can register its existence by the electrical method I described at the beginning. Suppose that we note down the angle. Now let us take another face of the same crystal and find the angle,—it will not be the

same if the face is not similar from a crystallographer's point of view. We may do this to several faces. We may prepare faces specially if they do not already exist; and it is to be observed that there is no need to polish the face or even to make it quite true, because the reflection is not at the surface but from the volume within, and the crystal will look after its own angles.

Now let us see what use we can make of the information we have got. If we stand in a vineyard we can see avenues running down the vines in all directions. If we were told the widths of these avenues we could make a plan of the vineyard. In exactly the same way, if we are told the spacings of various sets of planes in a crystal parallel to natural faces, or to faces we have prepared ourselves, we can, so to speak, draw a map of the crystal. This is in fact the procedure which is actually adopted.

It is to be observed that this does not tell us everything. To understand how much it does tell and how much it does not it is perhaps best to consider this simple case.

Here, say, is a wall-paper of very simple pattern (Fig. 1). If we take some representative point, say the tip of a certain ribbon, and mark it wherever it occurs on the paper, we have a kind of lattice of points. In the more complicated wall-paper (Fig. 2) exactly the same sort of thing may still be done. No matter how great the complication we arrive in this way at a simple lattice of points. It is in the unit which is repeated to form the crystal that we find greater or less complication.

In the crystal a certain unit must be repeated again and again, having always the same orientation in space, and always the same relation to its neighbours. If we pick out some one centre of an atom as representing each unit and mark it wherever it occurs we shall arrive at a simple space lattice. The unit itself may contain one, or any number of atoms; and may be quite complicated.

The first fruits of our measurements give us these lattice spacings and enable us to draw in space a map of the representative points. This part of the work is comparatively easy. When we take up a new crystal for examination, knowing already its symmetries and its crystallographic features, it does not take us very long to find the form of the lattice on which it is arranged. Knowing this and the specific gravity of the crystal and the weight of the individual atoms, a very short calculation tells us how many

atoms are contained in the unit which is repeated again and

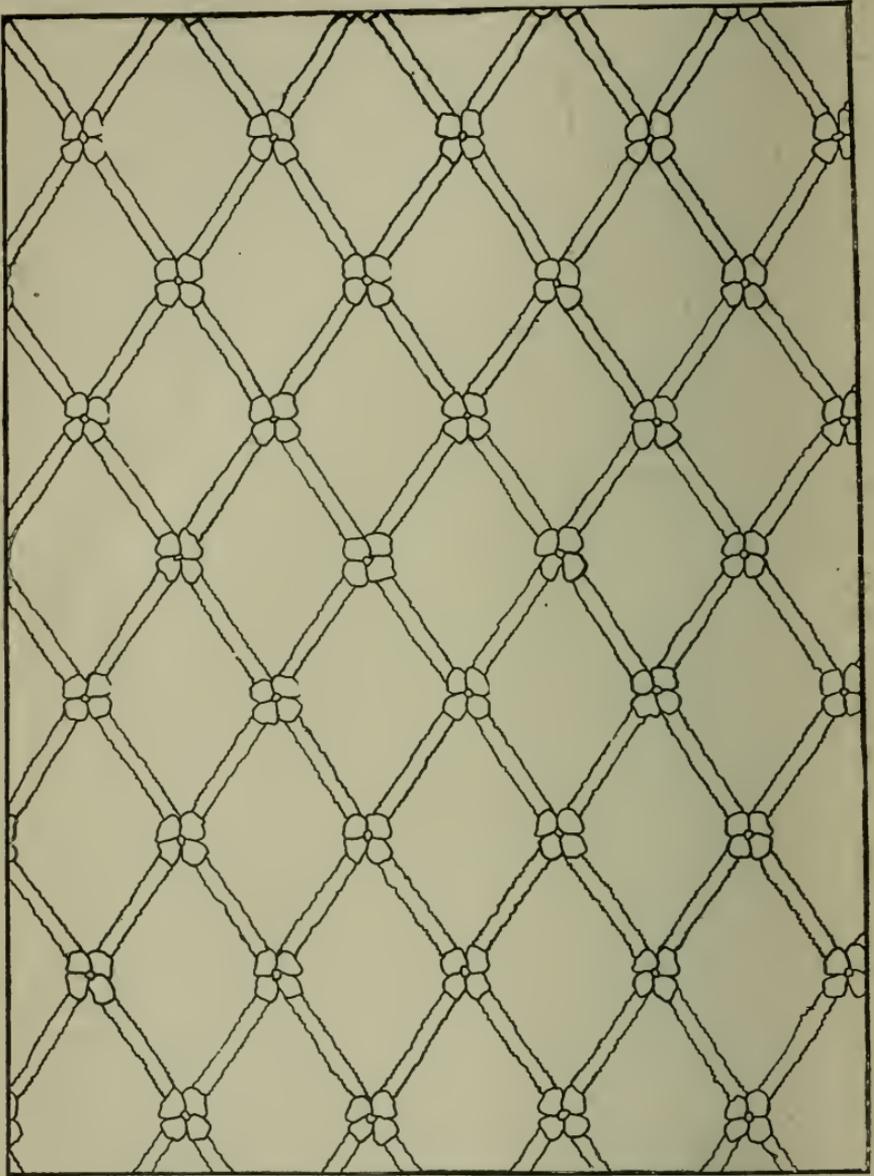


FIG. 1.—A very simple wall-paper pattern. Let the centre of each rosette (or any other representative point) be marked in ink. The ink spots will all lie on a simple lattice.

again through space. For example, in copper there is one atom

to the unit ; in antimony there are two ; in rock salt there is one molecule ; in calcite also one molecule ; in potassium chlorate there appear to be four.

There is a second part of the work which is in general much

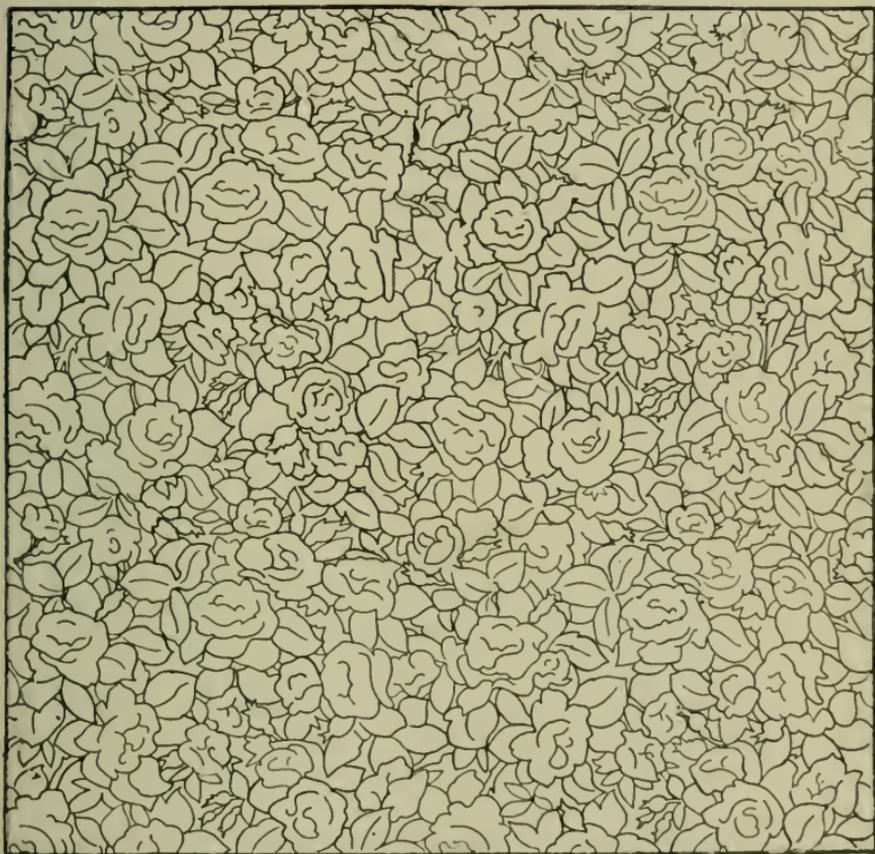


FIG. 2.—Exactly the same can be done in this figure as in the preceding, although it looks so much more complicated. Indeed the lattice is simpler than in Fig 1.

more difficult. It consists in the determination of how the atoms in each unit are arranged about the representative point. Let me try to explain this part of the work also.

It depends upon an entirely different principle, familiar to users of the spectrometer. When a diffraction grating is employed to produce spectra it is well known that the line that comes from the single slit can be resolved into spectra of several orders, and

moreover that these orders are not all equally intense. *The angles at which these spectra are to be found* is a matter of the *spacing of the lines on the grating*, but the *distribution of intensities* among the various spectra is a matter of the *form of the line* on the grating. Two different diamond points used to rule gratings of the same number of lines to the inch would give spectra in absolutely the same places, but there would probably be great differences in the relative intensities of these spectra because the diamonds would not rule grooves of the same form and depth.

Now we pass to the crystal case. Each face of a crystal gives reflections of many orders. Reflection flashes out, not only at one particular angle but one of a series of angles—when in fact the reflections of which we have already spoken lag behind one another by amounts of one wave-length, two, three, and so on. These constitute the different orders and correspond to the different orders of spectra in a diffraction grating.

Now these orders vary also in intensity. The intensities depend on how the atoms are distributed about the representative point of each unit. Our problem is to argue back from the observed effect to the distribution which has caused it. This is a task of much greater difficulty than that of finding the "lattice"; and here lies the explanation of why we have only succeeded as yet with the simpler forms and are obliged to move slowly in our attack on the more difficult.

It would be too great an attempt to go fully in one evening into the details of all the work that is being done,* and I must content myself now with showing you a few simple cases:

Here for example is a model of a crystal of rock salt, where the black balls may be taken as standing for chlorine and the white for sodium, or *vice versa*. You will see the simple cubical arrangement of the whole. Rock salt is well known to possess a cubic form of high symmetry.

Here again is one of fluor spar, also a crystal of very high symmetry and very simple outward form; the red balls here stand for calcium and the white for fluorine.

Here is the diamond, possessing an extraordinarily simple and well-balanced structure. Every atom stands at the centre of a regular tetrahedron formed of its four nearest neighbours. Zinc

* Examples will be found in the book already referred to.

blende has the diamond structure, but alternate layers are formed

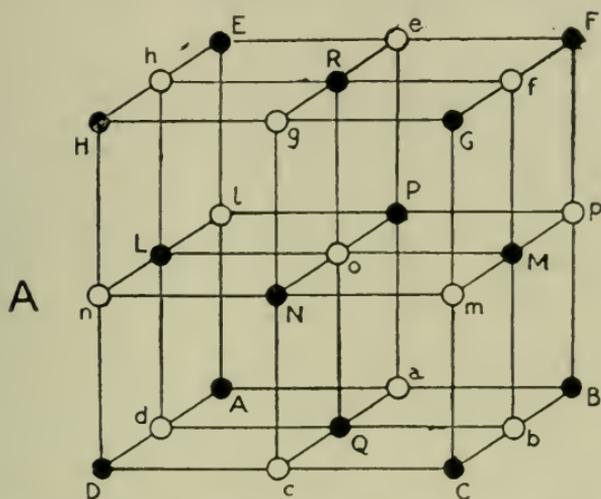


FIG. 3.—Diagram of rock-salt structure. Black dots represent sodium and white chlorine, or vice versa. The representation is as to position only, not to form or size.

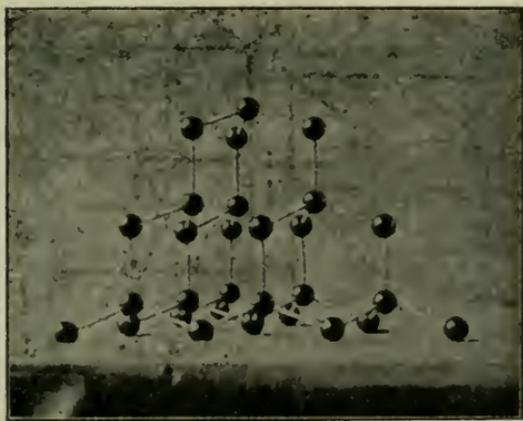


FIG. 4.—Diagram representing diamond structure.

of zinc and sulphur and it gives less symmetry to the outward form, as crystallographers know.

Here again is iron pyrites, showing a greater complexity of structure than in crystals we have had before and explaining the curious symmetry of the crystal.

Here is a very complicated-looking crystal* representing the spinel group, of which magnetite is a member.

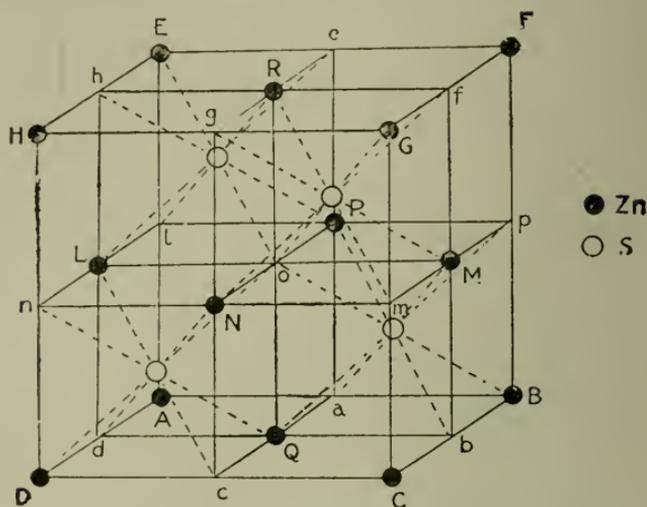


FIG. 5.—Diagram representing the structure of zinc blende.

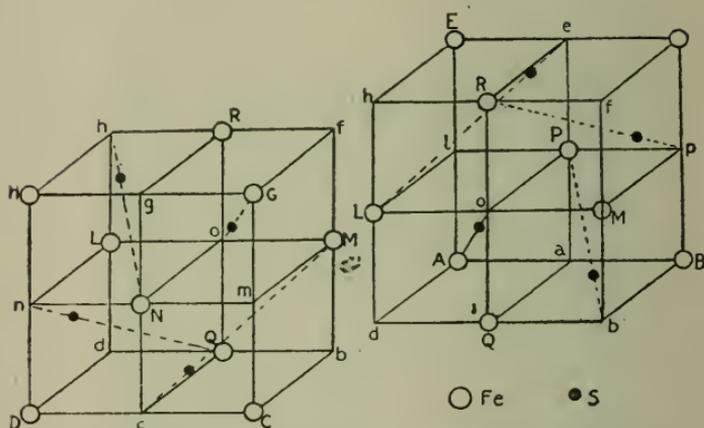


FIG. 6.—Diagram representing the structure of iron pyrites. Being rather complicated the model cube is shown in two halves separated from one another.

Copper possesses a constitution very easily described, for its atoms are arranged exactly like a pile of shot. As crystallographers have shown us, such piling can be of two kinds, one leading to a cubic crystal, the other to a hexagonal. Copper belongs

* This is too complicated to produce in a figure.

to the former class ; silver has lately been shown to possess the same structure ; no doubt gold has the same form. Bismuth and antimony were shown more than a year ago to possess a structure somewhat like that of the diamond. Recently it has been shown that the difference consists in the fact that the little tetrahedron of which we spoke in the case of the diamond is not quite regular, and that the atom which lies within is not at the centre but is pushed along the axis of symmetry towards the corner through which the axis runs.

Every atom in antimony or bismuth has, as it were, a great affinity to one neighbour and a lesser affinity in equal amounts to other three.

The study of iron crystals has hardly been begun. Perhaps at some future date I may have the opportunity of telling you more about them. You will understand that the circumstances of the time have put a stop to the ordinary development of these researches.

In conclusion, let me say that here are only the beginnings of a new science. I trust it will not be very long before we are able to describe the internal constitution of a number of the most important and prevalent crystalline forms, and that we shall be able to explain the inner meaning of allotropic forms. Indeed we have already made the beginnings of progress in this direction ; and, speaking more generally, we see dimly many directions in which the work will lead us to interesting and useful results. The methods are wholly new and open out to us fields into which we have never been before.

When once more we are able to prosecute these researches in peace, we trust that we shall find our hopes fulfilled and shall be able to build up on this foundation a structure which will be important both to pure and applied science.

[Of the numerous models and lantern slides used to illustrate the lecture figures 1-6 are reproductions, and for permission to reproduce these in the *Journal* acknowledgment is due to the Royal Society, the Chemical Society, and Messrs. G. Bell and Sons.—ED.]