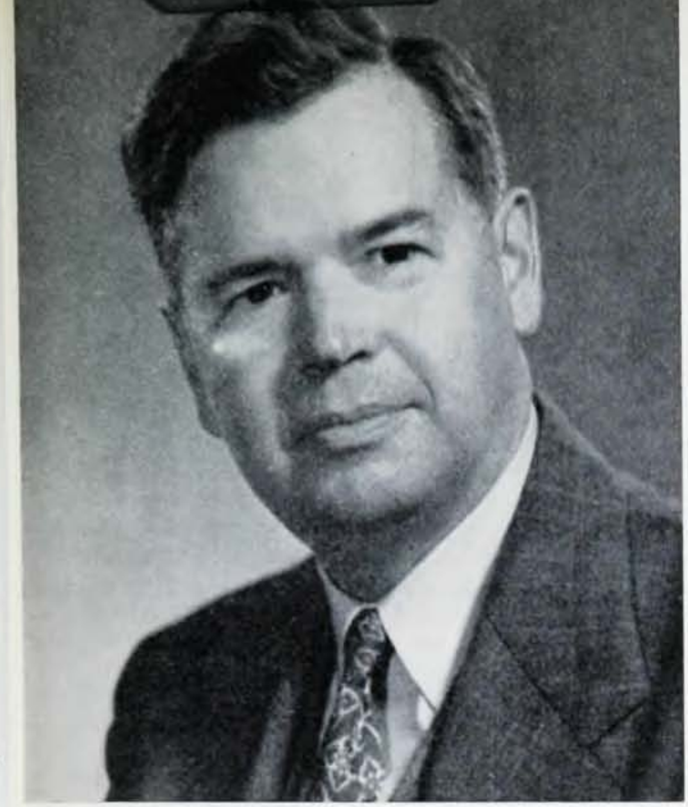
the Solid State

By *John C. Slater*

THE PHYSICS OF THE SOLID STATE is nothing new. In 1900 it was as well realized as now that mechanics, heat, electricity, magnetism, optics, all have their solid-state aspects. In mechanics we have elasticity, plasticity, elastic vibrations or sound. In heat we have specific heat, thermal expansion, heat conductivity. In electricity we have conductivity, dielectric constant. In magnetism we have paramagnetism, diamagnetism, ferromagnetism, the Hall effect. Optics involves the refractive index, optical absorption, double refraction, and so on. There are interrelations between different effects: Magnetostriction, the relation between magnetism and elasticity; pyroelectricity, the relation between heat and dielectric behavior; the Faraday effect, the relation between magnetism and optical double refraction; and a host of others. All these were known in 1900, there were tentative theories of many of them, and very elaborate studies of the interrelations of them with crystal symmetry, leading up to the proper mathematical description of many of the properties in terms of tensors, and such mathematical devices.

Why, then, is the physics of solids so much in the forefront just now? Why, in fact, has it had a very much more vigorous development in the present century than it had before? If we analyze the reasons, we see that they are largely two, each of enormous importance in the development of our understanding of the problems. The first is the discovery of x-ray diffraction, more recently supplemented by electron and neutron diffraction, and their application to the study of the properties of solids. The second is the development of the wave mechanics of the solid state, with the understanding it has given us of the motion of the electrons and nuclei which makes up the solid. I shall spend the first part of my talk saying some things about each of these developments, and the sort of results to which it leads; then I shall go over the various classical fields of solid-state physics—mechanics, heat, electricity, magnetism, optics—which still furnish a good classification of the subject, and say a little of the present stage of each, as illuminated by the new knowledge of the present century.

LAUE'S DISCOVERY of x-ray diffraction by crystals, in 1912, and the application of this method by the Braggs to the study of crystal structure, marked a wholly new era in the study of solids. In the meantime, methods have developed until crystals of more and more elaboration can be analyzed. It is worth while realizing that, though diffraction methods are powerful, they still have their limitations; it still takes skill on the part of the analyst to determine a structure. When x-rays fall on a crystal, scattered beams come off in certain definite directions, each beam consisting of a definite wave-length; thus to get all the beams, a continuous spectrum of x-rays must fall on the crystal. There is a very fine piece of mathematics connected with the process, based on the method of Fourier analysis. If we have a crystal with a three-dimensional periodicity, we can expand the charge density in a three-dimensional Fourier series; each of the terms corresponds to a sinusoidal variation of density similar to a plane wave, though standing still in space. Now it turns out that each of these pseudo-plane waves is responsible for just one of the scattered beams of x-ray; the scattering is what we should have by ordinary optics from a set of parallel reflecting planes, the spacing being the wave-length of the wave, and the intensity of the scattered beam depends, as we should expect, on the amplitude of the plane wave, or on the magnitude of the Fourier coefficient. Thus from the x-ray pattern we can directly read off these Fourier amplitudes. It would seem, then, that all we should have to do would be to add these Fourier components, or to perform the Fourier synthesis, and we should get the distribution of charge density in the crystal. This could be done, except for one thing: the intensity of an x-ray beam gives us the amplitude of one of the Fourier components, but not its phase. We can see this directly by the analogy of a diffraction grating: if we observe a diffraction spectrum from a grating, we can find the grating space from the positions of the diffraction peaks, we can even determine the details of the rulings by observing the relative intensities in the different orders, but we cannot distinguish between two positions of the grating which would differ only by a motion of a fraction of a wave length in the plane of the grating, perpendicular to the rulings. To supply this missing information, the



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phases, the x-ray crystallographers have developed a great many devices. Many crystals have enough symmetry so that we can be sure of the phases, except for an ambiguity of sign (which would correspond to a displacement of the wave through a half wave length). Then we can try out many combinations of sign of the most important terms, and see which combinations give sensible answers, which foolish ones, and eliminate the foolish ones. What would be a foolish answer? First, one which gave a density of electrons less than zero. It is the electronic charge density which does the scattering, the x-rays determine this density at all points of space, so that we get peaks of density at the various atoms, with the density going down almost to zero between atoms. Clearly the number of electrons per unit volume cannot really go negative, and this often eliminates most possible combinations of sign. Then the sign must be such that, if it predicts peaks which must represent atoms, these atoms must lie no closer together than we expect from the known sizes of the atoms. Such a criterion depends on previous experience: if, from the study of crystals starting with simple ones and going to more complicated, we have never seen a case where two particular atoms get closer than a certain value, it is highly unlikely that in a new crystal they would be found much closer. Again, we can more or less identify the peaks, and tell what atoms they represent, by their charge densities (careful work can determine the number of electrons responsible for a peak, to less than a single electron, and hence can determine the atom rather uniquely). We know chemically that some atoms will be found near each other, others will not, and this sort of information can eliminate certain possible arrangements. Finally a structure will be hit upon, by this type of argument; and once it is found, it can be almost uniquely verified, for it can be easily used to predict the missing phases, and then we can do what we could not do directly: synthesize the Fourier series to get the density. When this is done (and the process of synthesizing these three-dimensional Fourier series is a mathematical problem of no mean size, and one which has been mechanized in striking ways in the last years), we have a real picture of the atoms in a crystal. The process of analyzing a crystal is much like that of working a cross-word puzzle. There is no straightforward way to solve it; and yet when it is done, there are so many cross-checks that the probability that the final solution is wrong is vanishingly small.

This gives, then, a little insight into how the x-ray crystallographers work. What do they find? In the first place, of course, they find where the atoms are in crystals. Understandably, this gets increasingly hard as the crystals get more complicated; and while most inorganic crystals have been analyzed, and the simpler organic ones, the more complicated organic crystals are just beginning to be attacked, and very often a very large amount of chemical insight is needed to suggest likely structures, which can then be verified by x-ray methods, as Pauling has recently done in the case of some proteins. The structures which are found obviously fit in with chemistry, and a large part of the recent development in structural chemistry has been closely correlated with x-ray crystallography. Some solids, those held together by covalent bonds, are generally made of molecules, as one can show by finding that the atoms of a single molecule are really clustered together, separated a little more widely from the next molecule. The structure of the resulting molecule is found ordinarily much more easily by x-ray methods than by any other direct process; though the chemists have been so ingenious in the use of indirect evidence that in the vast majority of cases, the chemists had deduced the correct structure on the basis of other evidence before the x-ray method was used. Other kinds of solids show no molecular structure; bonds stretch all through the crystal, as in the familiar ionic crystals like NaCl, made up of ions Na^+ and Cl^-, with no ion being preferentially bound to a single other ion. Ionic crystals are all built this way. So are metals, the atoms all lying on a simple lattice. So are some crystals, like diamond, graphite, germanium, silicon, carborundum, which are not really either metallic or ionic, being held rather by covalent bonds, but nevertheless without molecular formation. This last group of crystals, some of which are among the hardest materials known, and others among the softest, give some very direct information about the strength of interatomic bonds. Diamond and carborundum are held by covalent bonds, and their hardness shows the great strength of covalent bonds; this is the same sort of strength that holds the atoms togther in an ordinary molecule, and which keeps them from breaking up until they reach very high temperatures. Graphite is partly held by Van der Waals forces, the weak type of force holding the molecules together in a liquid or solid, and its softness correlates with the ease of melting a solid or vaporizing a liquid, as compared with the difficulty of dissociating a covalent molecule.

These are just a few examples of the sort of information that we can get about types of solids, and the nature of the binding forces between their atoms. But x-ray methods can go far beyond this. Real crystals are not perfectly regular; and the irregularities are often of very great interest. Three common types of irregularity are those produced by thermal agitation; those produced by damage to the crystal, as cold-work in metals, or by irregularity in growth; and irregularities produced by impurities. X-ray methods are becoming increasingly useful in analyzing all these types of irregularity. We can give an illustration from the case of thermal agitation. The heat motion in a solid can be analyzed into a superposition of plane waves, like waves of sound, having all wave lengths from really long ones (like ordinary sound or ultrasonics) down to wave lengths of atomic dimensions. Each of these plane waves, if it is longitudinal, will produce planes of condensation and rarefaction of density, just like the pseudoplane waves which we mentioned in connection with crystal diffraction, and it can diffract a beam of x-rays in the same sort of way. Of course, to get reasonable angles of diffraction, the wave-length of the diffracted wave must be of something like the order of magnitude of the wave-length of the sound wave. Thus it comes about that light of ordinary wave-length can be diffracted by ultrasonic waves; this is a familiar optical experiment. But x-rays can be diffracted by the shorter waves of sound, and the wave scattered in a given direction gives information about the amplitude of the corresponding sound wave; this is what is called temperature diffuse scattering of x-rays. If we measure the amplitude of a sound wave, and at the same time know that it is produced by thermal agitation, and hence has the energy kT, where k is Boltzmann's constant, T the absolute temperature, then we can find its frequency, for the energy and amplitude are related by a simple equation involving only the frequency. We also know its wave length, from the relation telling the direction in which it is scattered. Then, knowing both wave length and frequency, we can find its velocity. When this is done for waves in real crystals, we find that the velocity extrapolates at low frequency to the observed velocity of sound determined by acoustic experiments, but that at higher frequency, of the order of 10^{13} cycles per second, where the wave length approaches interatomic dimensions, the velocity falls considerably; this is just what theory predicts, and the resulting experimental values, when they are known for more crystals, should be valuable aids in the theory of atomic vibration. This is a striking example of the way in which x-ray methods can supplement other fields, in this case acoustics, and can extend our information to ranges which could never possibly be reached by direct experiment.

Other types of problems where x-ray and other diffraction methods are proving of great value are in studying the electrical and magnetic properties of solids. In the ferroelectric crystals, like barium titanate and potassium dihydrogen phosphate, there is very good reason for thinking that the permanent electric polarization which sets in below a given temperature results largely from the actual displacement of certain ions in the crystal, rather than just the polarization of their electrons. The stable state of the crystal seems to be one in which the ions are displaced to slightly unsymmetrical positions, though raising the temperature makes the ions take up symmetrical positions of slightly higher energy, which do not involve electric moments. Obviously it would be very interesting to check this hypothesis. Until very recently, the x-ray methods were not accurate enough to detect such very small displacements of ions, of the order of a few hundredths of an angstrom. Within the last year, however, measurements of a new order of accuracy have been made, and have actually demonstrated ionic displacement of the general sort that had been postulated to explain these permanent polarizations.

For magnetic problems, neutron diffraction is the ideal tool. X-rays are scattered by the charge density of electrons in a crystal; electrons by the electrostatic potential, which is closely related to the charge density. Neutrons, on the other hand, are scattered by two sources: direct interaction with the nucleus, on account of nuclear forces between the neutron and the nucleons; and magnetic fields, on account of the simple fact that the neutron has a magnetic moment. Magnetic fields of many sorts exist in magnetic solids: fields all in the same direction, but localized largely within the inner shells of the magnetic atoms, in a ferromagnetic solid; in alternating directions in an antiferromagnetic solid; in random directions in an unmagnetized paramagnetic solid, with some preference for orientation in the direction of the field when such a substance is magnetized. In the hands of Shull, neutron diffraction has shown itself capable of giving very detailed information about the magnetic interactions in solids. This is of importance not only for magnetic problems themselves, but for wider reasons: the principal magnetic atoms are those of the iron group; these are among the most important of metals from a practical standpoint, and the same electrons which contribute to their magnetism also undoubtedly take part in their mechanical binding, so that there will certainly prove to be important connections between magnetic behavior and mechanical properties.

These are enough examples to give a suggestion of the many ways in which x-ray methods are giving vital information, beyond the straightforward determination of crystal structure; many other examples could be given, such as their use in investigating cold-work and other imperfections in solids. But next let us go on with the other great advance in the present century in our knowledge of solids, the wave mechanical theory of solid-state structure. I spoke about this in a good deal of detail in my Richtmyer lecture at the New York meeting of the American Physical Society last winter, and many of the present audience probably heard that talk; consequently I shall be rather brief in mentioning some of the points.

WE HAVE EVERY REASON for believing that the quantum mechanics, in its present form, furnishes the reliable and fundamental basis for explaining all the ordinary phenomena of the structure of solids. From our knowledge of nuclear problems, we are sure that the present form of quantum mechanics is not its ultimate form; there are too many parts of nuclear theory which do not follow satisfactorily from it. But no one questions it in the nonrelativistic range, and the simpler corrections of a relativistic nature are undoubtedly correct; and fortunately this is all that is needed for a quite complete study of the properties of molecules and solids. This then must affect in a rather profound way our whole approach to a theoretical understanding of problems in the structure of solids. We believe that we could derive their whole behavior in a theoretical way from quantum mechanics; hence we are not at liberty to look for alternative hypotheses to explain their properties. Unfortunately, the quantum mechanics of solids is a very difficult mathematical problem; we are dealing with the mechanical problem of the motion of a very large number of particles, all exerting large forces on each other, and whether we are using classical or quantum mechanics this is a problem so difficult that we must make drastic simplifications or approximations if we hope to get anything simple enough to solve. Fortunately there are simplifications available in the problem of the structure of solids, which seem to be adequately accurate and very useful.

These are the approximations leading to the well-known theory of energy bands. They follow the same lines as the Hartree self-consistent theory of atomic structure, and the molecular orbital theory of molecular structure. We know the limitations of the method fairly accurately, and they are serious; nevertheless it is a simple, usable method, it leads qualitatively to a great many results in agreement with experiment, and it seems to be in most respects the best simple approximation we have. In a few simple cases more accurate calculations have been made, by laborious methods which would not be practicable for more complicated problems. Such accurate calculations are of great service in estimating the accuracy of the approximation methods; we can compare the really accurate calculations with the approximate ones, and assume that the comparison is not very different in complicated problems from what it is in simple ones. In such ways we are building up a feeling of confidence in our approximate methods.

These approximations lead to results which by now have become familiar. They lead to an understanding of the difference between electrical conductors and insulators, and predict correctly what substances should be conductors, which ones insulators. They describe correctly the behavior of semiconductors, and this theoretical understanding has led very directly to the great experimental development of the last few years in the use of semiconductors. The theories lead to predictions about magnetic and dielectric behavior in agreement with experiment, and to an understanding of optical properties of solids. On the other side, they lead to calculation of the elastic properties of solids, of their mechanical behavior, specific heat, thermal expansion, and so on. In other words, theory has been applied to a great many of the properties of solids, and in general it works out properly. We should give a word of caution here. While a lot has been done by the theory there are many more things that have not yet been carried through. There is by no means complete agreement by all workers as to what methods of approximation are best in each case. The theory is far from finished, and there is a great deal more to be done. Nevertheless I believe that it is correct to say that we have good hope that the theory, developing as it now is, will prove able to describe the behavior of solids with qualitative accuracy, and that as we can make more accurate quantitative calculations of a higher order of approximation, we can assess better the errors inherent in our approximations, and allow for them. It is only in the last few years that we have begun to have this type of confidence in the theory, and it is clear that as a result of it, the whole understanding of the solid state is placed on a very different basis from what it was only a few years ago. For a proper theoretical treatment of a solid-state problem today should proceed without any arbitrary, adjustable parameters in it; only a few years ago that was too much to hope for. The encouraging thing is that an increasing number of calculations on such an absolute basis are being made, and that when they are carried through, they have proved in each case to agree with experiment to within the estimated errors of the approximation and of the experiment.

WE HAVE NOW SURVEYED the two techniques by which our knowledge of the solid state has been so greatly advanced during the present century. Let us spend the rest of the time in going over some of the properties of solids, to take a very quick look as to the sort of answers which we have got, by x-ray methods of theory or both, to the questions which naturally arise. Let us divide our analysis according to the conventional subdivisions of mechanics, heat, electricity and magnetism, and optics.

When we consider mechanical properties of solids, there are two sorts of behavior that concern us. First there is the elasticity: compressibility, elastic constants, and considered more broadly, all the forces that hold the crystal together, including those forces usually considered to be chemical. Here we know a good deal experimentally, and in principle we know how to get a great deal of information. The x-ray methods tell us how the atoms are arranged in their equilibrium positions; this tells us where the curve of interatomic energy versus atomic separation has its minimum. Measurements of elastic constants, including measurements like Bridgman's at very high pressure, give us the variation of lattice energy with interatomic distance. Heats of vaporization and dissociation tell us how much energy is required to break the bonds apart. Elastic constants are checked by accoustical measurements, and by the type of x-ray measurement I have mentioned earlier. Theory allows us to estimate the interatomic forces in simple cases, and allows us to extrapolate this knowledge to more complicated materials; it tells us that the interatomic forces are of electrical origin. We feel on quite sure ground as far as these ordinary elastic properties are concerned, though we must admit that real calculations have been made in only very few cases, and a great deal more work will be required before we have really mastered these problems.

The other, and more difficult, side of the mechanical properties of solids comes in the study of plasticity, creep, all those irreversible processes that are of so much practical importance. Here we are on ground which from its nature is much more difficult. A generalization has been arrived at, as a result of the interplay of theory and experiment: all these irreversible processes require for their understanding the assumption that we are dealing with imperfect crystals. Only an imperfect crystal would flow; only such a crystal would show a breaking strength of anything like the observed value; and so on. By purely geometrical study of how atoms can be arranged and disarranged, we have learned a good deal of the type of imperfection concerned in these problems, and we can begin to estimate whether such imperfections are in fact able to explain the actual behavior of solids. This type of problems is rapidly progressing toward a solution; it is a striking fact that far more work is being done at present on the study of imperfect crystals than of perfect ones, and as we shall see the nature of crystal imperfections is of profound importance in electrical and other problems, as well as in mechanical ones. But there are so many types of imperfection, and they are so hard to investigate by direct experimental means, that this branch of crystal physics is probably less advanced than the study of perfect crystals.

The thermal properties of solids are very closely tied up with the mechanical and elastic properties. We have already mentioned the heat of dissociation or of evaporation of a solid. The specific heat, the thermal conductivity, and a number of other properties are closely tied up with the elastic spectrum, since the thermal energy of the solid can be considered as a superposition of elastic waves of an acoustic or ultrasonic nature, with wave lengths extending all the way down to interatomic distances. Other properties with a thermal aspect to them, like viscosity, are closely related to the irreversible elastic properties like plasticity. Really the mechanical and thermal properties of solids are so closely related that they should be considered as forming a single category.

In the electrical properties, as in the mechanical, we find two types of problems: those which depend only on the lattice structure of the perfect lattice of the crystal, and those which are almost completely dependent on imperfections, and impurities. And here again, some of the most important problems in a practical way result from imperfections. Thus the general distinction between electrical conductors and insulators is a property of the lattice, and as we have mentioned, theory has advanced far enough to give a good account of the distinction. Impurities are important in determining electrical conductivity, as has been known experimentally for a very long time, and as we can now understand from the theory. But even more than this, the behavior of the semiconductors is determined almost completely by the impurities which they contain. Until this was understood, and until the experimental problem of preparing semiconductors with known amounts of impurity was solved, the semiconductors were considered to be unpredictable and unreliable materials; but now everyone knows that recent semiconductor developments have brought them into the forefront of the electrical industry and have focused attention on solid state physics as perhaps nothing else has done.

Not only electrical conductivity, but magnetic and dielectric properties of solids have attracted great interest in recent years. The magnetic behavior is tied up, through the electron spin and the Pauli exclusion principle, in a very important way with electrostatic energies and interatomic forces. Our knowledge of magnetism has greatly increased in the last few years. From the experimental side, we understand the domain theory of ferromagnetism very clearly, and now see how many of the most striking experimental phenomena of ferromagnetism, like initial permeability, hysteresis, retentivity, and so on, are results of the rather secondary domain behavior, rather than of the ferromagnetic properties of the individual domains and of the perfect crystal. The theory is in moderately good shape; though this is one of the cases where there is by no means full agreement among the theorists as to which approximate form of solution of the quantum-mechanical problem is most appropriate. Antiferromagnetism, the interesting behavior shown by a number of crystals, in which alternate planes of atoms are magnetized in opposite directions, has become of great importance and interest in the last few years. An antiferromagnetic material does not show its behavior by setting up a permanent magnetic moment, as a ferromagnet does, for the obvious reason that some of its elementary magnets point one way, the rest the other way. Its general behavior was worked out from its magnetic permeability, which shows anomalies in the neighborhood of the transition temperature above which it ceases to be antiferromagnetic, and from its thermal behavior in the same neighborhood. And now in the last two or three years neutron diffraction has proved to be an experimental tool uniquely fitted to investigate its problems, for a neutron, being esentially a magnetic probe, sees a great difference betwen an atom with its magnetic moment pointed one way or the other way, and it is able to give unique answers as to the arrangement of the magnets in antiferromagnetic materials. Here again, as in the ferromagnetic case, the magnetic behavior undoubtedly has a very close relation to the interatomic forces, so that an understanding of these problems is certainly necessary before we can fully understand the behavior of the substances concerned. This is a very important point, for the ferromagnetic and antiferromagnetic materials are among the most important ones from a practical point of view. And here, as with ferromagnetism, there is still far from unanimity among the workers in the field as to the exact nature of the theory to be used.

Finally we come to dielectric behavior, and to the closely related problem of the optical behavior of solids (for we remember that the dielectric constant is but another aspect of the refractive index). Here we find two rather different sources of dielectric effects; we can have induced dipoles on account of the displacement of ions as a whole, or of electrons in the individual atoms or ions of the crystal. The ionic displacement is important only at low frequencies. Ionic vibrations have their resonant or fundamental frequencies, in the infrared, where there is close relation between ionic vibrations and the high-frequency sound waves which we have already mentioned. At frequencies below this, the ionic vibrations are excited with large amplitudes, but they cannot follow frequencies much greater than their resonant frequencies, so that these vibrations are not of importance in the optical properties of solids in the visible and ultraviolet regions. They are essential, however, in a good many important types of behavior: in ordinary low-frequency dielectric constants, in dielectric losses, in the behavior of ferroelectric materials, and in the infrared absorptions of crystals. At higher frequencies, the electronic polarizations are the essential thing (and they cannot be neglected even at lower frequencies, for they have an importance even there which is quite comparable with that of ionic displacements). We have a moderately good understanding of the optical properties of solids in the visible and ultraviolet part of the spectrum; though when we come to details, there are very few crystals in which our knowledge is anything like complete, and there is a tremendous amount of work, both experimental and particularly theoretical, which should be done before this problem can really be said to be understood. When we come to the visible and ultraviolet region, however, our attention is not directed so much to the conventional optical problems, the index of refraction and absorption coefficient, but rather to more striking things like fluorescence, phosphorescence, photoconductivity, photovoltaic effect, photoelectric emission, and a variety of other phenomena. Here we are in another of those ranges of effects in which practically the whole thing depends on impurities and imperfections in the crystal. We are beginning to have a general qualitative understanding of how such irregularities of the lattice could allow electronic transitions between excited energy levels of the right sort to explain these phenomena. We begin to see how they correlate with the properties of semiconductors on the one hand, with the mechanical problems of plasticity and such things on the other. But these phenomena are of the greatest complication, and they are exceedingly hard to investigate, on account of the way in which they depend on minute amounts of impurities. The study of such things is a fascinating field, one where much work is being done, but where we cannot be said to have really got to the bottom of the problem in a unique and certain way.

I HAVE TRIED in this brief summary to give a short review of the present nature of our knowledge of the structure of solids, and of the way in which the two great tools, x-ray diffraction on the one hand, the quantum theory on the other, have been used to increase our knowledge. Things are moving fast enough in the field just now to attract much attention to it, and to bring more workers into the field. New tools are being added to those we have already had; for instance, the electrical and electronic types of experiments used in investigating semiconductors, and the related optical experiments. The further we get in understanding the interrelations between different types of effects, the more useful experiments and theories in each branch of the subject become. There is every ground for hoping that the next few years will see a development of our understanding of the solid state, not probably as spectacular as what has gone on so far, for we have already got a general understanding of most of the types of behavior, but on the other hand much solider and more satisfying. There is a satisfaction in taking a subject whose foundations are understood, as we believe the foundations of solid-state theory lie in quantum mechanics, and trying to see how those foundations lead to understanding of complex and interesting phenomena such as we find in the study of solids. It is different sort of satisfaction from that of nuclear physics, where we may hope to discover new particles and new fundamental laws; but it is no less real a satisfaction, and the pleasure of investigation is coupled with the realization that the problems we are dealing with are fundamental to technology and the practical affairs of everyday life.