Current Trends in Solid State Science

The Pollock Memorial Lecture

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It is my privilege to spend this hour honoring your great physicist Professor V. A. Pollock by attempting to give you a broad review of the field of solid state physics—a field which has not only been remarkably coherent during several centuries of the development of western science, but has also been highly productive both as a source of the kind of enlightenment for which we value science so much and as a contributor to technology.

In examining the evolution of any field of science, we may note that the process of development often resembles somewhat the evolution of a mining operation. In the early stages of mining for a new and relatively little used material, one focuses on very rich deposits which give the most concentrated products that can be recovered and used most easily or directly. In fact only such deposits may have significant value in the early stages of the mining operation. Later, as the material being sought becomes more useful, and as the technology for developing it expands, one may find that leaner, lower-grade deposits are exceedingly important. In fact, the major wealth associated with exploitation of the mineral may eventually be associated with the relatively leaner deposits, as is true, for example, for the highly mechanized production of gold in the South African mines of the Rand Area.

Something quite analogous to this pattern is visible in the history of the opening of major areas of solid state science, as the field as a whole has gone through successive cycles of advance. In any one stage of development, attention is focused initially on major principles. Many of the details stemming from the principles are, in the main, of intellectual interest only to those few who have a very special appetite for them. Ultimately, however, as the knowledge of a given area becomes absorbed into useful technology, what were initially regarded as secondary facets of the subject may come to have practical interest. Thus, as time goes on, the apparently leaner aspects of the subject can become of very great practical importance.

By way of introduction, let me remind you that the crystalline solids formed by the elements and their compounds can be classified into four broad categories, namely, the salts, metals and alloys, valence crystals, and organic or molecular solids. The alkali halides and alkaline earth oxides are typical salts. About 70 per cent of the pure elements are metallic, that is, are good electronic and thermal conductors and tend to alloy readily with one another. Carbon, silicon, germanium, gray tin, and silicon carbide are typical valence crystals. The organic, or molecular solids, comprise the most diversified group, ranging from simple systems like solid carbon dioxide to quite complex crystalline polymers, such as polyethylene, or the natural organic polymers which play such an important role in biological systems.

The four categories are not all pure, for many materials have properties that lie intermediate between these of two or more types. For example, there are many alloys which are very close to being electrical insulators and resemble the salts or valence crystals in composition and atomic arrangement.

A number of salts and valence crystals, which are good insulators at low temperatures, become electronic conductors at elevated temperatures because bound electrons become free as a result of thermal excitation. These solids are, of course, the semi-conductors; the electrons which become free may be either the normal bonding electrons in the valence shelves or may be associated with distinctive impurities or foreign atoms which are added.

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In a similar way, the various areas of development of solid state science may be broken into five major fields which interlock closely with one another, although the " mining " of each of the fields generally started at different times on the historical scale. The five fields are as follows :

1. Macroscopic Properties
2. Lattice Structure
3. Electronic Structure.
4. Imperfections
5. Surface Properties.

The macroscopic properties are concerned with those characteristics of solids that can be measured on specimens having substantial size, that is having linear dimensions of the order of millimeters, or larger. Initially, the studies were concerned with the geometrical relationships of natural-formed crystals, usually mineralogical specimens, and led to the formulation of laws such as those governing the constancy of angles between neighbouring faces in a given crystalline habit form of a specific compound. Eventually the study was extended to the measurement of mechanical, electrical, magnetic, and thermal properties of the specimens in various crystalline directions and various temperatures. The subject is sometimes referred to in terms of the " tensor " properties of crystals. Systematic studies of natural specimens of this type were responsible for the discovery of piezoelectricity and pyro-electricity. Although such effects were initially of purely scientific interest, they eventually led to very important applications of crystalline specimens, such as in polarizing prisms, piezo-oscillators, and sonic transducers.

A desire to broaden the range of available crystals, starting in the early part of this century, inspired the evolution of a number of techniques for growing large single crystals of interesting materials. Such crystals have turned out to have great technical value in their own right in numerous applications such as in relation to jewelled bearings, magnetic materials, transistors, optical lenses and prisms for the ultraviolet and infrared, and ultimately in the field of laser research. Among the techniques used for growing crystals are those of evaporation of aqueous solutions, stress annealing, the Kyropoulos method (drawing from the melt), the Bridgman method based on use of the thermal-gradient baffle, the boule or arc-melting method, the zone method and hydro-thermal techniques.

It is particularly interesting historically to note that natural radio-activity was discovered by Becquerel incidental to the study of the physical properties of many crystalline materials.

Similarly, superconductivity was discovered by Kammerlingh Onnes in 1911 as the result of a systematic investigation of the conductivity of metal at low temperatures.

Although we think of crystalline masers and lasers, which generate coherent electromagnetic radiation in the high radio or optical range of frequencies, in quite modern terms because they were developed in the recent past as a result of the study of quantum phenomena in gases and molecular beams, the action of these solid state systems actually can be regarded to lie in the macroscopic domain since the underlying phenomena depend on the co-operative interplay of the entire assembly of radiating atoms with the radiation field. Thus, even though the study of the macroscopic properties of crystals is old, the field continually yields new dividends as more and more techniques in which the macroscopic properties of crystals can play a role are developed.

Lattice Properties. At the time of Dalton, early in the last century, when the atomic hypothesis was gaining ground, the conjecture was offered that the regular form of natural crystals implies an orderly stacking of the constituent atoms into lattice-like array. In brief, it was postulated that crystals contain a basic geometric unit of atoms or molecules, the lattice cell, which is repeated over and over in a periodic way in three directions. This relatively speculative concept evolved steadily during the last century, until, near 1900, imaginative scientists began to propose detailed structures for the simpler crystalline compounds. In the meantime, the geometrical theory of three dimensional lattice arrays had been worked out in much detail by mathematicians, starting with Bravais in 1830, and extending on toward the end of the century.

The study of the lattice properties of crystals entered into a completely new era when in 1913 it was discovered that crystals diffract X-rays in a manner determined by the lattice arrangement. This discovery was augmented by the discovery of electron diffraction in 1929 and neutron diffraction in 1944. At first, diffraction techniques were used to determine the properties of the simpler inorganic crystals. Eventually, however, the methods were employed both in the investigation of more complex inorganic organic structures such as the silicates

and of relatively imperfect crystals. The highest points in the development of diffraction techniques achieved thus far occurred in the last ten years in connection with organic crystals, for example, in the discovery that the long molecules in crystals of polymers are folded, and in the discovery that the molecules of Deoxyribose Nucleic Acid (DNA), which enter in such a crucial way in gene material, are double spirals, each member of the spiral being closely correlated along the length according to precise rules of combination. One can only feel a sense of inspired awe when contemplating the fact that the early speculations on the lattice properties of crystals nearly 150 years ago eventually led to the evolution of techniques. for determining the pattern of arrays in the genetic material responsible for the replication of biological species.

Along somewhat different lines, it may be noted that the dynamic properties of the crystal lattice have made it possible to use crystalline materials to obtain valuable specialized information regarding nuclear energy levels in a number of elements. When a stationary, isolated nucleus emits or absorbs a gamma ray, the net momentum transferred to the nucleus is sufficiently large that the absorbed and emitted quanta have energies significantly different from the spacing of the nuclear levels involved in the transition. On the other hand, when the nucleus is in an atom bound into a crystal, it is possible, under proper circumstances, for the entire crystal specimen to absorb the momentum so that the energy of the absorbed or admitted quanta is very nearly the same as the nuclear level spacing. This effect, discovered by Mössbauer, makes it possible to use crystalline emitters and absorbers to obtain much detailed knowledge concerning nuclear energy levels.

Electronic Properties. In the 1880's, early in his long and productive career, the Dutch physicist H. A. Lorentz postulated that insulating materials contain bound charges which are held in position by harmonic forces, much like weights which are attached to a fixed point by an ideal spring. The existence of such changes had been surmised earlier from the laws of electrochemical equivalence but they had not been employed previously in considering the dynamical properties of atomic structure. In terms of this picture, Lorentz was able to explain the variation of the optical dielectric constant of crystals near regions where the crystals absorb light. In this way the concept of the electron entered solid state

science. Much more tangible evidence for the electron was developed a decade later when investigators began studying the fragments of atoms produced in gaseous discharges. Then, at the turn of the century, Drude proposed that metals contain a gas of free electrons which are responsible for their high electrical conductivity and started a very fruitful period of study of metals.

The understanding of the electronic properties of solids remained in a very primitive state until quantum mechanics was developed about 1925. Following that, it became possible to discuss the detailed behaviour of the valence electron in many crystalline materials. Investigation of the wave equation showed that the energy levels of electrons could be grouped into bands whose relationships gave, in turn, a simple and direct explanation, not only of the characteristic differences between metals and insulators, but of the ways in which transitions between the two types of materials occur. By 1940 one had an excellent semi-quantitative understanding of the behaviour of the valence electrons in many typical simple solids.

The development of electronic computers during and after the war made it possible to expand the detailed investigation of the electronic states in solids on a relatively enormous scale. Today, because of such computers, it is feasible to hope to obtain quite detailed knowledge of the levels or bands in many monotomic or diatomic solids. Studies of this kind have been accelerated substantially by the widespread practical interest in the detailed behavior of conduction electrons in the useful semiconductors such as silicon and germanium, and the compounds of elements in the third and fifth columns of the periodic chart.

One of the greatest triumphs of the electron theory of solids has been the achievement, within the last decade, of a high degree of understanding of the phenomenon of super-conductivity, particularly as a result of the work of Bardeen, Cooper, and Schrieffer. These investigations have shown that in cases in which the free valence electrons in the metal are disturbed sufficiently by the vibrations of the crystal lattice, or, to use the accepted language, interact sufficiently strongly with them, this interaction may have a significant influence on the behaviour of the motion of the electrons relative to one another. At relatively low temperatures, within a few degrees of the absolute zero, this effective electron interaction, originating in the inter-

action of the electrons with the lattice vibrations, may cause the electron gas to freeze into a mode of motion in which pairs of electrons which move in opposite directions with equal momentum are closely correlated even though they may be separated in space by many atomic distances. This correlation not only influences the way in which the electron gas conducts an electric current, inducing typical superconductive characteristics, but also determines the behaviour of the electrons in a magnetic field. In effect, the ideal homogeneous specimen behaves like a perfect diamagnetic for which the permeability vanishes (Meissner effect), that is it rejects lines of magnetic force.

The development of a consistent quantum mechanical theory of superconductivity has given an enormous impetus to the study of the entire field of superconductivity in recent years. Out of this work has emerged not only the discovery and refinement of many new superconducting compounds but also the discovery that the magnetic field associated with a supercurrent is quantized, that is, its intensity is restricted to discrete values which depend upon the geometry of the superconducting system. On the technical side, the refined studies have made it possible to construct permanent superconducting magnets which can produce magnetic fields in the vicinity of 100,000 Oersted. The superconductors used in such magnets, usually termed hard superconductors, have the property that they are not physically homogeneous and are able to retain lines of magnetic force that are trapped at imperfections in a way not yet thoroughly understood. The trapped lines of magnetic force reside near the centre of vortices of supercurrent.

Still further, there has been extensive study of the way in which conduction electrons flow from one superconducting metal to another as the spacing between the two is varied from zero to many atomic distances (tunneling effects). Such developments promise to yield an enormous amount of additional information concerning superconductivity, some of which may have very useful consequences.

The methods of mathematical analysis used in the theory of superconductivity are based on a combination of the methods of field theory, first developed in connection with high energy particle physics, and the methods of many-body theory, developed to handle problems involving the co-operative action of many particles. The success of this approach to the problem of superconductivity has opened a large doorway to the theoretical investigation of many other problems of solid state science.

Imperfections in Crystals. The concept of the ideally perfect crystal in which the lattice array is entirely unblemished is an abstraction normally realized only on a quite microscopic scale within a larger specimen. All real crystals contain varying degrees of imperfection. It was recognized very early in the history of the development of crystal science that imperfections are present in typical specimens. Indeed many irregularities could be seen with the naked eye, under the microscope, or discerned indirectly by chemical analysis. It was also recognized very early that imperfections must play a significant role in affecting the physical and chemical properties of specimens since the properties could be made to vary by altering the imperfections. On the technological side, the control of accidental or intentional additions or structural features has always been an important part of the practical lore in fields such as ceramics and metallurgy. Practical studies showed, in fact, that imperfections may be relatively inert in some cases; whereas they may have profound effects upon the properties in others, such as in the case of additions of carbon in iron.

To give another example, the entire field of crystalline luminescence underwent a vast development in the first quarter of the present century in the hands of the chemists, who studied the influence of various foreign additions on the luminescent properties of salts when irradiated with ultraviolet light, X-rays, or ionizing particles. Along similar lines, it was noted that the semi-conducting behaviour of many substances such as selenium, tellurium, and lead sulphide is critically dependent upon the presence of foreign atoms. Still further, it was found that the ductility of relatively plastic crystals such as metals and salts could be influenced enormously by changing the state of perfection of the specimens.

Following 1925 there was a strenuous attempt to catalog the possible imperfections that could occur in crystals and to sort out the influence which they have upon the physical and chemical behaviour of such solids. This work actually did not come to complete fruition until after World War II, when the subject received international attention on the massive scale which the postwar support of science made possible. It was then realized that the types of imperfections which can occur in solids are rather small in number. The great diversity of effects arising from the imperfections is to a

considerable degree a result of the complex interactions between imperfections which can occur.

Basically there are three families of imperfections, namely: point imperfections, such as foreign atoms present in the lattice either substitutionally or interstitially, or vacant lattice sites produced by removing atoms from the lattice (vacancies); electronic imperfections such as additional free electrons in an otherwise insulating matrix, generated, for example, by adding an atom with a loosely bound electron to the lattice; line imperfections, generally termed dislocations, such as may be produced by permitting the atoms on opposite sides of a planar area within the crystal bounded by a line or curve to slide past one another by one cellular distance in such a way as to cause a pattern of disregistry along the bounding line.

Each of these three basic types of imperfections can not only interact with imperfections of the same type but can also interact in various ways with the other two types to produce a wide variety of effects. It has been demonstrated, for example, that the plastic properties of simple crystals are closely associated with the ability of the linear dislocations described above to move through the lattice when it is placed under shearing stress. The interaction of dislocations with one another and with foreign atoms provides an explanation of the sensitivity of such plastic flow to cold work (extensive deformation) and to foreign atoms.

Although a large part of the research carried out in the field of solid state science between 1945 and 1960 was devoted to the clarification of the influence of imperfections on the properties of solids, the field still provides an enormously fruitful area for further research, particularly as new techniques for investigation are developed. Moreover, there are a number of facts which are not at all well understood. It is known, for example, that special crystals, such as zinc and cadmium sulphide, undergo a special type luminescence (electroluminescence) when placed in an oscillatory electric field. Investigations show that the emitted radiation probably originates near imperfections; nevertheless the nature of the interaction between the applied field, the luminescent centers, and the imperfections is not at all clearly understood at the present time.

Surface Properties. Every real crystal is bounded by a surface. Such surfaces have been studied systematically over many decades in an attempt to evolve systematic knowledge of the surface properties. The initiating investigations, in areas which still continue to be productive, were carried out by chemists concerned with such phenomena as surface adsorption and surface catalysis. In close relation to this, chemists and mineralogists studied the nature of crystalline layers formed by depositing one compound on the surface of another (e.g., epitaxy).

In a similar way, metallurgists have studied the influence of intercrystalline boundaries in polycrystalline materials (grain boundary effects).

Since 1945, several new types of studies have given added impetus to the investigation of surfaces. For example, Professor Mueller showed that one could obtain very interesting information about the atomic arrangements of the base material and deposited materials in the outer layers of point electrodes which were placed in electric fields sufficiently strong to induce field emission of electrons. I have been pleased to see important extensions of this work in the CSIRO laboratories in Melbourne. While this work has been rather specialized in the sense that it is focused on the use of a few metals, it has given a wealth of information concerning the influence of the underlying crystalline arrangement on foreign layers on the surface of such metals.

Soon after the war, John Bardeen pointed out that the conductivity of thin semi-conducting layers or filaments could be greatly influenced by the nature and condition of the surface. He emphasized that surface atoms had their own characteristic electronic energy levels, and that these levels could influence the number of conduction electrons present in a region near the surface. Since the pattern of surface atoms can be influenced in turn by adsorption, it follows that under proper circumstances there can be a correlation between volume conduction and surface conditions.

Still more recently, a number of investigators have developed techniques for studying diffraction of electrons of very low energy by crystalline surfaces. Such electrons, having energies near 100 electron volts, do not penetrate the specimen by more than a few atomic distances, so that the diffraction pattern is characteristic of the outer layers. Many individuals place high hopes on the promise of this new method of study for obtaining profound information on a wide diversity of surfaces. This approach to the study of surfaces

has been featured at the recent Melbourne Conference on Diffraction.

In spite of the progress that has been made over the decades in the study of crystalline surfaces, one must admit that the field is unfolding relatively slowly. Although there presumably will come a day when there is as much understanding of the surface properties of solids as we have at present of the volume properties, it does appear that a whole new regime of development will be needed to achieve that goal.

My own involvement in the science of solids now goes back somewhat over 30 years beginning with the early development of the theory of electron bands in solids. It is interesting to contemplate that a very major fraction of the quantitative and qualitative knowledge of solids which we possess at present has been developed over that span, in spite of the fact that the field is, in itself, several hundred years old. If I attempt to analyze my own experiences over this period, I find that one of the most remarkable features, apart from the advance in understanding, has been the fact that the interest in detailed facts has grown so much. In the 1930's, it seemed quite reasonable for one person to be familiar with practically all of the available literature concerning solids and much of the implication of the work. Now a typical good investigator may devote a number of years to one highly specialized facet of a given family of compounds and have relatively little knowledge of a topic which, although fairly closely related to his interest, is not immediately tied to it. Coupled with this increasing concern about detail has been a vast growth in the number of highly competent scientists working in the field and in the range of knowledge which has direct applied interest. From the detailed study of properties, there has been spawned families of devices including a large array of transistors, a spectrum of magnetic materials for transformers and recording devices, luminescent screens of varied use, superconducting magnets and crystalline lasers.

One might reasonably ask whether the field of solid state science is in its infancy or its old age. It clearly is not in its infancy for we now have far too much accumulated knowledge of the properties of a wide family of solids to assume that the field is not mature. Moreover, there are very few outstanding mysteries extant at present, as was true when I entered the field some 30 years ago. On the other hand, I cannot help but feel that there is still a vast amount of valuable " ore " left in the study of solids. The realization of that ore in the future will depend upon the careful and systematic study of detailed properties of many compounds, using all the battery of physical and chemical techniques which are now available and can be devised in the future. In a sense, the field can be looked upon henceforth as somewhat in the nature of a very sophisticated branch of chemistry, which will persistently yield significant new discoveries if a host of competent investigators continue to pursue a wide variety of investigations.