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THE STRUCTURE OF MATTER

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When the colloquium on "The Engineering Implications of the Physics of Solids" was in the formative stage of being programmed, this paper, the second in the series, was to be devoted to a discussion of the structure of matter, crystallography, and other related topics so that the average mechanical engineer could obtain a basic understanding of the properties of solids as they were to be discussed in the later papers of the colloquium, and in the engineering literature in general. For want of a better title the one that heads this paper was used although it does not describe the scope of the assignment except in a very loose sense. Something more than just a knowledge of the structure of matter is needed if one is to gain an insight into the current developments in the fields of the various engineering materials.

In order to understand why solids exhibit certain properties, it is necessary to know more than just the "Physics" of solids. One should also know something of the "Chemistry" of solids; the structure of solids, "Crystallography;" the non-crystalline solids or the "Amorphous" solids; the stability of solids, their "Thermodynamics;" environmental effects on solids or "Surface Chemistry." To handle these various phenomena and to reduce the experimental data to laws one needs "Mathematics" to express the findings in terms of suitable parameters and basic relationships. While one can show that from an historical standpoint each of these branches of science, with the exception of Mathematics, is an offshoot from the parent science of Physics, attempting to do so at this late date is apt to provoke some spirited controversy. Solids are of interest to large and varied groups of people: Physicists, Chemists,

Mineralogists, Ceramists, Polymer Scientists, Metallurgists and Engineers of all types. Each of those listed, and many others, has something to contribute to the general field of knowledge in this area and no one group is the sole depository of all truth. As you shall see in this symposium the problems in the area of solid state science are more than enough to keep all kinds of people gainfully employed for many years regardless of their background and training.

What can the various sciences tell us as Engineers about the properties of solids? The answer is surprisingly little in a quantitative sense except in a few specialized areas, but a great deal in a qualitative sense, or, as it is usually stated, "within orders of magnitude." Take, for example, the field of atomic and nuclear structure. There has been and continues to be a great deal of research in this area of the field of Physics. We know that all atoms are made up of certain basic units such as neutrons, protons, electrons, mesons, binding energy, etc. These basic particles and forces when found in certain combinations yield atoms which have certain characteristic properties. The rare gases are characterized by similar atomic and electronic structural features; the alkali metals such as lithium, sodium, potassium, etc., form an homologous group; the electronegative elements form another; the transition metals have certain unique configurations as do the rare earth elements, the transuranium elements, etc. When one finishes this analysis, based largely on spectral studies, one finds that he has reconstructed the old Mendeleef Periodic Table of elements which was initially put together on the basis of the similarity of chemical behavior by Chemists. It is true that

some of the kinks in the periodicity have been removed, certain anamolies explained and some new ones introduced, but in general we have a clearer picture of the basic structure of atoms; at least their electronic structure, their nuclear structures and nuclear forces are still very much an unknown quantity.

Working then only with the best known quantities of atoms, their extra-nuclear electrons, more specifically their energies, one can build up a fairly rational picture to explain the electronic properties of solids; electrical and thermal conduction; semiconduction; magnetic properties; dielectric properties, etc. In making this leap however from atomic structure to the resulting electronic properties one has left unanswered a whole host of questions such as: Why do atoms form molecules? Why do molecules condense to form solids? Why do only part of the electrons participate in the resulting electronic properties? It is not that there are not answers to these questions; the problem is that there are too many answers and none of them are really definite. It is helpful occasionally to remind ourselves that the bonding of two simple hydrogen atoms to form a hydrogen molecule is not entirely understood as yet and it is a huge step from this simple system to engineering materials such as cements, glasses and metals. To people outside the field looking in at the excellent qualitative and in some cases quantitative agreement, at present obtainable in applying electron theory, zone or band theory to electronic processes in solids, it seems only a question of time before exact solutions can be obtained to all our problems in regard to material properties. Such is far from the case since one is apt to overlook the fact that only fragmentary experimental data are used to test

the theories and quite obviously these data fit the theory. Their extension to additional systems usually discloses discontinuities, perturbations, and exceptions until the theory is warped so far from its original base that it is almost unrecognizable. This is of course to be expected since the magnitude of the problem that is to be solved is enormous. Most theories of the solid state are based on the energies of the electrons surrounding the atom; not all of them since the greater bulk never seem to enter the picture directly. Assuming that only one electron per atom is significant, one is faced with the problem of accounting for the energies of the order of 10^{22} electrons in a single cubic centimeter of an average metal. Obviously approximations have to be made and will continue to be made and one can never really say that he has an exact solution.

The question naturally arises in your minds as to how much of this material an engineer should know. To really follow developments in this field one needs a good grounding in classical physics, quantum physics, statistical mechanics, wave mechanics and more importantly, the mathematics associated with these fields. The average engineer does not normally have this background but it is not entirely beyond his grasp. The point I wish to make is that even if he has had all this training and background he would find that it is too qualitative to be of direct use to him as a practicing engineer. The gap between what we think we know in the sciences and what we can do in todays technology is quite large and has only been narrowed in certain selected areas such as magnetics, semiconductors and certain optical phenomena. Dr. Goldman in a subsequent paper will enthusiastically expand on these various applications of solid state physics

to the solutions of engineering materials problems and certain of these have been quite spectacular.

When one turns to examine the field of the mechanical properties of solids the contributions of Physics in these areas have been quite limited and will probably remain so for some time. Quite early it was recognized that geometric structure played a more important part in determining these properties than does atomic or electronic structure although admittedly the geometric structure must ultimately be traced back to the atomic structure. Since the mechanical properties are structural sensitive it is only natural then that we would turn to those sciences that are concerned with structure. This means the science of Crystallography if we are dealing with crystalline substances and portions of Physical Chemistry, Organic Chemistry, Polymer and Silicate Chemistry if we wish to discuss non-crystalline solids.

Crystallography is of course a completely closed branch of science in the sense that all crystalline solids can be classified as to crystal system, lattice type, crystal class and space group. This does not mean that all the work has been done in this field or that there are no new and interesting problems in this science. It simply means that once a given crystalline material has been classified and the various parameters determined, the crystal is completely described. This means that we have determined where atoms or atom groups are located in the unit cell, have located the principal axes, described its symmetry and in general have completely and unambiguously described the crystal. As tools for determining structure crystallographers utilize x-ray, electron and neutron diffraction techniques but also have used optical properties,

thermal properties, magnetic and electronic properties; as a matter of fact any tool to assist in the unraveling of the structure. They have rarely used mechanical properties, with the possible exception of cleavage studies, because they are so poorly behaved, non-reproducible, and ambiguous in meaning. One can however work from the inverse direction and from studies on the elastic and plastic behavior of crystalline materials make links back to the basic crystallography. The materials that are of interest to us as engineers are those with adequate strengths and if possible those with suitable plasticity; generally the metallic solids, since the ionics and covalents are not noted for their extensive plasticity while the molecular solids are characterized by low strengths.

Examining the metallic solids we find that those which are of the greatest engineering significance can be characterized crystallographically as simple, symmetric types of structures; face centered cubics, body centered cubics, or hexagonal close packed. Because of this simplicity of structure the basic deformation mechanisms of plastic deformation, slip, twinning, and kinking, can operate more readily. For ease of operation these mechanisms prefer planes of high atomic density and directions of high atomic density; characteristics of the structures listed. The lack of plasticity or limited amounts that can be achieved in materials such as concrete, ceramics, refractories and other crystalline solids is at least partially related to the relatively complex structures of these materials as contrasted to the common metallic structures. Here again however one must be cautious about relating properties to structure alone; the problem is not that simple. Considerations such as bonding, temperature, environment, method of loading, rate of loading, etc. all must be

considered. If one, for example, examines the mechanical properties of a single crystal he will find several things which seem to strike at the very roots of his engineering mechanics training. They are neither homogeneous, nor isotropic, nor do they obey Hook's Laws except in a very imperfect and quite unpredictable fashion. One also finds that the properties of this single crystal are very far removed from the properties that we normally associate with that material as an engineering material. It was this disparity between single crystal studies and the properties of the polycrystals that we use that triggered the extensive work that resulted in the development of the Dislocation Theory which Professors Gilman and Parker will detail for you in later papers.

When one goes from crystalline materials to non-crystalline materials one loses the guiding principles of crystallography, the strong bondings of the covalent, ionic and metallic solids and their relatively simple atom grouping characteristics and one must deal with huge molecules, a distinguishing and dismaying lack of orderliness, and weak bonding forces; the exact antithesis of crystalline solids. Needless to say the difficulties of working in the fields of elastomers, plastics, polymers, resins, non-vitreous glasses and the like are enormous. In spite of these difficulties however there is a large body of useful knowledge that has been developed in these fields. Much of this work is concerned with the chemical make-up and molecular structure of these solids and, as indeed is the case even in crystalline solids, there are so many parameters that have to be empirically evaluated and so many qualifying statements that must be made that one cannot really be very quantitative

in applying science to the study of these materials. As a metallurgist I am sometimes depressed by the complexities and difficulties involved in trying to make sense out of the metallic state but when I look at the problems of the amorphous state I am reassured that things could be much worse.

One of the most outstanding features of applying any science to an engineering materials problem is the metamorphosis that the science must undergo before it can be applied. Almost without exception one can examine a phenomenon and from a theoretical standpoint make rational deductions and draw conclusions and one will find that he is orders of magnitude from reality. This is what has become to be known euphoniously as the "zero'th order approximation." What one does then is to correct or amend the original hypothesis, recalculate the effect on the resulting answer and repeat the process until one has a working hypothesis. This happens so often that one can with some confidence claim that our current and future theories of solid state behavior are really based more on imperfections than on the perfection of the models. This is obviously a problem of semantics since one cannot have imperfections without prior perfection.

The imperfections that are so important to the understanding of the elastic and plastic behavior of materials are dislocations of which there are two principal types, edge dislocations and screw dislocations. Succeeding lecturers will spend a good portion of their time detailing how the interaction of these mobile lattice defects can affect mechanical properties. Two other types of structural defects which are related to dislocations are stacking faults, errors in planar placements of atoms in

structures, and epitaxial layers which are interfaces across which two dissimilar structures are in registry. In addition to these structural defects which are volume or planar in character there can also be what have come to be known as "point defects." Atoms may be missing from lattice sites to produce what are known as Schottky defects or holes in the structure. The atoms that are missing from the lattice points may be trapped into the interstices of the balance of the crystal to produce what are known as Frenkel defects or Frenkel Pairs. The holes in a Frenkel Pair may diffuse to the surfaces leaving the interstitial atoms behind in the lattice to produce what is sometimes called an anti-Schottky defect. Impurity atoms in the host lattice may either substitute for the host atoms or be held as interstitials to produce solid solutions. In many cases the impurity atoms may orient themselves about host atoms or between them to produce substitutional or interstitial compounds. There are even cases where the impurity atoms are located at the centers of edge dislocations. All of these structural defects are quite essential to the understanding of the behavior of crystalline solids since without them one cannot, on a theoretical basis, explain the properties of solids. The plasticity of a metal, the principles of alloying, diffusion in the solid state are but a few of the items which require the existence of the imperfections listed.

Even when one considers the electronic properties of solids one must develop the concepts of defects but this time on an electronic scale. Electrons may be present in materials as an excess or a deficiency as compared to the stoichiometric requirements and this gives rise to the

well known n and p type semiconductors. There are defects known as excitons which are an electron hole and an interstitial atom pair which are similar to the Frenkel Pairs mentioned under structural defects. In addition to these electronic point defects there are also regions within the crystals termed domains within which electrons align themselves as a function of the field that is applied which can either be magnetic or electric. Again it should be emphasized that the presence of these various types of defects is an absolute requirement in order to explain the known behavior of real materials.

Still another group of defects are those which might be termed surface defects. Since many engineering materials are polycrystalline and each crystal is separated from others but bound to them across an interface, or grain boundary as it is called, this represents a defect in the perfection of the crystal and it has as pronounced an effect on the resulting properties as any of those previously listed. Even within these boundaries we have other boundaries variously known as sub-boundaries, or polygonized structures, and these have been shown to be effective in controlling properties. Finally we have the free boundary where the solid terminates and this is as violent a discontinuity as one could hope to devise.

Combining now these various types of defects with the perfection that has been postulated by Physics, Chemistry, Crystallography and the other sciences one can begin to see the complexity of the analyses. When now as engineers we subject these materials to stress, strain, thermal, electrical and magnetic fields it is not too surprising that the difficulties of analysis are increased many fold.

There are two other fields of science that also touch on the field of engineering materials, Thermodynamics and Surface Chemistry. As mechanical engineers you are apt to wonder how Thermodynamics can have anything to do with materials but this is probably due to your orientation and training. Thermodynamics is the science which deals with the interaction of matter and energy and materials are certainly matter and will interact with energy. The energy interaction can of course be of several varieties. Mechanical Engineers are apt to think in terms of thermal and mechanical energy; Chemical Engineers in terms of thermal and chemical energy; Electrical Engineers in terms of electrical and magnetic energy. In dealing with solids all kinds of energy should be considered. When they are, all these supposedly new or neglected phenomena such as thermoelectricity, magnetostriction, piezoelectric, magnetocaloric, pyroelectric, etc., effects all drop out of the mathematics as thermodynamic functions. This is one of the powerful features of classical thermodynamics in that it predicts all of these effects. Unfortunately it tells one nothing about the magnitude of the effect nor does it tell anything about the mechanisms involved since it is based on a macroscopic model. To get to the microscopic level and to discuss mechanisms we must turn to statistical thermodynamics. Similarly the field known as Irreversible Thermodynamics is attempting to handle the problem of rates which is something that classical Thermodynamics excludes from discussion since all of its concepts are concerned with equilibrium; something that is rarely attained in solids. Since classical Thermodynamics is rather imperfectly assimilated and utilized by the

engineering profession as a whole I would hazard a guess that it will be some time before these newer types of thermodynamic concepts filter down to everyday usage. Their current applications lie largely in explaining existing phenomena and in many cases their applications while they may be a more rigorous approach to obtaining solutions, are quite tortuous.

The name of the field of Surface Chemistry might lead one to believe that this is the exclusive field of the Chemist but this is not the case. Physicists, Crystallographers, Metallurgists, Ceramists and many other groups are active in this field. In the final analysis we as engineers utilize matter in various environments and what we wish to know is whether the matter we have specified has the abilities to withstand certain conditions of stress, temperature, chemical, electrical and magnetic activity. While a knowledge of the structure of matter, its numerous defects, and its bulk thermal, electrical, chemical and magnetic properties will give an indication of the suitability of a material, it should be recognized that in isolating the system from the surroundings we are eliminating one of the more important variables. For example, the corrosion resistance of a stainless steel is not dependent on the crystallography of its structure, the chemical composition of the alloy, the energy states of the electrons of the atoms, the number of defects present, nor even the thermodynamic stability of the alloy. All of these factors have some bearing on the problem but only indirectly. The really significant part is the Chemistry, Physics, Crystallography, Thermodynamics and perfection of the surface layers where it is in contact with the environment. The solid state is really only a support for the surface state where the real mechanisms of protection are operating.

As you see this lecture has not really been on the structure of matter as viewed from a scientist's position but as viewed from an engineer's position. Some science, some near-science and some sheer empiricism is needed in order to understand the various properties of engineering materials. To persons not directly engaged in work in these fields the theories, modified theories, claims, counterclaims and the large outpourings of research efforts in these many fields can be quite confusing. The function of this colloquium has been to try and relieve some of this confusion. It is helpful at times to consider that the phenomena that we observe are real, the sciences, systems, or methods of analyses that we use to explain these phenomena are only good to the extent that they achieve that purpose. The problems facing us in attempting to understand the behavior of materials are so complex that we will need the assistance of any and all groups before we can come up with answers to the many questions that can be asked about the properties of materials.