CONCEPTS IN SOLIDS

Lectures on the Theory of Solids

固体中的概念

P.W.ANDERSON

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—— IN ——
SOLIDS

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Princeton University

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Vita

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Philip W. Anderson has been the Joseph Henry Professor of Physics at Princeton University since 1978. Professor Anderson received his Ph.D. in physics from Harvard University in 1949. He received the Nobel Prize in Physics in 1977 for work in condensed matter physics. He has taught at Cambridge University (1967-1975) and has been a Fellow and Honorary Fellow at Jesus College (1969-1975) and a Visiting Fellow at Churchill College, Cambridge University (1961-1962). From 1949 to 1984 Dr. Anderson served at Bell Laboratories as Chairman of the Theoretical Physics Department (1959-1961), Assistant Director of the Physical Research Laboratory (1974-1976) and as Consulting Director of the Physical Research Laboratory (1976-1984). In addition to the Nobel Prize, Professor Anderson's honors include the Oliver E. Buckley Prize of the APS (1964), the Dannie Heineman Prize of the Academy of Science at Gottinger (1975), the Guthrie Medal and Prize (1978), the National Medal of Science (1983), the Foreign Association Academia Lincei (1985) and an Honorary Fellowship from the Institute of Physics (1985). He is a member of the American Philosophical Society and has been a Foreign Fellow of the Indian Academy of Sciences, a Foreign Fellow of the Japan Academy of Sciences, a Foreign Member to the Royal Society and has been a member of the American Academy of Arts and Sciences and the National Academy of Sciences Council. He has lectured at the University of Wisconsin, Duke University, the University of California at San Diego, and Harvard University.

Special Preface

I reread *Concepts in Solids* with both pride and embarrassment. Pride, both because it was this set of lectures which inspired Brian Josephson to invent his effect--not every book can point to the precise Nobel prize it inspired--and because I did, in a very brief space, manage to touch some of the key topics which are still not adequately covered in your average solid state theory book. For instance, it is shocking that the main texts used in this country still do not touch on the Mott transition or the "Magnetic State." I was aiming at conceptual, not mechanical physics, and I hope I got there.

Embarrassment, because after all, there has been 30 years of physics since then. For instance, I note that I guessed absolutely wrong in dismissing tight-binding theory out of hand: it has not yet totally come into its own but it is, in my present opinion, the right way to think about most bonding in solids. I am not ashamed of skipping localization--only Mott was interested in it, and neither of us yet knew where to go next. I was prescient about broken symmetry—as Josephson realized—but left out phase transitions, as I myself noted.

Nonetheless, I believe that the average student will still be harmed less by this book than by any number of other books I should not name, and I welcome the reissuance.

P. W. Anderson
March 1991

Preface

These notes were for a course given at the Cavendish Laboratory, Cambridge, in the fall and winter terms of 1961-1962. Nominally, it was for second- and third-year graduate students who had had a survey course in solid-state physics, and were interested (at least) in theory; but I assumed very little formal theoretical background. I think the notes can be read by anyone who has had a thorough course in quantum mechanics, but the reader who knows something about solids will find them much easier, and will also not be misguided by my rather arbitrary and specialized choice of material.

The idea of the course was to teach a number of central concepts of solid-state physics, trying to choose those — band theory, nearly free electrons, effective Hamiltonian theory, elementary excitations, broken symmetry — which lay as near as possible to what I consider to be the main stream of development of the subject. Such a choice is necessarily arbitrary — whose fields, such as dislocation theory, transport theory and fluctuation-dissipation theorems, magnetic resonance theory in all its forms, and critical fluctuations, which could easily be argued to be quite as important, were ignored, simply because the course was of finite length. My choice of examples was even more arbitrary. For instance, the choices of the electric field case of effective Hamiltonian theory and of excitons to illustrate collective excitations were made because I thought the students were likely to encounter the more usual examples elsewhere. From time to time, to liven the course up a bit, I introduced original material; the discussions of the limitations of nearly free electron theory, of the philosophies of elementary excitation theory, and of broken symmetry are new, and that of the magnetic state is not widely available.

The language and presentation are very informal; very few changes were made from my original lecture notes as written. I might add that little effort has been made to bring them up to date. Both limitations are of course implicit in the idea of a lecture note volume.

I would like to express my gratitude for the hospitality of Professor Mott and the

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Cavendish Laboratory, the secretarial staff of which prepared the original version of the notes. Mr. Liu Sham was kind enough to edit the notes and write in most of the equations.

P.W. ANDERSON

Murray Hill, New Jersey
January 1963

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INTRODUCTION

A. PREPARATION AND TEXTS

The subject of these lecture notes is "Concepts in the Theory of Solids"— in
point of fact I should have said "in the *Quantum* Theory of Solids," because there is
very little of our understanding of the properties of matter which does not depend to
some extent on the quantum theory. Some acquaintance with the quantum theory
will be necessary: a certain understanding of the matrix formalism and trans-
formation theory as well as of elementary wave mechanics. For instance, time-
dependent perturbation theory and operator equations of motion will be used without
much further explanation but not techniques of modern field theory; these will be, if
necessary, derived from scratch.

What preparation in the solid-state area is necessary is determined by the intent
of this course, which is not to survey the phenomenology of the properties of solids
but to go somewhat more deeply into what is behind these properties. In many
cases, this means that we shall try to understand *why* solids behave as they do, but
in many others of course—perhaps more—we shall simply be coming to the
questions at which our real understanding fails. It will then, clearly, be a great
help to have a reasonably wide knowledge of what the properties of solids are.
Kittel's "Introduction to Solid State Physics" (1) is an excellent text which surveys
the field on a level preparatory to what will be said. In other words, some famil-
iarity with such concepts as Debye T^3 specific heat, Brillouin zones, free-electron
specific heat or spin paramagnetism, electron or nuclear paramagnetic resonance,
and others of the more or less standard theoretical ideas and experimental tech-
niques will be assumed. No texts have even attempted to cover solid-state theory
as a whole at any basic level since Seitz in 1940 completed "Modern Theory of
Solids" (2); and that is in fact by far the best text still. This may indicate that we
have not made much progress since 1940 in basic understanding, only in investi-
gating much wider classes of phenomena, which is to some extent true. In any
case, the only answer so far found to the problem of modernizing the "Modern
Theory" has been to issue a series of books containing review articles, the so-called

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"Seitz-schrift" or Seitz-Turnbull series (Solid State Physics — Advances in Research and Applications), which is probably the best single source at this point. Kittel's book is very good, but except possibly in the one field of crystal symmetry in the second edition, it is not very complete on any one subject. Special areas are covered reasonably well in certain books — e.g., Ziman's "Electrons and Phonons" (3) and other books on special subjects such as dislocations, magnetic resonance, etc. Wannier's "Elements of Solid State Theory" (4) and Peierls' book (5) should be mentioned, each of which is probably the result of some such selection as will be made here, but a quite different one. A magnificent, but quite advanced, and quite condensed text is Landau and Lifshitz' "Statistical Physics" (6). A forthcoming text which will cover a very wide area of solid-state physics from the point of view of group theory and symmetry principles will be M. Lax, "Symmetry Principles in Solid-State Physics" (6a). In any case, books and articles used for sources in any given area will be mentioned.

B. PLAN OF THE COURSE

1. First some general ideas about solid-state physics, including the classification of solids into types, and some broadly general things about the quantum chemical facts we might hope to explain from a deeper point of view: occurrence, properties, etc., of the different types.

2. The next and possibly most important and fundamental area is the purely one-electron band theory, since probably most of the basic questions such as binding, symmetry, band structures, etc., are primarily determined by the bands.

What we hope to lead up to, via some study of the older methods and results, are the more recent ideas of Phillips, Cohen, Heine, and others about the success of the almost-free electron model, and some of the speculations one can then make about binding-energy trends and the quantum chemistry of solids.

Another subject will be the modern developments in one-electron band theory in the presence of perturbations, external fields, impurities, etc.: i.e., effective mass theory.

3. Next we comment on the reason why such manifest oversimplifications as the one-electron theory discussed above work — namely, the idea of elementary excitations, probably the single most fruitful theoretical concept in all of solid-state physics. After discussing the theoretically simple case of insulators and the less simple case of metals, we go on to discuss various possible kinds of collective elementary excitation — excitons, spin waves, and phonons. There are also some more general remarks about collective excitations which apply to all of these.

4. In discussing spin waves we shall treat magnetism. Here the fundamental questions are why and when materials are magnetic — the question of the magnetic state, or when free spins occur — and what causes the interactions among the spins which lead to ferro- or antiferromagnetism. We shall also use this as an example of some general facts about condensation.

C. GENERALITIES AND CLASSIFICATION OF SOLIDS

I suppose any course on the theory of solids should start with a definition of a solid, although we all know that the physicist rejects the definition of a solid as (roughly) what hurts your toe when you kick it, and defines it as a regular array of atoms in the sense of having, to a good approximation, translational symmetry under some one of the space groups.

At this point we have already slipped past three of the most fundamental questions of solid-state physics: (1) Why is a solid? (2) How does one describe a solid from a really fundamental point of view in which the atomic nuclei themselves as well as the electrons are treated truly quantum-mechanically? (3) How and why does the solid hold itself together?

The first of these can be the subject of bitter semantic and philosophical argument, but as far as I know no one can give a real proof, or even a good qualitative reason, as to why the ground or lowest energy states of almost all assemblages of atoms are regular rather than irregular in nature. For instance, in the simplest possible case of a box full of rigid spheres under pressure, everyone assumes for obvious reasons that the regular closest packing (cubic or hexagonal) has the smallest volume and therefore, under pressure, the lowest energy; but I know of no proof that that is so.

Landau has expressed this point of view (7): that the ground state of such a system must have some invariance group. After all, the initial Hamiltonian H_{el} + H_{nuc} is invariant under the full space translation and rotation group. In one case we know about—He_4 at low pressure—and possibly another—He_3—the ground state of the system as a whole retains the full translation and rotation group, although in the latter it may be only full translation symmetry that is maintained. In all other cases, the system condenses, by which we mean it chooses a still lower symmetry, namely a periodic space group. It is quite unreasonable in fact to expect a system starting from a Hamiltonian with the full translation-rotation group symmetry to have a lowest state with no symmetry at all. Perhaps it is a more interesting question why there are not more quantum liquids, not why there are no cases of glass-like lowest energy states. I feel this is an interesting point of view but hardly a convincing argument.

The second question may be one which present interest in solid He_3 and He_4 will see solved in at least an approximate way fairly soon, although I have never yet seen a satisfactory fully quantum-mechanical description of a solid, with all the zero-point motion adequately included, starting from a realistic description of the atomic interactions.

As far as the third question is concerned—how and why a solid holds itself together—I think we will give an adequate if approximate account when we come to talk about phonons and collective excitations.

Knowing then, as an experimental fact, that solids do exist, we can ask in general what sorts of solids there are and how one might classify them. There are a number of phenomenological ways of classifying solids—for instance, one which you may find most familiar is by symmetry, which is a rigorous mathematical way of going about it, and a most useful one, but not directly related to the binding forces and other physical properties of solids.

In Seitz' and Kittel's opening remarks one finds a classification which is much more to the point of this course, according to the type of chemical bond which, from a phenomenological point of view, is responsible for the binding energy of the substances. Seitz' classification contained five categories: (1) metals, (2) ionic crystals, (3) valence or covalent crystals, (4) molecular crystals, and (5) semiconductors.

By now we realize that in every real sense the distinction between semiconductors and metals o, valence crystals as to type of binding, and between semiconductors and any other type of insulator as to conductivity, is entirely artificial; semiconductors do not represent in any real sense a distinct class of crystal. To the remaining four categories Kittel added a fifth, of great interest from the point of view of dielectrics and ferroelectrics but otherwise not distinct in any very important way from molecular or ionic crystals: hydrogen-bonded crystals. Thus we have a reasonable classification into 5 types (see Table 1).

I note in connection with each type of crystal the most significant properties, which can in almost all cases be shown to follow from ideas about the forces which bind the crystals. I hope these connections may become clear to you in the course of these notes. Finally, it is significant to put down as a last column the areas of the periodic table in which each category occurs.

There is one noteworthy thing about this table of occurrences which is not discussed very often. If we look simply at the elements on the left- and right-hand sides of the periodic table: the elements, say Li and Na, with one extra electron in the s and p bands, or even at Al with one p electron, as opposed to those elements with one, two or even three holes in the p bands, we find that the former are metals where the latter tend to form molecular or at best valence crystals. One is so often led to believe in a fundamental symmetry between holes and electrons that it is worthwhile to point out that chemically they are quite dissimilar. Later on, in discussing magnetism, we shall find quite the same dichotomy between the behavior of a few holes in the d shell as opposed to a few electrons. The two types of phenomena may be related and will be discussed later.

It is also important to discuss the extent to which this classification fails. Naturally one can think immediately of a number of obvious cases in which the classification fails, but the principle still holds — e.g., the ammonium halides, $(NH_4)^+ Cl^-$, etc.; here the NH_4^+ is molecularly bound, the crystal as a whole ionic with a slight overtone of hydrogen bonding. The occurrence of molecule-like groups in ionic crystals is quite common.

More important and interesting by far is the existence of a range of substances, which, it is by now understood, completely fill in the territory between the three strongly bound categories of metals, ionic and valence crystals. For instance, let us start from NaCl, which is certainly almost purely ionic in nature, and increase the valency of the two constituents in the same row of the periodic table. MgS still remains in the typically ionic NaCl structure, and obeys most of the relationships one expects for an ionic crystal. AlP, on the other hand, is already a member of the group of semiconducting valence-like crystals of ZnS structure (zincblende) of III-V elements; more completely investigated are the closely analogous InP and AlSb. We all know that Si itself is a valence semiconductor par excellence. With increasing atomic number the true ionic crystals become rarer and rarer; ZnS

TABLE 1

Type	Type or "canonical" case	Cause of binding	Properties	Occurrence
Molecular crystals	Ne or N_2	Van der Waals attraction: Mutual polarization, an n-body effect	Resistivity R high. Binding weak. n^2(refr. index.) ϵ (diel.const.) low: electrons seldom mobile. Close-packed structures	(a) rare gases (b) lower, right-side elements: C, N, O, H, F, S, P, Cl, etc. *No electropositive, few heavy elements*
Hydrogen-bonded crystals	H_2O	Hydrogen bonds — lowering of K.E. of proton by O—H—O	Moderately weak binding ($\sim$10-100 × molecular); n^2, low, peculiar dielectric properties because of mobile p. Loose structures	Same as above except always contain H and an electronegative element. O, F etc.
Ionic crystals	NaCl	Ionic bond: Madelung potential + shell effects which make ionization energies right	Very strong binding, close-packed structures (rather), R high, n^2 low, ϵ high (ionic pol.), ionic conduction, low-mobility electronic conduction	Metal from left (electropositive) side—Na, K, Ca—with a right-side, preferably low at.-wt. element—O, F, Cl
Metals	Na, Al	Metallic bond — low K.E. of electrons because of free motion in metal	Moderate to strong binding, close packing, R low, dR/dT>0 (metallic conduction). Metallic appearance (=low-frequency absorption band)	Widest occurrence: to left of H, B, Si, As, Te; if no atoms to right it is a metal; it often is anyway. Combinations of elements at random usually metals
Valence crystals	Diamond	"Valence bond"—like bond of organic chemistry. Distinct in principle from metal?	Hard, strongly bound, loose-packed structures. High n^2 and ϵ. R variable, but high mobility conductivity	Rare but important. Low Z, central elements: C, N, P, Si, B are typical constituents

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itself, CdS, CdTe are all very valence- or even metal-like in character. Ca, Sr, and Ba, on the other hand, tend to retain their property of forming ionic-like oxides and sulfides — although one could explain this on the basis that the next orbitals available to them, those which are filled in their neighbors Sc and V, are d and not p orbitals and so are unsuitable for tetrahedral bonding — e.g., in terms of a valence crystal argument. It has been shown quantitatively that most of the alkali halides are pretty good ionic crystals in the sense that the charges on the two ions are pretty much ± 1, but otherwise the quantitative degree to which this is so, even in oxides, is very much in doubt. The silicates, for instance, typically crystallize in valence-like, not ionic, structures.

Even more disturbing is the fact that the distinctions between valence crystals and metals and between ionic crystals and metals are gradually losing their clear-cut character with our increasing knowledge of the broad and little-investigated field of intermetallic compounds. I cannot hope to give you a reasonable insight into this area because there are few clear ideas as to the quantum chemistry behind the bewildering variety of phenomena. One example will show how bad things can be, namely, the stoichiometric intermetallic compound NaTl(8). This is a metal with good conduction, not a semimetal, of a structure such that the Tl's form a diamond lattice, the Na's occupying the large interstices in the Tl lattice which themselves also form a diamond lattice. Since the Tl is such a relatively large ion, this is by no means a close-packed structure, in fact it is one to be expected of a typically valence-type crystal. The only way one can make sense out of that is to suggest that the Na's have ionized to Na^+, donating the odd electron to Tl which is now Tl^-, having an sp^3 configuration suitable for the diamond lattice. The fact that the Na is indeed ionized is confirmed by nuclear resonance evidence, the details of which I shall not discuss here. Thus we have in a single substance metallic conduction of a reasonable order, ionic charge-transfer, and an open, valence-type structure.

This then is a brief survey of the general features of the quantum chemistry of solids. I would repeat that I have made no attempt at completeness, even relative to Seitz' first chapter, in which he discussed, for instance, order-disorder, atomic-size relationships, and the Hume-Rothery alloys, subjects I pass over only because of lack of time, and because they are well treated in the literature, not because of their lack of interest and importance. I would emphasize that a whole area, that of intermetallic compounds, remains almost unexplored.

Another way in which the lines, at least between valence crystals and metals, have begun to blur is the general realization that the basic electronic structure of a valence crystal like Si, which can be a fairly good insulator, is not noticeably different, when looked at in a broad sense, from the electronic structure of a good metal. That is, when one studies the electrons with a tool such as plasma resonance or positron annihilation, which resolves electronic density distributions and the like only on the scale of volts —i.e., tenths of rydbergs —rather than tenths of volts, they resemble quite closely the free electron Fermi sphere, as is also true of many good metals. It is to be emphasized that the nature of the binding forces in such crystals has as yet not been amenable to calculation, so that we do not have a clear quantitative idea as to the sources of the binding energy and whether they are more valence- than metallic-like.

A few other ways of categorizing solids might be discussed broadly here. There is, for example, the question of their magnetic properties. The great majority of all solids are either diamagnetic or, in the case of a fairly large number of metals, slightly paramagnetic with little temperature dependence. There are, however, groups of substances in which there is evidence that the atoms in the solid state retain free, orientable spin and in some cases orbital magnetic moments. This may be evidenced by the presence of strongly temperature-dependent paramagnetism, increasing at low temperatures, or by the phenomenon of ferro- or antiferromagnetism—i.e., ordered arrangements of magnetic moments, occurring most often at reasonably low temperatures.

The widest occurrence of such moments is perhaps in the more or less ionic salts of atoms with unfilled shells of 3d, 4f, or 5f (or to a lesser extent 4d and 5d) electrons - the iron, rare earth, and actinide groups. The canonical example is MnF_2. It is a fair generalization that these are electrons which are in inner shells, in the sense that the bulk of their density is to be found inside the last maximum in the density of the outer, valence electrons. The occurrence or nonoccurrence of such moments in ionic crystals follows fairly well-known and well-understood rules of the quantum chemistry of ionic complexes.

Another category, the magnetic molecular crystals, solid crystals of organic free radicals, is, while of considerable interest to chemists, probably only worth a footnote here.

On the other hand, in crystals which are not so ionic—oxides and sulfides of earlier members of the 3d group such as Ti and V, or of 4d elements—the situation is by no means as clear-cut, as Morin has shown in a series of investigations (9), and the boundary between the magnetic and the nonmagnetic state is still being drawn and is not completely understood.

The situation in metals is even more confused. Here, aside from the f groups, in all but two known cases only substances containing one of the later members of the iron group—Mn through Ni—are ever magnetic. There are a large number of compounds (e.g., $CoSi_2$, almost the first superconducting compound of nonsuperconducting elements to be found) of magnetic elements which are not magnetic, but so far only two metals, $ZrZn_2$ and $ScIn_3$, not containing magnetic ingredients, are found to be magnetic. I need hardly say that the quantum chemistry of this situation is almost a complete mystery at this writing.

Another phenomenon, superconductivity, seems to give us a broad classification of metallic elements, alloys, and intermetallic compounds,[1] depending relatively little on structural details and in some broad way on the basic quantum chemistry. Superconductivity seems to be the rule rather than the exception among metals. One can in fact state the requirements for its occurrence thus: Practically the only islands of nonsuperconductivity among nonmagnetic metals occur at

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[1]As an alloy I will hereafter define a substance with some perceptible range of composition variation and thus presumably at least a partially random atomic arrangement; as a compound, a substance with a well-defined stoichiometry and atomic arrangement. It is convenient not to use the word alloy for the latter.

very small valence-electron to atom ratios — normally two or less and around a few elements in the sixth column — W (no longer Mo) and alloys of similar valence to atom ratio. Magnetic metals and semimetals are also not superconducting. Again the reasons for these rules are at best only qualitatively understood (10).