Electronic Theory for Materials Science

HENRY EHRENREICH

Some of the important ingredients used in theoretical investigations of the electronic properties of materials are delineated by means of examples. The importance of examining the physical behavior of related materials is emphasized as a means of establishing the credibility of theoretical explanations. Since the ability to deal realistically with complex technologically important materials is limited by analytic and computational capabilities, theories for materials science must aim at the development of comprehensive and predictive models based on physically motivated approximations. The emergence of such models and their ability to describe a broad range of properties foreshadows an increasingly important role of theoretical analysis in the future development of the field.

THEORETICAL MATERIALS SCIENCE REMAINS TO BE INVENTED as a discipline, and for good reason. Materials processing, historically speaking, was a craft. Experimental materials science replaced empiricism at a much later time. At present, theory, although important, continues to play only a supporting role. This article describes that role as it pertains to the electronic theory of materials by elucidating some of the important theoretical ideas and their applications to metals and semiconductors.

The theory for materials science is basically concerned with the systematization of experimental information about different classes of materials within a unifying theoretical framework. The theory deals with physical properties that depend on the details of the chemistry, structure, and perfection of real materials that have possible technological importance. Frequently the theory is "applications driven." The complexity of the phenomena or materials under investigation implies that (i) theory must be closely linked to experiment, (ii) ab initio calculations without approximation are virtually impossible except in model systems, (iii) approximations are frequently based on prior experience rather than on theoretical justification, and (iv) the study of trends in the properties of homologous materials is a crucial ingredient of a credible theoretical framework.

Electronic theory, at least, must deal with materials science problems on a microscopic quantum-statistical level. Such descriptions are increasingly characterizing metallurgical problems. Cottrell noted some 30 years ago that necessary ingredients in the definition of the metallic state in the metallurgical sense include a "theory . . . which explains the properties of metallic solids and the explanation of the origin of this structure from the structures of individual atoms" (*1*, p. 2). A similar microscopic approach will surely be important in the future for polymers, colloids, and ceramics.

Contributions to the theory for materials science are made by theoretical physicists, chemists, and engineers. Solid-state physics, as defined by the subject matter of Kittel's highly influential *Introduction to Solid State Physics* (*2*) or the *Solid State Physics* series of Seitz and Turnbull (*3*), has played a significant role. Theorists in materials science use a large repertoire of techniques that generally originate within the parent disciplines. The range of applications is broad. Significant contributions require an understanding of both experimental and theoretical results for systems ranging from practical to laboratory-produced materials.

Theory can play a predictive role or it can furnish the environment for discovery. Turnbull, in collaboration with Cohen (*4*), suggested the existence of amorphous metals before their discovery and Zener predicted the occurrence of the martensitic transformation in alkali metals (*5*). The ambient effect of applied theory is well illustrated by the invention of the transistor. A Bell Laboratory *Memorandum for Record* (1949) entitled "The Genesis of the Transistor" states (*6*, p. 98):

> Bardeen's theory afforded a means of investigating the electronic behavior of surfaces. . . . There was also the possibility that . . . electronic semiconductor amplifiers might become practical. . . . The phenomena which led up to the invention of the transistor were discovered in the course of this fundamental research program.

For the most part, pure (rather than applied) condensed-matter theory is concerned with the description of basic phenomena having a degree of generality that transcends chemical or other details. This is the case for the Bardeen-Cooper-Schrieffer theory of superconductivity. Other examples deal with the universality of critical exponents of second-order phase transitions and the precise determination of Planck's constant from the observation of the quantum Hall effect as observed in metal-oxide-semiconductor field-effect transistors (MOSFETs). Liquid crystals are of interest to the pure theorist precisely because many of their fascinating properties are essentially independent of the detailed molecular chemistry. The understanding and methodology developed during the course of fundamental investigations serve as an important input when dealing with materials science. In this mode the theorist tends to be a consumer rather than a producer of theories.

The present theoretical approach to materials science, as it applies to the equilibrium electronic properties of materials, is illustrated by the ingredients shown in the flow chart of Fig. 1. The first three rows specify the systems under consideration: first, in terms of their composition, structure, symmetry, and number of dimensions (as in one-dimensional wires, two-dimensional charge distributions in a heterojunction inversion layer, or three-dimensional alloys); second, in terms of order (crystalline, amorphous, quasi-crystalline); and third, in terms of the importance of electron-electron interaction energies relative to, say, bandwidths. The relative magnitudes of these effects determine whether the electrons are itinerant (that is, free to wander around the solid) or localized to lattice sites or to regions in disordered solids having unusually deep potentials. These effects are all subsumed in a Hamiltonian, which in principle can be written unambiguously. In practice the Hamiltonian requires simplification because many-electron and disorder effects can only be treated in approximate form (*7*). Conventional band and alloy

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The author is a professor in the Division of Applied Sciences and the Physics Department, Harvard University, Cambridge, MA 02138.

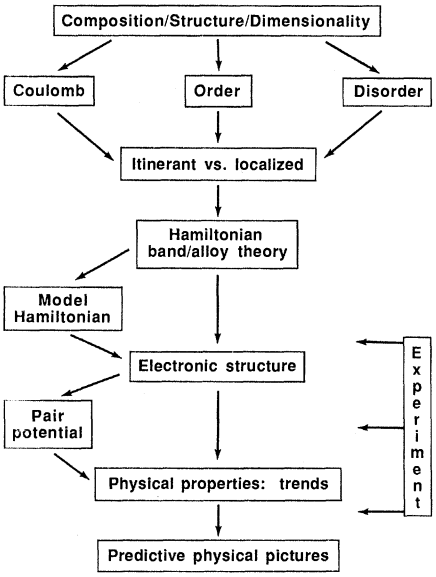

Fig. 1. Flow chart illustrating present-day approaches to the electronic theory for materials science.

theories, appropriate to itinerant electron systems, are applicable to many cases of practical interest. However, in instances in which the systems are chemically complex, highly disordered, or characterized by unusually large electron interactions, the electrons may be localized. The Hamiltonian then requires further simplification and the conventional techniques must be modified. Model Hamiltonians, for example, the Anderson Hamiltonian for localized magnetic moments, or that describing electron localization, focus on limited features of particular interest. Such Hamiltonians are useful since the problem can be pushed quite far analytically and limiting cases can be easily examined.

These considerations, together with experimental data, lead to the electronic structure (the band structure in crystals) that becomes the basis for theoretical investigations of the physical properties. For technical reasons such calculations can become difficult, particularly for structural properties of low symmetry such as cracks, dislocations, and stacking faults. The use of appropriate interatomic or pair potentials describing the interaction between pairs of atoms then becomes a virtual necessity.

The fundamental importance of examining trends in behavior among related materials has already been emphasized in connection with extracting physical information from complicated calculations. Thus, one ultimate aim of theoretical analysis must be the development of predictive physical pictures. Such pictures are beginning to emerge. Their predictive value foreshadows an expanding role of theory in the future development of the field.

Itinerant, Localized, and Interacting Electrons

In a paper presented at the 1928 meeting of the German Chemical Society, Sommerfeld stated (*8*, p. 593):

> Metals assume a peculiarly interesting position among all the materials with which the chemist deals. As in the past, we must still regard the existence of free electrons as characteristic of metals. According to recent calculations of Herzfeld, one can easily understand how the valence electrons experience an instability (*instabilen Zustand*) at high atomic densities and become dissociated from their parent atoms. It is therefore possible to predict which atoms assume a metallic character in the solid state.

Herzfeld's paper (*9*), which seems to have been largely forgotten, is instructive beause it shows how electrons tied to their lattice sites by springs according to the Lorentz insulator model become dissociated from these sites because the associated Hooke's law force vanishes as a result of polarization effects. The Drude free-electron model thus applies at metallic densities.

The itinerancy or localization of d electrons in $3d$ transition metals remained a controversial issue for over 30 years. In his classic 1928 paper (*10*), *On the Theory of Ferromagnetism*, Heisenberg discussed the possible models for describing exchange interactions. These are (i) the free-electron model introduced by Pauli (*11*) and Sommerfeld (*12*), (ii) itinerant electrons moving in a periodic potential, and (iii) electrons localized to lattice sites. He cautioned that "there are probably no a priori arguments for preferring any one of the approximation schemes. . . . I have chosen method (iii) because it alone permits a quantitative treatment of electron interactions" (*10*, p. 622). These cautionary remarks were frequently disregarded because of the success of the Heisenberg model in explaining magnetic phenomena. The itinerancy of d electrons was not fully accepted until Herring's incisive paper of 1960 (*13*).

The questions continue to be important for other materials. According to the Mott or Mott-Hubbard mechanism (*14*), an ordered solid is a metal or an insulator depending on whether the valence bandwidth is large or small, respectively, relative to the Coulomb energy among the involved electrons. Transition metals satisfy the metallic criterion; magnetic oxides such as CoO probably do not. (Band theory, on the other hand, is remarkably successful for many transition metal oxides.) Electrons in amorphous semiconductors may be Anderson-localized (*14*) or itinerant. The associated mobility edges are a consequence of the disorder in the material.

Electron interactions play a particularly important role in materials having dimensionality less than three, as for example, in surface states, in interfaces between materials, and in electronic conduction in thin wires. These features are of importance in microelectronic components. Electron interactions are also significant in materials containing actinide elements (for example, cerium and uranium) having partly filled f electron shells. These so-called "heavy electron" metals have exhibited a fascinating array of properties, including giant effective masses, superconductivity, and magnetism, which are still only partially understood (*15*).

Transition Metals: Trends in Cohesion

The technologically important properties of transition metals derive from the presence of the d shell. As indicated in Fig. 2, the electronic configuration of atomic copper and potassium differs only in that copper has a filled but weakly bound d shell whereas the d shell of potassium is empty. As a result a copper atom is only about half as big as a potassium atom, and its ionization energy is about twice as large.

These effects are most simply explained by means of the pseudopotential concept. This idea has had an enormous impact in explaining phenomena in both metals and semiconductors because it can be used to extract transparent physical pictures unobscured by heavy numerical camouflage. Although the idea dates back to Fermi's pseudopotential for nuclear scattering and other ingredients suggested by Herring's development of the orthogonalized plane wave method, its development, implementation, and subsequent widespread application are largely due to Phillips (*16*), Harrison (*17*), and Heine (*18*).

The orthogonality of valence $4s$ to core $3s$ eigenstates for both copper and potassium is associated with wave function oscillations in the core region. These oscillations imply a sufficiently large kinetic energy ($\propto |\nabla\psi|^2$) in the core region that one can assume a $4s$ electron to be entirely excluded from the rather small core. The resulting pseudopotential is shown at the bottom of Fig. 2. In the spatial

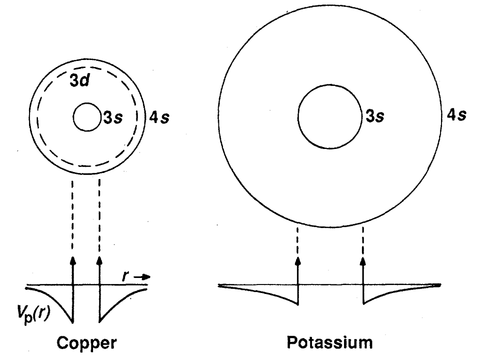

Fig. 2. Atomic and ionic radii of copper and potassium. The pseudopotentials $V_p(r)$ for each atom are sketched as a function of r, the distance from the nucleus. The atomic radii of copper and potassium are 1.28 and 2.35 Å, respectively; the corresponding ionization energies are 7.7 and 4.3 eV.

region permitted to the potassium 4*s* electron the potential is very weak. This fact explains why Sommerfeld's free-electron picture is valid for crystalline potassium. The presence of the *d* shell is responsible for the large cohesive energy, resistance to corrosion, magnetic properties, characteristic colors (copper and gold), and mechanical properties such as the tensile strength. The filled *d* shell of copper is neutralized by a more positive nucleus than that of potassium. The more attractive potential causes the core 3*s* radius of copper, which forms the repulsive "stop" for the 4*s* electrons, to be smaller relative to potassium. This effect leads to a stronger pseudopotential, a larger ionization energy, a smaller atomic radius, and reduced chemical reactivity.

An early and simple view of cohesion in the alkali metals is due to Wigner and Seitz (*19*). The atomic volume available to each potassium atom, represented by the spherical Wigner-Seitz cell, is smaller than that of the free atom. An electron placed in the field of a K^+ ion is therefore squeezed closer to the nucleus and the electrostatic attractive energy is increased. The energy of an atom in the solid is thus lower than that of an isolated one. Furthermore, since each atomic cell is automatically neutral, exchange-correlation effects are automatically included, but they are nuclear rather than electron centered.

This same idea can be applied to the transition metals by means of a straightforward generalization, termed the renormalized atom method (*20*). Each atomic cell is again replaced by a neutral Wigner-Seitz sphere. To construct the charge distribution appropriate to the solid, the atomic charge once again must be renormalized, that is, compressed into the sphere. The steps to be used in this process are illustrated for titanium in Fig. 3 (*21*). The cohesive energy can be visualized by examining the development of the full crystalline density of states beginning with the free atom. First, the atom must be prepared in the $d^{n-1}s$ configuration appropriate to the solid; second, the charge must be renormalized; third, the conduction band must be allowed to broaden; fourth, the same must happen for the *d* levels; finally, the conduction and *d* bands must hybridize. The atomic preparation steps (Fig. 3, A to C) make an unfavorable contribution to cohesive energy, whereas the remaining steps consisting of conduction- and *d*-band broadening and hybridization (Fig. 3, D to F) make an overwhelmingly favorable contribution. The lower and upper portions of the *d* band contain electrons that are, respectively, in bonding and antibonding states. The cohesive energy peaks near the middle of each of the 3*d* or 4*d* rows when the bonding *d* states are just filled, a fact recognized early by Friedel (*22*). The theoretical results shown in Fig. 4 illustrate how trends in band broadening and *s*–*d* hybridization explain cohesive energies (*21*). [State-of-the-art calculations are reported in (*23*).]

Bonding, Structure, and Energy Gaps

The physical picture just described for cohesion of transition metals is convincing beause it explains the expected trends in the 3*d* and 4*d* rows of the periodic table. A variant of these chemical bonding-antibonding and hybridization models appears in different guises in other classes of materials. These variants have the common feature that the energy of atoms in the condensed state is lower than that of the same atoms in isolation because new physically identifiable occupied electron states are created. This idea finds its simplest expression in covalently bonded solids. Other examples include the following:

1) *Refractories.* Materials such as the transition metal carbides owe their refractory properties to strong covalent bonding between the transition metal *d* and carbon 2*p* electrons. This results in a sharp peak in the density states below the Fermi energy of the metal, separated energetically from an empty antibonding band (*24*).

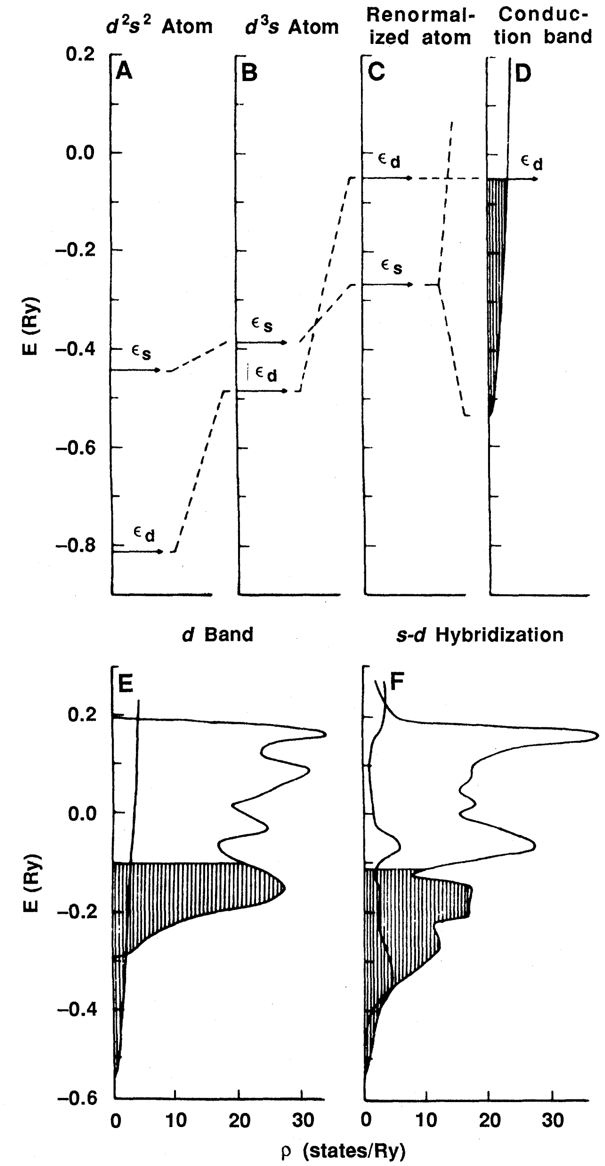

Fig. 3. Schematic electronic states for titanium at various stages in the development of the crystalline density of states, ρ, according to the renormalized atom method. (**A**) 4*s* and 3*d* levels ϵ_s, ϵ_d in d^2s^2 atomic ground state; (**B**) the same levels in d^3s atomic excited state involved in solid formation; (**C**) the same levels in the renormalized atom; (**D**) conduction band and (**E**) *d*-band broadening due to interatomic interactions in the solid; (**F**) the fully developed density of states including *s*–*d* hybridization. [From (*21*)]

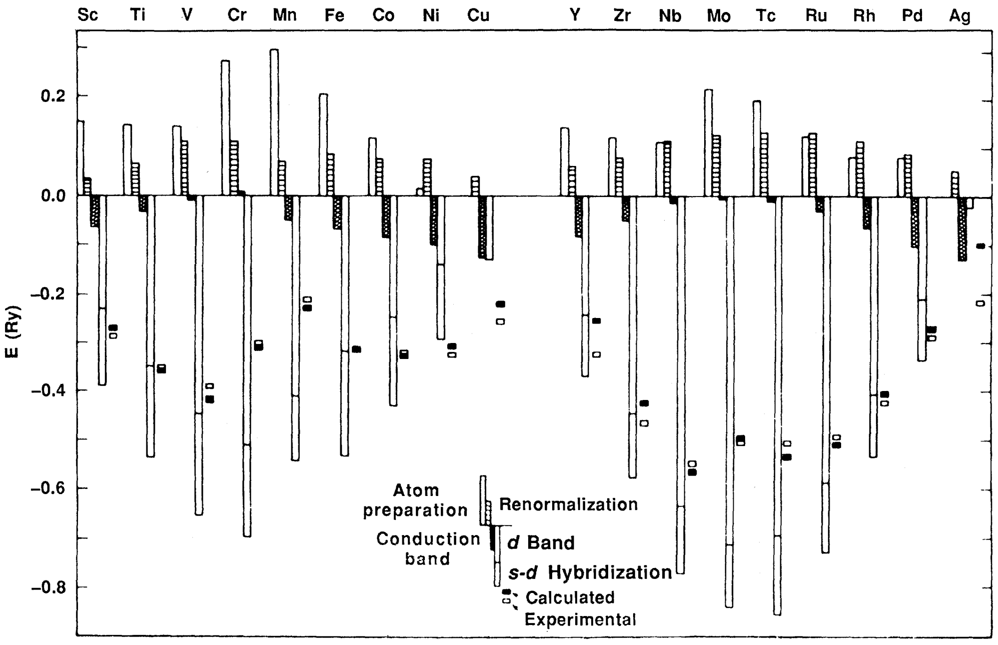

Fig. 4. Contributions to the cohesive energy for the 3*d* and 4*d* transition metals from atomic preparation, renormalization, *d*- and conduction-band broadening, and hybridization. For the 4*d* metals in particular, *d*-band broadening makes the dominant contribution to cohesion. This explains the trend that causes the heat of formation to be a maximum in the middle of the row. [From (*21*)]

2) *Hydrides.* One of the principal ingredients contributing to cohesive formation of 3*d* and 4*d* transition metal hydrides is the formation of a low-lying metal-hydrogen bonding band (*25*).

3) *Vacancy stabilization.* Although the presence of vacancies in solids is usually associated with entropic stabilization, it is possible for vacancies to lower the total energy through the creation of defect states below the Fermi level. In TiO, whose nominally stoichiometric form has about 15 percent vacancies on both sublattices, the energy is lowered because vacancies produce defect states. These states are probably associated with clusters of titanium atoms or anions, separated by vacancies, which appear in the gap between bonding *d–p* states and their antibonding counterparts (*26*).

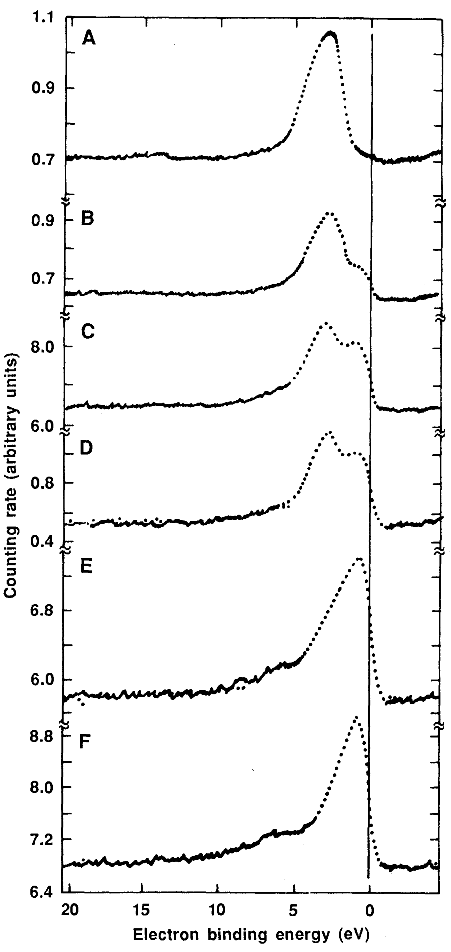

Fig. 5. X-ray photoemission spectra for (**A**) Cu, (**B**) $Cu_{0.74}Ni_{0.26}$, (**C**) $Cu_{0.46}Ni_{0.54}$, (**D**) $Cu_{0.44}Ni_{0.56}$, (**E**) $Cu_{0.12}Ni_{0.88}$, and (**F**) Ni as a function of electron binding energy relative to the Fermi energy. The structure observed experimentally closely reflects that of the electron density of states. Note that the copper *d*-band peak shrinks and that of nickel grows with increasing nickel concentration without shifting in energy. [From (*29*)]

4) *Hume-Rothery alloys.* Transitions between phases of certain alloys occur when the Fermi surface makes contact with the Brillouin zone boundary. The contact-induced energy gaps make the addition of further electrons energetically unfavorable and cause a change in crystal structure. The constituent concentration in copper-zinc alloys corresponding to the α, β, γ, and ε phases is well predicted by this rule (*2*).

5) *Dichalcogenides.* Transition metal dichalcogenides such as $TaSe_2$ and TaS_2 have layered structures, much like superlattices. As the temperature is lowered, they undergo structural transformations (Peierls distortions) due to the formation of charge-density waves that produce energy-lowering gaps (*27*).

6) *Ferroelectrics.* The occurrence of a soft optical phonon at sufficiently lower temperatures permits a point symmetry-lowering lattice distortion which depresses the electronic energy by splitting degenerate levels (cooperative Jahn-Teller distortions), thereby causing spontaneous electric polarization (*27*).

The last two examples differ qualitatively from the preceding ones in their explicit dependence on temperature. In these cases it is not sufficient to deal simply with enthalpies obtained from electronic structure calculations. Since calculations of the appropriate free energy involve difficult entropy estimates, the phenomenological but exceedingly versatile Ginsburg-Landau theory is frequently used (*27*).

Electronic Structure of Alloys

Early alloy theories tended to be based on empirical extrapolations of crystalline electronic structures. An example is that of the Hume-Rothery rules for alloy phases cited above. Slater formulated the so-called rigid band model for transition metals. This model (*28*) assumes that all 3*d* metals are characterized by a common density of states filled to the appropriate Fermi level determined by the number of available electrons. The density of states is much like that shown in Fig. 3E or like that seen in the x-ray photoemission spectra (XPS) of Fig. 5 (*29*). In copper, for example, the Fermi level would lie about 2 eV above the *d* level, thereby accounting for the characteristic color of the metal in terms of optical excitations of the upper *d* band. The ferromagnetism of nickel is due to the Fermi level position in the large density of states of the *d*-band complex. The overall success of the model is fairly limited. The virtual crystal model, in which the potential for the substitutional alloy is regarded as a weighted average of the potentials associated with its constituents, is also of limited applicability.

The coherent potential approximation (CPA) is based on a multiple scattering description of electrons in random media (*30*). The underlying formalism goes back to Lord Rayleigh and Ewald. It is also fundamental to the so-called "muffin tin" band theories. In alloys it accounts for many physical properties. The theory is exact for dilute alloys of arbitrary alloy scattering strength and for concentrated alloys having weak scattering strength. The mean field approximation, which is used in many practical formalisms pertaining to materials science (including the Ginsburg-Landau theory), interpolates between these limits and yields semiquantitative results that are valid for all concentrations and scattering strengths. The differing predictions of the three theories are illustrated by reference to the XPS data for copper-nickel alloys shown in Fig. 5. With increasing nickel concentration the peak associated with copper *d* electrons is seen to shrink, and a higher peak due to nickel *d* electrons is seen to grow. By contrast, the rigid band and the virtual crystal model both predict a single peak that shifts upwards from its position in copper relative to the fixed Fermi energy. The CPA yields the correct "split band" behavior observed in the experiment.

Theoretical Chemical Approaches

In contrast to the *k*-space methods that have been the mainstay of band theory, quantum chemistry generally utilizes real-space approaches such as the tight-binding method (*31*) that are particularly well suited for organic molecules and chemically or structurally disordered solids. Because of their simplicity, tight-binding and pseudopotential techniques can be applied to relatively complex problems. The fruitfulness of these techniques to the theory for materials science is well exemplified by Phillips' *Bonds and Bands in Semiconductors* (*32*) and Harrison's *Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond* (*33*).

In one recent example, the electronic structure of the group II-VI semiconductor alloy HgCdTe, important in far-infrared detectors, and closely related materials such as CdMnTe (termed "diluted magnetic semiconductors" because of their interesting magnetic properties), has been explored with the use of an empirical tight-binding approach (*34*). The tight-binding parameters are drawn from atomic and experimental information based on constrained empiricism.

Figure 6 shows the valence and conduction bands of HgTe, CdTe, and hypothetical zincblende MnTe. HgTe has a "negative" band gap, which becomes positive and larger as cadmium is substituted for mercury. MnTe contains a weakly bound occupied *d* band as in transition metals. In all of these materials, the upper valence band region has predominantly tellurium *p* and the lowest conduction band has largely cation *s* character. The increasing band gap is associated with the rising cation atomic *s* levels (also shown in Fig. 6). The upper valence band edge, associated with tellurium 5*p* states, in all cases remains essentially constant, in agreement with the still controversial common-anion rule. At a given site the manganese 3*d* levels are spin split with only the lower states of spin σ occupied. the spin states $-\sigma$ at the same site are higher by an energy corresponding to the Hubbard intrasite Coulomb energy, U_{eff}, and are unoccupied. These states hybridize with the valence states, thereby acquiring an appreciable bandwidth. The valence bandwidths can be determined either by using Harrison's empirical tight-binding parameters listed in his "Solid State Table of the Elements" (*33*) or by means of more sophisticated methods (*34*). This approach permits not only the identification of salient features of the electronic structure on the basis of a simple physical picture, but also the quantitative calculation of delicate properties such as exchange interactions (overwhelmingly antiferromagnetic and resulting largely from manganese *d*–valence band hybridization) and the prediction of trends in related manganese-based semiconductors and insulators. The chemical approaches are also well suited for examination of the separate and combined effects of the chemical, structural, and magnetic disorder (*35*).

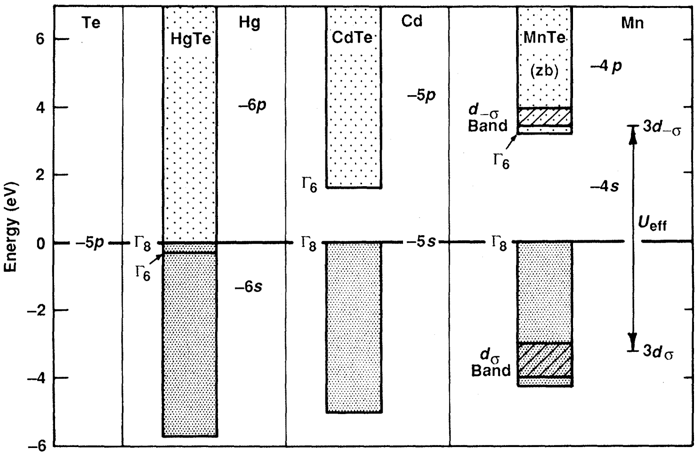

Fig. 6. The tight-binding calculated upper valence (heavily stippled) and conduction (lightly stippled) bandwidths for HgTe, CdTe, and hypothetical zincblende (zb) MnTe relative to the tellurium (Te), mercury (Hg), cadmium (Cd), and manganese (Mn) *s* and *p* atomic energy levels. The energy zero corresponds to the valence band maximum in all three crystals, and Γ_6 and Γ_8 denote symmetries of the wave functions at the band edges. The d_σ and $d_{-\sigma}$ manganese bands are indicated by the hatched areas. The occupation of a $d_{-\sigma}$ level on a given manganese site exacts a Coulomb energy penalty of $U_{\mathrm{eff}} \approx 7$ eV. The $d_{-\sigma}$ band is therefore part of the conduction band complex. Note the approximate coincidence of the tellurium 5*p* level with the valence band maxima and the concomitant rise of the conduction band minima and of the relevant atomic energies in the progression Hg (6*s*), Cd (5*s*), and Mn (4*s*).

Trends in Physical Properties

The importance of explaining physical trends has already been underlined in the examples of the cohesive energy of transition metals and band gaps in group II-VI semiconducting alloys. The ubiquitousness of this approach to the theory for materials science deserves further emphasis. Other examples include the following:

1) *Ionicity and structure*. Phillips (*32*) has provided a modern definition of ionicity in semiconductors that is firmly based on pseudopotential theory. Covalent and ionic potentials lead to average bonding-antibonding band gaps $E_g = E_h + iC$, where E_h and C are energies associated, respectively, with covalent and ionic effects. These three quantities, which are expressible simply in terms of pseudopotential parameters, can be used to define the covalent and ionic band character. The more ionic solids (for example, NaCl) crystallize in the rock salt structure whereas the more covalent solids (for example, GaAs) crystallize in the zincblende (or wurtzite) form. Phillips utilized his definition of ionicity to predict the structures of 68 compounds without error.

Trends in the structure of metals, alloys, and semiconductors have been discussed comprehensively by Heine and Weaire (*36*) who also used a pseudopotential viewpoint. Further contributions to the theory of structural trends have been discussed by Pettifor (*37*).

2) *Solid-state table of the elements.* Harrison (*33*) has constructed a widely applicable set of parameters that make possible tight-binding calculations for a range of materials involving virtually every element in the periodic table. The input consists of atomic energies, ionic radii, and pseudopotential core radii. Interatomic matrix elements are obtained by simple scaling rules and adjustments to optimize agreement with ab initio band calculations. As already noted, these parameters have yielded semiquantitative physical results. Important among these results are the still controversial values of valence and conduction band offsets in semiconductor superlattices (*38*).

3) *Miedema scheme.* The Miedema scheme (*39*) applies to the heat of formation ΔH of many solid binary alloys consisting of a transition metal, and a transition, alkali, or alkaline earth metal. It predicts successfully both the size and the magnitude of ΔH in terms of just two parameters, the work function and the electronic charge density at the metallic Wigner-Seitz radius. The atomic constituents are regarded to be macroscopic pieces of metal. The two parameters are chosen in a consistent manner, but not necessarily in agreement with the values in the solid. A recent analysis by Pettifor (*40*) suggests that these parameters must be regarded as purely phenomenological because the picture of macroscopic atoms, as originally proposed, is not supported by the quantum theory of alloys. This fact does not undermine the practical utility of the scheme when applied as Miedema intended.

4) *Excitation and ionization energies of impurities in semiconductors.* Insight concerning band theory, many-electron effects, and lattice relaxations has been combined to provide an impressive description of the chemical trends exhibited by most of the technologically important impurities in well-studied semiconductors (*41*).

Prospects

Despite uncontrolled approximations inherent in the theoretical treatment of electron interactions (*7*), it is now possible to describe most electronic and derived physical properties on a reasonable quantum mechanical basis in the simpler crystalline metals and semiconductors. One of several possible exceptions concerns the existence of spin-density waves at low temperatures in potassium. This idea, due to Overhauser, has recently received strong experimental support (*42*). The electronic properties of many substitutional alloys having structural, chemical, or magnetic disorder have also been reasonably explained. The degree of detail that is achievable depends on the complexity of the material. Thus, in descriptions of metallurgical alloys or ceramics of practical importance, the theory (if any exists) is likely to be substantially phenomenological. This is the case for brittle and ductile fracture, where continuum mechanics continues to play a leading role (*43*). In the future, the theory for materials science must bridge that gap.

Many of the important phenomena in condensed matter (including its formation) occur at finite temperatures. The earlier discussions of heats of formation and equilibrium structures presented here have been largely based on quantum mechanics alone. Little has been said about free energies and alloy phase diagrams. The fundamental calculation of entropic terms or partition functions is difficult and is only in its beginning stages (*44*). The important omission in Fig. 1 is the absence of statistical mechanics.

State-of-the-art calculations are sufficiently advanced that stable structures of simple solids can be predicted with a high degree of confidence (*45*). It is quite another matter, however, to predict the stable structure of an organic solid given only the composition and structure of the constituent molecules, or, for that matter, of a quasicrystal (*46*) given only the structure of the basic cluster.

Theoretical predictions of phenomena that are presently unobservable for technical reasons have been important. It has been possible, for example, to calculate the theoretical tensile strength of copper (*47*) and other materials. More recently, Freeman and collaborators (*48*) predicted that the structural transition to a metallic hexagonal close-packed phase in solid hydrogen occurs at 4 ± 1 Mbar. Theoretical inputs of this sort enable the metallurgist to assess the amount of effort worth expending in improving the strength of a material, or the high-pressure physicist to define the specifications of the required apparatus. Other theoretical inputs concern the utility of "man-made" structures such as superlattices, the size limitations of MOSFET gates, and the maximum efficiency of photovoltaics. Such examples will undoubtedly proliferate in the near future.

The computer in its present most advanced form, and as used in the conventional ways dictated by fundamental quantum theory, has limitations. Although there is a great deal of physical understanding of the atomic reconstruction of a solid surface such as the 7×7 pattern on [111] silicon (*49*), or the close-packed surface layers of [100] gold (*50*), ab initio calculations have thus far been computer limited. (For N atoms, the required computer time is roughly proportional to N^3 and becomes unfeasibly large when hundreds of atoms must be considered.) If there were to be no substantial breakthroughs in computer design (an unlikely happening), it would clearly be necessary to devise other perhaps less fundamental and less computer-demanding theoretical approaches.

Sophisticated pair potentials, including terms designed to simulate the effects of many-body interactions, are now being developed and applied to such problems (*51*). These time-honored approaches are useful also in applications to chemisorption, which is basic to heterogeneous catalysis, and a number of other surface and interface related phenomena. Present-day interatomic force methods are particularly promising in computer simulations.

Dynamic phenomena, such as crack propagation in solids, can be highly nonlinear. Substantial analytic progress on this and related problems on a microscopic level would be surprising.

In view of the complexity inherent in some of the materials and phenomena mentioned above, it is clear that the approach suggested in the last two entries of Fig. 1 should not be neglected because of the attraction of large-scale computation. The understanding of chemical and physical trends in simpler materials must be imaginatively combined to construct predictive physical models that apply to more complex systems. Some of these physical pictures will, in fact, derive from the results of supercomputer calculations on simpler materials. However, given the technical limitations of such calculations, the materials problems to be addressed in this fashion should be chosen to have optimal synthetic (rather than archival) value.

As Wigner and Seitz stated in 1955 (*52*, p. 97):

> If one had a great calculating machine, one might apply it to the problem of solving the Schrödinger equation for each metal and obtain thereby the interesting physical quantities. . . . It is not clear, however, that a great deal would be gained by this. Presumably the results would agree with the experimentally determined quantities. . . . It would be preferable instead to have . . . a simple description of the essence of the factors which determine cohesion and an understanding of the origins of variation in properties from metal to metal.

The same is true more generally today for the materials driving advanced technology.

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