Solid-State Chemistry: A Rediscovered Chemical Frontier

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Chemical bonding in solids is not completely understood, mainly because of the wide variation in the chemical properties of the elements. Many difficult challenges remain in predicting the composition, structure, and the properties of new materials. Consequently, the synthesis of novel solids is as much an art as a science. Discoveries of new compounds and structure types highlight the versatility that nature has allowed with the relatively small number of elements. This article explores the long-term challenges in solid-state chemistry and then focuses on efforts at Cornell to prepare new solids.

THE PREPARATION AND EXAMINATION OF NEW SOLIDS HAS led to technological advances as well as enormous progress in our understanding of materials properties (*1*). These include now commonplace devices and phenomena such as transistors and integrated circuits, lasers, superconductivity, supermagnetism, and high-strength materials. In the laboratory, hints of some future advances can already be seen. For example, as discussed later in this article, we can prepare very thin wires with diameters of only atomic dimensions. Can we invent ways to use them? As another possibility, consider high-temperature superconductors (*2*). Their advent caused considerable excitement that has abated somewhat because the properties of the superconductor are not what was initially expected. Can we find better materials with improved properties? Will we find room-temperature superconductors?

It is both recent discoveries, such as high-temperature superconductivity, and the expectation of future new discoveries that have contributed to a resurgence of activity in the synthesis of new solid compounds, a central activity in the field of solid-state chemistry. However, this article is not a review of the field of solid-state chemistry, as the field is too broad for me to give a balanced presentation in one article. Further, recent reviews of exciting advances in solid-state chemistry are readily available [(*2*) and the other articles included in this issue of *Science*]. Indeed, the field is large enough that journals devoted exclusively to a particular subtopic in solid-state chemistry are published (*3*). This article, therefore, was written with two objectives in mind. The first is to outline several major long-term challenges in the field, barriers that prevent us from being able to design and predict new families of solid-state compounds. The second is to further illustrate some of these topics by giving a review of current research directions in a few selected areas not covered by other articles in this issue. In the latter case, I draw heavily on my own research.

Solid-State Materials

It is convenient to divide solids into two groups based on the kinds of bonds that hold the solid together. Molecular solids consist of small groups of atoms (molecules) within which the interatomic bonds are strong, but between which the bonds are weak. These weak intermolecular bonds, known as van der Waals bonds, are manifest in the bulk solid by the small mechanical strength of the material. For example, substances such as candle wax are molecular solids and can easily be broken by hand. The second group of solids are called "extended solids." In these materials strong covalent or ionic bonds connect one atom to the next in a continuous network from one side of the solid material to the other. Although both kinds of solids are of considerable scientific and technological interest, I will only discuss extended solids.

Some solids fall between these two simple categories of materials. Polymeric solids are molecular, but the molecules are very long chains of covalently bonded atoms. As the polymer chains become longer and as cross-linking between chains is introduced, the solid behaves less and less like a molecular solid. Indeed, an extended solid may be thought of as one giant polymer molecule with cross-links at every atom. Consequently, we may describe diamond as the "ultimate" carbon-based polymer. Other solids, known as low-dimensional materials, show strong bonding in one or two dimensions only, with weaker van der Waals bonding in the remaining dimensions. Examples of such low-dimensional materials include micas, clays, and graphite. In the latter part of this article, I will discuss a few solids of this type.

Unresolved Issues and Long-Term Problems

The chemistry of extended solids is perhaps the oldest chemical science, beginning perhaps with the firing of clay pots in prehistoric eras or certainly with the smelting of ores in the bronze age. Yet many basic principles and concepts that serve well other branches of chemistry, such as organic chemistry, are lacking or only apply to a small fraction of solid-state compounds. These include the ability to understand and predict composition (stoichiometry), structure (the geometrical arrangement of atoms in a compound), and reaction pathways or reaction "mechanism" (the evolution of the formation of the structure). In general, our predictive ability is almost nonexistent, except in the simplest cases of substitution of chemically similar elements. It is the lack of predictability of these "simple" factors that considerably slows the pace of advance in solid-state chemistry. At the same time, this lack of understanding is a source of not only great challenge, but also of surprise, wonder, and excitement about the intricacy of nature. Thus, the science of solid-state chemistry includes elements of "art," such as intuition and insight based on experience rather than the use of predictive models. We next

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consider these three topics, composition, structure, and reaction mechanism, in more detail.

One of the greatest accomplishments of the early chemists was the development of the law of definite proportions, which states that the ratio of the number of atoms in a compound is always expressible as the ratio of integers (usually small integers). Later, on the basis of electron counting or more sophisticated quantum mechanical ideas, valence and oxidation-state rules were developed to help explain and predict the composition of both molecular and extended compounds. In extended solids these rules work reasonably well only for what are called "normal valence compounds." These are compounds that contain electronegative elements, those from the right side of the periodic table, combined with electropositive (metallic) elements from the left side of the table (Fig. 1). Although three quarters of the elements in the periodic table are metals, only a handful are quite electronegative. As an example of these rules, consider simple binary compounds, those that contain only two elements. Consider the metallic element vanadium and the electronegative element oxygen. Vanadium has five valence electrons; it will use some or all of them in ionic or covalent bonds to make a specific compound. Oxygen wants to gain or share two electrons. The compounds that vanadium commonly forms are V_2O_5, VO_2, V_2O_3, and VO. Oxidation state rules tell us to count the oxygen as O^{2-} and that to balance the oxidation-state "charges," the vanadium must be V^{5+}, V^{4+}, V^{3+}, and V^{2+} in the above compounds, respectively. The vanadium cations so formed give up (or share) five, four, three, or two electrons, respectively, to (with) the oxygen anions. The oxidation state rules then "explain" the occurrence of these compounds.

Other compositions (stoichiometries) of vanadium and oxygen also can be prepared, but these can be simply understood as compounds containing two different kinds of vanadium, each in a different oxidation state, so that again the total negative charge on all the oxygen is balanced by the total positive charge on the vanadium. For example, V_6O_{13} contains one V^{5+} and four V^{4+}. In those cases the crystal structure clearly shows two (or more) different vanadium sites that are differentiated by the number or arrangement of nearest neighbor oxygen atoms, or both. This possibility of variable valence, along with other phenomena unique to extended solids, such as the possibility of extensive vacancy formation (a missing atom from a normally occupied position in the structure), allows for the preparation of important classes of solids called nonstoichiometric compounds. Nonstoichiometric compounds do not have a fixed ratio between the numbers of atoms in the chemical formula; in fact, the ratio may be continuously variable over some range. For example, ferrous oxide has a variable composition, FeO_x with $1.05 < x < 1.13$, that does not include the stoichiometric composition $x = 1$. The possibility of forming nonstoichiometric compounds is unique to solid-state compounds, and it is never observed in molecular materials. It is fortunate that few of these compounds were known to early chemists, because ideas important to the formation of the science, such as the law of definite proportions, would not have carried the day and the progress of chemistry would have likely been delayed. Now we know that the law of definite proportions only applies to some compounds, and we understand why.

In contrast to the normal valence compounds, there are no general rules that predict or make understandable the stoichiometries of intermetallic compounds (compounds containing only metallic elements). For example, consider the binary compounds of the transition metals nickel and zirconium. They are Ni_5Zr, Ni_7Zr_2, Ni_3Zr, $Ni_{21}Zr_8$, $Ni_{10}Zr_7$, $Ni_{11}Zr_9$, NiZr, and $NiZr_2$. Why do these stoichiometries occur and why are there not other possibilities? There are many other examples of simple binary compounds that illustrate the point, such as Ca_3Cd_2, CaCd, Ca_2Cd_7, Ca_3Cd_{17}, and $CaCd_6$ or Nb_3Ga, Nb_5Ga_3, Nb_5Ga_4, Nb_4Ga_5, Nb_5Ga_{13}, $NbGa_3$, and $NbGa_4$. As seen above, different binary pairs usually have different sequences of stoichiometries. For elements that are closely related to one another, some regularity does exist. For example, hafnium is chemically very similar to zirconium and it forms a similar series of compounds to Ni-Zr, except that it contains one more compound, Hf_3Ni_7. Why this occurs is unknown. Our ability to understand the composition of more complicated intermetallic compounds, those containing three metals (ternaries), four metals (quarternaries), or even more elements, is essentially nonexistent.

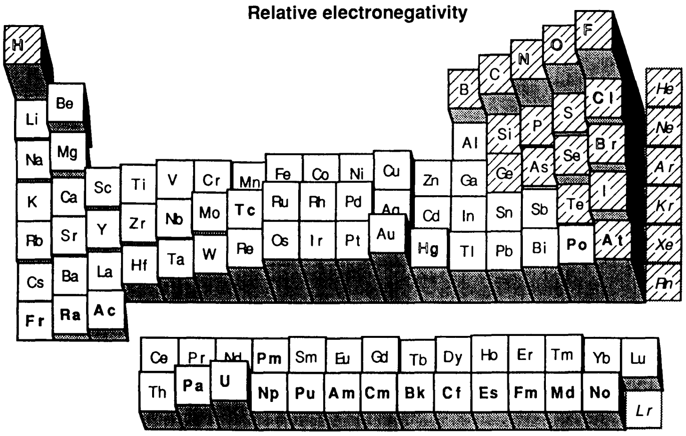


Fig. 1. The periodic table shows the approximately 100 elements from which all possible new compounds will be prepared. Combinations of only five elements theoretically could lead to many billions of new materials, many more than the perhaps few hundred thousand known solid-state compounds. The electronegativity of the element is indicated by height. The electronegative elements are found in the upper right-hand corner and the electropositive elements are on the left (with the exception of hydrogen). The elements marked by hatching are nonmetals; the remainder are metals (good conductors of heat or electricity).

Even in the case of normal valence compounds, where the composition of particular ternary or quaternary compounds can be understood from valence rules, our ability to predict the existence of new compounds is limited. One may be able to write hypothetical formulas for compounds that satisfy these rules, but, by present methods at least, one may not be able to prepare them. Although we may have general arguments that suggest why they cannot be prepared, in specific cases we cannot predict what will happen.

The crystal structure of extended solid-state compounds is an issue closely related to composition, but requires more detailed knowledge. In practice, we are able to experimentally determine the structure of a new compound by x-ray diffraction but are unable to predict it, unless the "new" compound is in fact a "derivative" compound obtained by replacing one or more elements by chemically similar elements. The prediction of new structures is virtually impossible by present techniques. For example, the new high-temperature superconductor $YBa_2Cu_3O_7$ adopts a structure that had never been observed in any other material. No scientist has yet claimed that such a structure could have been predicted. Even less so could anyone claim that high-temperature superconductivity was predictable in such oxide compounds.

This situation, especially with regard to the prediction and control of composition and structure of extended solids, is in great contrast to fields such as organic chemistry or even biochemistry. In those fields there is a "rational synthesis" strategy based on the nature of the covalent bonds between carbon and itself or a few other elements such as hydrogen, oxygen, nitrogen, and the like. These bonds have characteristics (such as number of bonds per atom, bond energy, bond length, and bond angles) that are essentially constant from one molecule to another. Thus the structure, and often the reactivity, of an enormous family of organic materials can be predicted with considerable confidence. In contrast, extended structure compounds can be prepared with virtually any element in the periodic table, so that bond strengths vary from moderate to very strong. The bond types also vary from mostly ionic to completely covalent. Likewise, bond lengths, bond angles, and the number of bonding near "neighbor atoms" in different structures vary considerably. In the last case, for example, the number of near neighbors may be as low as 2 or as high as 24 or more; considerable variability may be seen for the same element. It is in part this large range of possible bonding characteristics of the elements that makes the prediction problem so difficult and the chemistry so exciting.

Another central concern of chemistry is the reaction mechanism. In the reaction of solids there are two steps in the reaction kinetics: the atoms must first diffuse through the solid reacting material to reach an interface between different reactant particles where reaction can take place, and then the atoms must rearrange themselves into the new structure. We presently understand quite a bit about diffusion mechanisms and the relatively slow diffusion rates. However, again in contrast to other branches of chemistry, the mechanism by which reactant atoms initially rearrange to form the product structure is almost completely unknown. This is in part due to experimental difficulties. Reaction between solids takes place at the interfaces between the reactant solids (the places of intermaterial contact). During a reaction this interfacial region is usually obstructed by the as yet unreacted material in the sample, making direct observation of the reaction zone difficult or impossible. It is especially difficult to obtain information about atomic scale processes at this interface, although methods such as Rutherford backscattering presently allow in situ studies of reaction interfaces in films of materials with a resolution of perhaps 50 Å (*4*).

This lack of knowledge about mechanism makes it difficult to know why a new compound with a new composition does not form in a particular synthesis experiment. The problem may be thermodynamic (that is, formation of the compound may not produce the lowest energy state of the system), or it may be kinetic (that is, under the conditions of synthesis the atoms do not have the required energy or local concentrations to rearrange into the desired product). The latter problem is expected to become increasingly important as the number of elements in the compound increases. For example, a compound containing five different elements can only be formed if the five elements come together in the correct concentration (possibly in sequential steps) in an atomic-sized volume. This is likely to be difficult under most conditions of solid-state reactions.

The chemistry of solids has largely been the chemistry of thermodynamically stable phases. This is the result of the high temperatures used in synthesis to obtain reasonable diffusion rates and to promote atom rearrangement. The great richness of carbon chemistry, for example, is thus not possible with most other elements. Most organic compounds are only metastable; that is, for a given composition there are many possible structures, or isomers, with similar total energies, but with large enough thermal barriers to forming the most stable structure that near room temperature the different isomers are retained. Solid-state chemists have for some time been exploiting low-temperature solution techniques to prepare known oxide materials of commercial interest, such as zeolites (*3*) or ceramics (*5*). Occasionally, particular materials can be prepared from the gas phase at low temperatures. Producing diamond films at low temperatures from methane gas (*6*) is a good example of the latter approach. These methods overcome the diffusion problem inherent to the reaction of solids at high temperature by either having the atoms already mixed on the atomic scale in the correct stoichiometry or by adding the atoms to the solid one at a time from the gas phase. In the former case, precursor molecules are designed with appropriate "leaving groups" that are rejected by the material as the new extended structure grows. In contrast to this work on commercially important solids, relatively little work has focused on the preparation of new or metastable solid phases that might be expected to result from such low-temperature chemistry.

Although I have been emphasizing what we do not know, this is not to imply that little is known about the nature of solids. There is a large body of empirical data that can be organized by families of compounds, such as oxide materials, within which regular features are usually observed. Within these families, and especially within a group of compounds with the same structure, chemists can modify the composition in a predictable manner by chemical substitution, intercalation (insertion of extra atoms into a host structure), or other methods. That ability is very important when the object is to modify a particular property of a known family of materials to optimize technological performance, at least within that group of materials (*1*). There are also a few examples of materials design where desired structural and chemical characteristics can be rationally planned for and controlled. For example, zeolites are compounds based largely on silicon, aluminum, and oxygen (*3*). They have porous structures into which molecules of specific geometries may be inserted; they are very important commercial catalysts. Zeolites are produced by low-temperature Sol-gel methods in an aqueous medium, and organic "template" molecules are used to define specific pore geometries (7). Thirty years of research have resulted in the ability to tailor a zeolite material for a specific application.

Once the composition and structure of a new compound are known, there is a reasonable probability that some of its properties can be predicted. There are, however, still a considerable number of cases where our ability to predict properties also fails. For example, we still cannot explain most of the properties of the high-temperature superconductors, including the reason for the high transition temperature itself. Consequently, the properties of new materials must be measured to see if enhanced or novel behavior is present.

Beyond the Long-Term Challenges

Solid-state chemistry is the foundation on which the other solid-state sciences must build. However, it is apparent that many fundamental concepts concerning the preparation, structure, and predictability of formation of solids are yet to be developed. Although the problems can be simply outlined, they are incredibly difficult problems that will occupy researchers and theorists for decades to come. After considerable effort, many scientists, such as Linus Pauling, Roald Hoffmann, and Ken Wilson, have made only small steps toward these goals. Yet the drive to explore the periodic table for new science and technology is strong and cannot wait for answers that may be a very long time in coming, if ever. Indeed, by building a larger body of knowledge about the formation of new solid compounds, we may be providing the very clues that will be necessary for us to solve these puzzles.

Solid-State Chemistry: A Particular Effort at Cornell University

The research in my group is driven by an interest in novel or enhanced properties. Our approach is to synthesize and examine new compounds or recently reported compounds that have novel structures and whose properties have not yet been measured. Subsequently, we measure electrical, magnetic, and thermal properties as well as examine the chemical reactivity of the compounds with specific reactants. This approach has historically been the most productive route to new discoveries: novel chemical or physical properties are most often found in materials with unusual structures (*1*). Our present research focuses on two main topics: solid compounds containing metal clusters and new classes of materials that may be high-temperature superconductors.

Cluster Compounds

In the early seventies an unusual class of compounds were discovered by a group in Rennes, France (*8*). These compounds, commonly called Chevrel phases, contain clusters of metal atoms bonded to each other and then to the anions [one of the chalcogenides (X): sulfur (S), selenium (Se), or tellurium (Te)]. This structural arrangement is quite unusual. In the vast majority of normal valence compounds, the structure is such that the cations and anions alternate in a simple way so that cations are bonded only to anions and anions only to cations. The structure of these cluster compounds is shown in Fig. 2, where octahedral clusters of six molybdenum (Mo) atoms are quite apparent. The octahedral clusters are surrounded (capped) by chalcogen atoms and the intercluster spaces are filled with a metal (the "ternary" metal) different from molybdenum, to make a compound such as $PbMo_6S_8$.

There are other cluster compounds, most based on early transition metals such as molybdenum, niobium, tantalum, and zirconium combined with halogens such as chlorine (*9*). Although those materials show considerable structural variety, they are less interesting to me since most are electrical insulators and cannot be chemically altered at low temperatures. The Chevrel phases have a wide variety of interesting chemical and physical properties; there are compounds that are electrical conductors, superconductors, ferro- and antiferro-magnetics, superionic conductors, or chemical catalysts, depending on the ternary metal included (*10*).

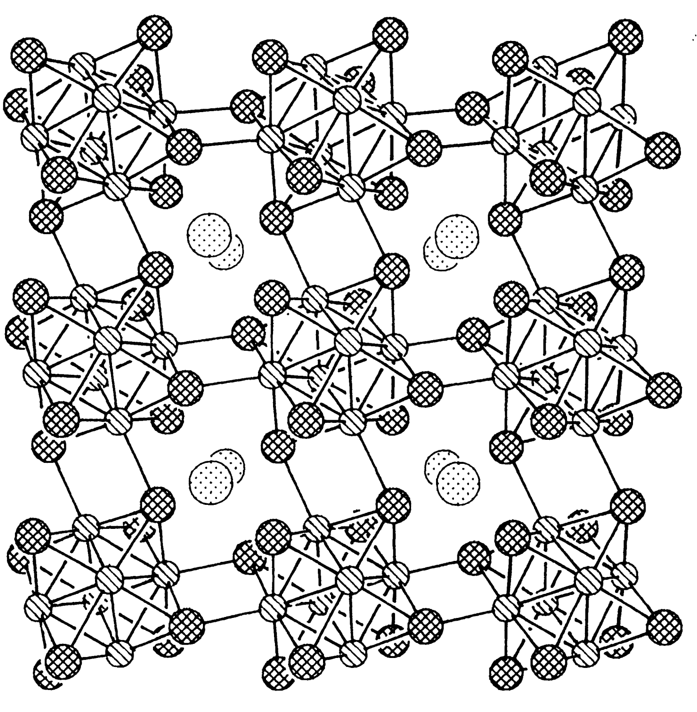


Fig. 2. The crystal structure of the Chevrel phases exhibits octahedral clusters of molybdenum atoms (small hatched circles) that are held together by strong metal-metal bonds (indicated by lines joining the atoms). The anions (crosshatched circles) are bonded to each face of the octahedron to make a cube. The molybdenum-selenium bonds are indicated by lines joining them together. A third element (large circles) inserted between the cubes is usually necessary for the compound to be prepared in this structure. The solid is held together by intercluster bonds between anions in one cube and a molybdenum atom on the face of the next cube.

The Mo_6X_8 cluster was found to be the smallest member of a family of larger clusters made by stacking Mo_3Se_3 units (*11*), of the formula $Mo_{3n}X_{3n+2}$ (n is an integer ≥ 2). The structure of these clusters is shown in Fig. 3. It was the large diversity of the properties of such cluster phases that attracted us to examine them in more detail and to search for new cluster phases. To illustrate the unusual nature of these cluster compounds, I will focus on a few examples of our recent work.

About 5 years ago, while I was still working at AT&T Bell Laboratories, my co-workers and I discovered that the "infinite" chains of the infinity member (n) of the $Mo_{3n}Se_{3n+2}$ cluster (Fig. 3) in the compound $LiMo_3Se_3$ could be dissolved in certain organic solvents (*12*). Because of the strong metal-metal bonding between the molybdenum atoms in the chain, the chains are quite rigid and they bend only slightly when in solution. Thus, this molybdenum-based "inorganic polymer" is unlike most organic polymers, which

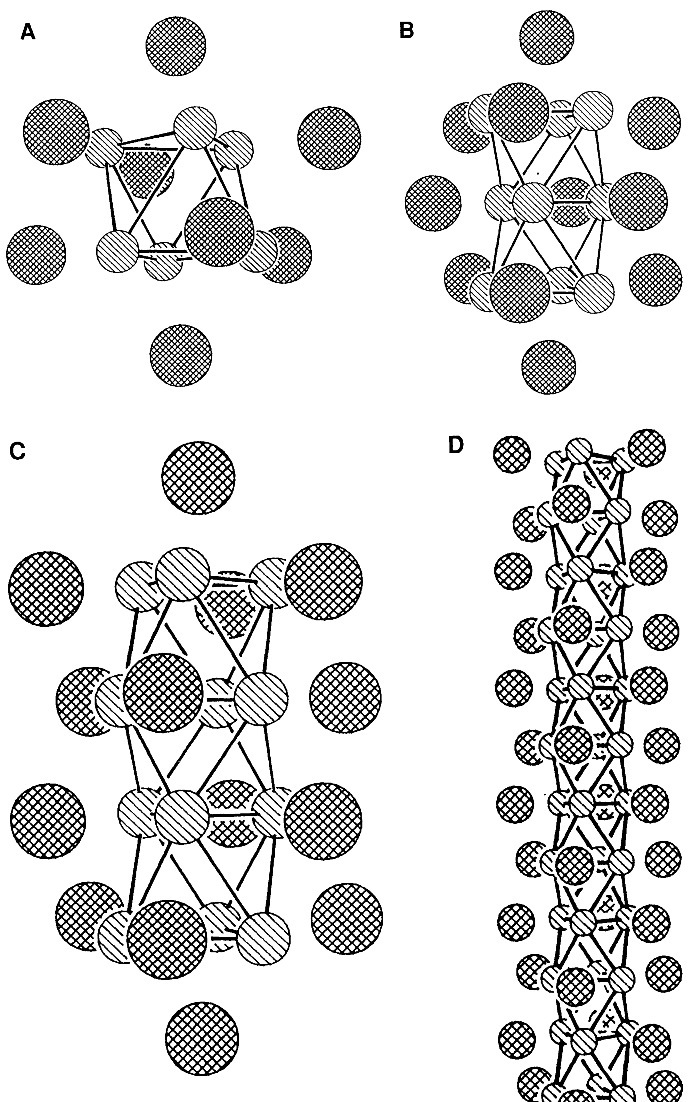
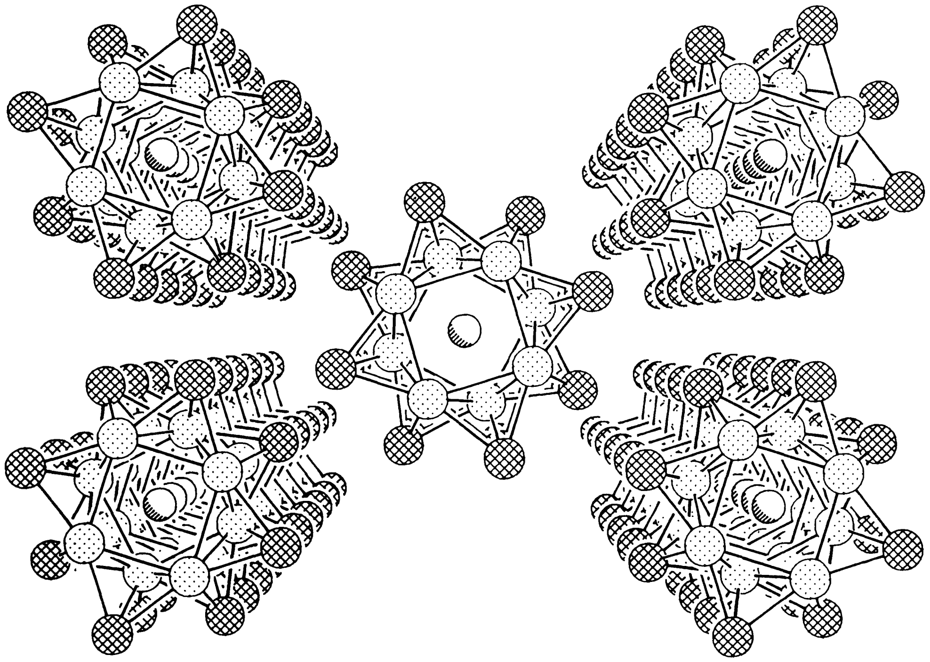


Fig. 3. (**A**) A single cluster of Mo_6Se_8 is shown oriented with the threefold cube axis vertical. Only the Mo-Mo bonds are shown as lines; the Mo-Se bonds are not shown for clarity. (**B**) When $n = 3$, a Mo_9Se_{11} cluster results. This figure shows the cluster oriented with the threefold axis vertical; again only the Mo-Mo bonds are indicated by lines. (**C**) At $n = 4$ a cluster containing 12 Mo atoms is obtained. (**D**) At n = infinity, a compound containing infinite clusters is obtained.

Fig. 4. A view of the chain structure of the new cluster phase Ta_4SiTe_4. The tantalum (Ta) atoms are represented by dotted spheres, the silicon (Si) by shadowed spheres, and the tellurium (Te) by crosshatched spheres. The Ta-Ta bond lengths are between 2.98 Å and 3.25 Å, only somewhat longer than the bond lengths in Ta metal (2.86 Å). The silicon atoms form a one-dimensional chain with Si-Si bond lengths almost equal to those in elemental Si. Ta-Si bonds are not shown for clarity. Interchain interactions occur through weak Te-Te van der Waals bonds.



usually fold into a loose spherical shape in solution, rather like a ball of string. Also in contrast to most polymers, the molybdenum chains are metallic conductors of electricity. Thus, we can prepare isolated metallic "wires" only 6 Å in diameter.

We have recently discovered that such solutions are stable for a year or more, even when water is the solvent, as long as dissolved oxygen is removed from the solvent. We have subsequently shown that homogeneous, mixed organic-inorganic polymer solutions and solids can be prepared as well. These mixtures are homogeneous only when the organic polymer contains polar groups. Examples of such polymers include polyethyleneoxide and polyvinylpyrrolidone. In those cases, the polymer is thought to coordinate to the Li^+ ions in solution, forcing an intimate mixture of the two types of polymers. Another class of mixed polymer systems can be prepared by replacing the Li^+ ions in solution with a polycation, such as polyallylammonium, $-[CH_2CH(CH_2NH_3^+)]-$. This is accomplished by mixing solutions of the two polymers in water to form a precipitate that contains both polymers, but no lithium. When the solvent is removed, a new kind of polymer blend results: one that has some imparted conductivity and usually higher mechanical strength. In collaboration with Jean Frechet, a polymer chemist in our department, we are just beginning to investigate the properties of these novel polymer blends.

Also of interest in these inorganic chain polymers is their electrical properties. It is known that the electrical properties of thin metallic layers or wires deviate from classical predictions (*13*), when one or two of the dimensions, respectively, of the material are below a few hundred angstroms. We have therefore begun a program whose goal is to measure the electrical properties of one single chain. Such a chain is about as small a wire as could ever be obtained or measured; the smallest measured to date have diameters of about 100 Å (or a cross section about 300 times larger than the chain). Many problems in carrying out the measurements must be overcome before such experiments can be confidently concluded, and we will rely heavily on the expertise of collaborators to succeed. One such experiment, undertaken in collaboration with Al Sievers in the physics department, is to measure the conductivity of aligned chains via an optical method, as the frequency is reduced into the far infrared. Other approaches involve attempting to make electrical contacts directly to the wires, perhaps with liquid metals.

Our research also focuses on the synthesis of new cluster phases. Building on the discovery in halide cluster compounds that small interstitial atoms can be inserted into the center of the cluster to "glue" the cluster together (*14*), we are searching for similar effects in cluster-chalcogenide compounds. We expected to prepare clusters with a structure similar to the Chevrel phases, but with an interstitial atom at the center of the metal octahedron (Fig. 2). Instead we found a new class of linear chain compounds built from square antiprismatic clusters that are centered with silicon or small transition metals. These are the first clusters composed of centered square antiprisms of metal atoms. From the structure of a prototypical compound of this type, Ta_4SiTe_4 (Fig. 4), it is apparent that the silicon atoms form a linear chain along the prism axis. Preliminary experiments indicate that individual chains of the Ta_4SiTe_4 can also be put in solution. It is likely that these kinds of cluster compounds are just the "tip of the iceberg" and that many more will be found. This chance discovery of the Ta chain compound illustrates further our inability to design or predict specific compounds and also illustrates the surprises that lurk in the attempted synthesis of new materials.

Solid-State Nitrides, New Materials, and Possible New Superconductors

Our second research program in solid-state synthesis is driven by an interest in a specific phenomena, high-temperature superconductivity (*15*). There are many thousands of groups worldwide attempting to understand and exploit the properties of the very unusual superconductors that contain copper and oxygen and several other elements. Even though the mechanism of high-temperature superconductivity is not yet known, it is still possible that we can make educated guesses, based on the known chemical and physical properties of the copper oxide materials, about the existence of such superconductivity in other classes of materials. There are many motivations for such research beside the search for even higher transition temperatures, such as the need for less brittle materials or materials that have a high critical current. Yet very little research is focused on non–copper oxide materials. This is precisely the interest of my group: to find whether such new classes of materials exist. A broader objective of this work is the synthesis of new compounds, especially those with unusual structures. Such new materials also have a reasonable probability of displaying other new or enhanced properties as well, as previously pointed out.

My purpose here is not to explain how we make our "educated guess" about where to look, since that is explained elsewhere (*16*), but to discuss the specific materials we are investigating. We have focused on solid-state nitrides, not only because they have the potential to be high-temperature superconductors, but also because relatively little is known about such compounds. There are tens of thousands of oxide compounds, including both synthetic materials and minerals, but only several hundred nitrides are known. However, even in this small class of nitrides, many useful materials are known. For example, Si_3N_4 is an insulating material used as coating on semiconductor circuits, and AlN and TaN are refractory materials being developed for use in high-temperature environments.

Nitrides are generally less stable than oxides. When heated to high temperatures they lose N_2 or O_2, respectively. However, because of the much higher bond energy of the N_2 molecule (941 kJ/mol) compared to O_2 (499 kJ/mol), the decomposition of the nitride occurs at much lower temperatures. Indeed, a number of the metallic elements do not form stable nitrides, whereas only a very few do not form stable oxides. For example, Li_3N is the only alkali metal nitride, but all the alkalis react with oxygen. The higher stability of oxides relative to nitrides means not only that nitrides must be prepared at lower temperature, but also that oxygen and water must be completely excluded from the nitrogen-containing reactant, usually nitrogen gas or ammonia. Perhaps it is these conditions of nitride chemistry that has led to a lack of activity in the field.

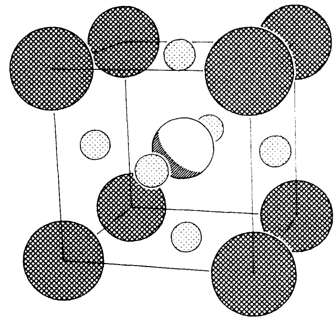
Since binary nitrides have been well studied, we wished to explore the formation of ternary nitrides, of which only a few are presently known. Our nitride strategy is to exploit an inductive effect common in oxides: the inclusion of electropositive elements from the left side of the periodic table stabilizes the formation of metal oxides of metals further to the right in the periodic table. In the case of nitrides then, we are examining the formation of ternary nitrides of the type $M_xM'_yN_z$ where M is alkali, alkaline earth, or a rare earth metal, and M′ is a transition or post-transition metal.

Our initial survey of these combinations indicates that many new compounds are indeed present. The presence of the new phases is easily shown by powder x-ray diffraction, even when the sample is not a pure or single-phase material. Subsequently, the composition may be determined by further synthesis experiments and by several analysis techniques. The crystallographic unit cell can then be obtained, if the phase is a well-crystallized powder. However, if single crystals cannot also be obtained, the final step in compound identification, the determination of the crystal structure with only powder diffraction, is the most difficult. This last step may take considerable time. Of course, the properties of the new material can be determined without knowing the crystal structure. A knowledge of the crystal structure is however necessary to understand the bonding and the properties of the compound.

Even though we only recently began to study solid-state nitrides, we have already determined the structure of several new compounds whose structures are simple enough to readily be determined from powder diffraction. Again, a few examples will convey the beauty of this chemistry.

We have prepared a series of compounds Ca_3MN where M represents P, As, Sb, Bi, Ge, Sn, or Pb by reaction of the element M with Ca_3N_2 at 1000°C in nitrogen gas. The structure of these compounds is a very simple and well-known type, cubic antiperovskite (Fig. 5). (The P and As compounds are distorted variants.) The stoichiometry and bond lengths (near neighbor distances) show that the post-transition element (Bi, Sb, or Pb) behaves as an anion of oxidation state −3. In the case of the group V elements P to Bi, this leads to filled atomic shells and the expectation that Ca_3MN will be a semiconductor. Electrical measurements suggest that this is the case, the P compound is essentially insulating, whereas the Bi compound is a degenerate semiconductor at room temperature. Ca_3MN with M representing Ge, Sn, or Pb should be metallic, since the Pb^{3-} anion has an incomplete electron configuration; there is one electron too few to fill the valence shell. In solid-state physics terminology, the Fermi level ought to lie in a Pb-based p band. Indeed, the electrical conductivity of Ca_3PbN is much higher than that of Ca_3BiN.

Fig. 5. The cubic structure of Ca_3BiN is shown. The atom at the cube center is N and the atoms at the cube corners are Bi and at the cube faces are Ca. The cubic lattice parameter is 4.89 Å.



CaNiN can also be prepared by the reaction of Ni and Ca_3N_2 in N_2 gas at 1000°C. It adopts a very uncommon but simple structure (Fig. 6), seen before only in RCoC, where R is Y or a heavy rare earth metal (*14*). The formal valence of the Ni cation is +1, a very uncommon valence for Ni in solids (usually it is +2 or +3), especially when no Ni-Ni bonding is present. The electron configuration is d^9, the same as that of Cu^{2+} in the high-temperature superconductors. CaNiN is, however, not a superconductor, but a good metal down to 4.2°K. We are now investigating the chemistry of Ni^{1+} in nitrides, searching for possible analogs to the copper oxide superconductors.

Although we are just beginning our study of ternary nitrides, it is clear that many new phases exist. However, much work remains to be done before the full scope of this new field is apparent. Whereas

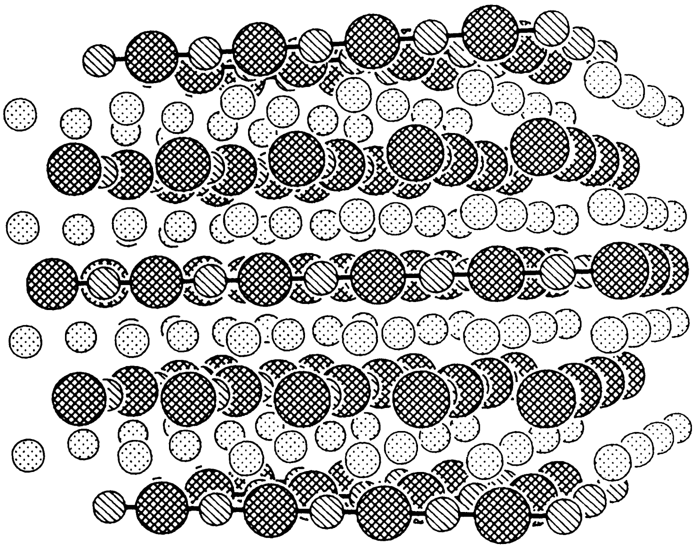


Fig. 6. The structure of CaNiN clearly shows the linear chain nature of this compound. N, represented by the large crosshatched spheres, is bonded to two Ni atoms, as indicated by the connecting lines. The chains are packed in layers and the layers are separated by Ca atoms. The closest Ni-Ni distance, 3.50 Å, is between the layers.

our initial thoughts about nitrides were motivated by high-temperature superconductivity, it has become clear that a broad opportunity to discover new chemistry and perhaps other new phenomena exist in solid-state nitrides.

Summary

Solid-state chemistry is very much in its formative years. Many challenges at even basic levels remain, including the understanding, control, and predictability of composition, structure, and reactivity of solids. Although "solutions" to these problems may be a long time in coming, the need for the discovery of new materials both for scientific study and technological progress is urgent. A number of strategies to discover new materials have historically been productive, including those based on structure, properties, or novel preparative methods. I have outlined two strategies from my research based on unusual structures or on specific phenomena and have shown how they lead to new and exciting solid-state materials even with our limited predictive abilities. Perhaps some day in the future theorists will be able to help us design specific materials that have new and useful properties; until then, progress will continue from forays into unexplored combinations of elements in the periodic table.

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18. The particular research work discussed here is not yet published and is the product of the perseverance and creativity of students and postdoctoral candidates in my group at Cornell. These include M. Badding, M. Y. Chern, J. Davis, S. Elder, M. Hornbostel, R. Mariani, C. Michelson, P. Rauch, Y. Vassiliou, D. Vennos, A. Wizansky, and R. Ziebarth. The research will be published in detail shortly. We greatly appreciate support for the cluster work from the Department of Energy, Basic Energy Sciences through grant DE-FG02-87ER45298 and for the nitride work from the Office of Naval Research. Setup support and support of R. Ziebarth by the National Science Foundation through the Materials Science Center at Cornell (NSF/MRL-DMR88-18558) is also greatly appreciated. Finally, I thank B. Carpenter, B. Cotts, F. Franzen, D. Murphy, A. Ruoff, S. Whittingham, and P. Wolczanski for their comments on this manuscript.

" It wasn't magic. It was mead contaminated with a recombinant DNA retrovirus."