Report from the third workshop on future directions of solid-state chemistry: The status of solid-state chemistry and its impact in the physical sciences[☆,☆☆]

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Executive summary

Foreword: Public awareness of solid-state chemistry, or more broadly solid-state science and technology rapidly grew along with the transistor revolution and the development of the integrated circuit. We are now at the half-way point in the solid state century [Scientific American The Solid-State Century 1997;8(1) [special issue]], a period of the last 50 years when the term ''solid state electronics'' was in general vernacular and ''solid state'' was prominently stamped on consumer electronics appliances, almost as a synonym for ''advanced'' or ''modern.''

Clearly without the Bell Labs discovery of the first transistor, which boosted an electrical signal a 100-fold, our personal computers would not be possible, and the information age it spawned would never have happened. It is clear with hindsight that those individuals, companies, regions and nations that have embraced the new information technology have flourished.

At the present time the solid-state age does not show any sign of stopping. In this the second half of the century, we have chips with 10 million transistors, solar photovoltaics and all—solid-state lighting, cell phones, displays, data storage, the insulated gate bipolar transistor (IGBT) revolutionizing power electronics, and enthusiasm is high for quantum-optical devices which may begin to dominate new technology.

The goal of the Solid State Chemistry Workshop was to assess the current state of solid-state chemistry and explore its impact on allied disciplines as well as industry. In this report we articulate the solid-state chemistry community's sense of the future opportunities and directions and make several recommendations. The findings of this workshop could act as a vehicle for informing the solid-state chemistry community of programs and opportunities for support at NSF and elsewhere.

This report aims to identify research directions in solid-state chemistry closely aligned with emerging or potential technologies, as well as areas of original research that could lead to new advances in materials science, solid-state physics and the solid-state sciences in general. Of course, judgment must be exercised to distinguish which of such efforts have true fundamental value, and sufficient patience must be accorded for fundamental research to ultimately bring about new technologies.

A major societal impact of the solid state and materials chemistry community is the education of students who are able to excel in multidisciplinary areas crucial to the competitiveness of American industry. Solid state and materials chemistry by its nature, with its interdisciplinary history, has the ability to prepare and educate its graduates to excel in a wide variety of industries including the fields of energy,

pharmaceuticals, optical materials and all manner of electronic devices, and nano and biotechnology. Since by their nature emerging technologies depend on the discovery of new materials and their properties, individuals with training in solid-state chemistry are key members of research teams and companies developing these technologies.

Which scientific disciplines are affected most by what goes on in solid-state chemistry? The focus of the proposed workshop was two-fold, we sought a close look at the discipline of solid-state chemistry in the beginning of the third millennium and explored its continued impact and relationship with allied disciplines in the physical sciences and also industry. This report highlights a number of accomplishments, emerging research directions and areas requiring increased effort but is not meant to be all inclusive and it is certain that we have left out a number of important aspects. An assessment of how solid-state chemistry is impacting the physical sciences, through continuing advances and the many ways of interacting across disciplinary boundaries, could help the National Science Foundation and the scientific community better appreciate its value and contributions in the greater scientific and societal context.

The report also includes discussions of existing and new modes for educating students, and the development and use of national facilities for performing state-of-the-art research in our field. A critical enabler of this societal benefit has been funding from the NSF and other agencies in this area, in particular our nation's premier national user facilities.

Recommendations: 1. There is great interest in developing methodologies for synthesis of materials with intended functionalities. To continue the pace of progress solid-state chemistry has enjoyed in the past we recommend sustained support for exploratory synthesis and directed synthesis aimed at new materials' discoveries and the development of methodological and design principles. Syntheses assisted by theory and modeling are only still emerging and should be encouraged.

2. Structure–property relationships are the fundamental underpinning of solid-state sciences. Be they experimental or theoretical, efforts and ideas that will make advances in this area should be supported with sustained funding from the Foundation.

3. The Foundation should encourage and support outreach ideas aimed at explaining, promoting and projecting the place and significance of solid-state chemistry to society. This could be done under the umbrella of Centers or smaller special projects.

4. Fundamental research and materials discovery emanating from NSF and other agency support of solid-state chemistry in academia ultimately affects the strength of industry and therefore the economy. Where appropriate, the NSF should seek the advice of industrial experts in solid-state chemistry as a development tool in formulating potential research directions. In addition existing programs aimed at supporting academic–industry collaborations leveraging industry resources and providing graduate students with goal-driven perspectives are viewed favorably.

5. Solid state and materials chemistry research will extract maximum benefit from NSF funding of personnel and support activities in national facilities. These often unique facilities enable the solution of important problems in solid-state chemistry. Greater utilization of these facilities is limited by lack of expertise on the use of these techniques amongst solid-state chemists and limited user support from the facilities. The NSF has an important role to play as an advocate for the needs of solid-state chemistry to the facilities.

6. The NSF should consider and implement mechanisms for supporting collaborative research between the solid-state sciences and investigators in far-ranging fields, which may require creative funding mechanisms involving other agencies.

7. Programs within NSF that foster collaborative research with international PIs, groups or Institutes such as the Materials World Network should be supported. Also recommended is funding for short term overseas career development 'sabbaticals' for faculty and increases in the number of US postdoctoral fellowships for positions abroad with a well-defined NSF affiliation.

Contents

Section 1. Synthesis and new materials

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1.1. Introduction

Synthesis is the bedrock, the essence of chemistry because it provides the objects of any further studies. After all, if no new compounds are synthesized, no new properties could be found. Synthesis is clearly one of the permanent frontier areas in the process of discovery of new materials. Different synthetic approaches often lead to different properties of the final material. Therefore, the development of new techniques for synthesis and subsequent processing is vital for achieving materials with complex collections of properties that may satisfy today's needs for multifunctionality. Exploratory and directed synthesis of solid-state materials and their characterization contribute to building a larger body of knowledge that will add insight into the syntheses of other new solid materials.

This report is an overview of the current status of synthesis in solid-state chemistry illustrated by selected new materials. Its main objective is to report on some of the most widely used synthetic strategies applied to a variety of materials, but most importantly to highlight future challenges and opportunities facing solid-state chemists. However, it is almost impossible to provide a comprehensive overview in such a short document due to the large number of existing approaches and their modifications. Thus, the document is rather a cross-section, a snapshot of current synthetic approaches, both classical and emerging new ones, and may reflect to some extent the specific interests of the panel members.

1.2. Synthesis

The approach to synthesis can be either exploratory or targeted. Exploratory synthesis has yielded numerous discoveries and continues to be a valuable and popular method in solid-state chemistry. Directed synthesis, on the other hand, targets specific properties and their optimization. There is great interest in developing methodologies for directed synthesis of materials with intended functionalities. Both approaches have resulted in major advances in materials science and continue to be important. Syntheses assisted by theory and modeling are only still emerging and should be encouraged. Another important aspect of synthesis is crystal growth, both for obtaining sufficiently large crystals for physical property measurements as well as for materials discovery. Combinatorial, high throughput and parallel syntheses are approaches that allow for rapid production of large numbers of samples and analysis of phase space and hold great promise for discovering and optimizing new materials.

The arsenal of synthetic methods for solid-state chemistry includes the direct combination high-temperature approaches, synthesis from fluxes and melts, hydrothermal synthesis, and synthesis from solutions. Some of the emerging approaches described here include synthesis of alloys from suspensions of pre-formed metal nanoparticles, synthesis of extended frameworks by directed assembly of large molecular building blocks, low-temperature synthesis of

nanostructured metal oxides and chalcogenides, salt-inclusion synthesis, and a palette of preparation techniques for porous materials.

Most research efforts in current solid-state chemistry are concerned with the design and prediction of new structures and materials [2,3]. In general it is difficult to design a phase a priori. Progress has been considerable and we have many cases in which "materials design" is actually possible, e.g. simple isoelectronic elemental substitutions, the intercalation of species into solids, the synthesis of coordination solids based on solid-state structures, and the assembly of templated materials (see elsewhere in this issue). Nevertheless, in most cases the ability to broadly design and predict new phases remains a challenge [4]. In addition to synthetic techniques, concepts of compound formation may be used in materials discovery. The challenge of designing solid-state compounds with predicted compositions and structures could be partly met using concepts that employ phase homologies. Homologous series of compounds not only can place seemingly diverse phases into a single context, they can also forecast with high probability specific new phases. A homologous series is expressed in terms of a mathematical formula that is capable of producing each member. Within a homologous series, the type of fundamental building units and the principles that define how they combine remain preserved, and only the size of these blocks varies incrementally.

1.2.1. High-temperature synthesis

Because of the very low diffusion coefficients in solids (in the order of $10^{-12}\,\mathrm{cm^2\,s^{-1}}$), the traditional solid-state synthesis requires high thermal activation. In this method, reactants are measured out in a specific ratio, ground together, pressed into a pellet, and heated to high temperatures. The temperatures needed to facilitate solid-state diffusion and reaction between grains—particularly with refractory borides, carbides, silicides, and nitrides—may require the use of specialized furnaces, arc welders, RF induction heating, or combustion (Fig. 1.1). Furthermore, the products are often powders and multiphase, and lengthy annealing is necessary in order to produce larger crystals which usually are large enough for single-crystal diffraction but not for transport measurements. However, many intermetallic mixtures are conveniently liquid at moderate temperatures, and synthesis of compounds

Ignition   Reaction front propagation   Cooling
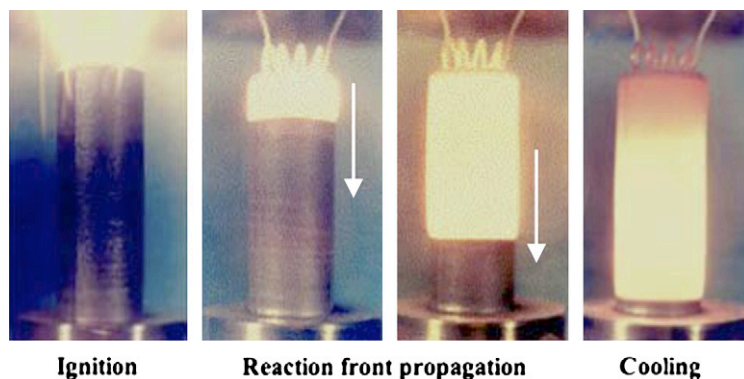
Fig. 1.1. Combustion synthesis by self-propagation.

by cooling such melts is not affected by slow diffusion rates. This synthetic approach, often referred to as "flux synthesis" is reviewed in more detail in Section 1.2.2. Generally, high temperatures allow for mainly thermodynamic control which, in turn, prevents subtle control of the reactions and, hence, limits rational design of desired products. High-temperature synthesis is perhaps the oldest approach in solid-state chemistry but even today it is still not amenable to detailed design and is still intrinsically an exploratory method. It suffers from the inability of current basic chemical principles and concepts to completely understand and predict composition, structure, and reaction mechanisms. Such eventual prediction of structures and development of synthetic routes towards them remains to be a coveted goal for every solid-state chemist. The progress in the field cannot conceal the fact that even at present there are no advanced methodologies to the rational synthesis of predicted solid compounds. In spite of the everlasting efforts in developing a rational approach, the generally successful high-temperature route to new materials is still empirical and based on a mixture of analogies, intuition, and accumulated knowledge. Hence, synthesis of novel solid materials is as much an art as a science and much of its direction is guided by rules developed from past serendipitous and intuitive discoveries.

Despite all these shortcomings, the importance of high-temperature synthesis in the fields of solid-state chemistry and condensed matter research cannot be understated. Numerous ground-breaking discoveries have been made by this approach, and yet tremendous opportunities lie ahead. Fairly recent examples that demonstrate the success include the cuprate superconductors, the fullerenes, transition metal borocarbides, CMR manganites, dilute magnetic semiconductors, half-metallic ferromagnets, mixed valence compounds, heavy-fermion intermetallics, etc. [5−9]. The discovery of superconductivity in MgB_2 ($T_C = 40$ K) [10], a compound that has been *known* for decades, suggests that additional discoveries, even among the most simple binaries, are yet to be made. Furthermore, it raises many questions about eventual existence of other materials of this category and how high their T_c may go. Thus, the high-temperature synthetic expertise of the solid-state community will remain crucial in this regard.

Another example of the importance of high-temperature synthesis can be found in the preparation of various transition metal borides, carbides, silicides, and nitrides that exhibit valuable properties such as oxidation resistance, thermal shock resistance, low density, and good mechanical strength. Due to their high melting points, the synthesis of these materials is very difficult and often requires the use of a combination of high-temperature synthetic techniques, such as reactive sintering, hot pressing, mechanical alloying, etc. A more creative approach in the form of self-propagation combustion synthesis has been developed recently (Fig. 1.1). This method saves time and energy and, yet, yields high-purity products. Furthermore, its non-equilibrium nature may allow for synthesis of metastable phases on account of the steep thermal gradient and fast reaction and cooling rates.

In general, exploratory synthesis approaches such as high-temperature synthesis are somewhat blunt instruments in the search for new compounds because they sample only a small fraction of the possible compounds. However, in light of the fundamental importance of condensed matter in the form of traditional or novel materials such systematic endeavors are readily justified. Nonetheless, exploratory materials' research is often overlooked and underappreciated. Thus, it is important to emphasize to all relevant parties such as academic institutions, industry, national laboratories, and funding agencies, that exploratory studies are crucial for the advancement of the materials science and for the discovery of new materials.

1.2.2. Synthesis from metal fluxes and melts

Synthesis from fluxes can be viewed as slow cooling of a melt that can have a composition very different from the resulting crystalline phase. Although flux synthesis is popular for crystal growth of oxides and chalcogenides from molten-salt fluxes, the technique is less well established for synthesis of intermetallics from molten metal fluxes. Given the increased recent interest in complex intermetallic compounds such as heavy-fermion materials, boride superconductors, quasicrystals and approximants, magnetic alloys, and hydrogen storage alloys, the molten metal flux technique is experiencing a renaissance. Developed in Europe in the early 1900s as a method for growing crystals of binary carbides, borides, and silicides, and expanded by a number of investigators in the 1980s, reactions in metal fluxes are now being used for exploratory synthesis.

Selection of a suitable metal as a flux medium is based on a number of criteria such as non-zero solubility of the reagents, low melting point, and inertness. The reagent solubility provides high reactivity while the low melting point allows for kinetic control over the reaction and eventual isolation of new phases. Removal of the flux is done in a number of ways such as chemical etching with various solutions or mechanical decanting/centrifuging at elevated temperature while it is still molten.

Hundreds of new complex intermetallics have been isolated in the last 10 years from molten aluminum, gallium, indium, or tin. Unusual fluxes and flux mixtures are being investigated to develop the technique from purely exploratory into a tool for the preparation of materials with specific structures. The most obvious method of tailoring products is by adjusting reactant ratios. For example, the number of $AuAl_2$ layers in the homologous series $Th_2(Au_{x-}Si_{1-x})[AuAl_2]_nSi_2$ depends on the concentration of gold in the aluminum flux [11]. Similarly, phase diagrams for synthesis of ternary phosphides of (Sm or Tm)/Co/P in tin flux have been successfully derived by fine-tuning the synthetic ratios [12]. Another important variable is the temperature and heating profile. A number of examples show that lower temperatures, as expected, favor kinetically stabilized phases. Structures such as β-SiB_3 and $Tb_{1.8}Si_8C_2(B_{12})_3$ cannot be grown without the use of a flux, gallium in this case [13,14]. One of the clearest demonstrations of kinetic control is the exploration of α and β-$RENiGe_2$ (RE = late rare earth) growth in indium flux [15]. The thermodynamically stable α form can be synthesized using high-temperature methods such as arc-melting; the kinetically stable β form has been achieved only in molten indium and only at lower temperatures and shorter reaction times (Fig. 1.2).

Another, particularly elegant example of controlling product formation by careful fine-tuning of both reactant-to-flux ratio and temperature is the growth of large single quasicrystals. These unusual materials with local 5-, 8-, or 10-fold rotational symmetry are often metastable alloys of aluminum or zinc with other elements. They possess unusual transport properties and some are potential spin glasses. Single quasicrystals $Ho_{8.7}Mg_{34.6}Zn_{56.8}$ and $Al_{71.9}Ni_{11.1}Co_{17.0}$ were successfully grown by the "self-flux" method which involves melts that are slightly different in composition from the desired material [16,17]. $Ho_{8.7}Mg_{34.6}Zn_{56.8}$ (Fig. 1.3) was grown from a magnesium-rich melt with composition $Ho_3Mg_{51}Zn_{46}$ that was slowly cooled until the quasicrystal precipitated and then the remaining liquid was decanted.

While the more commonly used Sn, In, Ga, and Pb inert fluxes have yielded very interesting results, relatively more reactive fluxes such as aluminum offer their own promise as it tends to incorporate in the product. Although referred to as "flux", the aluminum in this case is a part of the resulting compounds and, therefore, this should be viewed as if
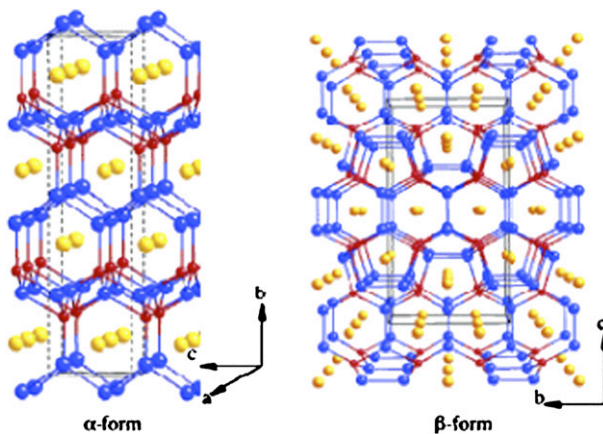
Fig. 1.2. The α and β form of RENiGe$_2$. The β form is only accessible by growth in indium flux.

studying the aluminum-richest part of a multi-component phase diagram. This is equivalent to simply growing crystals from multi-element melts as most of the intermetallics are made. Some of the Al-based intermetallics grown from such Al-rich systems, for example RE$_2$Al$_3$Si$_2$, RE$_4$Fe$_2$Al$_7$Si$_8$, and RENiAl$_4$(Si$_{2-x}$Ni$_x$), may be important components in advanced aluminum alloys and are, therefore, of industrial importance. Even more reactive fluxes, alkali metals for example, have been used as solvents to grow large crystals of nitride phases such as GaN, Ba$_5$Si$_2$N$_6$, and Na$_n$Ba$_{14}$CaN$_6$ [18]. The thermal decomposition of NaN$_3$ is used as a source of nitrogen and as a source of additional sodium flux. Carbides and borides have also been synthesized in sodium and lithium fluxes. The disadvantage of
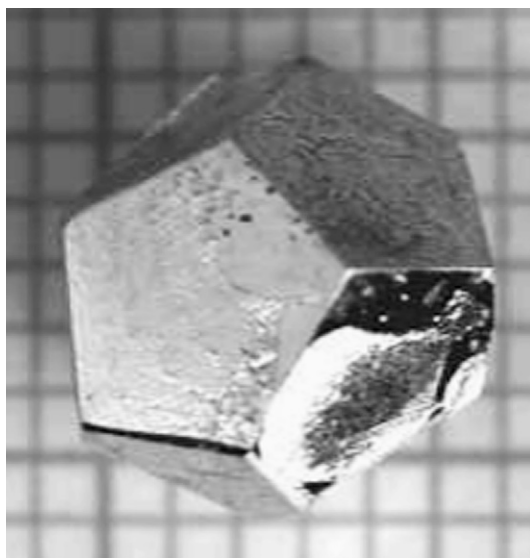
Fig. 1.3. A single grain of Ho$_{8.7}$Mg$_{34.6}$Zn$_{56.8}$ grown using the self flux method, showing pentagonal facets.

alkali-metal fluxes is that special containers must be used and most of the products are extremely air sensitive. To avoid this problem, flux mixtures of reactive and inert metal can be used. For example, a mixture of calcium and zinc can be used in a regular open steel crucible, and the eutectic formed at 7:3 ratio has been used to synthesize several new phases such as $Ca_{21}Ni_2Zn_{36}$, $Ca_6Pt_3Zn_5$, and CaPdZn.

Many of the metals and metal mixtures that can be used as solvents have not been investigated. Little is known about the possible mechanisms of these reactions or the solvated species and building blocks that form in these fluxes. As knowledge of binary and ternary phase diagrams increases, so will the ability to control syntheses in metal mixtures. Another unexplored aspect of flux synthesis is the use of lower temperatures. Most of the work mentioned involves reactions heated to at least 600–700 °C. New phases may be attainable with lower temperature reactions made possible in low melting metals or eutectic mixtures.

1.2.3. Synthesis in molten salts and salt inclusion

It is now evident that molten halide salts provide a good reaction medium for the crystal growth of refractory compounds. A wide spectrum of halide fluxes, alkali and alkaline-earth halides, provides a sizable temperature window (300–1000 °C) for synthesis and crystal growth. These fluxes include single salts, such as the monochlorides A^ICl (mp = 605 °C for LiCl up to 801 °C for NaCl), dichlorides $A^{II}Cl_2$ (mp = 782 °C for $CaCl_2$ up to 963 °C for $BaCl_2$), and eutectic mixtures such as $CaCl_2/BaCl_2$ (mp = 450 °C for 43.6/56.4 molar ratio). While the role of molten halides needs to be studied further, these flux techniques (in contrast to traditional, high-temperature, solid-state synthesis) allow new discoveries to be made through altered reaction conditions, such as acidity and basicity, solubility, and reaction temperature. It is also worth noting that these fluxes are inexpensive and have proven to be easy to work with in terms of retrieving crystals. Worth mentioning here are also the ionic liquids and their potential to be used as molten-salt solvents at lower temperatures. The ability of the ionic liquids to dissolve organic and inorganic compounds introduces the possibility of synthesis of hybrid materials.

It is realized that incidental incorporation of cations and/or anions from the flux is inevitable, and, thus this salt inclusion provides additional variety in structural features of the product [19]. Structural studies have revealed that often the extended salt lattices provide structure-directing effects in a variety of nanostructured covalent frameworks of incorporated transition metal oxides (Fig. 1.4). The composition of the incorporated salt and the coordination environment of the halide anions result in covalent oxide lattices ranging from sheets to clusters to porous structures. Due to the weak interaction between the two chemically dissimilar lattices, the salt lattice can be washed out in some cases, an effect that resembles reversible intercalation [20,21]. In some of these compounds, the incorporated salt sublattices are made of halogen-centered acentric secondary building units, thus forming non-centrosymmetric covalent oxide frameworks [22–24]. Furthermore, recent studies have shown some scattered salt-inclusion chemistry in non-TM-containing silicates and in mixed-metal chalcogenides.

The salt-inclusion compounds can be considered as a part of the larger class of compounds with open frameworks that includes zeolites. Such compounds with channels and cages have drawn much interest for their applications in catalysis, ion-exchange, separation, sensor, and molecular recognition. Transition-metal-containing open frameworks (TMCOF) have particularly drawn attention because of their unique properties including redox catalysis, magnetic ordering, and cathodic electrolysis. The synthetic endeavors, thus far, have
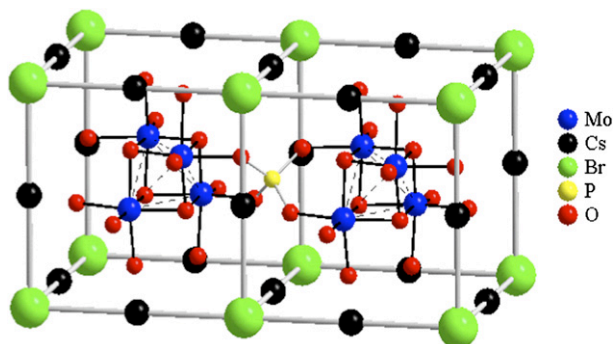
Fig. 1.4. Partial structure of $Cs_2Mo_4P_2O_{16} \cdot CsBr$ showing the $[Mo_4O_{16}]^{12-}$ magnetic clusters are caged in the Cs-Br lattice. The latter adopts the anti-ReO$_3$ structure with the cubane-like $[Mo_4O_{16}]^{12-}$ cluster residing in the center of the Cs$_3$Br cage.

almost exclusively concentrated on the systems consisting of inorganic/organic hybrid frameworks that are largely covalent [25−33]. The salt-inclusion open-framework solids are completely composed of inorganic hybrid lattices including a TM-oxide-containing co-valent network and an ionic salt lattice. Therefore, this new subclass of salt-inclusion frameworks is complementary to the organically templated TMCOFs. An example of such framework structures is the family of solids named CU-n (Clemson University) with compositions represented with general formula $A_2M_{2n-1}(M'_2O_7)_n$ where A = K, Rb, and Cs, M = Mn^{2+}, Fe^{2+}, Ni^{2+}, and Cu^{2+}, M' = P^{5+} and As^{5+}, and n can vary from 1 to 4. CU-2, for instance, with formula $A_2M_3(M'_2O_7)_2 \cdot$(salt) exhibits pores with diameters of ca. 5.3 Å and 12.7 Å (Fig. 1.5) [21]. The as-prepared CU-2−CuPO solid demonstrates high-temperature ion-exchange properties in molten salt media. Another compound from the family, $Na_2Cs_2Cu_3(P_2O_7)_2Cl_2$ (CU-4) [20], exhibits elongated pores (Fig. 1.5) occupied by smaller alkali metal cations and a less salt than in $K_2Cs_3Cu_3(P_2O_7)_2Cl_3$ (CU-2). Corre-lation studies of CU-2 and its structural cousin CU-4 revealed that the salt plays the role of a structure-directing agent. Changing the identity and amount of the salt can vary the shape and geometry of the open framework. Furthermore, several of the new $M_{2n-1}(M'_2O_7)_n^{2-}$ open frameworks crystallize in non-centrosymmetric (NCS) space groups due to the salt inclusion. Such NCS compounds are $Cs_2Cu_7(P_2O_7)_4 \cdot 6CsCl$ (CU-9; $n = 4$) which crystallizes
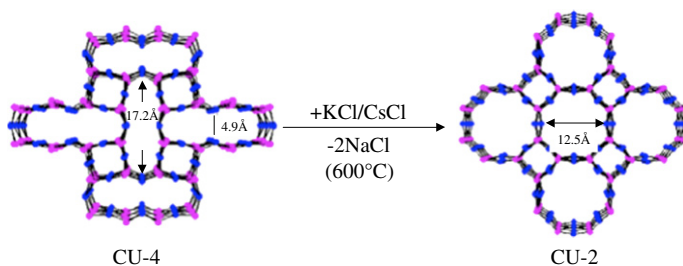
Fig. 1.5. Ball-and-stick representations highlighting the TMCOF of $Cu_3(P_2O_7)_2^{2-}$. These two structures are interconvert-ible by varying the concentration of salt (not shown), see text. The Cu^{2+} cations are drawn in blue circles, P^{5+} in pink, and O^{2-} anions are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in the space group 222 (D_2) and $Cs_2Cu_5(P_2O_7)_3 \cdot 3CsCl$ (CU-11; $n = 3$) with space group $mm2$ (C_{2v}) [24,34]. The Cu−O−P lattice in CU-9 wraps around the salt lattice which adopts the NaCl-type core (1/8 of the unit cell) along the 2_1 screw axis. The extended salt lattice of CU-11 literally adopts one-half of the NaCl-core in CU-9. As a result, the pore size in CU-11 is approximately half of that in CU-9.

1.2.4. Synthesis from solutions and suspensions

While low-temperature routes have become increasingly common for mixed-metal oxides and sulfides, analogous synthetic routes for accessing alloys and intermetallic compounds remain underdeveloped. Recent advances in this area, however, have demonstrated the importance of alternative low-temperature routes in order to access new structures that are inaccessible at high temperature.

The most common low-temperature strategies for synthesizing intermetallics are solution-based colloidal methods, which are gaining increased attention as the interface between solid-state chemistry and nanoscience expands. These methods employ either aqueous or non-aqueous solvents. The so-called "polyol process" uses a high boiling and gently reducing organic polyalcohol solvent to facilitate nucleation and growth of the metal particles. The general idea is that chemical methods, e.g. reduction or thermal decomposition of molecular precursors, can create a condition of supersaturation of zero-valent metals that results in the precipitation of metal particles, often as nanoparticles with organic stabilizing agents attached to their surfaces. Furthermore, subtle effects that can be neglected in traditional high-temperature reactions become important in defining the structure that nucleates, e.g. surface energy and the stabilizers that are used to preserve nanocrystallinity can influence the formation of a metastable phase. From a solid-state synthesis perspective, the key idea in these low-temperature solution reactions is that solid−solid diffusion is not the rate-limiting step in the formation of reduced metal compounds. While well developed for single metals, extending these ideas to multi-metal compounds, such as alloys and intermetallics, has challenges. For example, efficient co-reduction or co-decomposition to homogeneously incorporate multiple metals in the correct ratios into single particles can be difficult to accomplish. Appropriate modifications to these approaches have overcome these problems to yield quite a few known binary intermetallics in late transition metal and post-transition metal systems such as Au−Cu, Pt−M (M = Bi, Pb, Sb, Sn), M−Sn (M = Ag, Au, Co, Cu, Fe, Ni), and Co−Sb [35]. Nanoparticles of ternary ($AuCuSn_2$, $AuNiSn_2$, Ag_2Pd_3S) and even quaternary ($AgPb_mSbTe_{m+2}$) intermetallics have also been accessed using similar low-temperature solution methods [36,37]. Notably, $AuCuSn_2$ (Fig. 1.6) and $AuNiSn_2$ adopt an ordered NiAs-derived structure that is not observed in bulk systems synthesized through equilibrium methods, providing evidence that these methods can yield new intermetallics.

Intermetallics can also be synthesized rapidly at low temperatures by using pre-formed metal nanoparticles as reagents. In this case, nanoscale composites are formed in solution via surface-induced aggregation, and after precipitation to form a dry powder, the nanocomposites thermally transform into intermetallics and alloys of pre-determined compositions. The precursor powders are essentially nanoscale analogues of the mechanically mixed micron-scale powders that form the basis for "heat and beat" solid-state synthesis. The nanocomposite precursors avoid solid−solid diffusion as the rate-limiting step. This approach has also been useful for forming a library of binary and ternary intermetallics based on late transition metal systems [38]. Similar nanocomposite-based approaches have yielded intermetallics in systems such as
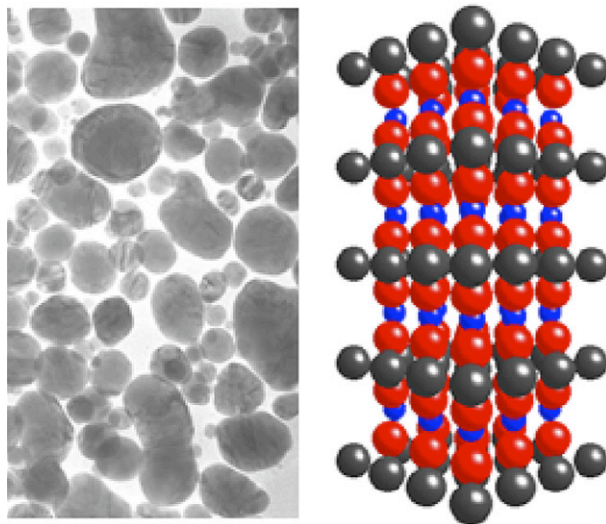
Fig. 1.6. TEM micrograph and structure of AuCuSn$_2$.

Mg−Ni, Ni−Al, and Zn−Sb, some of which have the additional challenge of extremely air sensitive and reactive precursors.

Another important issue that can be addressed with the help of synthesis from solutions is better understanding the relationships between small main group clusters and the corresponding bulk solid-state material. A question of fundamental importance is how properties and structures of small molecular clusters evolve into bulk intermetallics. Although the stepwise growth of large transition metal clusters has been clearly elucidated, similar routes to post-transition semiconductor clusters are scarce. It seems that, so far, no bulk material has been synthesized from an assembly of small well-defined molecular clusters that can clearly establish the direct relationships between the properties of the clusters and the bulk. The progress towards this goal has been slow, mainly because of the absence of unequivocal structural and mechanistic correlations between the solid-state phases and their relevant cluster derivatives. Zintl phases and polyatomic Zintl anions of group 14 may be considered as close derivatives of their technologically important parent elements and, hence, studies of their structures and properties may provide valuable clues to understanding the evolution from clusters into nanophase and into macroscopic solid. Thus, the approach is to oxidize such clusters (in ethylenediamine or more exotic media such as ionic liquids that can withstand higher temperatures) and study the resulting elemental structures. The lower temperature and kinetic control may lead to metastable structures for the elements. Similarly, oxidation of mixtures of clusters may lead to metastable intermetallics.

Another synthetic strategy to generate novel elemental structures as well as nanocrystals of Ge and Si employs a unique stepwise growth method via oxidative coupling of the corresponding anionic clusters. This strategy provides advantages over traditional growth strategies. First, due to the well-defined chemistry of the clusters, a high degree of control at the molecular-to-nanoscale growth is possible. This provides unprecedented handle and control of the growth process. Second, by controlling the reaction temperature and nature of solvent, one controls the Lewis acidity and coordinating properties of the solvent and can, ultimately, achieve

designed growth of nanostructures and porous crystalline structures that are otherwise inaccessible. Third, the strategy can be used to grow single crystalline nanophases and functional hybrid organic—inorganic nanocomposites. Fourth, the strategy can be readily adapted to heteroatomic systems.

In general, low-temperature strategies for synthesis of intermetallics demonstrate that high-temperature materials are also accessible by low-temperature "chemical" routes. Indeed, current methods have already established that a growing library of binary and ternary intermetallics are accessible, which paves the way to the formation of other compounds, including new and metastable structures. As the interface between solid-state chemistry and nanoscience continues to expand, including new synthetic techniques and complex target materials, intermetallics will become more popular because of their diverse compositions, structures, and properties. Low-temperature solution methods would allow control over nanocrystal size and shape, along with concomitant control over composition and crystal structure. Useful intermetallic materials such as films, coatings, and nanoporous mesh materials will also flourish when the appropriate intermetallic nanoparticles are synthesized.

Metal chalcogenides play an important role in solid-state chemistry not only because of their technological importance but also because of their role in the development of new synthetic concepts and methods in this area of chemistry. For example, the first report on alkali-metal intercalation into TiS_2 three decades ago highlighted the then-novel synthetic approach called "soft chemistry" ("chimie douce"). This low-temperature process allows for new compounds to be obtained while retaining the structural framework of the precursor. Related to this synthetic concept is the reactive flux method that has proven to be widely applicable to the preparation of multinary metal chalcogenides, especially low-dimensional polychalcogenides with unprecedented structures [12]. More recently, emphasis has been placed on developing approaches for low-temperature synthesis of metal chalcogenides in smaller length scales. The first synthesis of semiconducting CdSe quantum dots (semiconducting nanoparticles that show confinement effects and, thus, size-dependent band gaps) was possible through an organometallic synthetic route that utilizes tri-octyl phosphine selenide as a selenium source. Other II—VI quantum dot materials from the same methods include CdS, ZnSe, Mn-doped ZnSe, PbS and PbSe as well as CdSe@ZnS core/shell structures and their analogues. Overall, the synthesis of the most common quantum dots is reasonably mature. The original method has been refined in various ways for a better control of size distribution and shapes and for the use of more convenient cation sources and solvents. Nowadays, the focus is on controlled synthesis of new quantum dot materials and complex quantum architectures with tunable optical and electronic properties, on controlled incorporation of dopants to yield dilute magnetic semiconductors and tailored electronic and optical properties, on control of surface and interfacial chemistry to facilitate device integration and bioconjugation, on utilization of high throughput (microfluidic) and green methods for synthesis, and on integration of quantum dots into new photovoltaic, optoelectronic, bioanalytical, and other device architectures. More recently, CdSe and CdSe@ZnS quantum dots were successfully prepared by employing B_2Se_3, B_2S_3 and P_2S_5 as new chalcogen sources in the presence of primary amine (Fig. 1.7) [39,40]. The new synthetic method operates at much lower reaction temperatures, which allows microwave-assisted heating, high-throughput screening without a need of refluxing apparatus and facile surface functionalization. Nanoparticle-to-nanoparticle conversion also has been an important alternative to prepare metal chalcogenide nanostructures [41,42].

Fig. 1.7. Photoluminescence of colloidal CdSe quantum dots from microwave-assisted reactions at low temperatures.

Hydro- and solvo-thermal methods have been successfully used for the synthesis of inorganic−organic hybrid metal chalcogenides. They are used for preparation of open-framework structures with organic molecules as either templates for the formation of inorganic frameworks or covalent linkers in the frameworks. Notably, prepared have been framework structures of supertetrahedral clusters of metal chalcogenides and their properties have been studied for various applications such as hydrogen production and ionic conductivity [43−46]. A family of organic−inorganic hybrid structures ranging from one-dimensional chains to three-dimensional frameworks have been synthesized based on II−VI semiconductors [47].

Quantum dots are nanoscale semiconductors that show confinement effects and thus have a size-dependent band gap. The latter has motivated a large effort aimed at reproducibly controlling these morphological factors. Shape control of the CdSe system is well understood from an empirical standpoint, and theoretical understanding is quickly growing. For other systems, less is known. Thus, extending the ideas developed for CdSe to other semiconductor systems, such as InP and GaN, remains challenging. Seeded growth strategies, which yield nanocrystals and nanowires of controlled diameter and length, appear promising [48]. When successful, such synthetic endeavors yield new insights into the physics of these important materials, including scaling laws and rules that describe the effect of dimensionality on the optoelectronic properties [49,50].

Like quantum dots, nanoparticles of single metals have properties that differ from their bulk counterparts, and thus represent an important topic for the discovery of new materials. For example, nanoparticles of simple metals such as Au, Ag, and Pt continue to uncover new physical phenomena and new applications. Au is generally known as a catalytically inert noble metal, but 2 nm Au particles are highly active for low-temperature CO oxidation. Au and Ag nanoparticles also have optical properties that differ dramatically from their bulk analogous. The surface plasmon resonances of these nanoparticles are tunable by size, shape, and surface chemistry, and allow for advanced applications in bioanalytical and photonic devices. Pt-based nanoparticles are among the most studied catalytic metals, and multi-metal nanoparticles are gaining increased attention as well. FePt and related alloy nanoparticles have been a primary target of research in the past few years because of their magnetic properties and possible applications in ultrahigh density magnetic storage devices. Other multi-metal alloys of Pt, Pd, and Au are being studied for their tunable catalytic properties.

Nanoparticles, nanorods, nanowires, and other ''nanoshapes'' of metals, oxides, sulfides, and other materials are currently important targets for the design and discovery of new materials, as

their physical properties often depend on their shapes and, from a catalysis perspective, the crystal faces that are exposed. Strategies for controlling the morphology of nanomaterials include a growing number of solution and vapor-phase methods, as well as post-synthesis etching. Among the most studied materials from a size- and shape-controlled perspective, in addition to the quantum dots described above, are ZnO, Fe_3O_4, and TiO_2. An increasing effort is being placed on size and shape control of more complex solids, which remains challenging.

From a solid-state chemistry perspective, most of the materials that serve as targets of nanoscience studies (both synthesis and characterization) are primitive. That is, they involve primarily single metals, simple alloys, or simple binary oxides and chalcogenides. Only a handful of more complex materials, such as most of those that are at the forefront of modern solid-state chemistry research, have been studied. If the spectacular results obtained for these simple metals and compounds when their size is reduced to nanoscale dimensions is combined with the knowledge and capabilities that solid-state chemists have concerning the structures and properties of more complex and exotic materials, exciting opportunities will emerge for discovering new and more advanced materials. A challenge at the forefront of both solid-state chemistry and nanoscience, then, is to develop methods to synthesize and characterize nanoscale materials of compounds that are compositionally and structurally more complex than those currently under investigation. Doing so would greatly expand the complexity of size-dependent physical properties that could be accessed, studied, and exploited. In addition, it could possibly lead to entirely new materials with new structures, and thus provide new insights into structure—property—morphology interrelationships.

Along with the need for increased synthetic capabilities for nanoparticles of all types comes increased need for careful characterization of nanoscale materials. It is not trivial to fully characterize complex nanomaterials. Careful data collection and analysis, beyond simple observations of nanocrystal size and shape, are required to prove that a particular multi-element compound has been made. The combined use of techniques such as X-ray diffraction, electron microscopy, electron diffraction, elemental analysis, and various optical and electronic spectroscopies, as well as physical property measurements, are common for solid-state chemists and are necessary to fully characterize a solid-state material. However, these ideas and techniques must merge with mainstream nanoscience in order to fully characterize nanomaterials of analogous complexity. Issues of homogeneity, composition variation, local structure, and defects in complex nanoparticles represent an area where increased attention is warranted.

1.2.5. Directed synthesis of extended solids from molecular building blocks

Remarkable progress has been achieved in the field of synthesis of solids assembled from molecular building blocks linked by highly directional bonding, both based on coordination bonds between metal atoms and functionalized organic linkers and on charge-assisted hydrogen bonds between organic molecules. The latter is a part of the broader areas of organic solid-state chemistry and crystal engineering which have made substantial progress in recent years. Discussed in this section are specifically the compounds involving metal centers, but many of the general principles apply for the purely organic solids as well. Reasonable progress has been made towards the rational design of such frameworks. Work in this area has led to the discovery and development of materials that two decades ago belonged to our imagination and dreams. This important and successful field of inorganic synthesis constitutes fertile ground for the integration of a variety of solid-state synthetic techniques. It is interdisciplinary in nature requiring expertise in a number of different areas such as solid-state chemistry, coordination

chemistry, organic synthesis, crystal design and growth, structure elucidation, etc. The diverse properties of the resulting hybrid inorganic−organic materials provide potential for a variety of applications. The synthetic approach, essentially combining molecular components, allows access to a large class of diverse compounds that provide tremendous opportunities for development of multifunctional materials. A judicious choice of the type of molecular building blocks allows for designing the structural dimension and topology of the target material and for the deliberate introduction of new functionalities in order to achieve specific physical and chemical properties.

The preferred synthetic approach for building such frameworks is the hydrothermal, or more broadly, solvo-thermal synthesis. Indeed many of the coordination frameworks have been produced via this approach. Recent advances in this area include the use of multiple organic components to serve additional roles beyond direct coordination and assembly. Specifically, these include influence of redox state, templating (or structure direction), light harvesting as well as in situ ligand syntheses. With respect to structure direction, the use of non-coordinating organic species such as 4,4′-bipyridine in the presence of rare-earth carboxylate frameworks allows for not only tuning of pore topology, but also introduces chromophoric species capable of sensitizing luminescence from the framework lanthanides. Given the success of templating in zeolitic systems, it is conceivable that extension to coordination materials holds significant potential for design influence. Turning to redox influence, the use of multiple organic species allows for the selective oxidation of organic components to form simpler linker molecules such as oxalates. This in turn promotes reduction in the inorganic component and thus the potential to stabilize mixed valence compounds as well as oxidation states not commonly seen in aqueous systems. As the catalog of organic linker species utilized for construction of such frameworks has expanded, many of these observations have been noted serendipitously. The frequency of these results, however, suggests that use of this phenomenon as a design principle may be on the horizon.

The assembly approach for building networks is a ''bottom-up'' strategy that, when combined with the ''top-down'' structural knowledge accumulated by solid-state chemists (and certainly mineralogists), can become a powerful tool in the design of complex materials. Thus, a number of inorganic−organic hybrid materials in which the combined organic and inorganic moieties determine the topology and dimension of the overall structure have been prepared in recent years [51−58]. Although complete control of the properties of the materials obtained has yet to be achieved, this approach has brought us closer to making materials by design (Fig. 1.8).

The major problem, however, is the fact that modification of the chemical and physical properties of these materials generally requires the design and preparation of new building units. So, a flexible building unit that can be chemically modified to suit a range of applications is required. These units must first have good structural stability, their physicochemical properties must be easily modified, and their functionalization should be possible.

A promising yet challenging strategy is the use of well defined and stable metal clusters equipped with multidentate bridging ligands as building units for the assembly of hybrid materials based on discrete supra-molecular assemblies or polymeric extended supra-molecular frameworks. In contrast to frameworks based on mononuclear species, the unique properties of metal clusters, intermediate between mononuclear species and metallic elements, lead to a number of advantages of using clusters as building units. For example, larger clusters can potentially increase pore sizes in porous solids, and a larger number of ligands around the cluster core can potentially lead to a wider variety of topologies. Facile ligand substitution allows for precise control of structure and function through modular ligand substitution. In addition

Fig. 1.8. Comparison between the accuracies of preparation of materials by (left) traditional explorative synthesis, and (right) directed synthesis using the building block approach (pictures are courtesy of Tommy Murphy-WFU).

to their remarkable electronic flexibility and magnetic properties recent work indicates that some clusters release their coordinated ligands upon photolysis which presents a tremendous opportunity in photocontrolled modification of organic substrates. The ease by which metal clusters can be chemically modified, their robustness, and strong Lewis acidity and photocleavage ability should in principle lead to significant advances in chemical catalysis. Different metal clusters are being actively investigated; however, octahedral metal clusters have received special attention due primarily to the fact that they constitute the basic component of the so-called *Chevrel* phases (Fig. 1.9) which show unusual superconducting properties. Here, 0D octahedral metal clusters will be used to illustrate what has been achieved in the directed
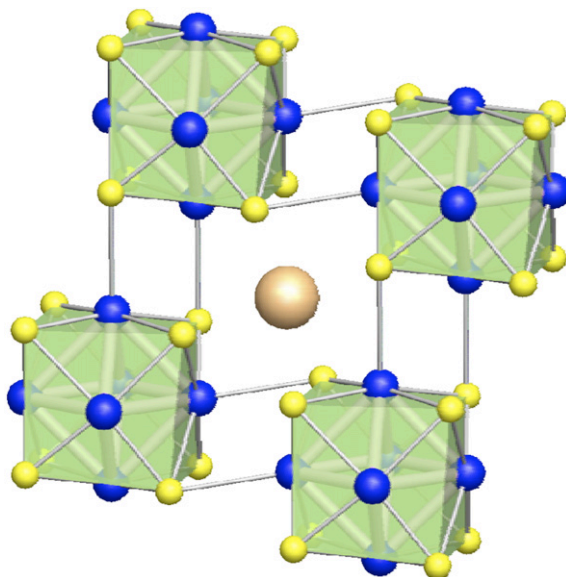
Fig. 1.9. The structure of *Chevrel* phases $A_xMo_6L_8$ built of octahedral Mo_6L_8 connected via all their inner ligands to generate a 3D framework and cavities occupied by the cations. Blue, Mo; yellow, L; brown, A.

assembly of extended solids using stable molecular building blocks and describe the opportunities and challenges ahead.

Octahedral metal clusters are the subjects of intensive studies because of the versatility of the design of the coordination environment around the highly symmetrical cluster core, with six apical labile ligands. Diverse neutral and anionic ligands with various donors have been used to substitute the apical ligands. Clusters equipped with cyanide ligands that have the ability to coordinate to two metal centers are being investigated as versatile building blocks of solids with extended structures [59—63]. Extended frameworks solids that incorporate octahedral metal clusters as building blocks in place of individual metal centers are expected to have expanded frameworks with larger pores. For example, recently investigated was replacing octahedral metal ions with octahedral clusters. The framework structures of $M_4[Re_6X_8(CN)_6]_3 \cdot xH_2O$ and $A_2[MNb_6Cl_{12}(CN)_6]$ are expansions of the Prussian blue structure and present a fascinating example of this approach (Fig. 1.10) [64—67]. In both cases, the cluster $[M_6X_n(CN)_6]^{4-}$ replaces the anion $[Fe(CN)_6]^{4-}$ as the basic building unit. The versatility and potential of this approach is further demonstrated in the synthesis of compounds that combine metal clusters with linking metal complexes. The specific geometry, coordination requirement, and functionality of the latter results in a variety of supra-molecular assemblies and coordination polymers with different dimensions and topologies. Two of the most fascinating examples are the formation of: (1) a series of supra-molecular assemblies resulting from progressive coordination of Mn(III) Schiff base complexes to $[Nb_6Cl_{12}(CN)_6]$, and (2) layered chiral coordination polymers with chains of copper complexes that are pillared by $[Re_6X_8(CN)_6]^{4-}$ (Fig. 1.11) [68].

The inertness of the $[M_6X_n]^{2+}$ core, which can be viewed as a nanometric-sized metal atom, opens up tremendous opportunities for the design, and directed synthesis of unprecedented materials. The availability of a large number of metal complexes with a variety of structural, electronic and optical properties, the recent development of supra-molecular arrays based on bimetal building units, and the availability of a number of different types of clusters, including the surprising oxo- and seleno-bridged siamese clusters, provides unlimited source of building units to be investigated.

1.2.6. Porous materials

As a result of intensive developments of new synthetic techniques during the last decade, porous materials can now be designed with great control over pore structure, periodicity of pores and particle morphologies at multiple length scales. Compositions of porous solids have been extended from a few main group elements (mainly silicates and aluminosilicates) to compounds drawing from a significant portion of the periodic table. Equipped with a large palette of
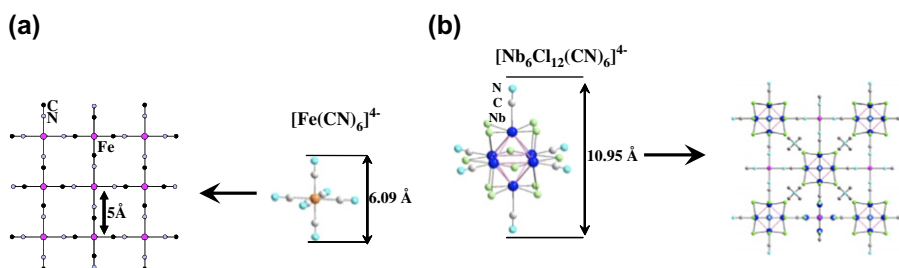
Fig. 1.10. (a) A unit cell of $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$. (b) A unit cell of $A_2[MNb_6Cl_{12}(CN)_6] \cdot xH_2O$.
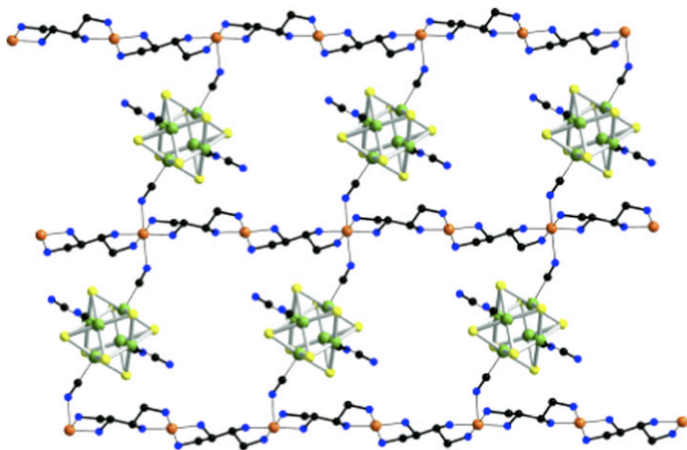
Fig. 1.11. Ball and stick representation of the chiral layered coordination polymer of $[Cu_2(threotab)_3(NH_3)]$ $[Re_6Se_8(CN)_6] \cdot 2H_2O$. Color code: Re: green; Se: yellow; Cu: orange; N: blue; C: black.

synthetic methods and advanced techniques for structural characterization at the atomic level and larger scales, solid-state chemists are now in a position to progress from synthesis to applications, and this progression has been the recent trend in the field. Many high-tech applications require greater complexity, multiple functionality and multiple compositions of materials. Here, the materials chemist can make important contributions by developing novel strategies for the generation of complex materials composed of multiple components, such as assemblies of nanoparticles incorporated into structures with larger feature sizes that can be interfaced to the tangible world. Significant advances can be expected from new assembly and self-assembly techniques for discrete components larger than molecules with dimensions ranging from several nanometers to millimeters. Hierarchies of pore structures and multi-component assemblies are often found in natural materials which exhibit high-performance characteristics or serve multiple functions. Some recent developments in porous materials, outlined below, indicate that we are on track to move closer to the complexity of structures found in nature.

On the small-pore length scale (micropores: 0.2−2 nm), zeolites have been the work-horse serving a multi-billion dollar energy industry [69,70]. Major recent advances in zeolite chemistry have involved the incorporation of organic functional groups into the framework of zeolites, preparation of supported oriented films, synthesis of polycrystalline membranes with low defect levels and especially the development of methods for syntheses of colloidal zeolites (nanozeolites) with narrow particle size distributions for diameters <200 nm (Fig. 1.12 [71]). Nanozeolites have large external surface areas, high surface activity, shorter diffusion path lengths compared to typical micrometer-sized zeolites and therefore highly accessible catalytic sites. The particle surface can be functionalized with organic groups to control dispersion in other phases and facilitate use of nanozeolites as building blocks for extended structures. Nanocrystals can be used as seeds for zeolite synthesis or as model systems for studying zeolite crystallization to answer the still open question of the role of small fragments during condensation of zeolites.

Progress in control over morphologies has been facilitated by a better understanding of molecular interactions between zeolite crystal surfaces and species such as solvent, cations and organic templates. Nonetheless, several challenges remain, including low synthesis yields for nanozeolites due to mild reaction conditions, inconsistent reproducibilities, greater structural
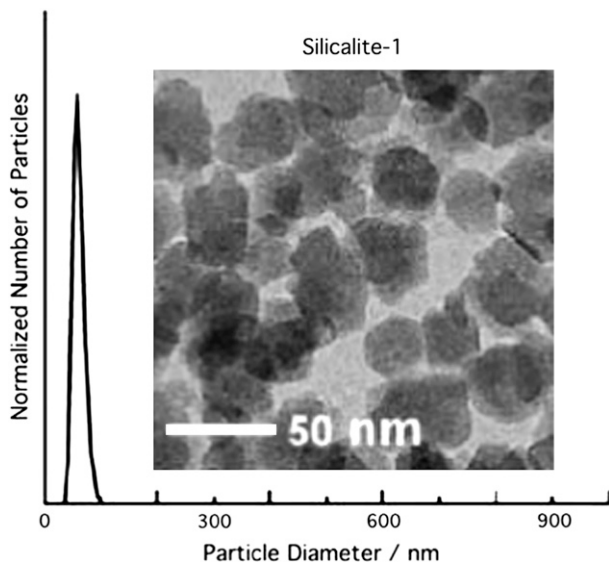
Fig. 1.12. Size distribution and TEM image of zeolite nanoparticles (figure adapted).

control for nanozeolites and issues of scale-up. Chiral zeolite topologies exist, which are of considerable interest in chiral catalysis; however, it is still difficult to resolve enantiopure zeolites. In this direction, some recent progress has been made by heterogenizing enantioselective homogeneous catalysts on the surface of zeolites.

Porous metal-organic frameworks provide a major extension of microporous structures to new compositions [72−74]. They are crystalline solids with 3D frameworks, assembled by connecting metal ions or clusters through coordination by molecular bridges. In these structures, the integrity of the building blocks and their properties (chemical functionality, rigidity) are maintained so that variable composition can be designed into the structure on a periodic scale. Although the as-synthesized products contain solvent molecules within the cavities, it is possible, in some cases, to exchange solvent guests or remove them completely while maintaining permanent porosity. Control over pore sizes is possible by impregnation with non-volatile guest species or by interpenetration or interweaving of multiple frameworks. In contrast to zeolites, metal-organic frameworks are held together by relatively weak bonds, which allows for solvent-driven, controlled structural transformations. Much excitement has revolved around the capacity of certain frameworks to store hydrogen and the observation that methane sorption capacity can be very high. Catalytic applications have not yet been widely studied and new opportunities may exist in this direction. As in the case of zeolites, the potential for chiral structures remains intriguing and challenging.

The field of mesoporous materials' synthesis (pore sizes 2−50 nm) continues to progress at a fast pace. Using surfactants, block copolymers and liquid crystals as templates, silicates with diverse mesostructures and high surface areas can now be synthesized in a much greater variety of forms than is possible for zeolites: powders, nanoparticles, self-standing thin films, supported films, fibers, monodispersed spheres, and monoliths. Surface functionalization with organic groups either during the synthesis or in post-synthetic procedures is widespread. Near the turn of the millennium this area has transitioned from synthesis and characterization towards applications and commercialization. Potential and actual applications include low-k dielectrics,

catalysis, separation, optics, magnetics, sensing, energy storage, thermal and acoustic insulation, bioencapsulation, and more. The concept of response of a mesoporous film to its environment has been demonstrated in materials functionalized with molecular gates, that allow controlled release or variable permeability, properties of interest in microfluidic applications. More recently, new opportunities opened up through the development of periodic mesoporous organosilicas (PMOs) and the development of new methods for forming non-silicate mesostructures. PMOs are composed of silsesquioxanes organized via organic bridges into mesoporous architectures. The stoichiometry of organic and inorganic components is well defined by the molecular building block. The organic bridges allow for chemistry within the channel walls of a material whose shape, chemical properties, interfacial character and stability can be tuned. As PMOs can also be functionalized with non-bridging groups, mixed properties can be built into the structure. Large-pore non-silicate mesostructured materials can be obtained by evaporation-induced self-assembly (EISA), ion-exchange cross-linking of soluble clusters and nanocasting [75,76]. In EISA, the condensation of inorganic precursors and their self-assembly into mesostructured phases is driven by a change in concentration upon solvent evaporation. This approach has several advantages compared to hydrothermal syntheses with fixed compositions: mesophase formation is fast, a large variety of mesophases are accessible, and homogeneous mother solutions or gels can be prepared in dilute form. The last factor permits the use of non-silicate precursors to obtain, for example, mesoporous titania, niobia or binary oxides. The evaporation process is a natural step in common coating and printing processes, so that spatial patterning is now accessible for mesoporous films. Ion-exchange cross-linking involves assembly of soluble adamantane clusters or binuclear Zintl clusters with platinum ions in the presence of long chain alkylpyridinium or alkylammonium surfactants via coordination reactions [77,78]. Nanocasting employs hard templates (pre-formed mesoporous silicates or carbons) or soft templates (polymeric liquid crystals) to form replicate structures [79—81]. With hard templates, precursors are incorporated into mesoporous channels and thermally decomposed to form nanoparticles or continuous frameworks with shapes dictated by the template. Nanocasting has proven to be a powerful method for creating non-siliceous mesoporous materials with new compositions, controllable structure and specific functionality for compositions that are not readily accessible by solution-based methods. In terms of numbers of new studies, mesoporous carbon prepared by nanocasting is beginning to take the place of mesoporous silica. Carbon replicas, which are synthesized from pitches, sucrose precursors or CVD precursors, can form film and monolithic structures that are easier to handle than mesoporous silica. Being conductive, mesoporous carbon is of interest for electrode materials in secondary lithium batteries, supercapacitors, biosensors, and electrochemical reactions. Surface modification of carbon is more difficult than with silica, and the field can benefit from new functionalization methods. In spite of the rapid progress in mesoporous materials' synthesis, a number of existing challenges can be identified. A more detailed understanding of mesostructural organization, defects, grain size and structure, and nucleation processes is important for engineering of these materials. For films, precise control of mesochannel orientation on different substrates and understanding of the substrate influence on the structure of very thin films will be necessary to facilitate membrane applications and other uses relying on mass transport. Nanocasting with hard templates can become even more widespread if the degree of channel filling with certain precursors can be increased.

The next larger range of pore sizes, macropores (>50 nm), is relevant because it provides enhanced mass transport of guest species and sufficient space for pore wall modification with functional groups ranging from small molecules to polymer layers to nanoparticle
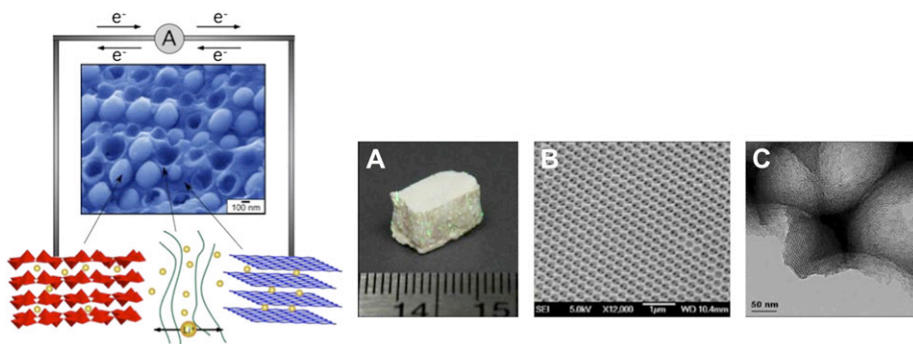
Fig. 1.13. Left: Schematic diagram and SEM image of a 3D interpenetrating electrochemical cell. Right: Monolith of silica (A) with periodically structured macropores (B) and mesoporous walls (C).

coatings. Furthermore, walls in macroporous solids tend to be thicker than in zeolites or mesoporous materials, so that control over the wall structure itself can be possible. Macroporous materials thereby offer great opportunities for hierarchical structuring and multifunctionality. Using colloidal crystal templating, a large number of 3D ordered macroporous (3DOM or inverse opal) oxide and non-oxide compositions can be prepared, including insulator, semiconductor, metal, polymeric and hybrid macroporous materials [82,83]. Alternate templates include bioskeletons and emulsions. Template-free syntheses of macroporous solids are attainable from two-phase composite structures after leaching of one of the phases [84,85]. Pseudomorphic transformations of these structures are possible, in which the general shape of the structure can be maintained, while its composition is altered. When macropores are periodic on the length scale of visible or infrared light, the materials can function as photonic crystals. Other applications that rely on the relatively large accessible reactive surface of macroporous solids require less periodicity. These include bioglasses, hierarchically structured catalysts and battery materials. 3DOM carbon can be prepared in monolithic form and can therefore provide a basis for complex assemblies, involving coatings with catalytic nanoparticles or even multifold interpenetrating structures. An example of the latter (Fig. 1.13, left) depicts a macroporous carbon anode, coated with a conformal thin film of a polymer electrolyte and infiltrated with vanadia gel. After lithiation, the resulting 3D nanostructured electrochemical cell produced an open circuit voltage and lithium could be shuttled between electrodes multiple times. Other examples of complex 3DOM structures include those containing zeolitic or mesoporous walls around interconnected macropores (Fig. 1.13, right) of a silica monolith with both macropores and mesopores. The structural hierarchy has been advanced to the next level, by combining colloidal crystal templating and surfactant templating with lithographic patterning. Such fractal structures mimic those widely found in nature, where mass transport needs to be directed from a major source to widely distributed destinations. The remaining challenges in synthesis of macroporous materials involve both the templates and the wall skeletons. Templates with symmetries other than face-centered cubic (the common symmetry obtained by natural assembly of uniform spheres) will be required to access different photonic crystal structures capable of photonic band gap formation. For optical applications, precise defect control and directed defect design will remain important targets. New template structures can also be used to alter mass transport of guests and the space available for post-functionalization of an inverse opal. Biomimetic templating can result in novel morphologies and possibly chiral interfaces. Lithographic methods, like direct laser writing, can also provide novel template forms. Materials'

aspects for improvement include minimization of shrinkage to avoid cracking and other defects during ceramic processing and methods of creating active phases at lower temperatures. For example, in the case of 3DOM electrode structures, electroactive oxide phases are usually obtained at higher temperatures which tend to result in grain growth and loss of ordered wall structures. From a practical standpoint, a greater understanding of correlations between structure and mechanical properties of macroporous materials as a function of surface modification, composite structure and pore architecture, needs to be developed.

Perhaps the biggest advances in the next few years will result from directed assembly, self-assembly or programmed assembly of multiple porous and non-porous building blocks into structures with hierarchical pore architectures [86–89], feature sizes on multiple length scales and discrete or inter-related functionalities. Because many building blocks are already available, the ability to create materials with complex organization will depend to a large extent on understanding and directing the interfacial chemistry that governs the organization of organic and inorganic matter. For components in the size range from tens of nanometers to millimeters, assembly will involve attractive and repulsive interactions created by electrostatic forces (as employed in layer-by-layer growth), capillary forces, fluidic shear, and for larger components magnetic and gravitational forces. Another important target will be the integration of these new materials into existing platforms. To achieve this goal, processing compatibilities must be considered throughout the complete nano-to-macro assembly process.

1.3. Materials

The synthetic toolbox of the solid-state chemist is vital for the discovery of new materials with useful properties. Tailoring the combination of specific properties in a material (electrical, magnetic, mechanical, etc.) in order to provide desired multifunctionality remains a challenge in solid-state synthesis. Highlighted in this section are some materials of contemporary interest such as thermoelectric materials, ferroelectric materials, materials for hydrogen storage, hybrid organic–inorganic materials, and materials for quantum computing.

1.3.1. Thermoelectric materials

Thermoelectric materials are used for both power generation and refrigeration. Power generation is based on the ability of the material to generate voltage from an applied temperature gradient while, conversely, thermoelectric coolers achieve a temperature gradient when voltage is applied. Their usage includes power supplies for navigation beacons and deep space probes and Peltier coolers. The advantages of such solid-state devices are obvious—no moving parts, high reliability, and small size. Thermoelectric materials must be able to maintain a temperature gradient (requiring low thermal conductivity κ) but carry an electrical current (requiring relatively high electrical conductivity σ) and they must be able to convert a thermal gradient into a voltage (reflected by the Seebeck coefficient S). Unfortunately, the known thermoelectric materials are hindered by inherently low efficiency because these three criteria are interdependent and optimum combination is difficult to achieve. For instance, improving the electrical conductivity results in an increase in thermal conductivity. As a result of this, the field of thermoelectrics stagnated after the initial investigations in the 1960s, and the currently used materials are the same systems that were studied 30 years ago. Small band gap semiconductors have the best combination of electronic characteristics in material-specific optimal temperature ranges. Bi_2Te_3 is used at low temperatures; doped PbTe or GeTe at moderate temperature; and SiGe alloys at temperatures above 700 °C.

Clearly, research in thermoelectrics involves an uphill struggle against the laws of physics. In order to achieve an optimal combination of high Seebeck coefficient, high electrical conductivity, and low thermal conductivity, it appears to be necessary to cheat. The field of solid-state chemistry has recently provided a number of examples of tailoring solids to address this problem, aided by new characterization techniques that can probe local environments combined with the classic solid-state characterization method of X-ray crystallography. This has produced a recent resurgence in the field of thermoelectrics and a number of breakthroughs. One very promising class of thermoelectric materials being studied are compounds with purposely designed or serendipitously incorporated nanocomponents. Since the pioneering work of Dresselhaus on semiconducting PbTe quantum well superlattices in the 1990s, research on low-dimensional thermoelectric materials has exploded [90]. Quantum confinement works to improve the efficiency via a number of avenues. Phonons are scattered at the boundaries of the quantum wells, lowering κ. The band structure is also affected by quantum confinement, enhancing the density of states at the Fermi level (which increases the Seebeck coefficient). In addition to quantum well structures of a variety of semiconductors (PbTe, Bi_2Te_3), quantum wire arrays of bismuth metal and quantum dot arrays are also being investigated to take advantage of the effects of quantum confinement on the thermoelectric figure of merit [91]. This work often edges into the realm of solid-state physics, involving CVD sample preparation and theoretical calculations. However, the theoretical discoveries made in the physics community are now beginning to explain some of the unusual results obtained by solid-state chemists.

A breakthrough was recently obtained in a doping experiment on a classic thermoelectric compound, PbTe. Varying levels of doping with Ag and Sb (producing $AgPb_mSbTe_{m+2}$) were investigated to see the effects on the thermoelectric behavior [92]. Unusually high efficiencies were observed for certain doping levels while other samples prepared by slightly different methods were quite worse despite having the same stoichiometry and identical X-ray powder pattern. The explanation for this conundrum was found by moving beyond the traditional characterization method of crystallography. These compounds were thought to be solid solutions of PbTe and $AgSbTe_2$. However, high-resolution TEM studies and pair distribution function (PDF) analysis of powder X-ray data of the high ZT samples showed localized non-uniformities. It is apparent that when the compounds are grown using a specific temperature profile, it allows nanocrystallites enriched in $AgSbTe_2$ to form in a PbTe matrix (Fig. 1.14) [93,94]. It is these endotaxially embedded nanoparticles that are responsible for the improved thermoelectric properties of the material; if a different preparation method is used which prevents their formation, the resulting ZT is much lower.

This result points out two factors that will be crucial to the future design, synthesis and characterization of improved thermoelectric materials. One is the beneficial effects of nanocomponents, whether serendipitously or purposefully incorporated. Synthetic methods can be modified to promote the formation of localized inhomogeneities that will scatter phonons (lowering the thermal conductivity) while optimizing the Seebeck coefficient. The other factor is the limitations of X-ray diffraction in characterizing these materials. X-ray diffraction averages out short-range structural deviations such as nanocomponents, mixed sites, interstitial occlusions and other localized disordering, and must be supplemented by other techniques that are better at characterizing these structural issues, such as HRTEM and PDF analysis. The combination of recent theories on optimizing thermoelectric behavior (such as quantum confinement effects and the phonon glass electron crystal theory of Slack—'PGEC') with new analysis techniques has led to a renaissance in thermoelectrics research. Solid-state chemists are constantly discovering new compounds featuring large unit cells, heavy atoms, structural complexity, and loosely
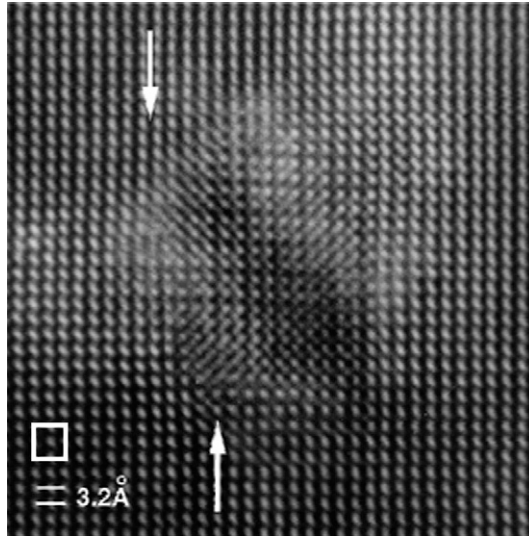
Fig. 1.14. HRTEM image of a AgPb$_m$SbTe$_{m+2}$ sample, showing endotaxial growth of a nanocrystal in the PbTe matrix.

bound guest atoms which have the potential to be good thermoelectrics. Families of materials such as Zintl phases and half-Heusler alloys are showing great potential, as are materials that occupy the boundaries between structural classifications. Future breakthroughs in this area will involve collaboration between solid-state chemists, physicists, and electrical engineers in deriving and utilizing further theoretical guidelines to design and discover materials with higher efficiencies than those that are currently used.

1.3.2. Magnetoelectric materials

Multiferroics possess two or more switchable properties such as spontaneous polarization, spontaneous magnetization or spontaneous strain. In particular, in those where magnetic and ferroelectric orderings coexist, their strong coupling (induction of polarization by a magnetic field and of magnetization by an electric field, magnetoelectric effect) is rare among the materials. Yet, such coupling is very desirable in order to make devices based on the mutual control of magnetic and electric states. Although investigation on magnetoelectric compounds is traced back to 1950s, a revival of interest in those materials is heralded recently largely by the discovery of the so-called colossal magnetodielectric or magnetocapacitance effect in rare-earth manganites [95,96].

Among the many multiferroic compounds, the magnetoelectric effect has been studied most extensively in the perovskite-type BiFeO$_3$ or BiMnO$_3$, the boracite family, and the families of BaMF$_4$ (M = divalent metal ion), hexagonal RMnO$_3$ (R = rare-earth metal ion) and the rare-earth molybdates [97−102]. Obviously, the largest coupling of ferromagnetism and ferroelectricity is expected when these properties originate from the same atomic sites in the structure. Transition-metal ions are not ideal for this purpose, however, because a partial occupancy of d-orbitals, one essential ingredient for ferromagnetism, conflicts with the usual requirement of empty d-bands for the ferroelectricity originated from the second-order Jahn−Teller effect. The lone-pair effect of heavy main group elements such as Bi^{3+} has been exploited in magnetic perovskites and yet the oxides have not shown a strong magnetoelectric coupling simply because the subunits in the

structure responsible for ferromagnetism and ferroelectricity are separated electronically. It remains to be seen if we can find compounds in which such subunits are coupled strongly electronically or structurally. An alternative approach has been taken for many years through preparation of composites of ferromagnets and ferroelectrics in the hope that the magnetoelectric coupling can occur through the structural contact between two separate phases. While this approach has not provided a significant improvement over the years due to the negligible coupling between thick slabs of layered magnets and ferroelectrics, recent studies have found that composite materials with nanometer-sized pillars of $CoFe_2O_4$ within a $BaTiO_3$ or $BiFeO_3$ matrix shows promising results [103,104]. The synthesis of the composites relies on phase decomposition upon vapor deposition, rather fortuitous formation of nanopillars and intimate lattice coupling between ferroelectric and magnetic materials. The criterion in choosing the right magnetic and ferroelectric materials for such nanocomposites is lattice match, chemical comparability, solid solubility and elastic properties which ultimately determine the morphology of the composite material and implicitly its functionality. Further exploration may provide more promising composite materials.

1.3.3. Materials for hydrogen storage

The problems inherent in the use of fossil fuels are becoming more evident each year. The drawbacks of pollution, geopolitical instability, and limited supply of oil are beginning to have serious effects, particularly in the transportation sector. The recent Hydrogen Fuel Initiative promotes development of clean, hydrogen powered automobiles. To allow for the use of hydrogen as a viable fuel, fuel cell technology must be optimized and storage methods must be developed to allow vehicles to carry enough hydrogen on-board to enable a greater than 300-mile driving distance. The storage method must fall within the vehicular constraints of weight, volume, efficiency, safety, and cost. The DOE has issued following technical performance targets: 2 kW h/kg (2 kW h of energy produced per kg of storage material weight; this translates to a storage material that contains 6 wt% accessible hydrogen) and \$4/kW h by 2010, and 3 kW h/kg (9 wt% hydrogen) and \$2/kW h by 2015 [105,106]. Conventional storage methods (high pressure compressed gas cylinders and liquid hydrogen tanks) can meet the 2010 standards, with tanks being developed for 10,000 psi pressures. However, due to the energy required to fill the containers and the danger of high pressures, this option is not realistic and not likely to meet the 2015 guidelines. Much of the promising work in hydrogen storage is focusing on storing the gas in solid matrices, and solid-state chemistry has an obvious role in the development and optimization of such materials.

For hydrogen storage materials, there are three mechanisms by which hydrogen is taken up and released—adsorption, absorption, and chemical reaction. Adsorption is a surface phenomenon commonly divided into two subcategories (physisorption and chemisorption) depending on the strength of the interaction between the H_2 gas molecule and the surface. Materials with large surface areas such as carbon nanotubes are being investigated for their hydrogen adsorption properties. The absorption process, exemplified by hydrogen storage alloys such as $LaNi_5$, involves breaking of the H_2 bond and intercalation of atomic hydrogen into interstitial sites in the lattice, forming hydrides such as $LaNi_5H_{5.6}$. Hydrogen storage by chemical reaction involves displacive chemical reactions for both hydrogen generation and hydrogen storage. Sodium alanate-based complex metal hydrides are an example.

Gas adsorption onto high surface area porous materials has been studied for decades and is used in industry in a variety of processes, such as gas separation using zeolites. Adsorption of molecular H_2 onto the surface of lightweight activated carbons and carbon nanotubes has been

studied by many researchers, with very inconsistent results. Initial measurements of up to 10 wt% hydrogen adsorption by carbon nanotube samples have been difficult to reproduce, and may have been due to the uptake of adventitious water vapor. Recent studies on a variety of sample preparations and gas loading techniques indicate that low temperatures (77 K) are needed to facilitate loading of up to 5 wt% hydrogen; this decreases to around 1% at ambient temperatures and requires high pressures [107]. It is likely that the weak van der Waals inter-actions between the hydrogen and the material surface, while favorable for allowing the release of hydrogen, work against the adsorption of large quantities of this gas at ambient temperatures. Variability of sample batches and insufficient characterization of the structural nature of acti-vated carbons and nanotube samples are also a major problem. Slight improvements may be possible using different carbon morphologies and metal dopants.

Another class of lightweight porous materials of interest for hydrogen adsorption are metal-organic framework materials. These are crystalline coordination polymers comprised of metal ions or metal oxo clusters connected by multidentate rigid organic linkers. Their ordered structure allows for consistent sample preparation and adsorption behavior, unlike carbon materials. The variety of possible linkers and metal clusters and the ease of synthesis has resulted in a very large number of 2D (layered) and 3D (network) materials; over 5000 structures have been reported in the literature. The porosity, large surface area (exceeding that of many zeolites in some cases), and low mass make these attractive materials for hydrogen adsorption. However, the studies that have been carried out on compounds in this family in-dicate that, like porous carbon materials, hydrogen adsorption in most of them is hindered by the weakness of the interactions between hydrogen and the metal-organic framework. In most cases, adsorption of significant amounts of hydrogen (2−4 wt %) requires low temperatures and high pressures [108].

Absorption of hydrogen by intermetallic compounds and alloys involves cleaving of the H_2 bond at the surface of the material and the intercalation of atomic hydrogen into the interstitial sites of the bulk structure. These materials are promising hydrogen storage materials due to their combination of high hydrogen capacity, close-to-ambient pressures and temperatures needed for charging and discharging, and cycling capability. The current state-of-the-art com-pound, $LaNi_5$ (or substituted analogues such as $LaNi_{3.5}Co_{0.7}Al_{0.8}$), can absorb one atom of hydrogen per metal atom forming $LaNi_5H_6$ at room temperature and 1−2 atm H_2 pressure. Moderate heating ($<100\ °C$) is required to release the hydrogen, and the process can be cycled hundreds of times. These intermetallics are comprised of an electropositive hydride-forming element A (alkali, alkaline earth, lanthanides, and early transition metals; elements that will combine with H_2 to form a stable hydride, such as CaH_2) and a more electronegative non-hydride forming metal B (a late transition metal element that does not form a stable hydride). The ratio of A to B determines the amount of hydrogen that can be taken up, and also the sta-bility and reversibility of the process. A high concentration of A element will increase the hy-drogen capacity, but will also increase the likelihood of an irreversible disproportionation reaction occurring, forming the stable hydride of element A [109].

The problems with the intermetallic materials are weight and cost. While the volumetric density of hydrogen in these compounds can exceed that of liquid hydrogen, the gravimetric density of hydrogen in hydrides such as $LaNi_5H_6$ or TiFeH is below 2 wt% and they are rel-atively expensive compounds. This works against their use in vehicles, but does not hinder their utilization as electrodes in nickel−metal hydride batteries. Achieving higher mass den-sities of hydrogen for vehicular use requires the use of lighter elements such as Li, Na, Mg, and Al. Work is underway in a number of laboratories to create new hydrogen storage

intermetallics with these elements. The kinetics of hydrogen absorption are often hindered by lowering the amount of transition metal; new activation procedures and different morphologies (ballmilling, amorphous phases, nanoparticles) are being investigated to overcome this problem.

Hydrogen storage by chemical reaction to form complex hydrides is the most recent endeavor in the field. Unlike the intermetallic hydrides described above, complex hydrides, such as $NaAlH_4$ and Mg_2NiH_4, are not metallic materials with interstitial hydrogen atoms but are instead ionic materials containing complex hydride anions such as the alanate ion AlH_4^-. The strong covalent Al−H bonds make accessing the hydrogen from this material difficult. Under normal conditions the hydrogen does not come off unless the compound is heated to above its melting point, and high pressures and temperatures are needed to rehydride the resulting mixture of Al and NaH. However, addition of a titanium compound as a catalyst allows dissociation of $NaAlH_4$ at moderate temperatures (180 °C), and the reaction is reversible [110,111]. The catalysis mechanism is not yet understood, and the full 5.5 wt% of hydrogen is not accessible without use of higher temperatures, but this promising result has lead to further interest in this class of materials. In addition to the alanates, other covalently bound hydrides being investigated for potential hydrogen storage applications include borohydrides ($LiBH_4$), amides ($LiNH_2$), and NH_3BH_3. Unfortunately, as the strength of the M−H bond increases, so does the temperature required to extract the hydrogen, and the reaction tends to become irreversible. To address these problems, activation by doping and morphology control (nanoparticles, ballmilling) is being widely investigated.

Each of the three hydrogen storage mechanisms has advantages and drawbacks. Advances in the field will require collaborations between solid-state chemists, metallurgists, physical chemists and engineers to determine ways to optimize the behavior of potential hydrogen storage materials. Composite materials (such as magnesium ball-milled with graphitic carbon) may allow for the favorable properties of multiple components to overcome their disadvantages. Synthesis of new materials will also be a key factor in the search for hydrogen storage materials—light element phases that fall between the metallic bonding of alloys and the ionic bonding of complex hydrides may allow for the high gravimetric hydrogen capacity seen in the complex hydrides to occur with the favorable cycling kinetics observed for the intermetallics.

1.3.4. Hybrid organic−inorganic materials

If the foundation of chemical creativity is in the synthesis of new compounds it is easy to realize how it can be done by increasing the complexities of chemical structures and stoichiometries. A classical approach to complex materials is by combining organic molecular groups with inorganic moieties into crystalline hybrid compounds. This is a powerful method for introducing unique properties and multiple functionalities into inorganic solids. In addition, the organic components may include metal ions as molecular coordination or organometallic complexes. New examples of crystalline organic−inorganic hybrid compounds with transition-metal and post-transition-metal ions with unprecedented structures are being discovered. Despite these examples, additional studies and substantial materials' advances are needed to meet applications that require complex and adaptable functions. The realization of targeted properties and functions through integrated structures is pervasive in biology and has been demonstrated with varying success in manufacturing and technology.

Hybrid materials are attractive because they consist of multiple components that can be organized into spatially identifiable domains with prescribed length scales and degrees of heterogeneity. As such, hybrid systems can be designed to utilize synergistic interactions between the dissimilar components, which can yield new properties and/or enhanced performance. Indeed, synergy will be critical in achieving targeted physical properties (e.g., electronic, optical, and transport properties). A key advantage of hybrid materials is that they can be synthesized from modular organic and inorganic components, which permits rational control over both structure and function. Furthermore, compared to single-component materials, multiple-component systems offer additional degrees of freedom in synthesis and thus an unprecedented ability to tune the materials' properties. Hybrid materials are often assembled and held together through covalent and non-covalent (ionic, dispersion, donor–acceptor type) interactions, unusual combinations of organic and inorganic materials can be produced in a cooperative manner. This feature greatly enhances the toolkit available for the synthesis of new materials. Thus, organic–inorganic hybrid materials combine the advantageous properties characteristic of inorganic solids (e.g. high carrier mobilities, thermal stability) with those of organic molecules (e.g. ease of processing).

The synthesis of low-dimensional organic–inorganic molecular composite semiconductors represents a highly promising area for the development of new and unique types of electronic and optical materials. Crystalline molecular composite materials are distinct from the more common intercalation compounds and nanoscale hybrid materials in that direct bonding exists between the inorganic host and the organic moieties. In addition, their stoichiometry is well defined as is the relative orientation of the organic fragments with respect to the inorganic component. In low-dimensional molecular composites, the immobile molecular species are successfully aligned in the crystal structure, and the potential for tuning the structure and properties of the composite is considerably enhanced. However, in many novel functional hybrid materials it is clear that the conventional view of "ship-in-a-bottle" in rationalizing the observed property and structure, as in framework compounds, cannot be applied effectively. The synergistic interaction between the organic and inorganic components is increasingly an important factor, particularly in highly polarizable inorganic systems.

Designing the structure and properties of organic–inorganic hybrids materials with regard to the possibility of fabricating molecular composites with specific properties can be based on the separate properties of the inorganic layer and the organic moieties. Through proper design and implementation, this approach even can be applied to low-dimensional systems leading to combined and/or enhanced materials' properties. Some possible combinations of properties in organic–inorganic molecular composite structures are highlighted (Fig. 1.15). Modulating the structures of organic–inorganic hybrids on the molecular scale may be done to tune their desired properties. Such a goal necessitates the establishment of useful structure–property-bonding relationships among complex chemical systems that incorporate a wide range of bonding schemes. We anticipate that the ability to tune the properties of these crystalline hybrid composites will facilitate the development of new materials for many novel device applications.

1.3.5. Extended solids for quantum computing

One of the most essential phenomena exhibited by single-molecule magnets (SMMs) is quantum tunneling of magnetization, QTM. We usually think of magnetic relaxation in terms of thermal relaxation through phonon interactions. SMMs can exhibit another form of
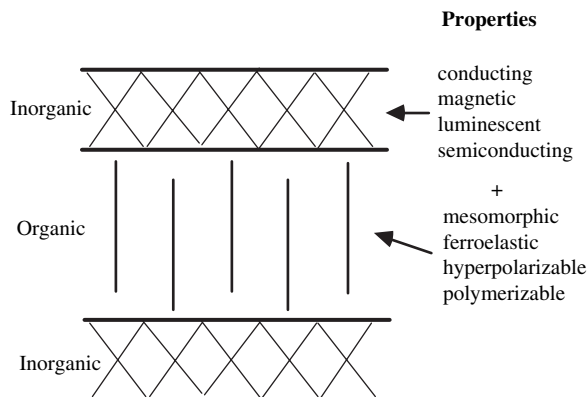
Properties

Fig. 1.15. Molecular composite depiction showing possible combinations of properties.

relaxation where the magnetic moment can reverse by tunneling through the energy barrier. These SMM quantum bits are useful for quantum computing by taking advantage of the super-position of states provided by QTM, which is evidenced in field-dependent magnetic data by magnetization steps at certain applied field intervals.

It has been now proven possible to achieve QTM also in extended solids that may have even an extended quantum regime beyond what SMMs have achieved. This observation is attractive since achieving quantum-mechanical effects in solids that are made of extended three-dimensional structures is theoretically unattainable due to itinerate electrons. However, solids consisting of electronically confined, low-dimensional magnetic nanostructures are thought to be capable of displaying magnetic quantum effects. Employing closed-shell, non-magnetic oxyanions (such as silicate and phosphate anions) as a rigid inorganic ''li-gand'' and linker, for example, one can synthesize a composite lattice containing periodic arrays of magnetic nanostructures [112,113]. Several compounds in this class of solids have shown ferromagnetic properties with magnetization steps in their hysteresis loops, a phenom-enon reminiscent of QTM in molecular-based magnets. Slow dynamics of the magnetization has also been predicted in chain compounds characterized by a strong uniaxial anisotropy. It has recently been observed in $Ca_3Co_2O_6$, a member of the large family of $A_3BB'O_6$ com-pounds [114,115]. This extended solid is a spin chain type compound, set on a frustrated triangular lattice, with ferromagnetic intrachain coupling and an antiferromagnetic interchain coupling. It is the 1D counterpart of many interesting frustrated magnetic systems like the 3D pyrochlore and the 2D Kagome lattices. Its magnetic behavior is characterized by a large Ising-like character with slow relaxation of the magnetization and step-like hysteresis ef-fects. While the prior reports on extended solids showing quantum-mechanical effects are few, some indications of a QTM process were reported in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ [116,117]. In any event, these extended solids have opened the door to study quantum ef-fects in a different class of materials. A wider investigation of the occurrence of QTM in magnetic solids with large-spin ground states showing strong uniaxial anisotropy and geo-metrically frustrated magnetic lattices should be encouraged. The growth of single crystals in this study is important in order to avoid problems associated with grain boundaries and random orientation of crystal lattices in polycrystalline materials. Single crystals are neces-sary in this research because they have been used to determine not only the crystal struc-ture, but also the anisotropic magnetic and transport properties.

Section 2. Structure−property relationships: current development, challenges, and future directions

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2.1. Introduction

Consideration of structure−property relationships plays a central role in the design and discovery of novel and important materials. Because solid-state chemists contribute to the development of materials exhibiting a very broad range of structures and physical and chemical properties, we can only briefly review here the status and opportunities in a few selected areas: (i) materials related to energy production and use, (ii) electronic and magnetic materials for emerging technologies, and (iii) nanomaterials.

Establishing structure−property relationships for a diverse body of materials exemplified by catalysts, dielectrics, and nanoparticles requires the use and availability of structural characterization tools that cover a significant range of resolution, extending from determination of average structures with diffraction to elucidation of bulk and surface point defects with electron microscopy. In many cases, developing relevant structure−property relationships requires that measurements be made under the ''in situ'' conditions of temperature, pressure, and atmosphere that match the performance environments of the materials of interest. For many such structural studies, central facilities, e.g., neutron and X-ray synchrotron, provide the specialized data-collection devices that are required. While not always routine, variable-temperature measurements are available via X-ray and neutron diffraction and scattering, NMR, and electron microscopy. The combination of controlled atmosphere and variable temperature is more challenging and greater capabilities beyond those currently available are desired, but the intense pulsed neutron source does offer powder diffraction measurements at high temperatures ($\sim$1000 °C) and at pO_2s from 1 to 10^{-20} atm.

Developing and establishing structure−property relationships is intimately connected to considerations in synthesis and advances in computational capabilities. For example, developments in areas such as low-temperature processing, shape-defined and patterned nanostructures, and laminated films are providing structural control at diverse length scales that correlate to new physical and chemical properties. In addition to detailed property measurements, understanding and developing these correlations can also be strongly supported through computational studies. The ability to move beyond selected experimental or time constraints in a theoretical framework provides a basis for prediction in structure−property relationships. A non-exhaustive list of materials' systems and applications that depend on our ability to understand structure−property relationships follows.

2.2. Energy-related materials

Our need for alternative energy sources and efficient ways of generating power is urgent. Important materials' advances have been made in the past, greatly enabled by the understanding of structure−properties relationships in the areas of catalysts, batteries, fuel cells, thermoelectric and optical materials (e.g., photovoltaics, phosphors) of both new and existing materials.

Research leading to new advances in all of these materials' areas is essential for the US to move to energy independence and away from a petroleum-based economy.

2.2.1. Catalysts

The petroleum, chemical, and pharmaceutical industries, contribute \$500 billion to the GNP of the United States and rely on catalysts to produce everything from fuels to polymers to drugs. Significant challenges for new materials include catalysts for production of new fuels and chemicals by selective oxidation of alkanes such as methane. Currently energy intensive indirect gas-to-liquid processes are used. Direct selective oxidation to liquid fuels would provide energy-efficient production, and lower CO_2 emissions. The development of new electrocatalysts for fuel cells is also a priority for materials' research. More efficient cathodes for oxygen reduction for operation at intermediate temperature (500−700 °C) and efficient anodes to allow direct oxidation of liquid fuels such as methanol are needed. Photolytic splitting of water to form hydrogen and oxygen is a second important area for new electrocatalysts.

The key kinetic processes in oxide catalysts can be divided into bulk processes (cation mobility, oxide ion and proton mobilities and electronic conductivity) generally governed by oxygen vacancies and electronic defects induced by doping and surface processes (oxygen and hydrocarbon adsorption, activation, and redox processes) that depend on the structure/composition of the outermost surface of the oxide. The coupling between the bulk crystal and electronic structure and the surface properties (composition, structure and electronic properties) under operating conditions determines the kinetic behavior. Our fundamental understanding of this coupling and particularly, the surface structures is not sufficient to predict or even to understand a given material's performance and therefore is an important topic for future research.

2.2.2. Batteries

The development of the lithium-ion battery has enabled many of the modern electronics that form an integral part of society in the 21st century. Solid-state chemists have played a central role in the field, the $LiCoO_2$/graphite cell commercialized by SONY in 1990 resulting directly from discoveries in 1980s by solid-state chemists. The SONY cell, while adequate for many low-power applications, will not meet all the requirements for high-power devices. The high-power applications include batteries for hybrid electric vehicles, where the current vehicles use nickel−metal hydride batteries. Advances are required as part of effort to reduce CO_2 emission and for fuel diversification, where power back-up is needed to couple with alternative energy sources (e.g., solar and wind). Even a fuel cell driven car will require a rechargeable battery.

Solid-state chemists continue to make significant contributions in this area, discovering new materials and widening the scope and types of electrode reactions. Work in the area of nanoparticles and composites has been significant [118]: Nanocomposites can in principle absorb the stresses that occur during the cycling of metals and alloys, which suffer from extremely large volume expansions/volume changes. The field was sparked off by the discovery of tin-based amorphous oxide anode materials and then by metal oxides such as CoO. The development of macroporous electrodes offers promise for improving charge/discharge rates and ensuring electrical contacts between particles [119]. Work in intermetallics (e.g., InSb, Cu_2Sb) has led to the development of a class of extrusion reactions and materials that couple both extrusion and intercalation (e.g., $Cu_{2.33}V_4O_{11}$) [118,120].

New materials involving multiple redox couples, e.g., $Li(NiMn)_{0.5}O_2$ (Ni^{2+}/Ni^{4+}) offer new approaches for increasing capacity [121]. Joint theoretical and experimental studies have provided considerable insight into the structure and function of these electrode materials, which has directly led to the optimization of new cathodes (e.g., $Li(NiMn)_{0.5}O_2$, Fig. 2.1) [122] or the understanding of electronic and ionic conductivity in layered materials and phosphates (e.g., $LiFePO_4$) [123]. New characterization approaches (PDF, NMR) and the use of national facilities (neutron and X-ray diffraction, XAS) have played an important role in this area.

In order to improve charge/discharge rates new materials are required with increased ionic (Li^+) and electronic conductivity throughout the electrochemical process (n.b., the standard positive electrode $LiCoO_2$ is very slow to charge and discharge). The properties of both new and existing structures require optimization, via both materials' synthesis and an understanding of the factors that control the properties. The control of size and shape of particles and the design of new nanostructures/composites (to "wire" particles together) will all play a role in increasing rate. However, an improved understanding of electrolyte-particle surface reactions

Transition metal	Co^{4+}	Ni^{4+}	Mn^{4+}	Ni^{3+}	Co^{3+}	Cu^{2+}	Ni^{2+}
Activation barrier (meV)	490	490	340	310	310	270	210
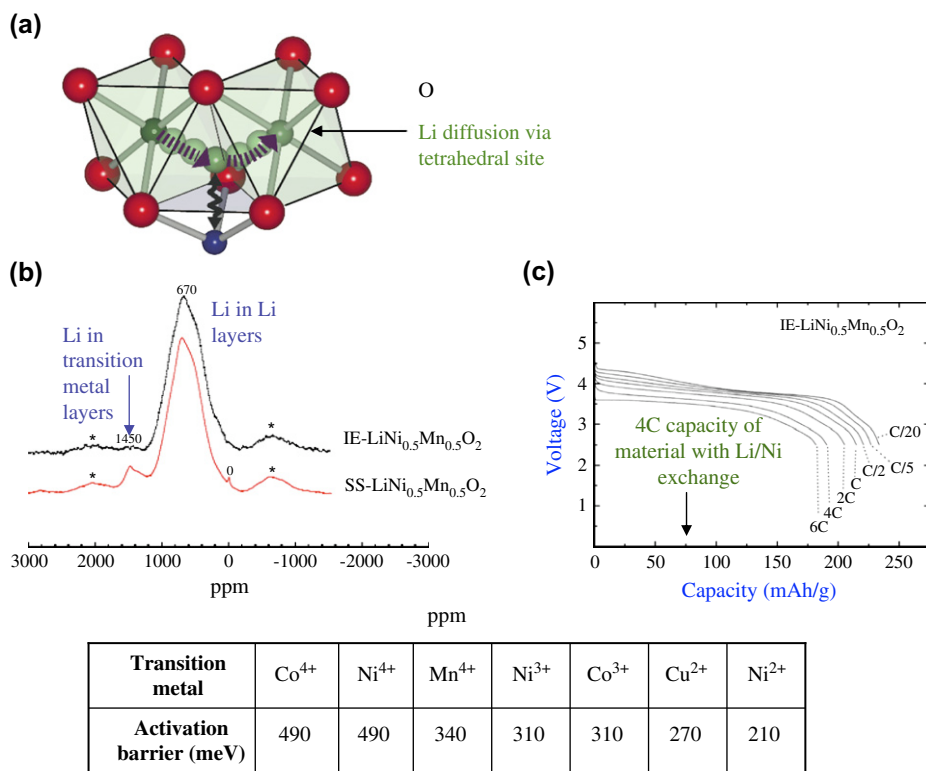
Fig. 2.1. A combination of theory and experiment was used to optimize the performance of the layered material Li-$Ni_{0.5}Mn_{0.5}O_2$. NMR and diffraction results demonstrate that the as-synthesized material (SS-$LiNi_{0.5}Mn_{0.5}O_2$) contains Li/Ni site exchange between the Li and Ni layers. (a) DFT calculations were used to identify the parameters that control ionic mobility in the layers. The activation energy for Li^+-ion diffusion strongly depends on the charge of the cation in the transition metal layer (Table) and the ideal layered form of $Li(NiMn)_{0.5}O_2$ should be a high rate material. (b) The ^{6}Li NMR results show that the material synthesized via the sodium form $Na(NiMn)_{0.5}O_2$ (ion-exchanged (IE) Li-$Ni_{0.5}Mn_{0.5}O_2$) does not contain a significant amount of Li/Ni exchange. (c) Electrochemical data for IE-Li$(NiMn)_{0.5}O_2$ demonstrate that this material does indeed retain its high capacity at high rates (C) [122].

and reactivity of materials, particularly at high states of charge, is needed in order to improve stability under a wide range of environmental conditions.

There is a need to increase capacity and to maintain the high capacity particularly at high C (i.e., a high charge/discharge rate) and to make use of the full theoretical capacity ($LiCoO_2$ only uses 50% of the theoretical capacity based on the Co^{3+}/Co^{4+} couple). An understanding of the factors that control correlations between voltage and structure and the factors that prevent full use of all the theoretical capacity are required. Materials in which the electrochemically active ions undergo redox changes of more than one electron (e.g., $Ni^{2+}-Ni^{4+}$; $V^{3+}-V^{5+}$) in a narrow voltage window are needed. A wider class of materials should be investigated beyond oxides, including nitrides, phosphides, fluorides, intermetallics, but moisture/air sensitivity issues will need to be considered. Although the development of Mg-ion batteries have so far been limited by the kinetics of Mg^{2+} diffusion, a move away from oxide systems may enable chemistry in this area. The development of a practical 3D or solid-state battery (with a solid-state electrolyte) will require continued work on macrostructure, materials' processing and interfacial issues. Although cost will restrict the utilization of many materials in batteries, unless the batteries are used in more ''exotic'' applications (medical, military, space, security applications), novel approaches and chemistries are required to make significant advances in this field, which justifies a wider exploration of materials.

2.2.3. Fuel cells

Fuel cells [124−127] represent an enabling technology, allowing fuel diversification, a method for reducing CO_2 emission (depending on the fuel source) and a potential improvement of efficiency over, for example, the internal combustion engine. The H_2/O_2 fuel cell relies on a proton- or oxygen-conducting membrane (the electrolyte) and electrodes; the latter must act as both a catalyst (for $H_2 \rightarrow 2H^+ + e^-$ or $O_2 + 4e^- \rightarrow 2O^{2-}$) and an electronic conductor for delivery and/or removal of electrons. Electrolytes must be stable on either side of the membrane constraining the choice of ionic conductors considerably.

The current proton-conducting fuel cells (utilizing fuels such as H_2 and methanol in direct methanol fuel cells (DMFCs)) are limited by the very high cost of the catalyst, Pt, and the membrane (nafion) along with issues of fuel/H_2O cross-over. The development of new catalysts has been constrained by the need to identify catalysts that are not poisoned by impurities in the fuel supplies. Recent advances have identified new, ordered alloys (e.g., PtBi, PtBi) [128] for use as possible catalysts in PEM/DMFCs fuel cells, which also represent a new avenue for research. Ru doping of Pt has improved tolerance of the catalysts to CO poisoning. Important challenges include an understanding of the surface structure, long-term stability of these new catalysts, stability under operating conditions and during processing of electrodes, along with a fundamental understanding of relationships between electronic structure and catalysis. Improved catalysts are also required to reduce the overpotential at the cathode side. The community should move some of its effort away from the very limited range of catalysts (for PEM fuel cells) studied by the majority of the community (Pt/Ru Pt/Sn).

Work on the development of solid-state electrolytes for H^+ conductivity may enable new technology and provide opportunities for new solid-state synthesis and understanding of structure−properties relationships. The key materials' issues are to discover new proton conductors that can operate in the range of 120−200 °C. Higher temperatures relax some of the catalytic requirements and may permit the use of non-platinum-based catalyst materials. Reduced platinum loadings or non-platinum catalysts are key issues. New catalysts must be stable in strong acid environments. New materials for bipolar plates are also needed.

Solid oxide fuel cell (SOFC) technology has been successfully established but costs remain too high to permit widespread introduction into the marketplace. Cost reduction requires both improvements in the properties of the materials, particularly the electrodes, and the development of inexpensive fabrication processes. Lowering the operating temperature of SOFCs offers the potential for significantly reducing cost through the use of less expensive materials. Operation of SOFCs at temperatures (500—700 °C) requires significant advances in materials.

For SOFCs, research if focused on improving the conductivity of the oxide-ion conductor (the electrolyte) and the three-phase composite or boundary of a mixed conducting oxide, and oxide electrolyte and pore space (Fig. 2.2) [129]. The fundamental atomistic/level understanding of the factors that control ionic mobility and trapping of defects is being studied, e.g., in perovskites with high ionic conductivity such as the ordered double perovskite $GdBaCo_2O_{5+x}$ and doped lanthanum gallates. Development in these areas should improve SOFCs as electrocatalysis of the oxygen reduction reaction becomes limiting as the operating temperature is reduced.

The transport reaction network in the porous three-phase boundary is very complex and consequently there is little fundamental understanding of how the properties of the mixed conductor determine the relative rates and contributions from the various processes and the overall electrode performance. It is clear that there are a great many interfaces to consider in materials used for applications in high-temperature electrochemical devices. There are homogeneous interfaces such as grain boundaries which can have a deleterious effect upon the transport of ions in polycrystalline materials, and heterogeneous interfaces in materials such as polycrystalline composites. Simpler architectures are needed to understand property/reactivity relationships. The study of stability (structure) of the electrodes under real operating conditions and the role that O-defects play in controlling mobility remains an important area for research.

2.2.4. Thermoelectrics

Thermoelectric (TE) materials can provide electricity when subjected to a temperature gradient or provide cooling when conducting an electric current without using any moving parts (Fig. 2.3). They are highly reliable, environmentally benign and maintenance free. TE devices
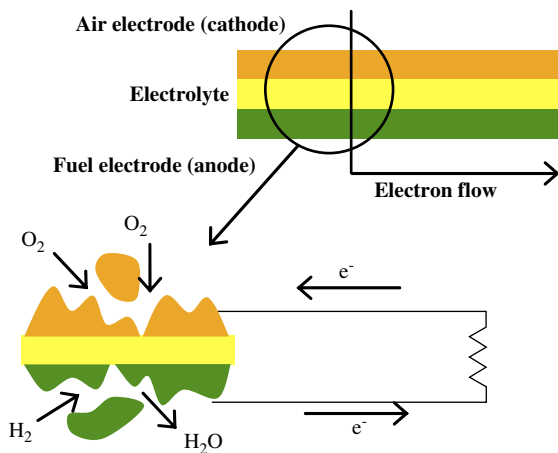
Fig. 2.2. Schematic of a solid oxide fuel cell.
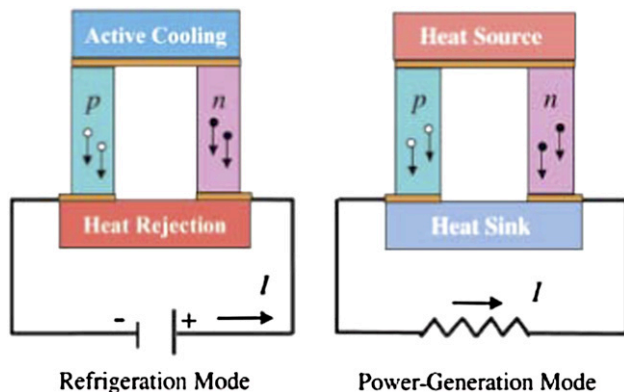
Fig. 2.3. Diagram of a thermoelectric couple made of an n-type and a p-type thermoelectric material. Refrigeration or power-generation modes are possible, depending on the configuration. I is current.

can be lightweight, small, and inexpensive, and in principle, can eliminate the need for compressor-based refrigeration units. In the realm of power generation, thermoelectric modules offer the ability to convert waste heat, particularly from combustion processes (automotive engine exhaust, utility stacks, etc.) into useful electrical energy, and may play a key role in addressing the global energy needs.

While the advantageous features of thermoelectric devices are well recognized, they are not widely available today because of their low efficiencies, which in turn, is a direct consequence of the difficulty in finding materials with desired electrical and thermal properties. At the heart of TE devices are materials with a unique combination of properties: high thermoelectric power, high electrical conductivity and low thermal conductivity. These properties define the thermoelectric figure of merit $ZT = (S^2\sigma/\kappa)T$, where S is the thermopower (or Seebeck coefficient), σ the electrical conductivity, κ the thermal conductivity, and T the temperature. Such a combination of properties, critical to obtaining high device efficiency, is difficult to achieve in a single material because often the properties are interdependent and any changes in one affect the other in a negative way. This situation creates a great challenge and an exciting opportunity for solid-state chemists, theorists and materials scientists to come up with creative approaches to optimize all relevant properties. The potential pay-offs for addressing this challenge are substantial, both in the realm of cooling and electric power generators [130].

The useful thermoelectric materials must not only exhibit high ZT over a wide temperature range, but must also be compatible with both donor and acceptor doping as the device consists of a pair of n-type and p-type elements that can be placed in parallel with a temperature gradient, but in series with respect to electron flow, and the voltage generated across each leg will be additive. Other thermoelectric devices, such as coolers and heaters, utilize similar device configuration.

The best commercial thermoelectric materials exhibit (bulk) values of ZT that are only in the order of 1, a milestone that was achieved in the 1960s. These are materials based on complex semiconductors, with optimized carrier concentration, high effective mass carriers, high carrier mobility, narrow band gap, and low lattice thermal conductivity. Examples include Bi_2Te_3, PbTe and $Si_{0.8}Ge_{0.2}$ (Fig. 2.4).

If one is to develop high efficiency thermoelectric devices, much higher values of ZT above 3 are necessary. Such targets should be possible as there is no fundamental limit to
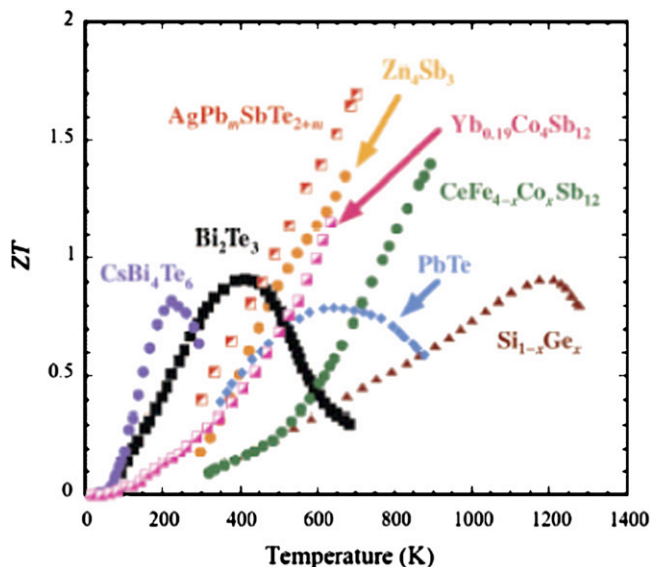
Fig. 2.4. Figure of merit *ZT* shown as a function of temperature for several bulk thermoelectric materials.

the possible value of *ZT*. As shown by the recent progress in this area, the new thermoelectric materials of the future likely to have very complex composition, crystal structures with "rattlers" in large voids, and high degree of atomic disorder, features that are needed to lower lattice thermal conductivity without sacrificing electrical conductivity and thermopower. Moreover, a single material is unlikely to exhibit high *ZT* over the entire temperature range of interest. Therefore, a sustained exploratory synthetic effort, that encompasses many classes of materials and structures (chalcogenides, pnictides, intermetallics, oxides, etc.) leading to the development of entirely new families of materials, must be pursued if the challenge of high *ZT* is to be met. In this context solid-state chemistry will play a definite center role. In addition to exploratory synthetic effort towards new thermoelectric materials, a strong computational/theoretical effort is needed as the shape and width of the bands near the Fermi level, the carrier effective masses, and mobilities are important to understand the fundamental properties that are needed for high *ZT* materials. The synthetic effort must also be matched by developing approaches and methods on measuring electrical conductivity, thermal conductivity and thermopower reliably and quickly. This necessarily brings together the fields of solid-state chemistry, solid-state physics, materials science and electrical engineering and close collaboration between scientists from these areas is of paramount importance.

2.2.5. Photovoltaics

Solid-state chemists have considerable opportunities to contribute to the development of new materials for thin-film solar cells. Thin-film cells are generally considered to comprise appropriate layers of polycrystalline inorganic materials, and it is their polycrystalline nature, demonstrated high efficiencies, and potential ease of manufacture that define their value. The highest efficiency thin-films cells ($\sim$17%) [131] currently operate on the basis of the absorbing semiconductors $Cu(In,Ga)Se_2$ (CIGS) and CdTe. While these cells exhibit high

efficiencies, it is difficult to forecast their widespread practical use, as In and Ga are scarce and Cd is toxic and banned for new uses throughout much of the world. CIGS and CdTe have been under development for more than two decades, and during this time very little effort has been directed to the design and synthesis of new materials that could provide higher efficiencies and solutions to the practical use of thin-film cells. In this context, new absorber materials with band gaps in the range of 1−1.7 eV are of interest for use in tandem-cell configurations to surpassing current efficiencies, and materials with band gaps >2 eV are of interest as transparent back contacts and transparent conductors. Development of these materials relies on an understanding of the relationships between crystal and electronic structures in predicting band gaps and carrier mobilities. In addition, understanding and controlling bulk and surface dopant and defect chemistries as well as band offsets between the different films in the cell are necessary for realizing electron- or hole-reflection properties that lead to effective charge separation.

2.2.6. Luminescent materials

Approximately 20% of the electricity budget in the US is spent on lighting and displays. Numerous opportunities exist for solid-state chemists to contribute to the development of new materials that could lead to greater efficiencies and energy savings in the generation and use of light. Mercury-based fluorescent lamps with efficiencies in the order of 100 lm/W represent the most efficient and cost-effective sources available for general lighting. Much higher efficiencies could be achieved through the use of xenon-discharge lamps in conjunction with quantum-splitting phosphors, i.e., luminescent materials exhibiting quantum efficiencies greater than unity [132]. The synthesis and development of such materials requires an understanding of the local crystal structure and its effects on the energy levels of a dopant ion. To make advances in this field quantum-splitting schemes must be identified; energy levels for absorption much be matched to the excitation source; energy transfer and migration processes must be thoroughly detailed (particularly host-to-dopant transfer processes); red, green, and blue emission must be realized for production of white light; and materials must have sufficient stability to survive in the discharge environment of the lamp. Solid-state lighting is also being developed on the basis of LED-excited inorganic phosphors. A critical understanding of the relationships between crystal and electronic structures is necessary to achieve the necessary energy match between the emission of the LED and absorption of the candidate dopant ion in a specific phosphor.

During the past decade, considerable attention has been directed to the development of organic light emitting devices (OLEDs). These devices function on the basis of favorable electron and hole charge injection in materials with subsequent recombination to produce light. While these devices can be made to produce bright light, they suffer from limited efficiency and operational lifetimes. An inorganic version of an OLED, i.e., an inorganic light emitting device (ILED), could provide a much improved efficiency and operational lifetime. Unlike a conventional inorganic light emitting diode, the ILED is a polycrystalline device that would operate through low-voltage electron and hole injection much like an OLED. The use of polycrystalline materials in an ILED relative to single-crystal technology in a conventional diode provides a means for large area coverage and low manufacturing costs. A solid-state ILED has not previously been realized primarily because of the very high work functions (8−9 eV) and associated energy barriers for hole injection in inorganic phosphors. The recent introduction of wide band gap inorganic luminescent materials having work functions near 4.5 eV [133] (Fig. 2.5) provides new opportunities

Fig. 2.5. Intrinsic luminescence of wide band gap BaCuSF.

for realizing low-voltage hole injection with light emission. To make progress in this field it is necessary to achieve a detailed understanding of the relationships among the crystal structure of a material, and its band structure, work function, and defect chemistry. In many ways, the materials' characteristics and device physics of an ILED parallel those of thin-film photovoltaic cells.

2.3. Electronic materials

Electronic materials are ubiquitous in our technologically advanced society and continued innovations and emerging new technologies continue to demand improved electronic materials.

2.3.1. Dielectrics

High dielectric constant (κ) materials are widely used in the microelectronic industry and, as of today, no single material satisfies all the requirements. High κ is required for capacitor function in microcircuits such as gate dielectrics in integrated circuits (IC), chip or embedded capacitors in passive components, memory elements in microcomputers such as DRAMs and FeRAMs (Fig. 2.6). As the device gets smaller and smaller, the circuit density increases exponentially and the need for finding better high κ capacitor material also increases.

In digital circuits, insulating dielectrics separate the conducting parts (interconnects and transistors) from one another. They are called interlevel dielectrics (ILD) and need to be as low as possible (<2). To make higher-speed chips, the transistors must be placed closer and closer together, and thus the insulating layer becomes thinner. This leads to charge build up and crosstalk, adversely affecting the performance of the chip. Reducing the κ of ILD lowers the parasitic capacitance and enabling faster switching speeds and enables heat dissipation. For example, the dielectric constant of SiO_2, the insulating material used in silicon chips, is 3.9. By doping it with fluorine to produce fluorinated silica glass, this is lowered to 3.5. Another approach is to make a porous dielectric. The pores lead to a smaller average dielectric constant. Future needs for the next generation of dielectric materials for emerging electronics are

$BaTiO_3$
TiO_2

**Embedded capacitors
(ferroelectrics & non-ferroelectrics)**

SiO_2
$HfSiOx$

**Gate dielectric: CMOS
(non-ferroelectrics)**

**Dielectrics
in electronics**

$SrBi_2Ta_2O_9$

$(Ba,Sr,Ca)TiO_3$
Ta_2O_5
$Pb(Mg_{2/3}Nb_{1/3})O_3$

**Chip and ceramic capacitors
(ferroelectrics and non-ferroelectrics)**

**FeRAM in computers
(only ferroelectrics)**
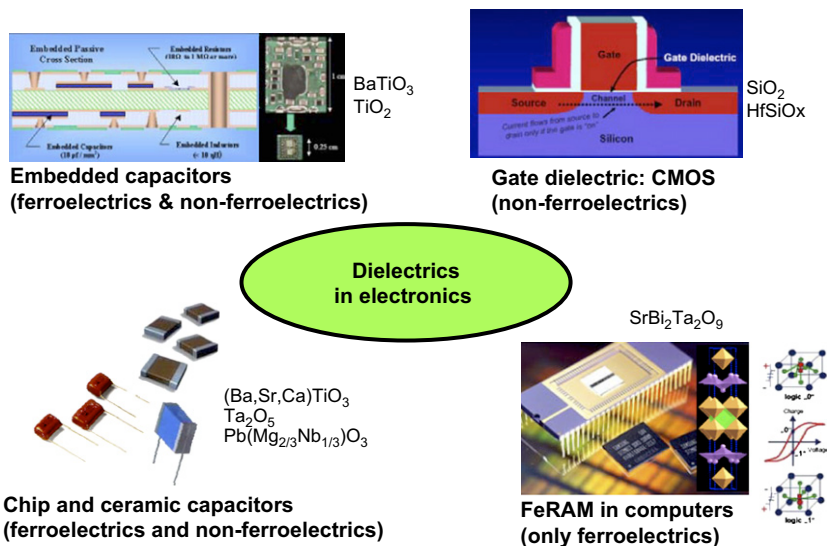
Fig. 2.6. Applications of dielectrics in electronics industry.

- high κ dielectrics ($>$5000) with high Q factor with temperature and frequency independent behavior up to several GHz frequencies;
- low κ dielectrics ($<$2) containing only inorganics compatible with current IC manufacturing process;
- free of Pb, Cd and other heavy metals;
- low temperature processable under reducing conditions for Cu interconnects.

The discovery of new materials is important for next generation devices, and solid-state chemistry will play an important role. In addition, studies should also focus on understanding the correlations between crystal structure, defects, non-stoichiometry and loss mechanisms, which are also important in the design of the next generation of dielectric materials. Many known materials remain untested and probably the next generation materials already exist, but no one as yet investigated them. Recent discovery [134] of high κ ($>$10,000) in non-polar $CaCu_3Ti_4O_{12}$ is an example; this compound was first reported in 1967 (Fig. 2.7).

2.3.2. Superconductivity

Research on superconducting materials remains a focus of intense scientific interest for both fundamental reasons of understanding basic properties of solids and potential applications for energy-related utilization. While several areas of materials science, for example fuel cells and thermoelectric, await a discovery of the breakthrough materials that would enable widespread development of new technology, such materials have been found in the field of superconductivity already 20 years ago [135]. Since then several hundreds structural variants of high-temperature superconducting layered copper oxides have been found in a worldwide effort of solid-state chemists and physicists.

Significant progress has been made towards commercialization of high-temperature superconductors for applications in electric power. Wire based on $YBa_2Cu_3O_7$ (YBCO) has been
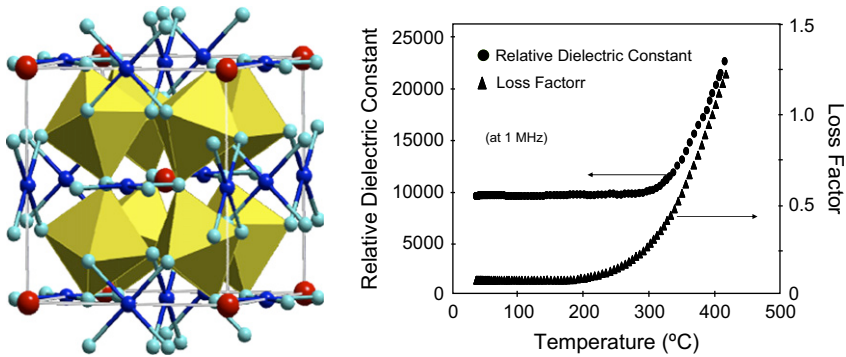
Fig. 2.7. Crystal structure and dielectric properties of $CaCu_3Ti_4O_{12}$.

developed by IGC-SuperPower, Inc and American Superconductor Corporation (AMSC) in the US and also in Japan (Fig. 2.8). A critical current performance of 219 (A/cm width) over 322 m, corresponding to performance of 70,520 A m has been reported by IGC-SuperPower for YBCO wire and the first commercial products, dynamic synchronous condensers, have been sold to the electric power industry by AMSC. Further work aimed at improving the current carrying capability and the magnetic field behavior is required for widespread utilization of high-temperature superconducting materials.

Materials' research to achieve increased pinning of magnetic vortices by special features of the crystal structure, the introduction of nanoparticles, as well as use of the crystal chemistry to
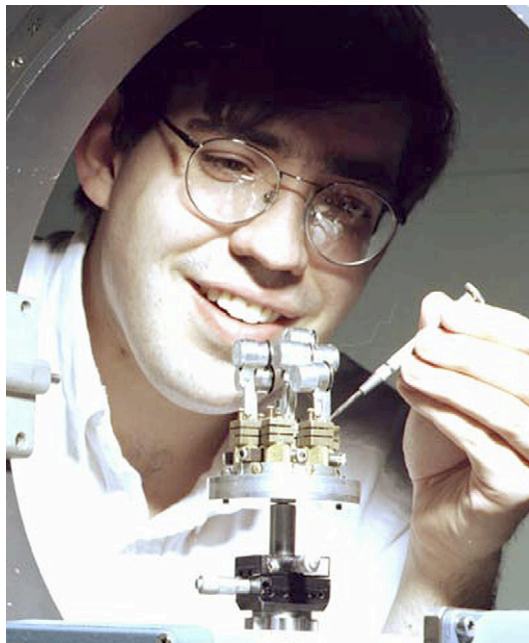
Fig. 2.8. W. Hardy and D. Bonn, UBC; Chalk River labs, the Canadian neutron scattering facility—a picture of graduate student Chris Stock aligning several large crystals of YBCO grown by their group.

Table 2.1
Summary of recent discoveries of novel superconductors

Compound	Year	T_c (max., K)	Author/country
MgB_2	2001	42	Nagamatsu/Japan [10]
Li (50 Gpa)	2002	20	Shimizu/Japan [136]
$Na_xCoO_2 \cdot yH_2O$	2003	5	Takada/Japan [137]
Y_2C_3	2004	18	Amano/Japan [138]
Diamond (C:B)	2004	11	Ekimov/Russia [139]
CaC_6	2005	12	Emery/France [140]

design crystal structures that accomplish texturing in bulk materials provides strong opportunity for solid-state chemists to contribute in the applied effort of utilizing superconductivity at liquid nitrogen temperatures.

Search for new superconducting materials constitutes another area of research where solid-state chemistry had a major impact and will continue to provide unexpected discoveries as well as will be used to validate theoretical predictions. Recent discoveries of novel superconductors are listed (Table 2.1).

The highest T_cs have been found for layer compounds with light elements. None of them was predicted; several have been explained ''a posteriori'' by strong electron coupling to the particular phonon modes. Current predictions are that such a strong electron−phonon coupling could possibly lead to T_cs of 450 K. This should motivate expanded search for new materials with T_cs above room temperature to a broader compositional phase space using novel synthesis techniques to achieve a wider doping range. Both first principles and empirical rules should be used to identify compositions and structure types not previously investigated in this context.

Exceptionally high T_cs of cuprates (max $T_c = 130$ K, 160 K at high pressure) continue to challenge theoretical explanation. It may originate from an electron-mediated mechanism that could lead to materials with even higher T_cs, but there is no guidance how to design them. The solid-state chemistry community can significantly contribute to this theoretical and experimental challenge by providing large and thick crystals for inelastic neutron scattering and synchrotron studies of intrinsic in-plane and c-axis properties. Exceptionally pure as well as substituted and intentionally doped or defect-containing crystals are needed to improve methods of flux pinning.

Table 2.1 shows that recent significant discoveries of new superconducting compound have been done in Japan and Europe. This is a high risk−high payoff effort, and the absence of discoveries in US may be traced back to a lack of commitment and sporadic funding by NSF, DOE, and other agencies. Similarly, scrupulous examination of intrinsic properties of improved bulk and single-crystal materials requires increased and sustained support for research on new synthesis and crystal growth techniques.

2.3.3. Thin-film transistors

Thin-film transistors (TFTs) pervade our daily lives as indispensable elements in a myriad of electronic/photonic products, such as computers, cell phones, displays, household appliances, and sensors [141]. Furthermore, the future demand for next-generation mobile computing, communication, and identification devices is expected to increase dramatically. For diverse multiple functionalities, the electronics of ideal mobile devices must achieve lightweight, low power consumption, low operating voltages (powered by household batteries), and compatibility

with diverse substrates [142−144]. Additional desirable features include optical transparency (''invisible electronics''), mechanical ruggedness, environmental stability, and inexpensive room-temperature/large-area fabrication. TFTs meeting all the aforementioned requirements have proven elusive and will doubtless require unconventional semiconducting and gate dielectric [142] materials and processing strategies. Conventional inorganic TFTs based on silicon and compound semiconductors have many attractions such as high carrier mobilities, but also limitations which include marginal mechanical flexibility and/or mandatory high-temperature processing (frequently >400 °C for II/VI and III/V compound semiconductors [145−149], >250 °C for Si TFTs [150,151]). Amorphous silicon-based TFTs have also been fabricated on plastic substrates at temperatures as low as 75−150 °C [152−156]. However, despite the great potential of these approaches, for active matrix-TFT driven display applications, this material still suffers low carrier mobilities ($\sim 0.03−1$ cm^2/V s on inorganic insulators) and optical opacity [152−156]. Organic TFTs (OTFTs) are promising and benefit from tailorable molecular functionality, low-temperature processability, and plastics compatibility [142,157−162]. Nevertheless, the low mobilities and modest environmental stabilities are factors currently limiting in their applicability. For all of these reasons, unconventional ''hybrid'' approaches [163] combining the favorable characteristics of both inorganic and organic materials, deposited at room temperature, would be of great interest.

2.3.4. Transparent electronics

Transparent conductors (TCs) constitute an unusual class of materials having two physical properties—high optical transparency and high electrical conductivity—that are generally considered to be mutually exclusive. Only a small number of highly conducting and visibly transparent materials are known, and among these, only n-type oxides are extensively used, primarily as *passive* electrical elements in applications such as automobile and airplane window defrosters and transparent contacts for solar cells and displays. With the exception of a few sensor applications, prior to 2003, the *semiconducting* nature of TCs had not been exploited. In 2003, the first example of a transparent thin-film transistor (TTFT), which operated on the basis of a wide band gap n-type oxide, was reported [164]. Since that report, device performance has continued to improve through the use of new materials in the fabrication of TTFTs and more recently complete circuits (Fig. 2.9) [165], demonstrating that TCs can serve as *active* electrical elements in the new field of transparent electronics. The next major challenges in this field are to produce transparent, high mobility p-type materials to facilitate the realization of high-performance complementary devices similar to those produced via silicon CMOS technology; develop an understanding of the trap and defect chemistries that affect device performance; and identify and synthesize wide band gap materials having higher conductivities than presently available. Advances in each of these areas would be considerably accelerated through collaborations with the computational community. Demonstration of high-performance devices and circuits with oxides and related semiconductors also provides new opportunities in fabrication through solution routes, enabling low temperature, additive processing of inorganic electronics [166].

2.4. Magnetic materials

Magnetic materials comprise an important class of inorganic solids. The fascination experienced by the ancients in response to the remarkable properties of naturally occurring inorganic magnets, such as lodestone or magnetite, continues to this day. All materials respond to the application of a magnetic field and the nature of this response gives important clues to the
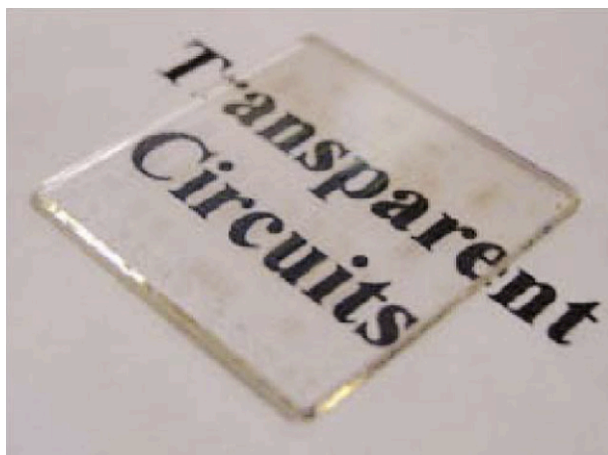
Fig. 2.9. All oxide integrated circuit.

underlying electronic structure. Our current understanding of the structure−property relationships in magnetic materials rests on the pioneering work of van Vleck, Anderson, Mott, Hubbard, Stoner, Goodenough, Kanamori and others in the mid-20th century (Fig. 2.10, [167]). Based on these ideas and using the principles of crystal chemistry, it has been possible to design materials in which the magnetic correlations are expressed in all possible real spatial dimensions—zero, one, two and three. As well, the dimensionality of the spin can be controlled by attention to the identity of the magnetic center and the crystal site symmetry, giving rise to the familiar Ising (1), XY(2) and Heisenberg (3) dimensionalities. The sign of the pairwise spin coupling, i.e., ferro or antiferromagnetic, can also be understood in a general sense and controlled.
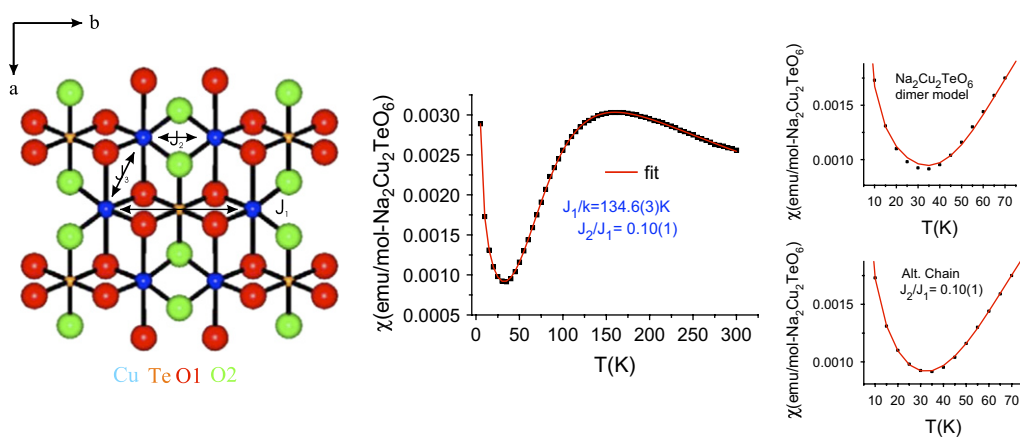
Fig. 2.10. Illustrative case history—subtlety of structure−property is shown $Na_2Cu_2TeO_6$—spin dimer analysis was applied to the $Cu_2TeO_6^{2-}$ layer. Signs and relative magnitudes of J_1, J_2 and J_3, determine the magnetic properties: $J_2 \sim J_3 \gg J_1$—2D honeycomb; $J_2 \gg J_1$, J_3—0D dimer; J_2, $J_1 \gg J_3$—1D chain or alt. chain. The result: $J_1/J_2/J_3$ = 1/.33/.01 indicates the alternating chain model, $J_1 > J_2 \gg J_3$.

The result of all of these factors has been the creation of a huge ''library'' of magnetic, inorganic solids which exhibit all possible types of magnetic property in a wide range of external parameters such as temperature, pressure or applied fields. Nonetheless, there is still much to understand in terms of the basic magnetism of real materials. Mentioning only a few issues, the importance of magnetic lattice topology—for example in the context of geometric frustration— in determining the magnetic ground state requires a much better understanding [168]. Claims of room temperature ferromagnetism induced by very low doping levels in semiconductors remain controversial. As well, magnetic materials based on 4d and 5d transition elements are still uncommon. The different oxidation states and structure types present new opportunities for materials design.

Progress will result in large part from the design, synthesis and characterization of new materials. But, the investigation of ''undercharacterized'' known materials should be pursued with equal vigor as, due to advances in instrumentation and basic understanding of magnetic phenomena, their earlier characterization can be considered to be inadequate by current standards. The application of advanced synthetic methods from the use of extreme conditions such as high pressure to very mild conditions such ''chimie douce'' and molecular precursor methods, designed to produce thermodynamically metastable phases and organic/inorganic hybrid materials, will result in a great expansion of the existing library. Characterization tools, once the domain of the specialist—such as SQUID magnetometers with fields in the >10 T range, calorimeters, and even neutron scattering instruments—are becoming, simultaneously, more sophisticated, more widely available and increasingly user friendly. These advances in synthetic methods and characterization hardware will be matched by advances in computational methods which will allow an unprecedented understanding of magnetic materials on a fundamental level—well beyond the quasi-phenomenological rules which have prevailed to date.

As well, the properties of ''doped'' magnetic materials will continue to be explored. Recall that the phenomenon of ''high-temperature superconductivity'' results from the ''hole'' doping of two-dimensional antiferromagnetic insulators and ''colossal magnetoresistance'' was discovered by either hole or electron doping of manganate antiferromagnetic insulators. The detailed pathway by which magnetic insulators are transformed by carrier doping into correlated metals is still not well understood.

Of course the application of magnetic materials will persist as a significant factor in driving the direction of research in this area. Magnetic materials, both ''hard and soft'', permeate much of modern technology from automobiles to hard drives to iPod head phones. Spintronics, in which both charge and spin information can be used may be important in the information technologies of the future. The materials needed are semiconducting and ''half-metallic ferromagnets'' [169]. Solid-state chemistry is uniquely positioned to contribute to the design and synthesis of such compounds. Magnetocaloric materials may compete with thermoelectrics in practical refrigeration. These are generally intermetallics in which crystallographic and ferromagnetic phase transitions near room temperature are strongly coupled [170]. On a similar theme, there is much interest in multiferroic materials in which both ferroelectric and ferromagnetic or at least ''weak'' ferromagnetic phase transitions can be realized and perhaps coupled, in the same material. This is a very difficult condition to achieve and thus presents a strong challenge. ''Nano magnetic materials'' will continue to be an active area. Most of these will exhibit superparamagnetic properties if the particle size is smaller than the width of a domain wall. Nano-magnets find application in biomedicine which opens a relatively under explored interdisciplinary pathway for solid-state chemistry.

2.5. Nanostructured materials

The last decade has witnessed tremendous progress in the nanomaterials research. Much of the effort was devoted to fundamental studies such as understanding and control of nucleation and growth, as well as elucidation of the structure−property relationship. The properties of nanostructured materials are determined by a set of physical parameters that include size, shape, composition, crystallinity, and microstructure. They can, in principle, be tailored and fine-tuned by controlling any one of these parameters, albeit the scope and feasibility of tuning depends on the specific parameter. As two typical examples, we choose to focus on metal nano-crystals and nanostructured crystals.

In the area of nanocatalysis, it has been established that the catalytic activity can be significantly enhanced by reducing the size of metal nanocrystals. The catalytic selectivity, however, is most sensitive to the shape and thus the facets exposed on the surface (Fig. 2.11). For example, Pt nanocrystals can selectively catalyze different types of reactions depending on the crystallographic facets involved, with the {100} and {210} planes best-suited for reactions that involve H_2 and CO, respectively. In the case of surface plasmon resonance (SPR) and surface-enhanced Raman scattering (SERS), it has been shown that the shape of metal nanostructures plays a critical role in determining the number, position, and intensity of SPR peaks, as well as the spectral region for effective SERS detection. Metal nanostructures of a specific shape may also be required for a particular application: for example, nanowires as interconnects for nanoelectronic devices and as plasmonic waveguides for nanophotonics. In the last five years, a number of strategies have been demonstrated for controlling the shape of metal nanocrystals [171]—the use of organic surfactants or polymers as the capping agents [172]; the introduction of an oxidative etchant to control the crystallinity of the seeds [173]; the use of chemical transformation that involve epitaxial growth and/or topotactic reactions (e.g., ion exchange) [174]. Some of these strategies have also been successfully applied to semiconductors [175].

In spite of their technological importance and the extensive efforts that have already been devoted to metal nanocrystals, the challenge to synthetically and systematically control the shape and thus properties has been met with limited success. Part of the reason can be attributed to the fact that very little is known about the details of nucleation and growth involved in a typical solution-phase synthesis of metal nanocrystals. For example, it is still unclear how a salt precursor is reduced to generate metal atoms, which then aggregate into clusters and finally evolve into nanocrystals. There is no conclusive account of the explicit functions of solvents, capping agents, and trace amounts of ionic species (e.g., contaminants) in both nucleation and growth steps. In addition, there is essentially no knowledge about the correlation between the structure of nuclei (i.e., clusters formed in the nucleation stage) and the shape of resultant nanocrystals. At the current stage of development, controlled synthesis of metal nanocrystals remains an art rather than a science. Thus a strong need to fully uncover the nucleation and growth mechanisms involved in the solution-phase synthesis of nanostructures, in an effort to decipher the fundamental connections between atoms, clusters, and nanocrystals, as well as to provide design rules for synthesizing nanocrystals of metals and semiconductors with superior electronic, magnetic, catalytic, and optical properties.

Another new area of nanoresearch concerns nanostructured crystals [47,176]. These are extended network structures assembled by incorporating inorganic (semiconductor) and organic segments at the nano- or subnanometer scale to form perfectly ordered crystal lattices (Fig. 2.12). While the semiconductor quantum dots have the strong capability to tune the
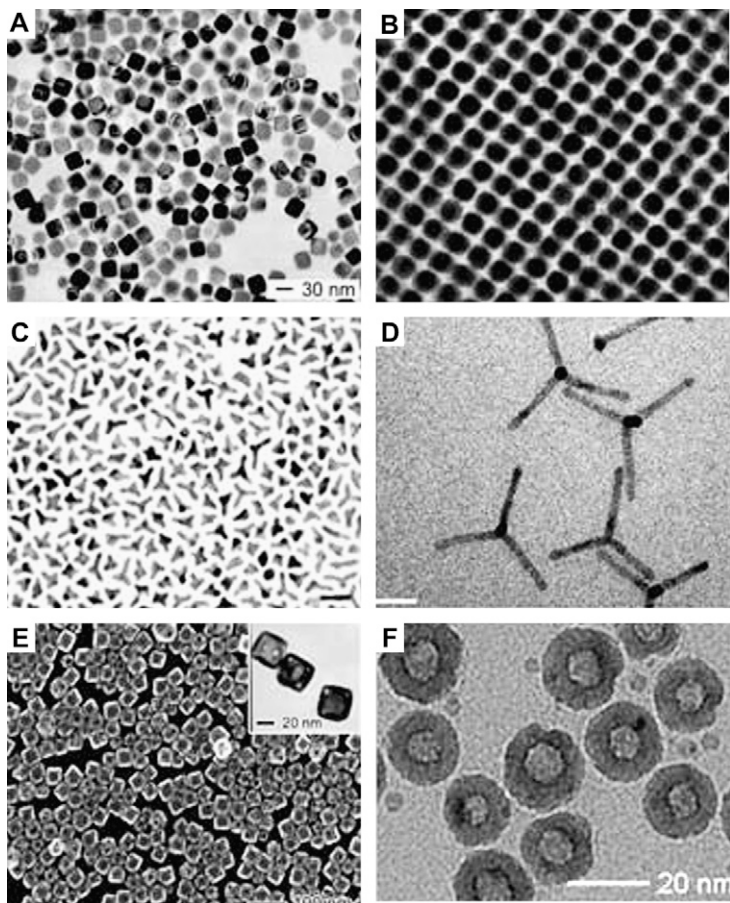
Fig. 2.11. TEM images of (A) Ag nanocubes of 30 nm in edge length synthesized via the polyol process; (B) FePt nanocubes of 6 nm in edge length synthesized with oleic acid as the capping agent; (C) Pt tripods with arm length of 10 nm in size synthesized with the mediation of silver; (D) CdTe tetrapods with arm length of 50 nm synthesized by controlling the structure of seeds; (E) Au nanocages with a wall thickness of 3 nm synthesized by galvanic replacement reaction between Ag nanocubes and $HAuCl_4$; and (F) Co_9S_8 nanoshells formed by reacting Co nanocrystals with sulfur.

electronic and optical properties of the bulk materials their utility in optoelectronic applications that require high carrier mobility and conductivity is limited due to the nature of the 3D confinement in these small particles. The nanostructured crystals are designed to specifically remove this limitation. Not only the semiconductor properties of the parent bulk are essentially retained in these structures, but more importantly they have the same level of property tunability as that of quantum dots which is independent of particle size, because the quantum confinement effect (QCE) is induced internally in these systems. Recent studies have shown that II−VI based nanostructured crystals exhibit numerous enhanced or modified features over conventional II−VI semiconductor bulk and dots, including an unusually large band gap tunability (a 2 eV window, exceeding what has been achieved by most other confinement approaches), very high absorption coefficients (an order of magnitude higher than the bulk), large carrier diffusion lengths and strong exciton binding energies.
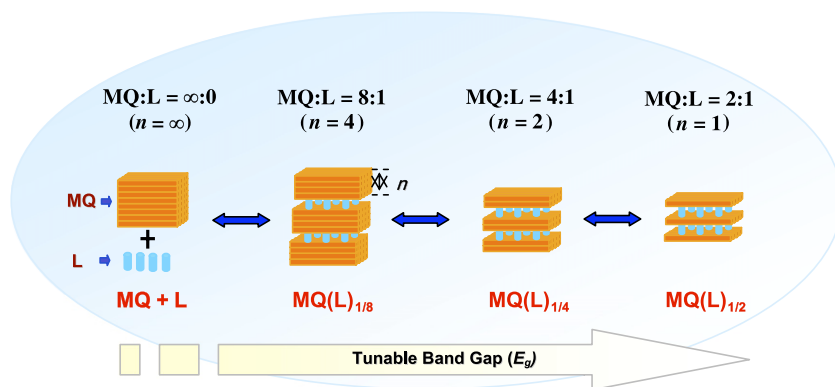
Fig. 2.12. Schematic drawing of nanostructured crystals of $MQ(L)_x$ (M = Zn, Cd; Q = S, Se, Te; L = diamine) where n is the thickness of a MQ slab.

The development of nanostructured crystals is still at a primitive stage and our knowledge on their structural, chemical and physical properties is very limited. While structure−property correlation plays a crucial rule in these hybrid systems a full understanding of the origin of such correlation remains to be achieved. Among the main challenges are structure and bonding compatibility between the organic and inorganic components, crystal growth control, and fabrication of cost-effective, high-quality thin films, to name a few. Nevertheless, the concept of size-independent nanostructures may be applicable to many other possible combinations of inorganic−organic hybrid systems and there is no question that continued efforts in this research area will have a strong impact on the advancement of nanoscience and nanotechnology.

In addition, surface properties of nanoparticles are of critical importance and these properties are dynamic and respond to the ambient environment. In nanoparticles of alloys, what is at the surface depends on the surface energies of the components and this is dependent on environment. For example, in nanoparticles of CuPd, Pd preferentially segregates to the surface in the presence of CO [177]. Theoretical approaches can make some important contributions to understanding this and similar phenomena.

Polymer nanocomposite technology offers exciting new opportunities for innovation in the plastics industry. These composites consist of layered materials, typically clays, exfoliated and uniformly dispersed in a polymer host matrix. Exfoliation of clay into individual platelets creates an enormous amount of surface area per unit mass. When dispersed in a polymer matrix, low weight loadings of clay—typically 5% or less—have profound effects on polymer properties including mechanical strength, gas permeability, tolerance of high temperatures, and flammability. These property enhancements suggest that polymer nanocomposites will replace conventional polymers in many applications and reduce the amounts of polymer mass and manufacturing energy necessary to achieve target performance.

Of the many facets of nanotechnology that have hyped as "revolutionary", polymer nanocomposites are the only commercial success to date. The first success story in this field was Toyota's development of a nylon-6/montmorillonite nanocomposite which, at low clay loadings, exhibits enhanced thermal and mechanical properties that enabled its use in automotive components in the engine compartment. Many successful nanocomposites have been developed since then, mainly for the automotive parts market. This success has prompted much additional research seeking a fundamental understanding of clay exfoliation and dispersion into

polymers, the mechanisms by which exfoliated clay platelets lead to dramatic improvements in physical properties, and the impact of dispersed nanoparticles on polymer synthesis and processing. A substantial body of knowledge has accumulated indicating that the physical properties of the clay platelets (e.g., aspect ratio) and their chemical interactions with the host polymer are the critical factors. To that end, synthetic platelet materials, such as synthetic clays, layered metal phosphonates and layered perovskites have been incorporated into polymer nanocomposites where the surface modification of these platelets is believed to improve the compatibility between the host polymer and the platelet material, improving the resulting physical properties.

2.5.1. Thin films

The electronics industry, providing devices and hardware for computation, data storage, and communication, relies heavily on thin-film technologies. Many of the materials described and proposed throughout this document will likely find use as thin films and contribute both to operational improvement of electronic and optical devices and the development of new technologies. Process integration and feature patterning play key roles in the utility of a material in a device, and these ''properties'' can be considered as additional elements in the design strategies for new materials development. Many opportunities exist to specifically use thin films in the production of novel phases having unique properties and to fabricate well-controlled layered structures across variable length scales to realize multifunctionality.

The growth, for example, of oxide epitaxial thin films on single-crystal substrates by physical and chemical deposition techniques can be used as an approach to the synthesis of new materials and in unique architectures for the measurement of physical properties; the compounds $BaCu_3O_4$, $NdMn_7O_{12}$, and $RNiO_3$ (R = Pr, Nd, Sm, Gd), which are not stable in bulk form, can be stabilized by epitaxial growth. Similarly, unusual polymorphs of stable phases, for example $BaRuO_3$, $RMnO_3$ (R = Ho, Y, Tm, Lu), TiO_2, and Mn_3O_4, can be obtained [178]. Thin films also provide an opportunity to produce known materials in forms ranging from single crystal to polycrystalline to amorphous. These different microstructures can be achieved by carefully controlling the growth conditions and substrate treatments. For instance, high-temperature annealing produces a pure TiO_2 surface termination on the (001) $SrTiO_3$ surface. The single-phase surface termination promotes the growth of single crystalline perovskite family thin films. On the other hand, with various miscut surfaces, the surface can be designed to obtain strain-free, strain-released, and strain-tensile heteroepitaxial films. The films grown with different microstructures allow the systematic investigation of structure—property relations and are particularly useful in studying the surfaces and transport properties at high temperatures. Multilayer, nanolaminate structures may also be used to enhance or modify properties. For example, the introduction during deposition of 40 nm thick CeO_2 layers between 0.75 μm thick $YBa_2Cu_3O_7$ layers dramatically enhances the critical current, and nanostructured chalcogenide films can be used to depress thermal conductivity and improve thermoelectric figures of merit. The introduction of interfaces that cause redistribution of ions in the space charge region is another instance. Qualitatively different behavior in ionic conductivity is expected when the interface spacing is comparable to the width of the space charge regions and has been observed in the two-phase system CaF_2 and BaF_2 [179].

2.5.2. Phase-change materials for data storage and reconfigurable electronics

Interest in phase-change materials (PCMs) has flourished recently, as a result of emerging technologies including, most notably, commercially available rewritable optical

media (e.g., CD-RW, DVD-RW, DVR) and the development of non-volatile phase-change memory (PRAM). Each of these applications employs a chalcogenide-based PCM film, which must be switchable between two physical states (i.e., usually amorphous and crystalline). The state of the PCM must also be detectable using some physical measurement, such as optical absorption, reflectivity, or electrical resistivity. There are a number of chalcogenide (S, Se, or Te) based alloys that exhibit phase-change properties in the binary, ternary, and quaternary systems including $Ga_2Sb_2Te_5$, $GaSb_2Te_4$, $Te_{51}Ge_{15}Sb_2S_2$, Sb_3Te and $AgInTe_2$. Of these materials the $Ga_2Sb_2Te_5$ composition has gained the most attention, in part due to the large change in resistance (four orders of magnitude) between the polycrystalline and amorphous phases, and the large change in index of refraction. Applications for such materials thus far include rewritable CDs and DVDs [180], non-volatile memory cells [181], and reconfigurable electronics [182]. In CD and DVD technology, the phase-change material (PCM) is heated with a focused write laser beam to crystallize a small section of the material, and change the local index of refraction. To erase this bit of information, the PCM is raised to a higher temperature (melting) and upon cooling returns to its amorphous phase at the original index of refraction. The difference in index of refraction is sufficient to be monitored by a focused read laser held at a lower power level. In the case of non-volatile memory cells, the change in resistance is the governing property. Electrical impulses can be used to locally heat the PCM and change its resistive state. This can be accomplished in very high densities of $Tbit/in^2$ non-volatile data storage [183]. Read/write times from 40 ns to 100 ns have been demonstrated, along with 10^{11} read/write operations and > 10 year memory retention at 110 °C [184], and these devices are radiation hard [185]. Controlled pulsing of the memory cells can lead to partial crystallization of the PCM. By controlling the amplitude and number of current pulses, percolation of nanocrystallites within the memory cell can be controlled, and multilevel logic can be realized with a single memory cell [186]. PCM materials have been developed in an empirical fashion over the last 25 years. The way these materials function at the atomic and molecular scale is not well understood. In fact, for this class of materials the technology is ahead of fundamental scientific understanding. Challenges that remain with these materials include understanding of the amorphous state, the study of kinetic and elucidation of the conversion mechanisms, decreasing the required current density for reset operations ($\sim 10^{12}\,A/m^2$ at present), decreasing the read/write times, and protecting the materials from degradation (oxidation, electromigration, and thermal effects at the electrode to PCM interface). In addition, reconfigurable electronics can include microwave applications (phase array antenna structures and microwave switching circuits) [187]. In such applications, improvements in microwave material characteristics of permittivity (dielectric constant and loss tangent) are also of great interest. For the memory cell applications, and reconfigurable electronics, material properties of the PCM significantly impact the behavior of the devices made from the phase-change materials. New PCM materials developed from fundamental studies may be superior to existing systems and tailor-made for specific applications [188].

2.6. Recommendations

Structure−property relationships continue to be a fundamental underpinning in the solid-state sciences. Efforts to make advances in this area and develop deep understanding of such relationships need sustained support.

Section 3. Modeling and prediction through theory

**Committee and Participants: Tahir Cagin, Ulrich Häussermann,
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Nicola A. Spaldin**

3.1. Methods and approaches

Our ability to quantitatively predict and explain the properties of strongly correlated materials has advanced dramatically over the last decade, with the implementation of several methodological developments in electronic structure theory. Early electronic structure calculations were performed using the local spin density approximation (LSDA) to density functional theory [189]. Although the LSDA is a well-established technique that continues to make many invaluable contributions, it has a number of limitations. For systems containing localized electrons with strong Coulomb correlations such as transition metal oxides, the use of the LSDA can be totally inadequate, since it can lead to metallic solutions for systems that are known experimentally to be insulators [190].

With respect to the study of strongly correlated materials, therefore, the development of methods that facilitate a realistic description of the electronic structure of magnetic systems containing strongly localized d or f electrons has been very important. Two methods that cure some of the deficiencies of the LSDA in the treatment of localized electrons are now in widespread use: the so-called "LSDA plus Hubbard U" method (LSDA+U) [191] and the self-interaction corrected pseudopotential method ("pseudo-SIC") [192]. Although the physical underpinnings of these two methods are different, they lead to very similar improvements in practice, in most cases yielding band gaps and band structures, magnetic moments, and crystal structures in good agreement with experiment. Other promising developments, which are currently still too computationally expensive for routine studies, but which will likely to find wider use in the near future, are the LDA+DMFT and GW methods, both of which offer a more rigorous physical foundation at the expense of computational effort.

Simultaneous with the tremendous improvements in the first-principles description of strongly correlated materials, developments in the so-called "modern theory of polarization" have revolutionized the first-principles study of the dielectric behavior of materials [193−195]. This theory provides both conceptual understanding of the spontaneous polarization in bulk crystals (which is complicated by the periodicity of the crystal lattice) and computational tools to calculate it within a density functional framework. Ferroelectric polarizations, dielectric constants and piezoelectric coefficients, as well as the behavior of materials in the presence of finite electric fields [196] can now be routinely computed from first principles. A particularly exciting recent advance is the development of first-principles methods for calculating the properties of metal−insulator heterostructures at finite bias. The electronic and structural nature of interfaces is becoming increasingly the domain of solid-state chemists, and the ability to calculate their properties using ab initio techniques will undoubtedly prove invaluable in understanding their behavior.

Where system size and/or computational complexity (e.g., systems which are intransigently resistant to SCF convergence) preclude the use of DFT calculations, carefully parameterized tight-binding calculations continue to play an invaluable role. Even in these circumstances,

DFT calculations often provide important benchmark calculations with which parameterization is performed [197−203].

Quantum DFT methods are generally limited to $\sim 10^{-12}$ s and $\sim 10^3$ atoms and even tight-binding methods are limited to $<10^5$ atoms; with classical interatomic potential systems about a million times larger in both space and time can be simulated. Of course, many problems of interest in solid-state chemistry require modeling of such larger systems. Theoretical approaches used for these problems have been advanced by growing use of hybrid QM-MM methods, where QM (Quantum Mechanics) is applied to a zone where chemistry (reactions, change of coordination number, etc.) is critical and MM (molecular modeling) is applied in a zone where interactions can be treated with classical interaction potentials. QM-MM approaches require careful consideration in the QM ''imbedding'' in the MM ''surroundings''. The past two decades have also seen the introduction of new functional forms for interaction potentials that allow chemical reactions and phase transformation in condensed phases to be accurately reproduced through classical simulations. The potentials that are more complicated in form but carefully parameterized by quantum chemical calculations have been developed for semiconductors, ceramics and more recently for organic solids. Especially, the bond order dependent reactive potentials opened up an avenue where one can treat materials chemistry through classical potentials using molecular dynamics and Monte Carlo techniques [204−206].

3.2. Areas of application

3.2.1. Synthesis

To date, the primary role of theory in solid-state synthesis is implicit, but powerful nevertheless. Over the past two decades, the role of theory in providing motivation for exploratory synthetic programs has grown dramatically. Theoretical/physical understanding of phenomena ranging from thermoelectricity to magnetism has improved to the point that synthetic chemists are assisted in identifying target systems where desired properties might be found. Of course, theoretical guidance can only fairly be described as a supplement to accumulated experience of previous synthetic explorers.

Despite this state of affairs, concrete and important examples where theory has actively played a role in guiding synthesis can now be cited. Prominent among these are found in (i) battery materials, where electrochemical properties inferences from theory have helped to guide the direction of synthetic exploration [122], (ii) metal-organic framework synthesis, where computational modeling has been useful in identifying appropriate SBUs for use in synthesis of frameworks with predictable topologies [207] and in hybrid materials preparation [208−211], and (iii) multifunctional compounds, where the results of first-principles DFT calculations have helped in formulation of synthetic targets [212].

3.2.2. Phase stability

Two key issues in studying phase stability in solid-state systems are determining the likely competing phases and then obtaining accurate thermodynamic models for those phases (Fig. 3.1). When appropriate candidate phases cannot be guessed from experiments, likely candidates can often be determined by considering zero-temperature energies, which is closely related to the problem of finding ground states of a Hamiltonian. Thermodynamic models are then built only for phases that might be competitive. The thermodynamic models in the solid state must take into account contributions from configurational,
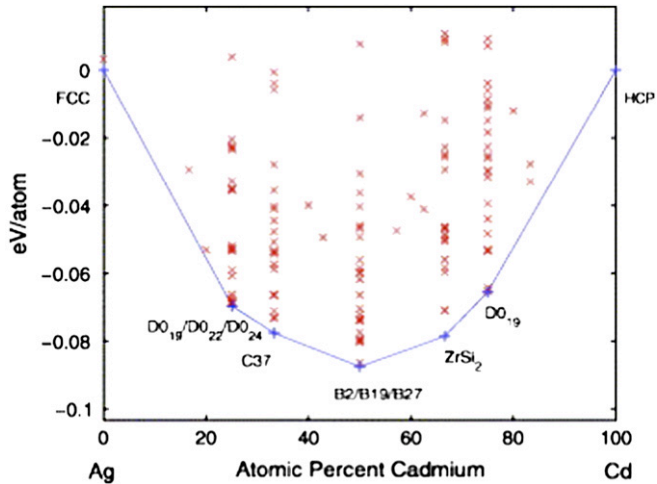
Fig. 3.1. Predicted formation energies of Ag−Cd compounds. The convex hull formed by the connected line segments gives the predicted stable structures and the other points are the structural "competitors".

vibrational, electronic, and magnetic degrees of freedom, although often many of these are not relevant and can be ignored.

Metal hydrides may play a role as future hydrogen storage materials—and have been a recent proving ground for phase stability studies by theorists and experimentalists. The focus has shifted from transition metal alloy hydrides to light-element hydrides from the upper left corner of the periodic table (Li, Na, Mg, B, Al) in order to reach hydrogen storage capacities of above 6 wt%. Recent years have seen a tremendous amount of research activity, especially centered around alanates A^IAlH_4 (A^I = alkali metal), $Mg(AlH_4)_2$, and MgH_2 [213−218]. These represent joint efforts between experimental and computational groups, exemplifying modern materials research.

The problem of identifying stable structures has been transformed by the ability of first-principles methods to yield accurate total energies. Direct comparison of many candidates can yield a list of ideal structures to pursue for more detailed thermodynamic modeling. This direct comparison approach is particularly enhanced by the advent of "high-throughput" DFT. Recent advances in DFT modeling have made codes robust enough that large numbers of calculations can be performed through automated scripts, with minimal human intervention. High-throughput DFT has been used to construct a database of over 14,000 structural energies for prediction of intermetallic structures [219,220], as well as to explore large numbers of compounds for key properties such as band gaps [221], hydride stability [222], lattice parameters and bulk moduli [223,224], and impurity surface segregation energies [225]. In order to apply these high-throughput methods one still needs methods to identify a tractably small list of potential structures to explore. This can often be obtained through data mining experimental results, or studies with approximate Hamiltonians, such as interatomic potentials or the cluster expansion [226]. The use of rigorous search methods, as applied to ionic compounds, has been put forward in a valuable review by Jansen [2].

Once stable structures have been identified, thermodynamic models can be constructed. Direct exploration of the state space of the system is very time consuming, and can only

be done either semi-analytically or numerically with a Hamiltonian that can be evaluated very quickly. As an example of a semi-analytic approach, phonons in the quasi-harmonic approximation [227] are analytically very tractable, and their thermodynamic contribution is straightforward to include once the dynamical matrix has been established [228]. First-principles Hamiltonians generally cannot be evaluated quickly enough to use them directly for studying phase stability (e.g., direct DFT molecular dynamics for order−disorder transformations is generally not practical), so methods to extend the reach of DFT to thermodynamic modeling are needed.

One such method which has proven very powerful for alloy studies is the cluster expansion approach [226]. The cluster expansion represents the alloy energetics as a generalized Ising model, with parameters fitted to DFT data. It can yield accurate energies for relevant configurations many of orders magnitude faster than full DFT, and for very large systems sizes (hundreds of millions of atoms if necessary). Direct Monte Carlo simulation with the cluster expansion representation can be used to study configurational thermodynamics and order−disorder phases transitions, both for bulk materials [226], and more recently near surfaces (Fig. 3.2) [229] and in nanoparticles [230]. Intuitive structure maps for intermetallics including complicated structures can be assembled from combined LDA-DFT and μ_2-Hückel calculations [231].

3.2.3. High pressure

One of the earliest total energy DFT calculations predicted successfully the phase transition from diamond to β-tin structure in silicon [305]. Since then a huge number of static lattice zero Kelvin work on high pressure and metastable phases was performed. The predictive power of calculations increased tremendously with the availability of fast and
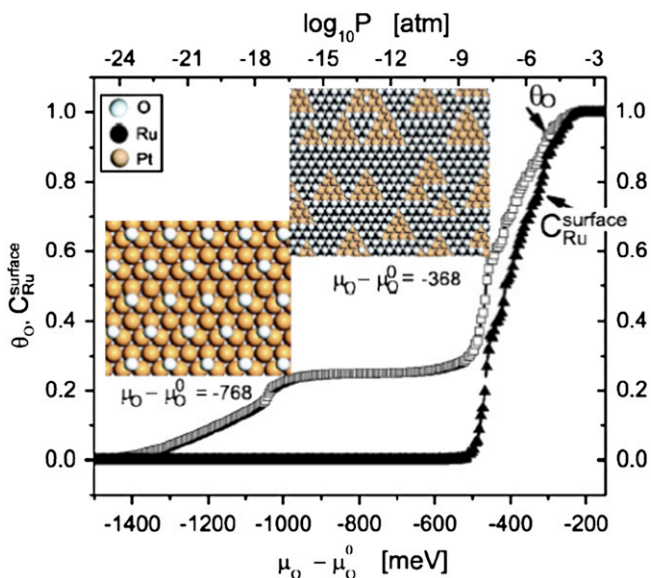

Fig. 3.2. Predicted (111) surface structure of Pt−Ru alloys in oxygen ($T = 600$ K, $m_{Ru} = -1750$ meV).

reliable static relaxations (e.g., Abinit, PW-SCF, VASP codes) and the inclusion of phonons. To reach the ultimate goal of predictability one wants the capability of performing constant pressure molecular dynamic calculations. Recent years have seen a remarkable renaissance of high-pressure science by new advances in techniques and instrumentation, which resulted in numerous spectacular discoveries, e.g. spin transformation of Fe at the enormous pressures in the Earth's lower mantle, the occurrence of unusual open packed or complex high-pressure structures in simple main group metals, the general enhancement of superconductivity of materials under pressure, or the polymerization of small inert molecules, like CO_2, into framework structure. High pressure research is now leading to the identification of new families of materials with previously unknown structures and combination of properties [232]. Theoretical calculations will play an increasingly important role for guiding high-pressure synthesis towards quenchable, metastable phases.

3.2.4. Kinetics

Calculation of rates for simple kinetic processes has now become relatively straightforward with first-principles approaches. The basic approach is to identify a reaction path (using, e.g., the elastic band or dimer methods), find the activation energy of the process, and then apply transition state theory [233] to derive the rate. This has been particularly powerful for studying catalysis. Important results have been obtained for simple reactions on simple surfaces, e.g., on (111) metal surfaces [234], and more complex reaction paths on interesting surfaces can be explored, e.g., CO oxidation on Au nanoparticles [235,236]. Another important application of kinetic modeling has been the calculation of solid-state diffusion. Both in solids and on surfaces, mobilities of atoms and atom clusters can now be routinely studied. One of the most interesting areas of recent development has been in the marriage of thermodynamic and kinetic modeling tools to provide full thermokinetic models for diffusion constants in alloys. In alloys the hopping barriers depend on the local short-range order, which requires a thermodynamic model to simulate. In addition, diffusion in alloys depends on the so-called thermodynamic factor, which also requires a thermodynamic model. All these thermodynamic and local environment dependencies can now be included through DFT-based cluster expansion and regular and kinetic Monte Carlo methods [237,238].

Many of the major challenges in phase stability and kinetic modeling are somewhat universal to simulations: accuracy, complexity, and length and time scales. As noted above, the accuracy of DFT methods is often very good, but highly robust and reliable methods are still quite slow, and the approximations in standard density functional theory are still unreliable for correlated electron systems. However, DFT+U methods, with self-consistent U values, were recently shown to produce far more accurate values for transition metal redox reactions compared to traditional LDA/GGA methods [239]. Compared to LDA/GGA, DFT+U also predicted qualitatively more accurate phase stability in the Li_xFePO_4 system [240]. The accuracy of next generation electronic structure methods for calculating phase stability and kinetic parameters will require much more exploration.

Another area that is challenging is identifying complex reaction paths, particularly when cooperative events involving many atoms are involved. This can be partially alleviated by using molecular dynamics (MD) to explore possible transitions, but the time scale limitations of MD make this difficult. Accelerated MD schemes can be used to overcome this challenge, and these

techniques were recently used to identify unexpectedly fast diffusion of relatively complex interstitial clusters in irradiated MgO [241].

3.2.5. Magnetism

An important division between the ways that chemists can *understand* magnetic properties of homogeneous solids can be drawn between systems where exchange coupling can or cannot be appropriately described by local pairwise interactions. For compounds in the first group (molecules, and insulating metal oxides and chalcogenides in the solid state) exchange coupling is described with Ising and/or Heisenberg Hamiltonians. Exchange coupling can generally be understood in terms of embedded molecular fragments and studies of dinuclear or small polynuclear systems by use of the broken-symmetry approach in DFT, useful in molecular magnetism, can be applied to obtain parameters for these phenomenological Hamiltonians. These results of these studies augment strategies that date from the rules devised by Goodenough [242], Kanamori [243], and Anderson [244]. Synthetic chemists with training in molecular chemistry have been able to make important recent contributions to solid-state chemistry using these rules and ''building-block'' synthetic strategies. The semi-empirical spin-dimer approach to obtain exchange parameters continues to make valuable contributions to understand magnetic properties of such systems [199]. When band structure methods are applied to magnetic insulators, the energies of competing ''spin patterns'' are evaluated with the purpose of finding a set of local pairwise exchange coupling parameters $LaCu_2O_4$ and $LaMnO_3$ [245−247].

3.2.6. Spin polarization in complex intermetallics

Magnetic metals belong to the group of compounds where pairwise coupling descriptions are usually inappropriate and, as indicated above, even when computational approaches to magnetic systems are successful in reproducing magnetic properties, a qualitative rationalization for the result is often elusive. Consequently, chemists' study of magnetic intermetallics and alloys has been comparatively moderate, despite these materials' potential for yielding new and interesting magnetic phenomena—from either a fundamental or practical perspective. Intriguing and useful properties such as giant/colossal magnetoresistance and half metallicity are based on metallic magnetism. Chemical understanding and prediction of metallic magnetism in transition-metal intermetallics is challenging because of delocalization of d-electrons and complicated bonding pictures in the compounds. Unlike the case of magnetic semiconductors and insulators, the formal electron-counting scheme is not generally applicable due to the extensive metal−metal bonds that blur the boundary between valence and conduction bands.

Over the years, the spin-density functional electronic band structure calculation method has been a predominant tool for description of those intermetallics by allowing electrons of different spins to have different spatial densities. In many cases, the predicted ground state and spin polarization density, the difference between the two different spin densities, from the spin-density functional calculations are consistent with experimental observations. However, mere agreement between numerical calculations and experimental results is often not satisfactory, unless an apprehensible rationalization—an explanation couched in words and accessing physicochemical trends—is given. In the solid-state-physics community, the Stoner condition derived in 1930s has been useful as a well-defined guideline in predicting spontaneous spin polarization by using Stoner exchange parameters calculated in 1970s through linear response theory (Fig. 3.3). The concept of ''covalent magnetism'' was
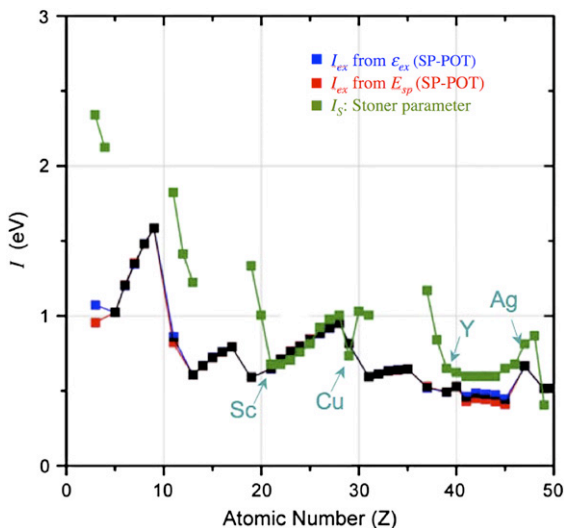
Fig. 3.3. Stoner's parameters have been validated by spin polarization perturbational orbital theory (SP-POT) calculations.

devised in 1980s to reconcile the non-rigid band behavior of many magnetic metals. In solid-state chemistry, Dronskowski renewed theoretical interest in metallic magnetism five years ago when he suggested ''antibonding conjecture'' for the origin of ferromagnetism in magnetic metals. As he properly put it in 2004, however, a quantum chemical operational theory, intended to deliver semiquantitative signposts for the synthesis of new ferromagnets and antiferromagnets, is still needed at the beginning of the 21st century. More recently, a perturbational treatment of spin polarization within density functional theory provided atomic exchange parameters for atoms and hence allows chemists to understand spin polarization from atomic orbital point of view. Future theories of metallic magnetism will be required to ''quantitatively'' explain the non-rigid band behavior of magnetic metals, antiferromagnetism and non-collinear magnetism in the language of orbital interactions and also the relative stabilities of different magnetic ordering patterns. Connections to more strongly correlated systems and magnetic insulators can be pursued through unified theories of magnetic exchange interactions.

Recent progress in treatment of magnetism of gadolinium-containing compounds is promising [201−203]. In selected molecular and solid-state examples, it has proven possible to use GGA-level DFT calculations to evaluate series of competing magnetic spin patterns (ferromagnetic and several potential antiferromagnetic orderings) amongst which the ground state magnetic structures are computationally favored. Analysis of these examples (e.g., Gd_2Cl_3) [201] has shown that they are well interpreted by considering the 4f−5d and 4f−6s exchange as intra-atomic quantities, i.e., as contact interaction—in the same spirit as in the RKKY interaction, *but applied to tight-binding bands.* Adopting this approach in tight-binding calculations (in a similar vein as the LDA+U method in DFT), the magnetic structures of several more complex Gd compounds are reproduced. For example, this method correctly predicts ferromagnetism in the important magnetocaloric compound, Gd_5Si_4, (Miller, Gschneider) and antiferromagnetism in Gd_5Ge_4 (for which a spin pattern that has not yet been determined experimentally) (Fig. 3.4) [248].
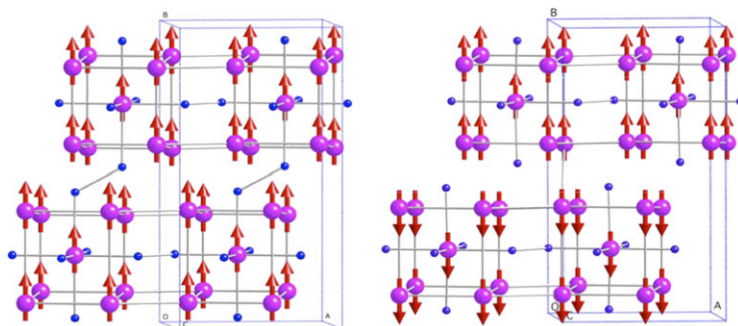
Fig. 3.4. Predicted ground state spin patterns for Gd_5Si_4 (ferromagnetic, left) and for Gd_5Ge_4 (antiferromagnetic, right).

The results of these spin pattern calculations cannot be even approximately reproduced with an Ising Hamiltonian (unless, of course, the number of exchange constants is taken large enough to equal the number of independent calculated energy differences). Thus, even for Gd-containing intermetallics, computation of temperature-dependent behavior has not been attempted because no phenomenological Hamiltonians are available to construct partition functions. One potential avenue for addressing this problem would be computation of a sufficient number of spin patterns that an adequate k-dependent exchange function, $J(k)$, might be obtained by interpolation of results at discrete k values to each spin pattern. In any case, prediction of magnetic/thermodynamic properties poses a major challenge insofar as intermetallic magnets are concerned.

3.2.7. Thermoelectrics

DFT calculations have been useful in evaluating the intrinsic properties of ''perfect'' crystals and insofar as real thermoelectrics' properties are related to such intrinsic properties, the results of theoretical treatment of a series of compounds, trends concerning thermoelectrics are revealed. In Bi_2Te_3, for example, the small band gap, the presence of many nearly degenerate band maxima at the valence band edge, and many nearly degenerate minima in the conduction band edge all bear on this compound's favorable thermoelectric properties (Fig. 3.5) [249].

Defects and disorder often improve the performance of thermoelectrics and there are several ways that theory can help in understanding this fact as well. An interesting example of the significance of disorder is found in β-Zn_4Sb_3 (Fig. 3.6) [250], where the disorder is presumed to be responsible for increasing the thermal conductivity. DFT calculations also show the true stoichiometry of this compound, $Zn_{3.9}Sb_3$ ($=Zn_{52}Sb_{40}$) [251], shifts the Fermi level such that the electrical conductivity is higher than implied by the ''salt-like'' composition. It is worthwhile noting that according to the computed 0 K Zn−Sb phase diagram, β-Zn_4Sb_3 is metastable with respect to decomposition into ZnSb and Zn.

3.2.8. Multifunctional materials

Magnetoelectric multiferroics are materials that exhibit both magnetic order and ferroelectricity in the same phase. In the last few years interest in multiferroic materials has
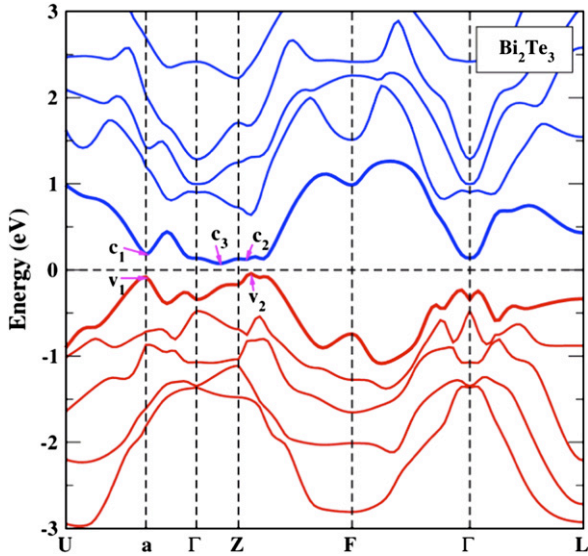
Fig. 3.5. Band structure of Bi_2Te_3.

seen tremendous growth, initiated in part by computational first-principles studies explaining the basic physics underlying their scarcity [189]. This resurgence of interest was anticipated in the 2002 report, which identified multiferroics as an emerging and important class of materials with numerous challenges for solid-state chemists. The recent flurry of research
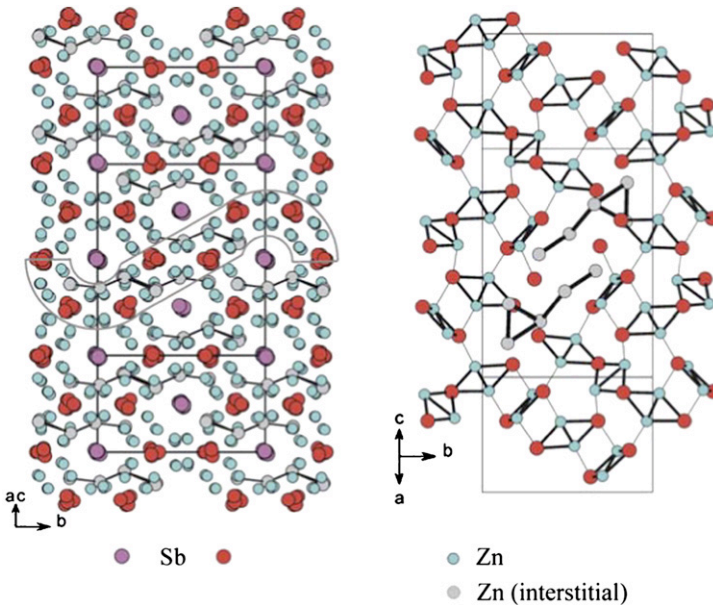
Fig. 3.6. Random Zn disorder in β-Zn_4Sb_3 yield an ordered superlattice with islands of interstitials in β-Zn_4Sb_3 [251].

activity has led to the discovery of several new multiferroic materials, as well as the identification of various strong coupling effects between their magnetic and ferroelectric degrees of freedom [252]. First-principles computations have made major contributions both in explaining experimentally observed properties and in predicting novel effects and systems [253].

Five years ago, the scarcity of magnetic ferroelectrics was already understood to result from the chemical incompatibility between magnetism, which requires localized electrons, and conventional ferroelectricity, which is driven by the off-center displacement of d^0 cations through the second-order Jahn−Teller effect. Since the source of localized electrons in many magnetic systems is the transition metal d electrons, this conventional mechanism for ferroelectricity cannot occur. Multiferroics therefore fall into the class of contra-indicated multifunctional materials, since the basic factors that favor ferromagnetism prohibit ferroelectricity and vice versa.

Two options exist for combining magnetism and ferroelectricity: If ferroelectricity is caused by a d^0 cation, then a different cation is needed to introduce magnetism; alternatively, if the transition metal ions are magnetic and have partially filled d shells, then an alternative mechanism for ferroelectricity is required. All of the new multiferroics identified in the last five years adopt the latter scenario, and indeed the search for new multiferroics has been instrumental in identifying the following alternative mechanisms for ferroelectricity:

- The stereochemically active lone pair in cations such as Pb^{2+} or Bi^{2+} can induce a ferroelectric distortion. The multiferroics $BiMnO_3$ and $BiFeO_3$ are the most well-studied examples, and in both cases, first-principles computations were invaluable in identifying the mechanism for ferroelectricity [254,255].
- In geometric ferroelectrics such as $YMnO_3$, the low symmetry distortion is driven by steric and Coulombic effects. Again, the origin of the ferroelectricity was elucidated through a combination of detailed structural analyses and first-principles computations [256].
- In the "lock-in" ferroelectrics, such as $TbMnO_3$ [257], a non-centrosymmetric spin state lowers the symmetry to a polar space group, resulting in a small but non-zero ferroelectric polarization.
- Charge ordering can result in a polarization, provided that the crystal structure favors a non-centrosymmetric ordering pattern; $LuFe_2O_4$ is an example [258].

We note, however, that none of these multiferroics has simultaneously large magnetization and large polarization above room temperature, a necessity for technological applications. The incorporation of magnetic behavior into conventional second-order Jahn−Teller ferroelectrics, for example by using rare earths to introduce f-electron magnetism, is as yet largely unexplored, and a ripe area for future research.

A scheme for using first-principles computations to predict new multifunctional materials in advance of their synthesis has been devised [212]; the scarcity of magnetoelectric multiferroics has rendered such ahighly desirable approach. One promising recent prediction exploits the strong antiferromagnetic superexchange that usually dominates the magnetic ordering in transition metal oxides to create ferrimagnetic ferroelectrics by combining two magnetic ions with different magnetic moments. For example, the ordered double perovskite system Bi_2FeCrO_6 was suggested as a candidate material, and a ferroelectric ground state with space group $R3$
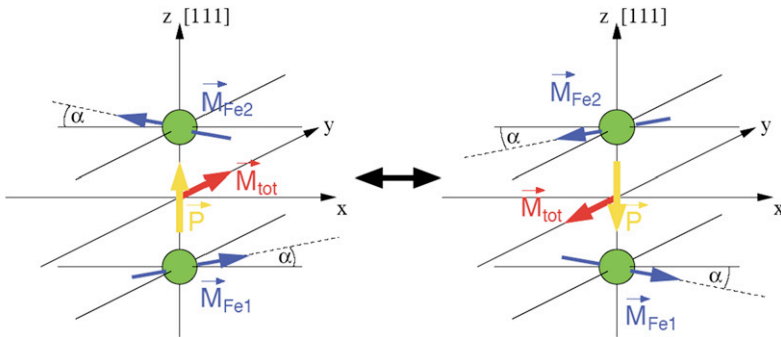
Fig. 3.7. Possible realization of E-field induced magnetization switching in a weak ferromagnetic ferroelectric: if the polarization (*P*) is reversed, the canting of the antiferromagnetic sublattices and the resultant magnetization (*M*) are also reversed.

was found by structural optimization using first-principles calculations within the LSDA+U method [259].

Calculations of the coupling between magnetism and structural distortions in $BiFeO_3$ showed that the Dzyaloshinskii–Moriya interaction, which leads to the canting of the magnetic moments and the appearance of a macroscopic magnetization, is a result of the symmetry-lowering structural distortions in this material (Fig. 3.7) [253]. In the case of $BiFeO_3$ there are two different symmetry-lowering distortions that together reduce the symmetry from the cubic perovskite structure ($Pm\overline{3}m$) to the ferroelectric rhombohedral ground state structure ($R3c$). One is a non-polar R mode that leads to a unit cell doubling compared to the simple perovskite structure and rotations of the oxygen octahedra around the rhombohedral axis, and the other is a polar Γ mode that displaces all ions relative to each other along the same rhombohedral axis. It was shown that the Dzyaloshinskii–Moriya interaction in $BiFeO_3$ is caused by the non-polar mode and that reversal of that mode also inverts the magnetization direction [253].

This has important consequences for the possible realization of electric-field-induced magnetization switching, which was believed to be impossible due to symmetry reasons. Such an effect is in principle possible in weak ferromagnetic systems in which the polar distortion, which results in ferroelectricity, also leads to the appearance of a Dzyaloshinskii–Moriya interaction, which results in weak ferromagnetism [253]. In such a scenario, the magnetization will be strongly coupled to the ferroelectric polarization and reversal of the ferroelectric polarization by an electric field will be accompanied by reversal of the macroscopic magnetization (Fig. 3.7) [253]. The search for a material where this effect can be realized is another area that is ripe for further study.

As time goes on, first-principles calculations will further broaden the field of magnetoelectric multiferroics. For example, efforts are underway to describe effects of spin–phonon coupling, and to identify material that electric-field switchable weak ferromagnetism. In addition, new classes of multiferroic materials remain to be explored, for example the orthorhombic and hexagonal rare-earth manganites, which show a variety of interesting coupling effects between magnetic and ferroelectric properties [257,260]. Nanostructured magnetoelectric composites [103] offer a new way of coupling magnetic and ferro- or piezoelectric properties, and the multitude of possible material combinations represents a way to tune the properties of the

heterostructure to the desired values. Again, first-principles calculations offer a powerful tool to study the properties of such heterostructures and to predict the characteristics of different material combinations.

3.3. Challenges and goals

Advances in density functional methodology and computational power have had a tremendous impact on solid-state chemistry. During the past 20 years electronic structure theory developed from a descriptive to an analytical tool and is now an integral part of research with important consequences: Electronic structure theory facilitates the interpretation and rationalization of experimental results, helps to uncover essential crystal structure—property relationships and directs further experiments. A variety of robust codes for accurate total energy calculations are now available and being utilized by an increasingly diverse range of researchers, including experimental groups. The outcome has been impressive, as summarized in the preceding section.

The next 10 years will see the transition of theoretical methods from an analytical tool into a more and more predictive instrument. The key phrase is "computational design of materials." High-throughput DFT methods that now permit calculation on thousands of compounds at a time (e.g., for band gaps, elastic, and simple energetic properties) should soon allow screening of compounds for desired properties, such as magnetic order and for multifunctional that depends on combinations of properties, such as thermoelectric performance, hydrogen storage capacity, and catalytic activity. Computational methods can be used to model the simultaneous presence of potentially competing properties (e.g., multiferroics) and suggest target compositions and structures for synthesis. The future will see a broader use of increasingly powerful computational methods to make major impact on the development and understanding of new materials. Ultimately, the rational design of solids, by strongly coupling synthesis and theory, has the potential to help society meet its tremendous demands for materials with new or improved properties. In the following we suggest a (far from exhaustive) list of goals and challenges for the years ahead:

3.3.1. More efficient algorithms

In addition to the need for more accurate band structure methods, there are new challenges to be addressed by computational materials chemistry: to develop fast, efficient and accurate methods to suggest material composition and constitution for particular a property in guiding materials development efforts. In the development of new generation materials we are observing emerging importance of interfacial interactions (as in the quantum dots or nanostructured thermoelectrics, for example) whose length scales are much larger than can be handled by conventional DFT methods. The development of robust, flexible, and easily available O(N) DFT methods [261—263] would be very helpful in extending the length scale over which DFT can be used. (This is a long-range goal; similar comments were made in the 1998 report.)

3.3.2. Molecular crystals and other weakly bonded systems

Amid the general optimism we have expressed concerning the role of DFT in solid-state chemistry, some of the current shortcomings of DFT deserve emphasis. Current

functionals are well known for their inability to handle van der Waals forces and hydrogen bonding. Thus, DFT is unable to usefully contribute to structural modeling of layered compounds such as graphite, BN, MoS_2 and molecular solids wherein these are the dominant intermolecular forces. Improved (non-local) functionals are necessary to describe generally systems with regions of sparse electron densities. The hitherto suggested non-local functionals are computationally expensive and need further development [264,265].

3.3.3. Excited states

For excited states, the situation for DFT is improving with progress in time-dependent DFT (TDDFT). Calculations in molecular codes already include TDDFT options—the obstacles to extending this methodology to solids are not within the sphere of expertise of this panel.

3.3.4. Electron transfer reactions

The importance of electron transfer throughout molecular chemistry has sparked intense research effort for decades. In solids, the scope of this important class of reactions is similarly broad, for example: electrode surface reactions, reductive intercalation reactions (e.g., in battery operation), photo-electrochemical reactions, and electrocatalytic reactions. The latter class of reactions is likely to become increasingly important as synthetic chemists strive to extend progress made in porous materials' synthesis to include conductive materials with sufficiently large pores to permit molecular inclusion. Theory will seek to couple understanding of electron transport with an understanding of the local details of solid/molecule electron transfer processes.

3.3.5. Balancing computational power with conceptual models

Despite our focus on the progress that theory is making in handling problems in phase stability and in helping to guide synthesis aimed at exploiting some theoretically motivated structure−property relationship(s), it is undoubtedly true that synthetic research programs will continue to be mostly guided by overarching generalizations regarding bonding or properties (i.e., experimental strategies generally derive from simple ideas!). It is therefore very important that along with computational power, theorists strive to find straightforward interpretative frameworks for their results—no matter how rigorous their origin. The constraints of system size and/or computational resources are not the only reason that simpler models will continue to hold an important place in solid-state chemistry—such models are most likely to find use by experimentalists in ''materials design'' for a long time to come.

3.3.6. Accessibility of theory, enhancing communication with experimentalists

A 'weakness' of a different sort should be mentioned: solid-state chemists still lack some tools in the literature for making DFT fully accessible to non-experts who wish to add DFT-based computations to their repertoire of ''techniques''. Solid-state chemists have a need for monograph(s) explaining the strengths and weaknesses of DFT, in the style of, for example, ''A Chemist's Guide to Density Functional Theory'' [266], but applied to problems in solid-state chemistry.

Section 4. Societal impact

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4.1. Introduction

The significant contributions of solid-state chemistry to societal and economic welfare generally go unnoticed. The following example is illustrative. At the time of this writing, Sony has just announced the release of the first, entertainment-oriented laptop capable of playing, editing, and recording next generation, high-definition videos in the Blu-ray™ format [267]. A Blu-ray™ disc exceeds the data-storage capability of a conventional DVD disc by more than a factor of five, enabling very demanding video applications. The key component of this advance is the blue-violet laser ($\lambda = 405$ nm) employed in reading and writing data to the Blu-ray™ disc, which allows the increase in data-storage capacity.

Light from the Blu-ray™ laser is generated by a multi-quantum-well InGaN device. The high efficiency of the device results from a spontaneous phase separation within the quantum wells, generating a nanostructure consisting of In-rich InGaN quantum dots embedded in a Ga-rich InGaN matrix (Fig. 4.1) [268−270]. Injected carriers are preferentially collected and trapped in the lower-band-gap quantum dots, where the probability of radiative recombination is much higher than in the surrounding matrix. The critically important phase separation and resulting compositional modulation within the quantum wells is induced by the miscibility gap in the InN−GaN pseudobinary phase diagram. Thus, the very success of the Blu-ray™ technology depends critically on fundamental solid-state chemistry developed over the past decades.

Unfortunately, the general public will not realize the important contribution of solid-state chemistry to this emerging Blu-ray™ technology, which is destined to become extremely popular. Nor is the public likely to attribute the advance to solid-state science or solid-state technology in general. Public awareness of solid-state science and technology has gradually faded since the transistor revolution and the rise of the integrated circuit, when the term "solid-state electronics" was in the general vernacular and "solid-state" was prominently

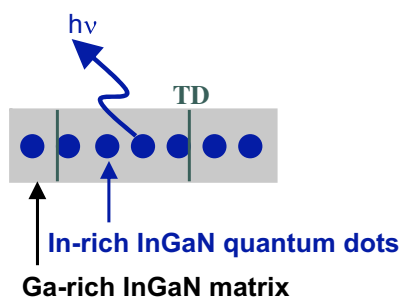Fig. 4.1. Schematic diagram of a phase-separated, compositionally modulated InGaN quantum well responsible for light emission in the Blu-ray™ laser. The vertical lines are threading dislocations, which would normally quench or severely diminish emission from the well. The modulated nanostructure, however, results in deactivation of only a small fraction of the emissive, In-rich InGaN quantum dots.

stamped on consumer electronic appliances, almost as a synonym for ''advanced'' or ''modern.'' Ironically, as familiarity with the ''solid-state'' *terminology* has declined among the general public, consumer hunger for solid-state *technology* has become voracious. Consequently, this mislaid public familiarity is a loss for solid-state chemistry and all allied disciplines.

An additional problem for solid-state chemistry is the typical separation of its contributions, in both time and stage of development, from the ultimate emergence of a new solid-state technology. Solid-state chemists tend to work at a fundamental level, the discoveries of which may not appear in technological developments for years or decades. Furthermore, solid-state-chemistry discoveries are typically passed to materials scientists and engineers, through several stages, in the process of developing a new technology. Awarding greater value and recognition to the disciplines contributing more closely to the ''bottom line'' of technology development is normal and generally appropriate. However, a moderate evolution in the research practices of the solid-state-chemistry community could raise the public profile of its contributions.

In terms of *recognized* societal impact, the solid-state-chemistry discipline would benefit from more of its practitioners committing a greater fraction of their efforts to research directions closely aligned with emerging or potential technologies, or to research directions of sufficient originality and significance to capture the imagination of the public. An example of the latter was the emergence of the high-T_c superconducting oxides in the late 1980s. Obviously the discovery of significant new research fields cannot be systematically planned. However, research efforts can be designed to explore important new dimensions, in consultation with and informed by the discoveries of related disciplines. The solid-state chemist should not hesitate to leave behind the old, the familiar, and the comfortable.

In terms of *real* societal impact, the necessity of continued fundamental developments of an initially more esoteric kind must be appreciated. For example, the steady, fundamental developments of semiconductor chemistry and physics were essential to the inventions of the transistor and integrated circuit, which spawned the revolutions in information and communication technologies that continue today. Judgment must be exercised to distinguish which of such efforts have true fundamental value, and sufficient patience must be accorded for fundamental research to ultimately seed new technologies.

The goals suggested above for achieving increased societal impact are

- commit greater research efforts to emerging technologies;
- increase emphasis on significant and original research directions;
- identify new research directions from exciting developments in parallel fields, such as condensed matter physics, solid-state electronics, materials science, and the various engineering disciplines;
- exercise judgment in identifying basic-research efforts of true fundamental value.

In pursuit of these goals, this section aims to identify solid-state-chemistry directions closely aligned with emerging and potential technologies, and directions of sufficient originality or immediacy to impact public awareness. Human-resource development is a primary contribution of solid-state chemistry, and training and pipeline issues are addressed. Nanoscience has undeniably emerged as a considerable, modern cohort to solid-state chemistry over the past two decades, and exerts a large influence over the opportunities to be discussed. Areas of current and future contribution to technology, energy, and health are listed. Environmental risks and

benefits of new directions in solid-state chemistry are analyzed in some detail. Relevant national-security concerns are also described.

4.2. Human-resource development

A major societal impact of the solid-state-chemistry community is the education of students able to excel in multidisciplinary areas crucial to the competitiveness of American industry. Solid-state chemistry, with its interdisciplinary history, has the ability to prepare its graduates to excel in a wide variety of industries including catalysis, pharmaceutical processing, environmental technologies, optical materials and devices, nanotechnology, and electronics. Since many emerging technologies depend on the discovery of new materials and their properties, individuals with training in solid-state chemistry often are key parts of teams and companies developing these technologies. A critical enabler of this societal benefit has been funding from the NSF and other agencies in this area.

The basic-research skills imparted by traditional graduate training in solid-state chemistry are essential to the technical needs of employers. However, the community should do more to provide the additional teamwork and adaptive skills required for individuals to excel in non-academic settings. Educational programs should strive to develop abilities to communicate effectively, cooperate with and manage coworkers, solve problems from a broad perspective, and work with others of differing technical backgrounds. Increasing interactions with industry through internship and co-op opportunities for both graduate and undergraduate students is one avenue to expand this impact. This will require faculty and educational institutions to change existing attitudes towards off-campus experiences for students, and may require action at a programmatic level. NSF IGERT programs will perhaps provide data on the impact of off-campus experiences on the productivity of graduate students during graduate training, their time to degree completion, their ability to find employment, and their ultimate career success.

Many industries that could benefit from solid-state-chemistry expertise do not commonly hire from this community. As most solid-state-chemistry graduates are employed in the private sector, the impact of solid-state chemistry on society and industrial competitiveness could therefore be increased. The disinclination of some potential employers who do not traditionally hire solid-state chemists in part reflects a failure of graduate programs to provide specialized training optimized for specific industries.

The internship program recently initiated by universities in Oregon with the semiconductor industry provides an excellent example of how such specialized training can be delivered. A materials revolution is underway in the semiconductor industry as a result of the switch to copper-interconnect technology and the need to meet semiconductor-roadmap goals. The number of elements used in the manufacture of integrated circuits is increasing rapidly as new materials are introduced, such as high- and low-κ dielectrics, diffusion barriers, and contacts. The Oregon schools have created a graduate-internship program in partnership with several major semiconductor companies to provide graduate students with the additional background required for them to excel in the industry. The program also transitions students from undergraduates to researchers, and reduces their time to degree. Students are immersed in a full-day, 10-week summer program at the start of graduate school in which they receive practical training in semiconductor-device fabrication. Group work is emphasized. The accompanying lectures on fundamental solid-state

chemistry, device physics, and experimental design, combined with some intermediate goals enable the students to problem-solve their way to functioning devices. To be successful the students need to communicate precisely, learn to work in teams, and solve problems by seeking information, designing experiments, and interpreting data. The reward for participating in this program is a nine-month internship in one of the participating companies where they join project teams solving pressing issues. The typical student participating in this program graduates before his/her classmates, despite the nine month off-campus period, and achieves employment in the industry. As previous NSF studies have indicated, the only parameter that tracks with time to degree is the availability of a job afterwards. Similar programs designed to address the specific needs of other industries should enjoy similar success.

As noted below, highly trained US citizen scientists are also needed to support national-security demands, so human-resource development must remain a major emphasis for the solid-state-chemistry community.

4.3. Nanoscience

The emerging field of nanoscience appears to have captured the imagination of the public, through its novelty and aesthetics, its real and perceived technological applications, and the salesmanship and even hyperbole of its proponents. Although one may argue that nanotechnology has yet to make a widespread economic impact, the indicators are certainly promising. For example, semiconductor quantum wells are employed in commercial optoelectronics such as CD drives and DVD players, which are in the hands of most US consumers. There is clearly a public expectation that nanoscience and nanotechnology will figure prominently in the future economic landscape.

Presently, the solid-state-chemistry community does not agree about whether nanoscience is a relevant partner discipline for solid-state chemistry, a subdiscipline of solid-state chemistry, or a separate, non-aligned discipline that competes with solid-state chemistry for resources and attention. However, large areas of research within nanoscience are obviously derivative of fundamental solid-state chemistry, are based on compositions and crystal structures developed by solid-state chemistry, are informed by the methods and principles of solid-state chemistry, and would best be advanced by solid-state chemists. Solid-state chemists should not ignore the opportunities to explore valid new research directions and physical phenomena that arise at the nanoscale, to establish connections to new applications and technologies, to benefit from the increased public awareness, and to access the additional avenues of funding that nanoscience will likely provide. The solid-state-chemistry community should move aggressively to claim and own its share of the nanoscience field.

One area in which solid-state chemistry and nanoscience overlap strongly is the study of inorganic nanoparticles, nanotubes, and nanowires. These materials are composed of metals, ceramics, and semiconductors previously studied by solid-state chemists as bulk phases. The interesting optical, electrical, and magnetic phenomena exhibited by these nanostructures are correlated with those previously characterized by solid-state chemists for the bulk phases. The selection and optimization of compositions, structures, morphologies, and physical properties are squarely within the skills of solid-state chemists. Exciting potential applications for inorganic nanostructures in catalysis, data storage, light emission, communications

and information technologies, detection, solar- and thermal-energy conversion, spintronics, biological labeling, medicine, environmental management, and national security are currently under development. Several of these applications are listed in the following sections. Clearly, solid-state chemists are well positioned to advance these efforts, which will have significant societal impact.

4.4. Technology, energy and health

Traditional solid-state chemistry contributes to a rich variety of technology, energy, and health fields through the discovery and development of materials exhibiting a wide range of physical phenomena. The list of material types includes thermoelectrics, phosphors for solid-state lighting, laser materials, superconductors, gas-storage and gas-separation materials, magnetoelectrics, phase-change optical-recording materials, battery-electrode materials, ionic conductors, nonlinear optical materials, transparent conductors, materials for solid-oxide fuel cells, photonic band gap materials, ferroelectrics, medical-implant materials, microporous materials for petrochemical catalysis, and others. Many of these families are discussed elsewhere in this report. The discussion here selects a few technological opportunities having a nano-science dimension.

4.4.1. Semiconductor technology

The imminent demise of Moore's law has been predicted for several years [271]. Moore's empirical law accounts for the dramatic increases in computing speed and memory density that have occurred over the past four decades by means of progressive device miniaturization and the attendant increases in the number of transistors per chip. Presumably, fundamental limitations will soon be reached that are imposed by the wavelength of the light used in the photolithographic patterning, and the width of the gate oxide. Even so, the device half-spacing has continued to decrease from 130 nm in 2001 to 65 nm in 2004, well into the nanometer regime, and the end of conventional-microlithography era is not yet in sight. When and if the end arises, a disruptively new semiconductor technology may become attractive.

One such disruptive approach is the bottom-up assembly of integrated nanoelectronic circuitry from nanotube and nanowire components. Individual carbon nanotube or semiconductor-nanowire field-effect transistors, single-electron transistors, p-n diodes, rectifiers, and logic circuits have been constructed and tested at the proof-of-concept level. Crossed-nanowire device arrays have also been fabricated [272]. At least initially, nanowire and nanotube electronics would require integration with existing CMOS technology [273], which is currently a challenging prospect.

At present, nanotube and nanowire devices are generally constructed in a serial, one-at-a-time manner, whereas means for the massively parallel assembly and interconnection of nanostructures are required for integration and competition with existing technology. Lieber and co-workers are developing strategies for the large-scale, hierarchical, Langmuir–Blodgett assembly and registration-free, statistical interconnection of nanowires [274,275]. However, considerable efforts will be necessary to solve this assembly-and-interconnection problem, and a variety of strategies should be developed and compared. Solid-state chemists could contribute creatively to these efforts.

The development of a nanoelectronic technology faces another, more severe device-density limitation imposed by heat-dissipation requirements. The International Technology Roadmap for Semiconductors projects that current CMOS technology will have scaled to a device half-spacing of 22 nm by 2018 [273]. That spacing approaches the theoretical limit of bit-storage stability for any *charge-based* device operating at acceptable switching speeds and levels of heat dissipation [276]. The additional device densities that might be achieved through nanowire-based electronics prior to reaching this fundamental thermal-management limit are likely insufficient to justify the development expense for a new, nanoelectronic technology [273].

Therefore, the search for alternative logic devices to support further Moore's-law increases in device density should seek nanoscale devices operating with logic-state variables other than electric charge [273]. Considerable latitude may be exercised in identifying such alternative state variables, with the possibilities including biological, mechanical, optical, electron-spin, and nuclear-spin systems. The rich array of physical phenomena exhibited by solid-state compounds, with which solid-state chemists are deeply familiar, should enable the community to contribute significantly in the search for new logic-device strategies based on new logic-state variables.

4.4.2. Energy

Identification of new, carbon-neutral energy sources and technologies is arguably the greatest problem now confronting our society, and indeed all world societies. Vast amounts of solar energy are available at the earth's surface, but capturing and converting it in an economically viable manner is truly a grand challenge. The dimensions of this challenge have been outlined elsewhere, and will not be reproduced here [277].

Solid-state chemists have participated in advancing silicon-based solar cells, thin-film photovoltaics, semiconductor liquid-junction solar cells, and nanocrystalline dye-sensitized solar cells. None of these yet afford economical alternatives to the use of petroleum and natural-gas reserves. A recent DOE report [277] summarizes important future research directions for solar-energy utilization, including further developments of nanostructured photovoltaics, inorganic–organic hybrid cells, solar-powered catalysts for fuel formation, and multiple-exciton generation in quantum dot cells [278]. Many of these areas involve solid-state chemistry, and represent important opportunities for contribution by the solid-state-chemistry community.

4.4.3. Health

Traditional solid-state chemistry has participated in health technologies in various ways, such as in biomedical imaging and the associated detectors, and in the selection and design of implant materials. Recently, semiconductor quantum dot materials have been developed for biological-labeling applications. In an exciting recent example, quantum dots were modified for use in an *ex situ* clinical test for respiratory syncytial virus (RSV) infection [279]. The results indicated that the quantum dot RSV detection was faster and more sensitive than the existing Western-blot and real-time-PCR methods. The solid-state-chemistry community should seek stronger ties to health fields, and actively pursue research directions relevant to advancing health technologies for diagnosis and treatment.

4.5. Environment

The development and use of solid-state materials impact society through the influence of these materials on environmental quality. Environmental impacts of solid-state chemistry and nanoscale science occur through three primary mechanisms: (1) advanced applications for environmental treatment and remediation technologies, (2) changes in the lifecycle impacts of products that utilize solid-state chemistry, and (3) potential new risks to human health and ecosystems posed by the production and distribution of new materials. This discussion focuses primarily on applications in environmental technologies and then describes several issues associated with lifecycle impacts and environmental-risk assessment.

4.5.1. Environmental applications of nanostructured materials

Environmental nanotechnology benefits from unique properties of nanostructured materials. The high surface-area-to-mass ratios (i.e., specific surface area) of these materials can benefit any technologies that rely on reactions at solid−water and solid−gas interfaces. Such technologies include adsorption used for water and exhaust-gas treatment and photocatalytic processes for contaminant degradation [280]. Nanoscale sizes can also influence the chemical reactivity of materials by the predominance of near-surface regions with compositions distinct from bulk regions, quantum effects on (photo)catalytic processes, and the increasing contribution of interfacial free energy to the free energy of dissolution−precipitation reactions. The physical size of nanoparticles allows them to be incorporated into existing products to enhance performance or minimize cost. Small low-cost sensors of environmental parameters, which are often measured by optical or electrochemical methods, can now be deployed in smaller solid-state devices. Incorporation of metal-oxide nanoparticles into polymer membranes used in water and waste-water treatment can improve flux and inhibit fouling [281,282]. Finally, nanoparticles can have increased transport in environmental, especially aquatic, systems for the delivery of solid-phase reactants for groundwater remediation. Two applications are described below to illustrate the benefits of nanoscale science to environmental technology.

New nanostructured materials are already finding applications as adsorbents for water and exhaust-gas treatment. The adsorption of numerous contaminants in water occurs with greater mass-normalized capacities (contaminant removed per unit mass of sorbent) for nanostructured materials [283]. Adsorption of arsenic for drinking water treatment is a high-impact application of new materials; many small public-water systems in the United States will need new technologies to meet the recently lowered standard of 10 μg/L (lowered from 50 μg/L as of January 2006), and effective technologies are needed internationally for regions such as West Bengal, India and Bangladesh where arsenic exposure is a public-health crisis. In the field of air-pollution control, inorganic nanostructured sorbents can play a leading role in helping coal-fired utilities reduce mercury emissions [284] to meet the Clean Air Mercury Rule, which was passed in March of 2005.

While nanostructured materials have higher mass-normalized capacities, when the adsorption is normalized to surface area, the nanostructured materials have generally been found to have lower adsorption capacities and affinities (i.e., strength of adsorption) [285−287]. The mechanisms underlying the effects of size on adsorption remain elusive. Integrated experimentation, characterization, and simulation work by solid-state chemists can elucidate these mechanisms and provide information to aid in the synthesis of more-effective adsorbents. Matching

the scales of reactions and transport is an additional challenge in applications of nanosorbents. Effective adsorbents must have large surface areas that are both highly reactive with the target contaminant and also readily accessible (not diffusion limited) to the aqueous or gaseous phase being treated.

The delivery of solid-phase reactants for the remediation of contaminated groundwater is another example of the environmental benefits of nanostructured materials. Zero-valent iron (other metals are also used) is a relatively cheap material that can reductively dechlorinate solvents (e.g., trichloroethylene, which is the most widely observed groundwater contaminant) [288], transform high valence inorganic contaminants (e.g., perchlorate) [289], and immobilize high-valence toxic metals (e.g., Cr(VI) and U(VI)) by reducing them to lower-solubility oxidation states [290]. The application of granular zero-valent metals is limited to shallow contamination, but the development of nanostructured materials makes it possible to deliver iron nanoparticles to less-accessible zones of contamination. The nanoparticles have been found to reduce greater amounts of contaminants per unit mass. A remaining challenge in the application of zero-valent iron nanoparticles is treating the particle surfaces so that the nanoparticles remain stable in well-dispersed suspensions and can be effectively transported to the contaminant zones. Without stabilization, many nanoparticles may be removed by aggregation and interactions with aquifer solids.

4.5.2. Lifecycle impacts of products and pollution prevention

A recent review of environmental nanotechnology identified pollution prevention as one of three areas of greatest impact [291]. The application of nanostructured materials as well as other solid-state materials can impact the overall life cycle impacts of products. The positive impacts on the life cycle can involve reduced use of raw materials, water, and energy in product manufacturing. The impacts can also involve the replacement of hazardous materials with more environmentally benign materials. For example, through life cycle analysis a recent study found net environmental benefits of replacing automobile catalysts with ones based on nanotechnology [292]. Nanofabrication techniques enabling precise control over the shape, size, and positioning of nanoscale Pt-group metal nanoparticles should result in reduced metal loadings. Conversely, new synthesis methods or the production of nanostructured materials could involve the use of greater amounts of energy and raw materials or the use of more hazardous materials. These impacts may be most significant in the earliest (e.g., materials acquisition) and latest stages (e.g., disposal) of the product life cycle. For example, new materials often use rare elements because of their unique properties. The impacts of mining and processing steps to acquire these elements as well as their environmental fate following disposal are part of the overall life cycle impact. While most nanostructured materials will probably have net positive environmental impacts, determining these net impacts must examine the entire material life cycle.

4.5.3. Environmental risk assessment of new materials developed by solid-state chemistry

Assessing the environmental risks of new materials before deploying them in technologies is imperative. Such an approach will avoid past mistakes in developing products that were widely adopted because of their performance in specific applications but were later found to have negative environmental impacts (e.g., DDT, chlorofluorocarbons, and

tetraethyl lead). The same unique properties that make nanostructured materials useful in environmental technologies can also pose new environmental risks. The small size of nano-particles potentially increases the risk of human exposure because of their enhanced trans-port in water and atmosphere. Once taken up through ingestion or inhalation, the high surface areas of certain redox-active nanoparticles can produce reactive oxygen species that damage tissues, and the enhanced solubilities of nanoparticles containing toxic elements can increase their bioavailability. Current work is creating plans for assessing and minimiz-ing negative environmental impacts of nanotechnologies [293]. While concern over new en-vironmental risks is merited and is required as part of new product development, it is reassuring that most studies of the environmental risks of nanoparticles found few unusual risks [294]. This does not mean that production and use of nanoparticles is devoid of risk, but rather that the risks are similar to those associated with the production of a wide variety of chemicals and materials.

4.6. National security

The nanoscience and solid-state-chemistry communities have the potential to solve many national-security problems facing the intelligence, defense, and energy communities. The needs of these communities outlined below comprise challenges for which the societal im-pact resides, for the most part, outside the realms traditionally addressed by academia and industry.

Specifically, the intelligence community monitors assets (physical and human) and col-lects and analyzes complex data. Advances in optical and acoustic receivers, stealth com-munication, chemical and biological sensors, ultrasmall power supplies, and enhanced (e.g., solid-state quantum) computing are needed. Nanoscience and solid-state chemistry can impact each of these areas. For example, nano-metal-enhanced fluorescence (from either organic or inorganic semiconductor fluorophores) can be used to improve sensitivity in chemical and biological sensors that are based on optical signatures from analyte capture. Infrared nanocrystal quantum dot (NQDs) emitters can provide new efficient, tunable sour-ces for gas analyzers or stealth fluorescent tags for labeling assets. Alternatively, infrared NQDs may be used to construct a new generation of wavelength-tunable mid-IR detectors for multi- and hyperspectral imaging.

The needs of the defense community that can be addressed by solid-state chemistry and nanoscience typically center on the survivability of the soldier. For example, the US Army recently began to address this issue by funding The Institute for Soldier Nanotechnologies ($50M contract established in 2002). MIT, in collaboration with a number of industrial part-ners, researches energy absorbing, mechanically active materials, and sensors that could in-clude, for example, nanoscale organic−inorganic composites, such as polymer-nanoparticle and dendrimer-nanocrystal systems. Therefore, a larger challenge is to develop means for coupling organic, inorganic, and biological components at the nanoscale to yield structures and composites possessing complex, multifunctional properties. In addition, the ability to prevent ''friendly fire'' is of great concern. Here, again, advances in labeling, detection, and communication are required, and could benefit from advances being pursued in the con-text of ''intelligence science.''

National security is integral to the Department of Energy's broad mission: ''National, Economic and Energy Security.'' Nanoscience and solid-state chemistry research is being conducted in support of (and supported by) the national-security interests of the intelligence

and defense communities as described above. More generally, however, nanoscience is the scientific thrust behind the establishment of five new national user facilities: The Center for Integrated Nanotechnologies at Sandia and Los Alamos National Laboratories, Lawrence Berkeley National Laboratory's Molecular Foundry, The Center for Functional Nanomaterials at Brookhaven National Laboratories, The Center for Nanophase Materials Sciences at Oak Ridge National Laboratory, and The Center for Nanoscale Materials at Argonne National Lab. At these facilities, an interdisciplinary group of researchers is available for collaboration at various levels with members of the larger solid-state chemistry, nanoscience, and materials communities.

Finally, important science is being conducted in the name of national security. While much of this work can be conducted in open facilities, even universities, many of the customers of this research are unwilling to work directly with foreign nationals. And, often, direct contact between the researcher and the end user of the new science and technology under development is critical to the ability of the researcher to be truly relevant to these communities. At the very least, this requires a US citizen to conduct the work. It has been increasingly difficult to identify qualified home-grown talent in all of the physical sciences, including solid-state chemistry and nanoscience. In an attempt to find a solution to this problem, the CIA has established a postdoctoral fellowship program for US citizen postdoctoral associates ($120K/year) at universities and national labs for projects relevant to the intelligence community, hoping to cultivate home-grown talent and excitement about applied science and intelligence. (The PI may be a foreign national.) The CIA is also considering expanding this program to the graduate and, possibly, undergraduate levels. The recognition by this community of the dearth of qualified US citizen scientists is one small step, but could be coupled with existing efforts by the NSF to encourage promising young scientists.

The solid-state chemistry and nanoscience communities can contribute to these national-security goals through human-resource development, and further engagement with intelligence and soldier technologies.

4.7. Summary

Although the contributions of solid-state chemistry to society are varied, numerous, significant, and indispensable, the public profile of solid-state chemistry is not high. A more-vigorous emphasis on technological advances serving the communications, defense, energy, environment, health, information, and security fields would benefit the solid-state-chemistry discipline. Solid-state chemists should not cling to the comfortable and favorite themes of the past, but aggressively seek renewal by pursuit of the newest and most-significant technological challenges facing society.

There are now tremendous opportunities for nanoscale solid-state chemistry and for elaboration of solid-state materials into complex systems and architectures. However, public investments in fundamental nanoscience and solid-state-chemistry research must ultimately pay off in the creation of profitable technologies and nanotechnologies, or public support for such investment will erode. Thus, public education and outreach are important responsibilities of the solid-state-chemistry community. Training and human-resource development remain as vital responsibilities, and creativity in those endeavors will be necessary to cultivate the solid-state scientists of the future for industry, government, and the academy.

Section 5. Industrial impact and relevance of solid-state chemistry

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5.1. Introduction

The potency of the solid-state-chemistry community at large affects the strength of industry in specific ways. The most tangible, lasting impact of academic research is the production of well-trained chemists and engineers who go on to develop profitable products. Concomitant with their training are the discovery of new materials and the exploration of the characteristics of known materials. Future needs include an expanded scope to non-traditional materials, utilization of additional characterization tools, and increased collaboration mechanisms.

5.2. Trained scientists

The training and development of young scientists who are able to effectively contribute in the industrial setting is a primary focus of the solid-state-chemistry community. Their traditional skills are valued by industry, such as knowledge of the following:

- Synthesis methods
  - Solid−solid, flux, exchange reactions
  - Hydro- and solvo-thermal techniques
  - Sol−gel chemistry
  - Crystal growth
  - Safe handling of sensitive materials handling (drybox, Schlenk).
- Characterization techniques
  - Crystallography (X-ray, neutron, powder diffraction)
  - Microscopy (optical, electron, scanning probe)
  - Electrical and magnetic properties
  - Thermal analysis (TGA, DSC)
  - Spectroscopy, IR, UV, NMR
  - Adsorption.
- Simulation
  - Empirical
  - Semi-empirical
  - First principles.

More important than their technical prowess, however, young solid-state chemists often have developed crucial, professional skills as well. The nature of solid-state chemistry research results in fertile ground for developing skills of immediate utility in industry. Industrial research involves issues such as the following:

- Broad experience base
  - Projects shift quickly in industry

- ○ Industrial scientists must become local expert in minimal time
- ○ Independence, including during project start-up, are expected in industry
- ○ Solving complex problems, deep thinking.
- Interdisciplinary teamwork
  - ○ Scientists
  - ○ Engineers
  - ○ Legal experts
  - ○ Marketing and sales professionals
  - ○ Financial experts, including purchasing and accounting.
- Networks
  - ○ Communications–presentation, written, interpersonal
  - ○ Critical to finding information and solving problems
  - ○ People skills.

Of these, communication skills strongly affect an individual's success in an industrial setting. Solid-state chemists should continue to develop these through the use of local, regional, and global presentations. Various graduate experiences contribute to skill development as well, including through interaction with industrial scientists in collaborations, internships, seminars, and conferences.

As mentioned, the nature of solid-state chemistry is somewhat unique in preparing young scientists for meaningful industrial careers. For example, the following academic environment incubates skills which accompany such individuals into their later careers.

- Broad experience base
  - ○ Multiple focus areas in research groups
  - ○ Variety of projects and project shifts.
- Team skills
  - ○ Collaboration with other disciplines
  - ○ Co-authorship
  - ○ Leading and participating.
- External networks
  - ○ National labs
  - ○ Other universities
  - ○ Industrial collaborations, coops and internships.
- Multidisciplinary approaches
  - ○ Chemistry
  - ○ Physics
  - ○ Materials Science
  - ○ Surface Science.

Solid-state chemists have historically found employment in industries as diverse as their training backgrounds. Most obvious, perhaps, are industries such as lighting, catalysis, gas separations, electronics, energy storage, and energy conversion. Often overlooked, however, are contributions in the health industry, such as pharmaceuticals, medical/dental composites, and other biologically relevant areas.

In summary, academic training in solid-state chemistry provides a unique environment for developing important industrial skills. Broad reading and exposure, technical flexibility, and their

inquisitive attitudes facilitate solid-state chemists' transition into an industrial setting. Well-trained individuals are ultimately the source of innovation and competitive advantage for industrial products, and industry will continue to rely on solid-state chemists for profitable contributions.

5.3. Materials studies

Presently there is a decline in industrial support for basic research, including research in solid-state chemistry. This is a reflection of historical trends that shows undulations as new materials and applications (encouraging basic research) lead to new industries and the subsequent maturation of those industries (focusing industry on development). In addition, the regulation of large companies and economic competition has further focused large companies that traditionally supported basic research on shorter-term company products. One metric is the reduction in industrial publications in the open literature even in the face of increased publication rates, as well as the founding of new journals related to solid-state chemistry and the sciences more generally. Additionally the challenges faced by industry to cut costs and focus on engineering and development are seen by decreases in industrial employment for scientists.

The decline in industrial involvement in basic research has increased industry's reliance on academic research. Industry may focus more on known materials for development, to engineer and to optimize their performance for applications. Academia provides the environment to pursue basic research both for the fundamental materials and device understanding and the development of new materials that may offer a discontinuous (step function) development in materials from which industry may benefit. While industry may provide a priority list of applications, academia should intentionally be chartered with the broader exploration of new materials synthesis and characterization. This is supported in industry through university partnerships as a route to connect university research important to industry and industrial investment in academic research either directly or through consortia (e.g., NRI—which is joint NSF/SRC supported). In addition NSF-supported academic research may support student research in industrial research settings offering students both an exposure to industrial research and development and an opportunity to utilize materials and tools not available in academia.

One basic tenet behind solid-state chemistry is the understanding of structure−property relationships in technologically or scientifically interesting materials. As such, the successful implementation of this discipline potentially has a very tangible impact on industrial research. Examples include luminescent materials (as phosphors, LEDs and lasers), giant magnetoresistance materials (magnetic storage), support and separation materials (gas/liquid purification, household detergents), heterogeneous catalysts (energy/petroleum, environmental, chemical conversions), energy conversion materials (batteries, fuel cells, photovoltaics), superconductors (medical imaging, analytical), piezoelectrics (scanners, telecommunications, memory, sensors), thermoelectrics (coolers for communications and consumers), and nanotechnology (absorbents, polishing compounds, and many more some of which are to be determined).

For example, high-brightness LEDs are emerging as an important lighting technology. Currently used to backlight portable devices, LEDs promise to displace more traditional lighting, due to an increased lifetime, smaller size, lower environmental impact, and increased energy efficiency, the latter becoming more topical as traditional energy sources become scarce and expensive. These LEDs utilize phosphors which convert short-wavelength (blue) light into white light. Almost without exception, the traditional phosphor producers employ solid-state chemists who collaborate extensively with their academic counterparts to discover and optimize these performance-determining materials.

In developing materials with tangible application potential, environmental impact should be considered. For example, the replacement of Cd and Hg with Zn in a compound of interest is always preferred. In synthesis methodology, the use of benign solvents (e.g., water) should be preferred over toxic ones. These environmental considerations are not just issues of social responsibility; they often determine commercial viability. When thinking further down the line, issues of scale-up feasibility are also important. A synthesis with low yield and no effective purification, for example, or erratic in its outcome, should be worked until it is reproducible and the pure compound can be consistently obtained.

While in the past, the primary focus in the solid-state community has been on empirically directed synthesis, a future emphasis on developing techniques for theory-guided synthesis would be valuable to develop. Although still not generically feasible, computational power and techniques have evolved significantly over the last decade. The possibility of "discovering" new materials with desired properties using theoretical and modeling approaches is getting closer to reality and could have a huge impact on the costs of developing new functional materials.

Additionally, it would be very valuable to extend beyond the traditional realm of solid-state chemistry, i.e., crystalline inorganic materials. Organic solids are of significant interest for organic and potentially flexible electronics, sensors, displays, and biological applications among others. Organic—inorganic hybrids and other composites (e.g., combinations of two or more inorganic materials) provide the opportunity to build multifunctionality into new systems. Organic molecules provide the possibility for luminescence, electrical transport, and templating capabilities, while the inorganic component may provide superior electrical transport properties, thermal and mechanical stability and magnetic transitions. The combinations of these attributes can be both a combination of the two components, as well as providing the opportunity for new properties arising out of the interface between the organic and inorganic components.

Amorphous materials are technologically very valuable as well (e.g., phase-change materials for optical memory, glasses, amorphous transparent oxide conductors) and yet have been largely ignored by the solid-state community. As the tools for examining the local and intermediate range structure of glasses and amorphous materials has developed over the last decade, this should provide an important opportunity for the solid-state-chemistry community to examine the structure—property relations in these systems.

Many technologically significant chemical processes occur on surfaces and in thin films. These systems would also benefit from the type of analysis brought to bear by the solid-state-chemistry community. Finally, although this should not be used as a substitute for directed research, the expansion of high throughput and combinatorial approaches into the solid-state chemistry tool set would be valuable to introduce, both as training and as a mechanism for materials exploration.

In summary, fundamental research and materials discovery from academia affect the strength of industry. Application of the rich materials discovery and analysis tools of traditional solid-state chemistry to additional areas would increase this impact. Expanding the interaction of industry and academia will seed additional fruitful areas of solid-state chemistry.

5.4. Consultants and collaborators

As emphasized previously, the solid-state community is particularly rich when it comes to advancing programs through collaboration. Oftentimes this occurs between disciplines or departments. Equally influential, however, are collaborations between academia and industry. Experts can be identified from their public activities, such as publications and conference presentations.

Consultants are often utilized to quickly advance programs or to serve as consultants for program reviews. This is not unique to solid-state chemists, but such experts are quite versatile when it comes to broader reviews for the chemical industry.

Academic centers of excellence are another important source of advancing industrial solid-state chemistry. When such departments organize outreach programs, industrial development is advanced through pre-competitive information exchange. Access to both specialized equipment and expertise in such academic departments can accelerate industrial research programs.

A number of mechanisms exist for industry and academia to collaborate. Among them are traditional contract and sponsored research. Other industrial problems can include a greater training element. Funding programs, such as NSF's GOALI program, facilitate materials research in such situations. Matching funds from industry and funding agencies are advantageous for reducing the risk of industrial and academic collaborations.

Outside of traditional enterprises, numerous small companies collaborate heavily with academia. Start-up companies often have limited equipment for development and analysis. Obvious advantages include access to required equipment, original inventors, and infrastructure. Small Business Innovative Research (SBIR) programs are available to small enterprises to encourage collaboration and provide support for student training facilitate their transition to industrial research settings.

5.5. Future prospects

The continuing support of cross-disciplinary, solid-state research in academia trains students to work effectively on cross-functional teams in industry. The global competitiveness and sustainability of industry relies partially on broadly-trained, highly-flexible chemists. Therefore, solid-state chemists are often well suited to have significant industrial impact.

It is also imperative that longer-term, fundamental research continues. Exploration of material space with targeted, practical applications also fills an increasing gap in industrial research. Collaboration with industry strengthens the impact of such research, and mechanisms for such collaborative work with mutual benefit should be expanded.

There is a need in the graduate research experience of students to be driven by goals of some sort, which may be discovery of new materials, solving of a characterization problem, or synthesis of a material with a particular physical property. Although the goals of industrial R&D may be more mission oriented, the graduate student benefits from being driven by goals during their education.

An anti-intellectual sentiment has emerged among some in the population, an attitude which undermines innovation and influences the career choices of some of the brightest, young minds. Solid-state chemistry demonstrations can be visually striking and inspiring. Involvement of professional chemists with the public is critical to dispelling anxiety about solid-state chemistry and ultimately promoting positive impressions of the chemical industry.

Finally, the expertise of solid-state chemists can be brought to bear in areas that have not traditionally been explored by solid-state chemists but are critical to the vitality of industry. These include the study of glasses, surfaces, composites, multi-component systems, and crystalline−amorphous phase-change materials.

In summary, the relevance of solid-state chemistry on the strength of industry is significant, in terms of people, ideas, and tools. Industrial needs and the mission of the NSF are generally aligned, particularly in the training of a skilled, flexible workforce. Furthermore, the discovery and characterization of materials, as well as the development of tools, have historically contributed to industry. Strengthening the academic-industrial linkage will enhance further the impact of the solid-state chemistry.

Section 6. Education

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6.1. Introduction

Effective education in solid state and materials chemistry is vital to ensure the future health of the discipline. Deficiencies at the undergraduate, graduate or postdoctoral level can have an adverse impact on the educational enterprise. Since the previous workshop in 2002 did not include a panel on education, the charge of the present group was to review the status of education in solid state and materials chemistry since the first workshop, which was held in 1998, and to look towards the future. Our panel chose not to undertake a systematic review or to provide any statistics but rather to take a holistic approach to assess how this community is addressing education and what might be future challenges and opportunities to consider. With this in mind, the current status and educational needs of three populations, namely undergraduates, graduate students, and postdocs, are outlined below followed by a set of specific recommendations, described in detail.

6.2. Issues in undergraduate education

What is the optimum training and skill set that undergraduates in chemistry need and in particular, those students who might continue in solid state and materials chemistry? Aside from an introduction to and basic knowledge of the structures, bonding, and properties of solid-state materials, undergraduates need an introduction to problem solving skills and analytical thinking, as well as exposure to modern instrumentation and theory, and the power of interdisciplinary teams. Another overall goal of the ideal undergraduate curriculum should be to train students how to effectively communicate science to a variety of potential audiences. This should include writing and the presenting of scientific results for a community of experts in formal publication styles (most typically, laboratory reports, oral presentations, or poster sessions) as well as explaining the science behind issues of societal importance to a more general audience. Most in the scientific community would agree that research experience should be a critical component of a modern undergraduate curriculum, although many of the same benefits might also be attained through an industrial internship. What should unite and underlie all of these curricular aspects is that an undergraduate education should serve to excite students about science and ignite a lifelong passion.

Within the solid state and materials chemistry community, there are a number of models in practice to achieve these goals. The critical question is how best to introduce and integrate solid state and materials chemistry into the undergraduate chemistry curriculum. Historically, solid-state materials were noticeably underrepresented if not entirely absent. With the steady increase in the number of solid-state and materials chemistry faculty in chemistry (and related) departments across the spectrum of institutions in higher education, this situation has begun to improve. In some colleges and universities, undergraduate courses in solid state and materials chemistry have been developed; some of these include laboratory experience. In many cases

however, the undergraduate curriculum suffers from curricular gridlock. The list of required courses and topics for a chemistry major is already long; realistically, many students do not have the time for an elective course in solid state and materials chemistry, and faculty may not have the luxury of time to teach these courses. Moreover, such courses are limited to those institutions that have a solid state and materials chemist on the faculty. A more practical model to introduce solid-state materials in the undergraduate curriculum may be to integrate these topics into existing inorganic and physical chemistry courses. Many examples of successful integration can be found at institutions with a solid state or materials chemist on the faculty.

Looking to the future, the ideal would be that throughout the undergraduate chemistry curriculum, this integration of solid-state materials topics continues to spread and to grow. The primary limitation or impediment to achieving this goal is the lack of widely available teaching resources. Many faculty colleagues in inorganic chemistry would like to include more solid-state chemistry in their courses, but do not know where to begin. Textbooks offer minimal help. The majority of inorganic textbooks, for example, offer very little in-depth information on inorganic materials, particularly more recent advances and discoveries. These texts may present the basic inorganic structure types, but solid-state structural chemistry has moved far beyond NaCl. Simple descriptions of bonding in metals, semiconductors, and insulators may be briefly introduced, but often a connection to molecular orbital theory is lacking as well as an extension of the discussion to properties. Thirteen years ago, the seminal book, *Teaching General Chemistry*: *A Materials Chemistry Companion* was published. This resource book for teachers and related products has had a profound impact on the introduction and incorporation of topics in solid state and materials chemistry into general chemistry courses. The time is right to extend this model to advanced courses in the chemistry curriculum. Although it is unlikely that such an all-encompassing project would be assembled for inorganic and physical chemistry, the same ends might be achieved via more modest projects and dissemination of teaching resources within the chemistry community. These will be described in more detail in the recommendations below.

6.3. Issues in graduate education

The education of graduate students is one of the core missions of the solid-state community, one that has been and continues to be very successful. As it is carried out by the large number of individual researcher advisors, it is by its very nature quite diverse and individual: Graduate students enter the workforce with different, yet overlapping, skill sets. In fact, there are certain core competencies that all the students typically acquire during the course of their Ph.D. experience, such as synthetic skills, understanding structure−property relationships, expertise in materials characterization and, most importantly, strong analytical and problem solving skills. In addition, other skills specific to each research group are acquired as they are used by the graduate student for the completion of the Ph.D. degree, and these, of course, differ as widely as the research problems being investigated by the solid-state community. As a group, these highly trained graduate students are desired by industry as they possess the skill set generally perceived as necessary and essential by industry. The skill set is not static, but rather continually evolving as new instrumentation and new techniques and methods are introduced into the research laboratories. Thus by working at the forefront of scientific research, these graduate students continue to receive up to date skills. Quite naturally, these skills are passed down the educational ladder via an inherent feedback loop whereby Ph.D. students enter the workforce as teachers at undergraduate and graduate institutions, where they in turn educate the

next generation of chemists. This continuous upgrading of the skill set clearly benefits industry, as these students bring these new skills and methods to bear on the scientific research problems faced by industry.

There is, not surprisingly, a distinct difference between the undergraduate and graduate education program. While the undergraduates need to learn general chemistry knowledge and be exposed to a broad range of topics, graduate students tend to focus on a specific area in which they become experts by the time they graduate. Typically, in addition to acquiring advanced and specialized chemistry knowledge, they also learn to work in interdisciplinary teams, collaborate with industry, take advantage of national facilities and polish their writing and public speaking skills. This latter set of skills is particularly desired by industry, where most of our students end up.

This diversity in the skill set of graduate students brings about its own problem with respect to the availability of teaching resources, such as comprehensive textbooks. There exist no modern texts that include all the many topics that are required for the education of this group of students and the diverse set of areas in which they receive training. Thus, a modernization of the currently available teaching resources is in order. This need is widespread and could be solved by the generation of teaching modules, each of which would focus on a different topic. If handled properly, this would become a living project that is updated and expanded as necessitated by the ever changing research landscape. An additional benefit will be its applicability to the teaching of advanced undergraduates, where it also will represent a needed instructional resource.

In addition to preparing graduate students for industrial positions, a second mission of graduate education is to prepare a smaller subset of students for jobs in academia. This necessitates, with rare exceptions, that the graduate student continue his/her education at the postdoctoral level, where they need to acquire additional skills, some of which are particular to academia. Most research groups hire postdocs and thus bear responsibility for preparing these individuals for life in academia. The postdoctoral position, unfortunately, is ill defined in the academic system and its status varies widely between different institutions, which is typically reflected in the benefits that are, or are not, available to postdocs vs. students and staff. Defining the postdoctoral status, through rules set by the funding agencies and possibly new postdoctoral funding opportunities, is a suggestion well worth considering.

6.4. Issues in postdoctoral education

Postdoctoral associates are at a transitional stage between graduate students and faculty in the educational feedback loop. Although postdocs are still clearly involved in the educational system, the knowledge base that postdocs should acquire is less clearly defined than the educational goals for undergraduate and graduate students. In many cases, additional experience in the field of solid-state chemistry is good for the education of postdocs by diversifying their research experiences via exposure to a broader range of techniques to approach research problems and also by making additional contacts in the field of solid-state chemistry. In general, the research experiences of postdocs are thought to be positive. Nonetheless, there are a number of ways in which the further education and training of postdocs could be enhanced, particularly for those who hope to join the faculty at either research universities or primarily undergraduate institutions.

First of all to facilitate the transition to the postdoctoral experience, the NSF could support a searchable webpage containing a listing of links to academic, government, industrial, and international postdoctoral opportunities. A centralized listing would be beneficial for graduate

students in their search for research opportunities after finishing their Ph.D. dissertation. Once in a postdoc, the availability of funding to attend meetings and present research should be maintained and encouraged as an invaluable mechanism for exposure and further career development.

Some government postdoctoral opportunities, such as the National Research Council fellowship, offer a potential educational advantage in that the postdoc manages his or her funds and formulates a yearly budget for the costs of experimental supplies and travel. These are all crucial skills to develop early for those who will go on to manage research groups in academia. It is uncertain how to integrate these aspects into a more traditional academic postdoc, but such exposure to issues of financial and resource management could ease the transition from postdoc to new faculty member and have a particular impact on initial writing of research proposals. Along these lines, the installation of personnel management techniques, i.e. overseeing a research group, may be another potential educational component. Resources to improve interviewing skills and grant and research proposal writing would be helpful. The opportunities to provide service to the research community, such as reviewing manuscripts, should also play a role in the education of postdocs. This could easily be accomplished by the editors of journals, but there needs to be a mechanism for a postdoc to 'volunteer' to review for a journal. The opportunities to obtain combined teaching−research experience as a postdoc should also be available for those who are interested in four-year universities.

6.5. Recommendations

1. Develop tools for the incorporation of solid-state chemistry into the curriculum, specifically: (a) a peer-reviewed series of modular texts and (b) a living web-based library of solid state and materials chemistry teaching resources.
2. Continue to increase support for the involvement of undergraduates in solid-state chemistry and materials research.
3. Science for All—Educate the public in solid state and materials chemistry.
4. Enhance support for training of students in the effective use of national facilities.
5. Provide support for international exchange and collaboration for students and postdocs.

1. Develop tools for the incorporation of solid-state chemistry into the curriculum, specifically (a) a peer-reviewed series of modular texts and (b) a living web-based library of solid state and materials chemistry teaching resources.

An in-depth education in solid-state chemistry should begin at the advanced undergraduate to beginning graduate student level, however there is a consensus that there is no satisfactory modern solid-state chemistry textbook available to meet these needs. At the undergraduate level, many faculty are willing to incorporate solid-state chemistry topics into the inorganic or physical chemistry curriculum but are limited by unfamiliarity and lack of experience in teaching these topics. This is exacerbated by a lack of resources that can be used to supplement typical textbooks and lab manuals. To address these issues, a series of modular texts should be developed that could form the basis for a complete solid-state chemistry course at either the undergraduate or graduate level. The modular approach offers instructor flexibility in tailoring the content of such a course through selection of some subset of modules. Alternatively rather than offering a separate solid-state chemistry course, these modules would enable and facilitate the incorporation of selected solid-state chemistry topics into existing inorganic and physical chemistry courses.

Examples of topics for these modules might include synthesis methods, diffraction techniques, magnetic properties, optical properties, electronic properties, catalysis, thermal properties, phase diagrams, and structure−property relationships. A typical module would begin with introductory and background material as well as case studies drawn from the recent literature to illustrate key concepts. These modules would be peer-reviewed and published on the web as pdf files so as to facilitate updates as needed. This project should receive NSF support, such as summer salary for the individuals creating the modules, as well as for the main editor who will coordinate the project. This modular concept could function as a model for other disciplines, whereby experts are invited to write within their specialty, thus eliciting greater participation from the research community and concomitantly increasing the quality of texts available for use in courses.

Another way to satisfy the need for additional teaching resources in solid state and materials chemistry is to provide a mechanism to share best practices. A website, perhaps the same as the site for the modular texts, could serve as a living library of a diversity of materials generated by community members and reviewed by an editorial board and subsequent users. For example, this website might include syllabi illustrating the incorporation of solid-state chemistry topics into general, inorganic, and physical chemistry courses, tested laboratory experiments, particularly for the inorganic and physical chemistry lab courses, lecture notes, PowerPoint slides, homework problems, and references to current papers in solid-state chemistry used to introduce students to the scientific literature.

2. Continue to increase support for the involvement of undergraduates in solid-state chemistry and materials research.

As demonstrated by a survey of recent past participants (1998−2004) in the NSF Summer Research Program in Solid State Chemistry and Materials, this long-running program continues to draw students to the field of solid-state chemistry. While most students who entered the program did so primarily for the purpose of gaining research experience, over 50% of these students, once exposed to materials chemistry research, went on to pursue materials chemistry in graduate school. The implication of these results is that research exposure to materials concepts during the undergraduate years, whether during the summer or during the academic year, can influence student choice of research field in graduate school; in light of this, two specific recommendations emerge:

(1) Continue supporting the very successful, ongoing NSF Summer Research Program in Solid State Chemistry and Materials.

(2) Increase funding for support of other undergraduate research experiences in materials chemistry including those supported via REU programs and, more importantly, those supported on individual investigator grants at both research universities and primarily undergraduate institutions (PUI). This could be accomplished by direct grant support, by supplemental funding requests to existing grants, and by fostering collaborations between PIs at Ph.D. granting institutions and faculty and their undergraduates at PUIs.

3. Science for All—Educate the public in solid state and materials chemistry.

The impact and importance of solid-state chemistry is not generally appreciated by the general public or even by the large numbers of students taking non-majors and general chemistry courses. If these groups better understood the role of solid-state chemistry in our economy and the benefits to society as a whole, then the public perception of chemistry would be more positive. Solid-state chemistry is not instantly recognizable in the public mind as is, for example, the field of biochemistry. But nearly everyone interacts on a daily basis with technologies and applications that are deeply connected to solid-state chemistry: cell phones, batteries, LEDs,

magnetic storage devices, and petroleum products, to name a few. These examples offer unprecedented opportunities to educate the public in science, on the unique structures, properties, and applications of solid-state materials, and on the value of supporting fundamental research in the physical sciences.

Potential future chemists receive minimal early exposure to solid-state chemistry and materials, which limits the recognition that this discipline is an integral part of chemistry. If uncorrected, these attitudes persist and perpetuate in the more traditional molecular chemistry community, particularly in academia. Given that many students make critical career choices, beginning as early as the first year, the lack of exposure of solid state and materials chemistry in first year courses may limit the pool of students that is attracted to the discipline. For these reasons, continued efforts to introduce solid-state materials alongside discrete molecules in the first chemistry course that students encounter should be supported and encouraged. Given the limits of time and the already substantial amount of material normally covered in this first course, this addition would need to be in the form of solid-state examples of existing topics. Natural places to include such solid-state examples in the curriculum are periodic properties, stoichiometry, structure, bonding, and electronic properties.

4. Enhance support for training of students in the effective use of national facilities.

Solid-state and materials chemists are, potentially, a very important group of users for the nation's major synchrotron and neutron facilities, as they are the source of many scientifically and technologically interesting new materials. However, their university education often does not immediately equip them to make good use of these facilities, and members of the facility staff are often spread thinly and are unable to provide adequate support for new users. The provision of intensive short courses at national facilities provides the background needed to identify an opportunity for a valuable measurement, successfully design an experiment, conduct an experiment, and then analyze the resulting data. While there are already some short courses available, such as the Argonne synchrotron and neutron summer school, there are additional needs for courses that go into more detail regarding a specific measurement type, for example powder diffraction. Individual PIs may find it difficult to provide support for a student to attend these courses despite the fact that doing so would enhance the student's training and the potential outcomes of a research project. Thus, NSF should provide travel support where needed to enable students to receive the training necessary for the effective use of national facilities. Moreover, NSF should leverage their support with DOE to encourage further development of such short courses, online tutorials, and easy-to-use data analysis software by staff scientists and personnel at the national facilities.

5. Provide support for international exchange and collaboration for students and postdocs.

In order to train students to effectively join the global workplace, collaborations with international solid state and materials chemistry groups can offer an invaluable opportunity for cultural and scientific exchange. Research groups in different countries may offer a different approach to science as well as different priorities of current challenges within the field. These collaborations will most naturally arise through contacts between individual research groups and could involve undergraduates, graduate students or postdoctoral researchers. Providing ready access to such international learning opportunities would benefit the solid-state community as a whole. Potential mechanisms for funding these opportunities include the International Office of Science and Engineering, the Materials World Network, and joint funding with foreign counterparts.

Section 7. National facilities

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7.1. Introduction

National user facilities represent a considerable investment by the US and provide essential and unique capabilities for solid-state chemists. Premier facilities are available for experiments, such as neutron and X-ray synchrotron scattering, that simply cannot be accomplished in a routine laboratory setting. In addition, user facilities provide an inherently dynamic, collaborative, and interdisciplinary environment for conducting research and training students at the forefront of materials science. National scientific user facilities are increasingly available to scientific communities in many countries; for example, there are 58 synchrotron light sources in 29 countries, with 7 in the US. The availability of such facilities is changing scientific approaches and is leading to complex and interdisciplinary studies not possible a decade ago. However, the use of these facilities by solid-state chemists is not as widespread as it could be. This may in part be because solid-state chemists are not aware of the contributions that such facilities can make to their research. There are also various ''activation barriers'' associated with obtaining and interpreting data at national user facilitates which deters some scientists from using them. Our national facilities generally do a good job of serving expert users, but they do not always meet the needs of less experienced users who can bring scientific problems of equal importance. The charge to this panel was to examine how we can improve the link between solid-state chemists and the national facilities to summarize current and future capabilities that may be of interest to solid-state chemists, and to suggest strategies for improving accessibility and ease of use.

In this report we will highlight opportunities and challenges related to the involvement of solid-state scientists in research at national facilities. Advances in instrumentation and techniques have created extensive opportunities to probe the structures as well as the properties of solids with increasing sophistication. New scientific problems in solid-state chemistry, particularly those requiring extreme environments, also provide opportunities and challenges for the national facilities to develop new instrumentation. The major barriers to optimized use of the national facilities are user education and support (both financial and scientific). These issues are immediately pertinent to the mission of the NSF to train scientists and support the advancement of fundamental science. We further suggest that a reexamination of the importance of the activities of government scientists (especially DOE) in support of national facilities would be helpful in determining how to make the most of our national investments.

7.2. Local and regional user facilities

Though not directly in the charge to this panel, discussion at the workshop highlighted the importance of multi-user instrumentation at local and regional facilities to solid-state chemistry. We briefly highlight needs and opportunities in this regard, and recommend this as a topic that should receive specific attention in a future workshop. Such intermediate-scale instrumentation ($100 K to $1 million), largely based at universities, provides the backbone of characterization methods for solid-state chemists. In-house single-crystal and powder diffractometers are essential characterization tools, and are as critical to a solid-state chemist as is a solution NMR to

a molecular chemist. Though not as extensively utilized, or available, instrumentation such as variable-temperature diffraction, SAXS, and solid-state NMR is also critical for the structural characterization of solids. Similarly, solid-state chemists need access to SQUID and physical property measurement systems (PPMS) for characterization of magnetic and electronic properties, and microscopy facilities are of increasing importance with the advances in nanoscience research. These capabilities, while often managed by a single research group or department, need to be regionally accessible (within a 4 h drive) to facilitate collaborative research; students need these facilities on a regular basis to gain hands-on experience and develop real expertise in data collection and analysis. Such facilities are also critical to maximize the impact of science done at national facilities: the collection of preliminary data is essential in order to optimize experiments on local/regional instrumentation before more costly experiments are performed at large national facilities.

The CRIF and MRI programs sponsored through NSF's Divisions of Chemistry and Materials Research, respectively, have been critical to the solid-state-chemistry community in supporting the acquisition of local/regional instrumentation. Some concern (with contrasting perspectives) emerged from workshop participants regarding discontinuation of the requirement for cost matching from host institutions. This has helped many institutions with limited resources to acquire necessary and costly equipment. Nevertheless, given the finite pool of resources, this has also resulted in the funding of fewer awards. We recommend that NSF consider directing a portion of mid-scale instrumentation funds to the creation of regional facilities (i.e., for magnetic resonance, microscopy, magnetic and transport measurements), particularly if such facilities are staffed with scientists to facilitate collaboration and user training. However, funding for such regional facilities should not replace support for high-usage instrumentation critical for individual research programs. A need also exists for responsiveness to larger-scale emergent technology such as high-field solid-state NMR spectroscopy, small-scale synchrotron-type radiation sources, and atom-specific mapping instrumentation—these techniques are poised to have significant impacts on materials research.

7.3. Synchrotron and neutron facilities in the US

The past decade has seen an unprecedented surge in capabilities for the rapid and precise characterization of materials using a variety of tools at national facilities. In addition, specialized user centers dedicated to nanoscale materials research are currently being developed at Argonne, Brookhaven, Lawrence Berkeley, Los Alamos, Oak Ridge, and Sandia National Laboratories. The first of these, the Center for Nanophase Materials Sciences (Oak Ridge), is complete and the center is accepting user proposals. Other user facilities in the US of interest to solid-state chemists include the National High Field Magnet Laboratory, and those specializing in electron microscopy and mass spectroscopy; however, the present report will focus primarily on US synchrotron and neutron facilities.

During the early 1990s, a significant program of financial investments in the DOE synchrotron facilities was carried out in upgrades and instruments at second-generation sources (National Synchrotron Light Source (NSLS-Brookhaven) and Stanford Synchrotron Research Laboratory (SSRL-Stanford)), as well as construction of two state-of-the-art hard X-ray third-generation sources (Advanced Light Source (ALS-Berkeley) and Advanced Photon Source (APS-Argonne)). These national investments have been of enormous scientific benefit and have quadrupled the US synchrotron user base. Looking forward, the planned construction (starting in 2008) of a fourth-generation NSLS-II facility at Brookhaven, with capabilities

exceeding both the ALS and APS by factors of more than 100 in photon brightness, is a key element to maintain US leadership in the areas of synchrotron and materials science.

Beginning in the mid 1990s, revitalization of the nation's neutron scattering capabilities also became a focus of US funding agencies (DOC, DOE and NSF). Investments were made in upgrading existing reactor facilities as well as construction of the world's most powerful spallation neutron source facility. This led to a significant expansion in capabilities at the NIST Center for Neutron Research (NCNR), including the Center for High Resolution Neutron Scattering (CHRNS). A similar expansion at the High Flux Isotope Reactor (HFIR-Oak Ridge) to incorporate a new cold source and suite of instruments is almost complete. Several new and upgraded diffractometers have completed commissioning and joined their respective user programs at both the Manual Lujan Jr. Science Center (MLNSC-Los Alamos) and the Intense Pulsed Neutron Source (IPNS-Argonne). Together with the very recent completion of the Spallation Neutron Source (SNS-Oak Ridge) and production of its first neutrons, neutron scattering capabilities in the US have truly been revitalized. As the SNS and HFIR facilities ramp up to full power and instrument utilization, complementing the currently operating NCNR, MLNSC and IPNS facilities, the US solid-state community will have access to an unparalleled suite of world-class neutron diffractometers and spectrometers.

7.4. Capabilities at the major facilities

Conducting scientific research at a national user facility requires a different culture than is typically found in university-based research groups. The delay between writing a proposal and acquiring beamtime, condensing experimentation into only a few blocks of time per year, traveling to remote sites, round-the-clock experimentation at the facility, and extensive data processing are challenging for experienced users, and too often pose insurmountable barriers for new users. Nevertheless, the benefit in science that is possible when the activation barrier is overcome is considerable. Investments by the NSF are important to catalyze broader use of these national facilities which will pay significant scientific dividends. In this section we discuss what a solid-state (materials) chemist may gain by using the national facilities, focusing on synchrotron and neutron facilities which are most broadly relevant.

When a solid-state chemist synthesizes a new material, he/she will frequently examine the product first using powder (or if possible single-crystal) X-ray diffraction using an instrument in or nearby the laboratory. The diffraction pattern can be used to determine whether the sample is amorphous or crystalline, a mixture or single-phase, and by searching various databases, may reveal whether a known or new structure has been found. Why is this not enough? Why does one need further characterization using the national facilities? The major reason is that today we are dealing with increasingly complex materials, both structurally and chemically, and with many atoms in the unit cell. Determining the atomic positions of each element in the unit cell presents the preliminary challenge in understanding the nature and properties of materials. The sample may have complex superlattice ordering, information which is often hidden below the noise of a laboratory X-ray diffraction experiment. Moreover, the structure may not be perfectly periodic, and the real structure may deviate significantly from the average structure. Diffraction of neutrons may offer the ability to discern elements with comparable atomic numbers, or reveal the positions of light atoms. Such complexities are beyond the capabilities of conventional laboratory instrumentation and require more sophisticated methods available only at national facilities in order to accurately characterize the structure of the solid.
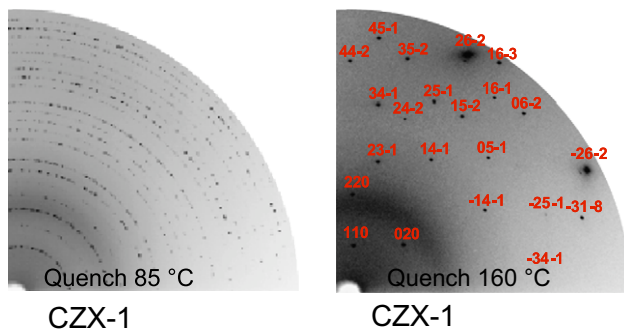
Fig. 7.1. Quadrants of image plates that show multiple nuclei formed by quenching a 230 °C melt of CZX-1 to 85 °C and single crystal growth when quenched to 160 °C (J.D. Martin, unpublished).

Other examples where national facilities enable science include the study of materials under high pressures, which may yield insight on phase transitions important for understanding geologic processes or changes in physical properties such as conduction. High-energy X-rays or time-of-flight neutrons are further required to investigate changes in local structure and/or pressure-induced amorphization that is often observed at high pressure. Time- and temperature-resolved diffraction experiments in high-intensity beam lines with fast detectors allow unprecedented opportunities to study the mechanism(s) of nucleation and crystal growth (Fig. 7.1). A reactive-gas sample environment containment apparatus can be used to study the structure−activity correlations of catalysts or sorbate materials under actual operating conditions. While basic studies can be readily performed under ambient conditions in a home laboratory, high-intensity radiation (X-rays or neutrons) is required to penetrate extreme-environment sample containers, such as a diamond anvil cell. These are but a few examples of cutting-edge science that is possible only with the instrumentation available at national facilities.

7.4.1. Synchrotron radiation facilities

Synchrotron radiation facilities provide: (1) high-resolution powder diffraction with an analyzer crystal to resolve overlapping peaks ($\Delta Q/Q \sim 10^{-5}$, $Q = 4\pi sin\,\theta/\lambda$, θ; diffraction angle, λ; wavelength of the probe). (2) High intensity and low background that allows the measurement of diffuse scattering. (3) High-energy X-rays (100−150 keV) for diffraction up to large Q ($Q_{max} > 50$ Å^{-1}). (4) Sample environments for measurements at low and high temperature and under pressure. (5) Fast data acquisition and time resolution (up to 30 Hz). (6) Tunable energy for EXASF and XANES spectroscopy.

7.4.2. Neutron facilities

Neutron facilities provide (1) capability to determine the atomic position of lighter elements and (often) elements with similar atomic numbers. (2) High-Q access for amorphous and local structure determination. (3) Capability to determine the magnetic structure and (4) dynamics of lattice and spin. (5) Neutrons penetrate many structural materials (e.g., quartz, steel) allowing complex sample environments.

The high Q_{max} provided by high-energy X-ray scattering or pulsed neutron scattering makes it possible to use the atomic pair-density (distribution) function (PDF) method. The PDF is obtained by Fourier-transforming the structure function determined by X-ray or neutron
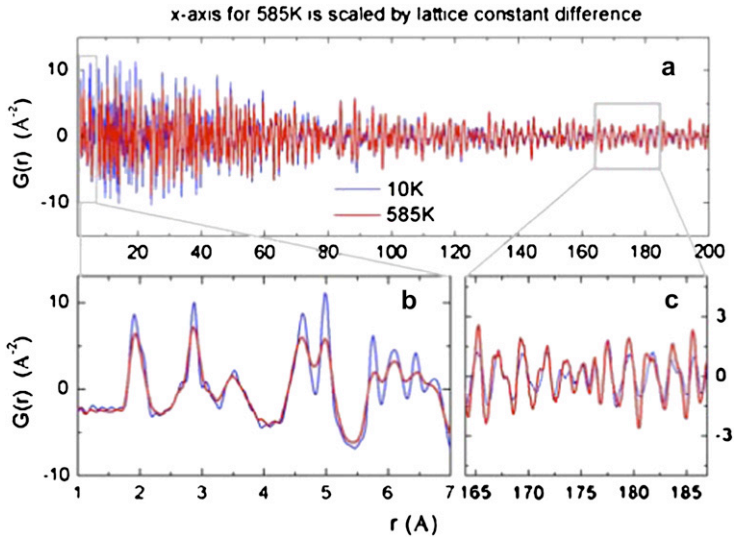
Fig. 7.2. The PDF of LiNiO$_2$ as determined by pulsed neutron scattering.

scattering, and describes the distribution of distances between atoms in the material. The method has long been used in the study of liquids and glasses, but the advent of synchrotron radiation and pulsed neutron sources made it possible to apply the technique to crystals. Now the PDF can be determined up to 300 Å (Fig. 7.2 [295]), connecting the local structure with the long-range structure. This method is particularly useful for nanoparticles and nanomaterials, since it can determine not only the particle size but also the atomic structure in the nanoparticle. When the particle size is small the Bragg peaks become broad, and it is often difficult to differentiate nanocrystals from nano-size glasses. The PDF allows us to differentiate the two (Fig. 7.3 [296]).
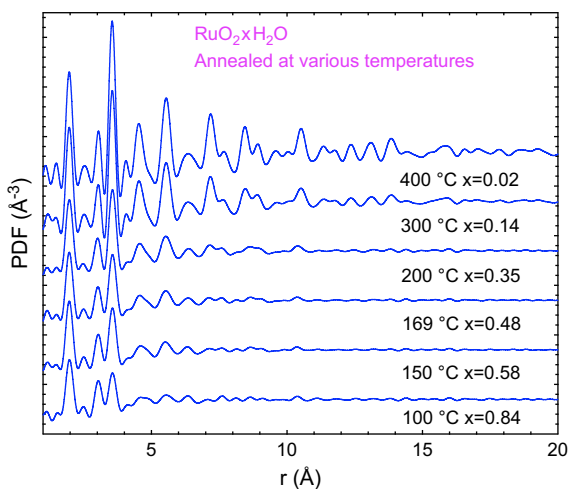

Fig. 7.3. The X-ray PDF of hydrated nanoparticles of RuO$_2$. Even with a particle size of 5 Å the PDF peaks agree with the bulk, suggesting that the 5 Å particles are nanocrystalline, not amorphous.

The variability of the energy of the incident X-rays at a synchrotron facility makes it possible to perform anomalous (resonant) X-ray scattering. Since the X-ray scattering factor of an atom changes abruptly in the vicinity of the absorption edge, by performing scattering measurements at two or more energies near the edge, the differential PDF (DDF) that describes the distribution of distances from a specific element can be determined. Similar data can be obtained using isotopic substitution with neutron diffraction experiments. The DDF yields information about the chemical environment of an element—not only the nearest neighbors, but those located at up to mesoscopic distances. Neutron facilities can be used to provide information on lattice and spin dynamics through the inelastic neutron scattering of phonons and spin waves (Fig. 7.4 [297]). For disordered systems, it is possible to study the local lattice and spin dynamics by a dynamic PDF study.

In addition to PDF methods, local structure can be probed via spectroscopic methods such as EXAFS and XANES. These techniques require a variable-energy X-ray source. Spectroscopic techniques can be exploited for local structure measurements of quite complex systems, since each constituent element can be probed individually by tuning to the appropriate absorption edge. For example, XANES was used to differentiate phosphate binding in Fe- and Al-based minerals, which is relevant to the environmental problem of the binding/dissolution of phosphate from excess fertilizer in various soil types (Fig. 7.5 [298]).

Table 7.1 has been prepared to provide an overview of the instruments and capabilities commonly used within the solid-state community. Users with interesting scientific problems are encouraged to visit the websites of the national facilities to review more detailed information about the individual instruments and techniques. Each instrument normally has at least one beamline scientist, who is ideally the first point of contact. If it is determined that the experiment is feasible, users are encouraged to submit a proposal for beamtime through the facilities general user programs. More complex experiments usually create a greater demand for both instrument time and participation from beamline staff and often pose increased challenges
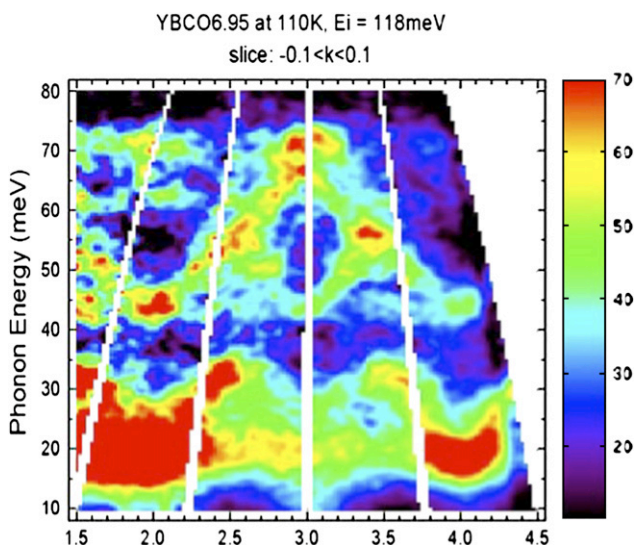

Fig. 7.4. Inelastic neutron scattering intensity showing the phonon dispersion in $YBa_2Cu_3O_{6.95}$ obtained with MAPS at the ISIS.
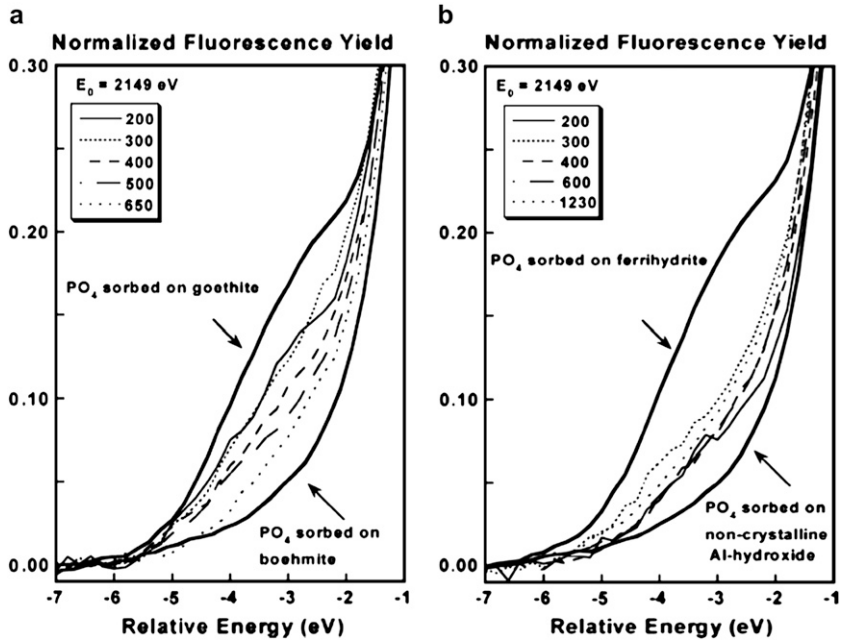
Fig. 7.5. Comparison of the pre-edge region for normalized XANES spectra for phosphate sorbed in mineral mixtures (a) oethite/boehmite mixtures; (b) ferrihydrite/non-xl Al-hydroxide mixtures.

Table 7.1
List of instruments commonly used by solid-state chemists and the instrument locations

Synchrotron radiation	
High-resolution powder diffraction	[APS] 1-BM, 5-BM, 5-ID, 6-ID, 16-BM, 16-ID, 33-BM; [NSLS] X7-A, X10, X14, X16, X17, X18, X23
PDF measurement	[APS] 1-ID, 11-ID; [NSLS] X7-A
Anomalous scattering	[APS] 4-ID, 9-ID, 15-ID, 33-ID
Time-resolved diffraction	[APS] 6-ID, 8-ID, 11-ID; [NSLS] X6-B, X7-B, X10, X14, X17, X20, X23
High-pressure diffraction	[APS] ID-1, 13-BM, 13-ID; [NSLS] X-17; [CHESS] B1
EXAFS, XANES	[APS] 9-ID, 11-ID, 12-ID, 20-BM; [NSLS] X-9, X10, X11, X15, X18, X19, X23; [CHESS] B2
Neutron scattering	
High-resolution powder diffraction	[LANSCE] NPDF; [IPNS] GPPD; [NCNR] BT-1; [SNS] POWGEN (2007)
PDF measurement	[LANSCE] NPDF; [IPNS] GPPD, GLAD, SEPD; [SNS] NOMAD (2011)
Magnetic structure	[HFIR] HB-1; [NCNR] BT-1; [SNS] POWGEN3
High-pressure diffraction	[LANSCE] HIPPO; [SNS] SNAP (2008)
Dynamics	[HFIR] HB-3; [LANSCE] Pharos; [IPNS] QENS; [SNS] ARCS (2008), SEQUOIA (2010), VISION (2012)

APS = Advanced Photon Source (Argonne National Lab.), CHESS = Cornell High Energy Synchrotron Source, HFIR = High-Flux Isotope Reactor (Oak Ridge National Lab.), IPNS = Intense Pulsed Neutron Source (Argonne National Lab.), LANSCE = Los Alamos Neutron Science Center (Los Alamos National Lab.), NCNR = NIST Center for Neutron Research (National Institute for Standard and Technology), NSLS = National Synchrotron Light Source (Brookhaven National Lab.), SNS = Spallation Neutron Source (Oak Ridge National Lab.).

for data reduction, analysis, and interpretation. Nevertheless, persistence often will pay large scientific dividends.

7.5. Making the most of our investment

7.5.1. The changing nature of user facilities

User facility instrumentation is entering a new era. In 2007, for the first time, dedicated high-throughput synchrotron and neutron powder diffraction instruments will become available not only through the customary types of on-site visits, but also via mail-in access. These instruments are therefore poised to produce at least an order of magnitude more datasets than previously. These data will be of world-class quality. Similar usage modes are planned or under consideration for a wide range of other techniques that are utilized by the solid-state-chemistry community, though few are as central to the field as powder diffraction. The steep increase in characterization rate will result in dramatic and far-reaching changes. The remote-access and high-throughput paradigm is highly beneficial to the community, which has been starved for access to world-class facilities, and which has found obtaining travel funds difficult. Nonetheless, these changes create several challenges for both the facilities and their users.

Historically, beamlines have been supported by on-site research scientists who would "hand over the keys" to experienced users who could work unaided, but who would also work closely with newcomers to instruct them on safe and productive measurement techniques. The resident scientists would provide tutorials on data reduction and analysis and were available for collaboration over the lifetime of the research project. In the new paradigm, instruments will be staffed at levels not significantly larger than the current mode, despite the much higher rate of data production.

7.5.2. New challenges facing users and facilities

Training: As we try to mainstream use of these characterization facilities, where will new scientists learn? Increasingly, solid-state chemists are trained as "consumers" of results from national facilities (crystallography, magnetic scattering, EXAFS, neutron spectroscopy…). Researchers are decreasingly likely to choose (or be chosen for) academic careers around the development of physical characterization methods; few chemistry departments have in-house experts to consult or collaborate on instrumental design.

Staffing: If most samples arrive via mail to a service facility, in contrast to a student/PI conducting hands-on measurements, where will the user facilities find scientists who are inspired to staff beamlines? Will sufficient resources be allocated to attract and retain them on a continual basis?

Data overload: At present, data reduction and analysis requires a significant fraction of a Ph.D. thesis. How will the benefits of accelerated collection rates be realized if the rate-limiting step remains data analysis? The currently available software programs for data reduction and analysis are not well integrated and can be charitably described as idiosyncratic. How will users be trained to use this software?

With the great wealth of computational power now available, one can envision software that supplies expertise to a user, rather than requiring expertise as a prerequisite for productive use. Where will this next generation of software come from?

7.5.3. The inverted pyramid for facility investment

Of necessity, the US invests billions of dollars in the construction of user facilities in order to create world-class sources. The sources in turn require instruments, which typically cost

millions of dollars to build. One or two scientists usually staff these instruments, sometimes with a technician, at a cost of hundreds of thousands of dollars. Many user facilities run summer schools or training workshops (which usually provide overviews rather than comprehensive instruction) at a further cost in the range of tens of thousands of dollars. While facilities typically develop some data reduction software in house, data analysis software has typically been produced as a labor of love, with essentially zero ''official'' funding. A noteworthy new development is the DANSE project, which was recently funded by the NSF. The goals of this project are to integrate existing software packages into the data analysis framework to be used at the SNS; however, little if any new software is expected from this effort. A larger investment in software development would facilitate greater impact of the foundational investment in the equipment and facilities themselves, and would enable increased use by a broader contingent of scientists.

7.5.4. A new generation of software

The ultimate goal of data analysis software is to directly fit experimental observations, deriving in this process the desired model parameters. Crystallographic analysis is an example of central importance to solid-state chemistry, wherein the desired model presents the atomic description of the material to the researcher; however, crystallography is one of many areas where atomistic models can be used to quantitatively model experimental results. Software is thus an essential part of the analytical process. Typically, the programs for these tasks have been written by expert practitioners of the experimental techniques, and are used by other experts. Most commonly the programs are large monolithic tools which prevent their use in combined analysis operations, for example, where EXAFS and neutron diffraction data are combined to derive a single model. Further, these tools were created to use older versions of programming languages (usually Fortran-77), which are difficult to maintain and repackage, since programming constructs of that era (for example common blocks) make it very difficult to separate program modules. For this reason, the current generation of codes is reaching the end of their life cycle.

Rather than writing large monolithic software, new codes should be written as modules that can be knit together as needed in projects. This will allow combinations of experimental fits and theory as needed to derive a single model. Software should be written with non-expert users in mind. Where possible the software should narrow choices and validate input. Where multiple fitting options are appropriate, the software can try all of them and select the option that provides best agreement without expecting that a user know to do this. Software should consider the needs of the experimenter who will need to repeat the same reduction and analysis steps on a large number of datasets, as required for parametric studies.

Software development is a never-ending task. While one can create specifications, hire a team of programmers, and create a program, the real value of an effort is established only through a continual process of fixing bugs, educating users, improving confusing bits and developing new features as scientific needs evolve. Software development must therefore be done with the goal of keeping the development expertise involved throughout the life cycle of the product, not only in the most active development phase. The national laboratories have historically been an excellent host for these sorts of long-term development efforts; e.g., ORTEP. However, the Departments of Energy and Commerce no longer see this as part of their core missions.

Recommendation: The National Science Foundation should lead a policy dialog to ensure that national facilities provide user-accessible data reduction and data analysis tools. Criteria for NSF funding of such projects should include definition of how the code will be developed

and supported over the project lifecycle. NSF matching or seed funds directed to user facilities through individual users could help initiate these types of projects.

7.5.5. *Training*

Few universities have faculty members who are prepared to provide instruction enabling students and postdocs to transition directly to productive facility users. The existing facility-run short courses and summer schools primarily focus on overviewing capabilities and providing examples of successful research results. This has great value in showing potential users how their research can be furthered through use of user facility resources. These short survey courses, however, do not provide enough experience to create independent users. While in many cases, documentation and instructional materials can be found for the basic techniques used in data analysis, the expert modes of analysis are typically not documented and are difficult to learn without instruction, requiring the need for advanced and more specialized short courses.

Recommendation: The existing facility-run courses need to be augmented by discipline-specific in-depth courses, for example the recent "EXAFS College" at the Advanced Photon Source. These courses should not skimp on length and may therefore need to be offered as successive modules, wherein participants may attend subsequent courses to obtain expertise they did not originally need.

Despite the high impact value of training courses and student−instructor interactions, it should be recognized that due to costs, schedules, and the limits on effective class sizes, it is unlikely that the full breadth of the potential user community can be educated through instructional workshops. Resources for self-instruction are also needed.

Recommendation: The world-wide-web has revolutionized the delivery of training materials. User facilities should be encouraged to develop web-accessible training resources, following the lead of many universities in distance learning. Facility−university collaborations can utilize these materials and provide discussion sessions to create accredited courses.

7.5.6. *Distribution/closing of facilities*

When the SNS is fully operational, discussions of closing other US neutron centers may ensue with the intent of freeing up funding. The DOE needs to consider not only the reliability of the source, but also the range of deployed instruments. The solid-state-chemistry community depends on access to user programs in liquid and amorphous scattering, powder, and single-crystal diffraction. Continuity in these areas must be ensured. When evaluating the potential impact of closures, the value of regional facilities to local universities should be considered. These facilities have spawned synergistic interactions between universities and local facilities to develop collaborative efforts. The resulting high-quality research has attracted faculty and positively impacted educational programs. These interactions will be hampered without the proximity of regional facilities.

Travel and accommodation expenses play a significant role in deterring access to user facilities. This will be particularly acute with the SNS, since airfares can be high and at present no on-site housing options exist, thus adding car rental and high hotel costs to the anticipated financial burden. The NSF and DOE can address this by offering travel supplements to grant recipients who successfully compete for user time at DOE user facilities, in a similar fashion to what the NSF does with access to NIST.

7.6. Future developments for solid-state chemistry research

Solid-state chemists have and will continue to have a significant involvement in and impact on science being done at National Laboratory facilities. Neutron and X-ray science accounts for the vast majority of this community's use of such national facilities. There are, however, extensive national user facilities including the high magnetic field lab, nanomaterials facilities, microscopy facilities, radiation facilities, etc., that offer great potential for collaborative research in the solid-state sciences. Currently under development are a number of DoE-sponsored nanomaterials research centers (at LBNL, ANL, BNL, ORNL, LANL, and SNL), all of which are contemplating a different operating model compared to the current national facilities. These developments are in progress and user input has been requested. This report, however, focuses primarily on synchrotron and neutron national user facilities. In the US the construction and operation of large national user facilities is funded primarily by the Department of Energy. Nevertheless, NSF researchers play a critical role in both developing and sustaining the operation of such facilities. A critical function appropriate to the NSF mission is to support and vitalize the interface between the national facilities and the people who use them (Fig. 7.6). An effective Facilities/People interface will involve program advocacy by NSF scientists, and NSF support for user education, training, and travel as well as provision of resources for instrument development (e.g., sample environment, detectors, etc.) and acquisition. Investments in these areas are poised to have a critical impact on the success of the proposed American Competitiveness Initiative because they directly increase the scientific return on the national investment in user facilities.

Significant barriers to PI initiation of experimentation at national facilities result from a lack of mechanisms for training and support of researchers at all levels. From the facilities perspective, this also exacerbates a shortage of instrument scientists capable of operating the facilities. As a result, national facilities hire a significant fraction of their scientists from overseas. To address these training and support needs, the following recommendations are proposed.

7.6.1. Summer schools and short courses

Summer schools such as the Neutron and X-ray scattering school offered by Argonne National Laboratory are an extremely important point of entry for a student's involvement in experimentation at national laboratories. However, participation in this program often requires
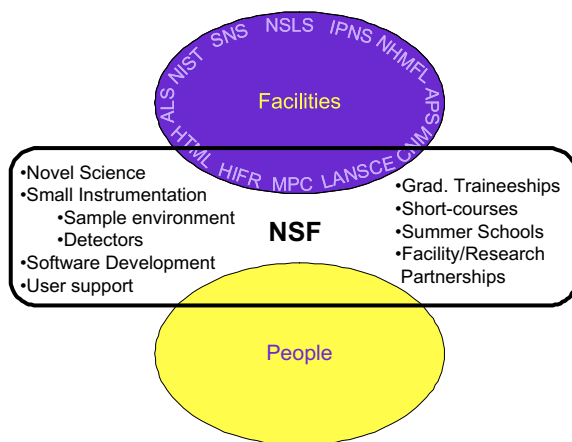

Fig. 7.6. Schematic of the role that the NSF maintains between the national facilities and users.

that the PI be attuned to the scientific opportunities accessible by neutron and X-ray scattering science. Thus it would be helpful to sponsor symposia at national meetings such as the ACS and MRS which showcase the scientific opportunities at national facilities. Furthermore, a hands-on short course that brings PIs to the facilities and provides exposure to data collection and analysis (analogous to the student/postdoc Argonne school) would be invaluable to enhance participation in national facilities research.

7.6.2. Graduate traineeships

More extensive training than that obtained in a short course is necessary to develop truly successful users and future scientific leaders at the national facilities. To address these needs, we recommend the creation of a Solid-State Chemistry/National Facility graduate traineeship program. Such a traineeship (to include stipend, tuition, and travel support) would be awarded to second-year graduate students whose research makes significant use of scientific capabilities at national facilities. Some support must also be provided to the PI and the facility scientist serving as the sponsor. During the course of a three-year fellowship the student would spend approximately six months in residence at the national facility in the first year of their fellowship, and be provided regular facility time and travel support throughout the remainder of their fellowship period. Such a traineeship would facilitate participation in research at the national facilities, as well as equipping the next generation of national facilities scientists with both solid-state chemistry and facility-specific expertise.

7.6.3. Collaborative research groups

Collaborative research groups (patterned after NSF's chemical bonding centers or collaborative research initiatives), consisting of 3−5 research groups and one or more national facility scientist(s), could be a mechanism to maximize investments in specific areas of science. For example, solid-state chemistry research groups focused on magnetic structures, amorphous materials, local structure determination, high-pressure science, catalysis and separations, etc., will have needs for similar sample environments and data analysis. Collective development of such resources, as well as support for multi-group postdoctoral fellows in residence at the national facilities, would be invaluable for efficient use of facility time, support of graduate student users, and the overall advancement of science.

As another facet of the national facilities/people interface, the solid-state-chemistry community has much to offer the future developers of instrumentation at national facilities. The contribution of new science provides the primary justification for our national investment in large research facilities. Research problems in materials chemistry continue to stimulate the design and development of instrumentation. Specialized beamlines delivering higher spatial, time, and angular resolution have been and are being commissioned at synchrotron and neutron facilities. Samples with sizes ranging from the micron to the nanoscale are being investigated using tools as varied as X-ray spectro-microscopy, small angle scattering, and high-resolution powder diffractometry. In parallel with these developments, and of great interest to solid-state chemists, is the construction of devices and beamlines dedicated to non-ambient and *in situ* studies. Such devices allow unprecedented investigation of ''real systems'' under ''real conditions'' and facilitate the investigation of systems of increasing complexity.

7.6.4. Special environment instrument components

The NSF, in conjunction with groups of individual PIs has a unique opportunity to contribute to the development of small to intermediate scale components to facilitate research under

non-ambient, extreme and/or *in situ* conditions. While much of the initial major instrumentation at neutron and synchrotron facilities is funded by the DOE, there are critical sample environment and detector needs, often more experiment-specific, which must evolve with the progress of research and which the NSF is encouraged to support. For example, the worldwide interest in high-pressure research is improving our fundamental understanding of the behavior of materials and is of particular interest to those studying geological processes. This research requires the development/acquisition of high-pressure cells as well as integrated structural/analytical probes for materials characterization. *In situ* catalytic and separations studies require sample environments with variable temperature/pressure capabilities as well as reactive-gas manifolds. Studies of reaction mechanisms, nucleation and growth, as well as structural dynamics and distortions require the purchase and development of ever faster and more sensitive detectors to exploit the research possible with high energy/intensity synchrotron and neutron facilities. A coordinated effort to support the science and unique instrumental needs of special-environment data-collection capabilities is extremely critical for advancement at these frontiers.

7.6.5. *Software for science*

As discussed above, critical needs exist for the development and support of user-friendly software for instrument operation, data collection, and data analysis. Specifically, to increase the use of national facilities by solid-state chemists, software is needed to readily convert data into a chemically useful form. Teams of programmers, instrument scientists, and solid-state chemists are needed to provide software that appropriately interfaces with facility instrumentation, rigorously treats data, and reduces data to a user-friendly form. In particular, general users need to be confident that they have effectively and accurately processed their data so that they can focus on the materials science without becoming an expert in the physics of the technique. The involvement of solid-state chemists in this process is critical to obtaining software that is useful to the community.

Fundamentally, the future of solid-state chemistry research at national laboratories is dependent on the quality of science pursued by the solid-state-chemistry community, facilitated by the national laboratories, and funded by federal as well as private sources. The proposed American Competitiveness Initiative offers the possibility of the largest investment in the physical sciences since the post-Sputnik era. After years of sparse and declining budgets, we must utilize this investment wisely. This demands a responsible balance between national, regional, and local (university based) facilities, as well as critical investments in personnel to utilize, develop, and maintain such facilities so that effectiveness, productivity, and impact are maximized.

A significant challenge confronting the long-term health of our national scientific enterprise is to re-capture a holistic balance between fundamental and applied research. National laboratories, as well as university researchers, have critical roles in this challenge. Over the past decade(s), with ever more competitive funding and heightened pressure to publish or perish, we have witnessed an explosion in both scientific hype and rapid data generation at the expense of high-quality *fundamental* science. Figuratively cartooned as the scientific food chain (Fig. 7.7), relentless pressure exists to produce the Big Fish served with a choice wine that will generate the Big Splash, save the world, and generate inordinate commercial profit. While laudable in theory, no big fish can grow unless there are little fish, and ultimately plankton, to provide the required nutrients. Arguably, to be globally competitive, research at universities and national facilities, with healthy support from the NSF, must be a primary source of nutrition to feed the scientific food chain.
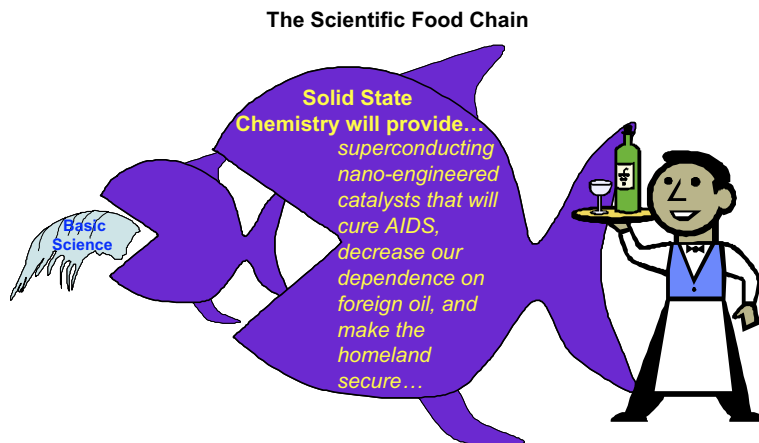
The Scientific Food Chain

Fig. 7.7. Cartoon of the relationship between basic science and large impact applications.

Notwithstanding the critique of over-hyping science, the challenge exists to ensure that fundamental research is truly ''nutritious''. Extensive (and derivative) data generation is not necessarily fundamental science. Syntheses, structure−property measurements, mechanistic and theoretical studies need to be focused to extract scientific principles and test hypotheses. In addition, this research must be carried out by globally aware scientists, perceptive to where these discoveries can have significant societal impact. As nutritious fundamental research is digested, transformational, non-incremental advances will be enabled.

For a healthy future, national facilities must provide a setting where scientific staff and external users can pursue science that cannot be conducted elsewhere. Solid-state chemists need facilities and support for materials characterization, experimentation under extreme and/or *in situ* conditions, and for addressing problems of increasing complexity.

7.7. Summary of recommendations

The nation's major facilities support a large and diverse body of high-quality work. However, the long-term return on our existing investment in these facilities could be further enhanced by careful attention to their operation, user support/education and long-term development. All of the issues and recommendations listed in the 2001 workshop remain valid, and the consensus opinion is that they remain insufficiently addressed with regards to improving access to national facilities by the entire spectrum of user type, from occasional to expert. A survey was undertaken to rank the 2001 issues by priority and the results are given here. A clear picture emerges of a ''people support gap'' that prevents increased use, and *making the most of*, the large national investment in user facilities. All of these issues, from travel support to user-friendly software that can be used to properly interpret data, appear to be activation barriers. The ''weak link'' in maximizing the scientific return on the investments in national facilities consists of insufficient resources to support the associated human costs—for those who need the support as well as for those who provide it. Considering that the DOE provides most of the funding for the construction and operation of national user facilities, it seems appropriate that the NSF should specifically target funding for the support activities and personnel needed to support the users of these facilities, thus enabling the US research community to achieve maximum return

from the large national facility investments. It has, however, come to our attention that there remain institutional policy issues between the organizations of the NSF and DOE that limit which organization can provide funds for what and whom (i.e., whether DOE can provide travel/financial support to NSF funded projects/personnel). Such administrative issues need to be evaluated and possibly revised to ensure the maximum scientific benefit from national facilities that are high priorities for both organizations.

The issues from the 2001 workshop report are again listed here, priority-ranked according to scoring provided by attendees of the 2006 Workshop:

1. An online resource providing guidance on the availability of instrumentation/facilities, the design of experiments, data analysis software, the fundamentals of techniques that are useful to the community, and the effective analysis of data should be constructed and maintained.

2. The operation of short courses on the design and execution of experiments and the analysis of the resulting data should be financially supported. Expert hands-on guidance is of great value to people who are learning a new technique. The cost of offering such a course is small compared to the real cost of the beamtime that might be poorly used in the absence of such training.

3. In selecting funding priorities for new instruments, the needs of the user community at large must be carefully considered. This community includes those who employ national facilities as an occasional tool as well as those who are major users.

4. The nation's major facilities will only realize their full potential if there is an ongoing investment in new instrumentation. Without good instrumentation, the world's best X-ray and neutron sources are of little value.

5. The part time operation of some instruments in a service mode or the development of dedicated service instruments should be carefully considered. Samples could be mailed in and data taken quickly by on site staff. This would lead to reduced travel costs and greater scientific productivity. Single-crystal diffraction, powder diffraction, and EXAFS measurements may be amenable to this approach.

6. The proposal mechanisms adopted by major facilities should allow for very rapid turn around on simple experiments such as SAXS, powder diffraction, EXAFS, etc. A response in a few weeks rather than a few months would enable close coupling between in house work on a material and major facility experiments.

7. Travel costs are a significant impediment to attracting new users to major facilities. NSF should consider the provision of a travel supplement to existing grants for unanticipated major facility experiments and offer summer/sabbatical support to faculty wishing to expand their knowledge of these facilities.

8. The geographical diversity of the nation's synchrotron and neutron facilities should be maintained. Short travel distances facilitate closer coupling between the work performed at major facilities and experiments at the home institution.

9. The construction and operation of instruments that are dedicated to one type of experiment should be supported. Simple experiments such as powder or single-crystal diffraction cannot be efficiently done on the very flexible instrumentation that is often constructed at synchrotron beamlines.

10. Security clearance procedures for access to major facilities should be kept as simple as possible. A common security clearance and ID requirement for all major facilities would be valuable.

11. Remote control capabilities should be further developed so that some experiments can be performed without the need for security clearance and travel.

Section 8. The place of solid-state chemistry within other physical disciplines

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8.1. Charge of the subpanel

The charge of subpanel 8 was focused primarily on assessing the role and impact of solid-state chemistry on other physical disciplines, specifically

- assessing the role of solid-state chemistry in the physical sciences through continuing advances and the many ways of interacting across disciplinary boundaries;
- assessing the potential impact of solid-state chemistry on disciplines in which the role of solid-state chemistry has not been fully appreciated, but for which substantial opportunities may exist, particularly those that have significant societal implications;
- assessing how to make the NSF and the scientific community more aware of the impact of solid-state chemistry on other disciplines;
- Assess how solid-state chemistry impacts other fields with respect to understanding and predicting the properties of materials, as well as stimulating the discovery of new materials.

This charge was based on the premise that the greatest opportunities and scientific advances often exist at the interdisciplinary boundaries. The NSF already recognizes the importance of interdisciplinary activities through its substantial investments in numerous initiatives, for example, the Materials Research Science and Engineering Centers (MRSEC), Engineering Research Centers (ERC), Nanoscience and Engineering Centers (NSECs), Nanoscale Integrated Research Teams (NIRTs), Focused research groups (FRGs), the Industry/University Cooperative Research Centers (I/UCRC), and the Integrative Graduate Education and Research Traineeship Program (IGERT).

Solid-state chemistry is naturally interdisciplinary. Many materials synthesized by solid-state chemists—energy storage materials, membranes, organic light emitting diodes, field-effect transistors—feed the activities of physicists, chemical engineers, materials scientists and engineers, and electrical engineers. Conversely, materials synthesis often is aided by these other disciplines, and the future is promising for even more interactions. For example, the aims of solid-state chemistry can be advanced considerably by chemical engineers who have a growing interest in green processing and in microfluidics, which can accelerate synthesis optimization while reducing reagent quantities. Most important, with a principal focus on the design and synthesis of new materials, solid-state chemistry plays a foundational role for fundamental studies by other scientific disciplines, particularly physics, and it is vital for many key technologies. As such, solid-state chemistry should continue to seek actively key collaborations with the customers of its materials, and the NSF as well as other agencies should encourage these.

In addition to turning its attention to other disciplines, solid-state chemistry would be well served by recognizing the diversity of expertise and materials within its own

boundaries. A more concerted effort to unify its inorganic and organic sectors by striving to identify issues common to both components—including synthesis, crystal nucleation and growth, structure−property relationships, structure prediction, theory, structure classification, characterization—would likely reveal substantial conceptual overlaps and would strengthen solid-state chemistry overall. The continuing growth in hybrid materials would seem an ideal platform for this aim. Furthermore, the re-emergence of organic solid-state materials for field-effect transistors and light-emitting diodes, and the growing recognition that pharmaceutical development requires improved understanding of solid-state chemistry, present solid-state chemistry with new growth opportunities that will undoubtedly increase its interactions with other sectors while expanding its impact on society.

Solid-state chemistry also may benefit by viewing itself as a branch of "materials chemistry," as this may allow it to connect more easily to other disciplines, including biomaterials, materials science and engineering, chemical engineering, and polymer science and engineering. There is some risk, however, that solid-state chemistry would lose its identity because materials chemistry is broad in scope and includes other fields (e.g., polymer science).

Although the specific examples below illustrate the role of solid-state chemistry in a few selected disciplines, this collection of examples is by no means comprehensive. Rather, they were chosen to illustrate that solid-state chemistry has the potential to be wide ranging in its impact and how it can appear (sometimes unexpectedly) in fields of research outside the conventional boundaries of solid-state chemistry. It seems advisable, therefore, for the solid-state chemistry program to commission a study, possibly by the NRC, that analyzes the impact of solid-state chemistry throughout science and engineering. The subpanel thought that a properly configured study would reveal that solid-state chemistry infiltrates numerous disciplines, including many with significant societal impact. This would not only provide guidance for future interdisciplinary activities for solid-state chemistry, but it would expose the broad impacts of solid-state chemistry through science, engineering and technology. This survey could include, but not be limited to, the following questions:

- How much solid-state chemistry is embedded within interdisciplinary NSF programs?
- How much solid-state chemistry is embedded within other agencies (DOE, DOD, etc.)?
- How is solid-state chemistry currently impacting other disciplines? Is the impact growing? How do we measure this? How do we increase the awareness of this impact?
- What is the impact of solid-state chemistry in the context of societal needs that can be addressed only through connections to other disciplines?
- What are the future growth opportunities for solid-state chemistry in other disciplines?
- How do investigators in different disciplines connect, particularly those that extend beyond the physical sciences?
- What are the best mechanisms for promoting these ventures?
- Are the current funding mechanisms for interdisciplinary research sufficient in terms of efficacy and financial support?
- Should new mechanisms be considered, for example, more support for interdisciplinary collaboration between small groups of investigators?

Finally, the mission statement of the NSF includes the following clause: "to promote the progress of science; to advance the national health, prosperity, and welfare; to secure the national defense…" Solid-state chemistry is well poised to influence emerging technologies

of vital national importance that ultimately will be reduced to practice by the engineering sector, which will rely on materials synthesized by the solid-state-chemistry community, for example: (i) high-performance membranes and catalysts for fuel cells, (ii) lightweight, high capacity fuel storage materials, (iii) new magnetic storage materials for information technology, (iv) energy-saving solid-state lighting, and (v) materials for long-term radionuclide sequestration. Therefore, to maximize its impact solid-state chemistry needs to maintain its traditionally strong alliances with the physics community and strengthen its ties to the engineering sector. Solid-state chemistry also needs to recognize its potentially significant impact on disciplines it may ordinarily regard as outside its purview, particularly in areas of high visibility and societal impact, for example, environmental science, health, and medicine. These efforts, however, need special attention to reduce the cultural gap that often exists between the physical sciences (like solid-state chemistry) and other fields, a particularly acute problem for collaborations with the health and clinical research sector. Building interactions with the health sector provides another path for expanding the scope of solid-state chemistry while expanding further its impact on society in a highly visible and tangible manner.

8.2. Role of solid-state chemistry in biological sciences and engineering

''Biomaterials'' most often are regarded as materials used for medical devices such as artificial hips, catheters, contact lenses, heart valves, and pacemakers. These materials typically are metals, metal alloys, polymers, ceramics, and glasses. Preserved tissues (e.g., porcine heart valves, human umbilical cord vascular grafts) also are, in effect, synthetic biomaterials. On the micro- and nanoscale, MEMS, nanotubes, and other nanomaterials are being proposed for several biomedical and bioengineering applications. Biomedical applications emphasize the use of synthetic materials that must be compatible with the adjacent biological tissues (beyond simple issues of toxicity) and must meet mechanical specifications appropriate to the application. Biomaterials often are designed to also induce a particular biological response (e.g., tissue in-growth and/or osseointegration). In addition to implants designed for short- and long-term use, biomedical devices include sensors, wound dressings, drug delivery constructs, therapeutic gels and fluids (e.g., intraocular gels, artificial blood), surgical life support systems (e.g., extracorporeal membrane oxygenators), and other products.

8.2.1. Modeling of bio/material interactions

There are no ''inert'' biomaterials. All materials placed in the body produce some type of biological response at the molecular and cellular level. In this light, we may regard the discipline as ''bio/materials,'' with more or less emphasis on one side of the interface or the other depending on variables such as conditions present at the site of material use, duration of use, and intended application. Although there is a very strong recognition of the role of interfacial properties of materials in biological response—surface analyses and surface modifications are integral to the research and development of biomaterials—there has been little input from solid-state chemistry expertise to the understanding and prediction of bio/material interactions at the atomic and crystalline levels. We have yet to understand whether proteins and/or cells can reliably detect (and, therefore, have a differential response to) different crystal structures of either inorganic or organic materials. Theoretical modeling of molecular events, for instance, at the protein- (or simpler yet,

peptide-) solid interface has been only a small part of the biomaterials toolbox to date. Most modeling software available to biological scientists and engineers is adept at modeling protein conformation in the solution state, but introduction of even a simple crystalline interface is a challenge. In the future, modeling also should be flexible enough to consider effects on both sides of the bio/material interface. Not only does the material affect the conformation and adhesive strength of adsorbed proteins and, through the adsorbed proteins, the responses of cells, but the biological film (particularly the cells and cellular products) can actively affect the nature of the solid material. Such modeling advances can improve the understanding of key physiological problems, from bone growth to certain disease pathways, such as the formation of kidney stones and gall stones, which are solid-state materials that nucleate, grow, and aggregate in vivo as a consequence of (poorly understood) interactions with proteins and other biomolecules (Fig. 8.1 [299,300]).

8.2.2. Nanomaterials

Owing to longstanding, negative clinical effects of particle generation from "traditional" devices (e.g., artificial hips), the biomedical community has concerns about the long-term biological effects of nanomaterials. "Nano" may be more than just "small". Are there negative effects on cells (or particular types of cells) that have not been adequately anticipated? What are the experimental protocols that must be designed and performed to evaluate and predict biological response to these materials? While individual particles eventually may be shown to be benign, under what conditions will the particles aggregate and induce negative biological effects? Similar issues arise in use of nanoparticles for drug delivery, diagnostic imaging, and genetic engineering.
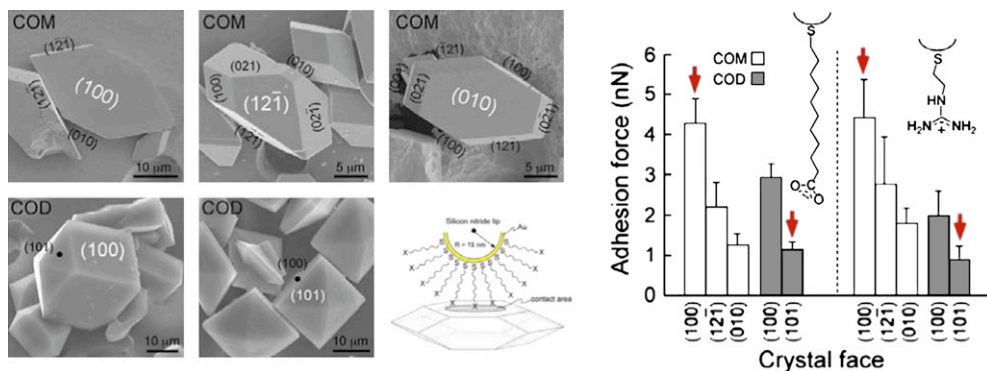

Fig. 8.1. Solid-state chemistry and disease. The panels on the right depict three different crystal faces of calcium oxalate monohydrate (COM), the primary constituent of most kidney stones, and calcium oxalate dihydrate (COD), which is regarded as benign form that does not aggregate to form stones. The adhesion force between these crystal faces and biologically relevant functional groups on an AFM tip reveals that COM (100), the largest face *in vivo* of this pathological crystal form, is the most adhesive. In contrast, COD (101), the largest face *in vivo* of this benign crystal form, exhibits the weakest adhesion. This illustrates that a knowledge of solid-state chemistry can resolve a key biomedical question, in this case the different pathological activities, associated with the different strengths of adhesion between crystals in aggregates of two forms of calcium oxalate.

8.2.3. Regenerative medicine and combination products

Over the past 10−15 years, there has been explosive growth in materials research related to the field of regenerative medicine (e.g., tissue engineering, wound healing, drug delivery). Tissue engineering considerations include not only the development and selection of appropriate synthetic scaffolds (often bio-absorbable polymers or bioactive glasses), but also culture technologies (e.g., static vs. dynamic flow) and the organization of the tissue, itself, as the bio/material construct extends into three dimensions. While solid-state chemistry concepts and techniques are being applied and refined for the design and evaluation of new drugs, solid-state chemistry has had minimal impact to date on tissue engineering or wound healing. Solid-state chemistry holds considerable promise, however, in the design of more effective scaffold materials that can be used for integrated tissue growth and healing. Solid-state chemistry is implicit in the reconstruction of bone, which is a mineralization process (Fig. 8.2 [301]). As such, solid-state chemistry has the capacity to make substantial contributions to the design of regenerative materials with the proper texture, porosity, structure, and composition for stimulating cell adhesion and bone growth. Well-defined crystalline materials, including those in thin film form, need to be explored further as templates for organization of biological molecules for implant biocompatibility as well as biosensors. There is a critical need for sound fundamental experiments that address these issues.

Researchers in industry and academia, alike, are moving strongly into the area of "combination products", wherein a product or application combines aspects of a traditional device with those of a drug and/or with those of a biological molecule. Examples include
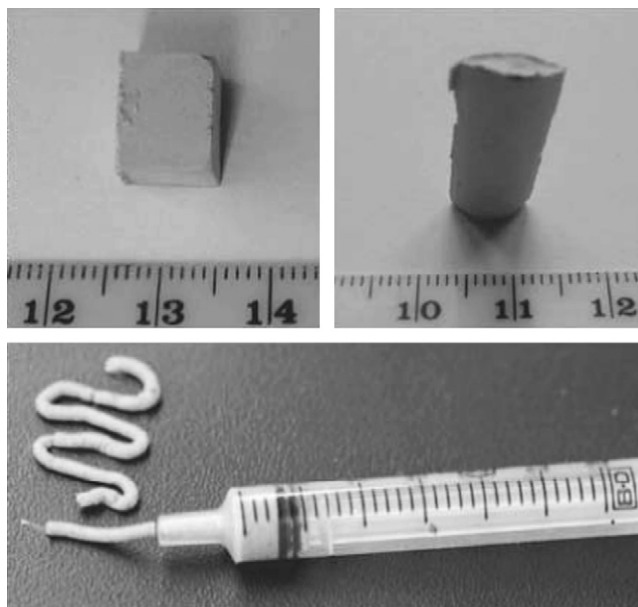

Fig. 8.2. Plastic but rapid setting cement from mesoporous bioactive glass in ammonium phosphate solution that has potential as a bone reconstruction material, which must be sufficiently plastic to inject into defects but must harden quickly and form hydroxyapatite crystals that bind osteoblasts and stimulate bone growth. This particular paste accelerated *in vitro* calcium-deficient hydroxyapatite nanocrystals ($Ca_{10}(PO_4)_6(OH)_2$) during setting, within 30 min.

drug-eluting stents and encapsulated islet cells (the latter to produce and deliver insulin). Although regenerative approaches are attractive for many reasons, they also present difficult regulatory hurdles in terms of sterilization, manufacturing controls, and shelf life. As a result, traditional materials (metals, metal alloys, polymers, ceramics, and glasses) will maintain a dominant presence in biomedical science and engineering for several decades to come. The need for input and leadership from the solid-state-chemistry community will not diminish in the foreseeable future.

8.2.4. Combinatorial chemistry and high-throughput screening

Over the past few years, a small number of academic researchers have begun to explore the use of combinatorial chemistry and high-throughput screening for design and selection of materials for biological applications. These efforts range from the development of chemical libraries and molecular assays to rapid screening of *in vitro* cellular responses to model materials. Although high throughput screening may advance the rate of development of new materials, this shotgun approach is a signal that the full potential of solid-state chemistry to basic bio/material understanding has not yet been realized in the biological sciences.

8.2.5. Other examples where solid-state chemistry can make a contribution

MRI-compatible materials: With the increasing use of MRI as a diagnostic imaging tool, and with the recognition that more and more people have implants of one type or another, there is a strong need for the identification of materials that are diamagnetic and, importantly, are compatible with a range of tissues and mechanical conditions. One example is the pacemaker battery case: it must be compatible with soft tissues on its external surfaces and with the lithium battery inside; it must be reliably sealed for the long term and must withstand sterilizing conditions.

TiO_2 and photocatalysis: There are many more applications than simply cleaning windows in skyscrapers. Consider medical facilities (operating rooms, waiting rooms) and emergency shelters, including means for decontamination and detoxification of biological and chemical agents. Are TiO_2 quantum dots applicable to surface decon/detox?

Titanium (commercially pure titanium) in contact with proteins, cells, and tissues: It has been observed that commercially pure titanium elicits a much less vigorous foreign body response and more rapid healing (e.g., in the case of bone implants, osseointegration proceeds sooner) than do other types of metallic and metal alloy implants. Is there a ''dark field'' response of the titanium to cells that apparently reduces or shuts down the foreign body response in tissues?

Organic templates for crystallization and their interaction with crystal surfaces: Understanding how organic molecules (and which molecules) can be arrayed to induce biological crystallization is a key to several areas of biological science. This includes promotion of mineralization (e.g., bone growth or repair), as well as the prevention (e.g., kidney stones, gall bladder disease, cataracts). Solid-state chemistry concepts and tools should be used to accelerate progress in these areas.

8.3. Role of solid-state chemistry in pharmaceutical research

In the last decade, pharmaceutical researchers recognized that the different solid forms of a drug significantly affect its physical properties. The solid forms of a drug include its crystalline polymorphs, its salts with different counter-ions, its co-crystals with inert ingredients,

and its amorphous solid. For drugs that are chiral, special crystal forms exist as a result of different enantiomeric compositions. These solid forms have significantly different solubilities, dissolution rates, and bioavailabilities. Identifying and controlling the solid forms is an important but previously neglected component of pharmaceutical research. This is an area where solid-state chemistry plays a role and has natural interdisciplinary activities with pharmaceutical scientists, organic chemists, physical chemists, chemical engineers, materials scientists, and mechanical engineers. Pharmaceutical formulations based on small-molecule crystalline drugs are estimated to be a $100 billion enterprise. The field is ripe for innovative solutions aimed towards regulating polymorphism. These solutions may include high-throughput screening based on combinations of experimental parameters (solvent, temperature, etc.), use of tailor-made impurities in solution that prompt or suppress certain polymorphs, as well as surfaces designed for selective heterogeneous nucleation.

Solid-state chemistry plays an important role in the study and control of pharmaceutical solid forms. Solid-state chemists help discover the solid forms of drugs, select the correct solid form for development based structure−property studies, and control the crystallization processes to produce desired solid forms. The pharmaceutical industry is now a major employer of scientists and engineers trained in solid-state chemistry.

8.3.1. Relation of organic and inorganic solid-state chemistry

Organic molecules such as drugs are flexible, chiral, and irregularly shaped. They assemble in the solid state through a variety of weak interactions, ranging from hydrogen bonding to dispersive forces. As such, the assembly of organic molecules into solid-state structures involves weak intermolecular interactions that are significantly different from those that bind most inorganic solids together. Organic solid-state chemistry requires methods of synthesis, characterization, and modeling that are distinct from those appropriate for inorganic solid-state chemistry. Nonetheless, there are many features common to both organic and inorganic solids. Nucleation and crystal growth, which are important to both organic and inorganic solid-state chemistry, provides a natural interdisciplinary bridge to other disciplines, including physics, chemical engineering, and material science. Many organic materials exhibit optical, magnetic, electronic, and light emitting properties (see above), which also draw in other disciplines. Organic solid-state chemistry requires methods of synthesis, characterization, and modeling that are distinct from those appropriate for inorganic solid-state chemistry. For pharmaceutical applications, however, bioavailability, mechanical properties, purity, and crystal habit are critical properties.

8.3.2. Crystallization in polymorphic systems−an area of special challenge and opportunities

Carbon forms diamond, graphite, and buckminsterfullerene (C_{60}). In the same way, complex organic molecules such as drugs, pigments, and explosives form polymorphs. Polymorphism is important because different polymorphs have different physical properties.

Polymorphic systems of increasing complexity have been studied. The system ROY (which stands for red−orange−yellow; Fig. 8.3) is a pharmaceutical intermediate and is currently the top system for the number of polymorphs of solved structures (seven) [302]. Systems such as ROY are ideal for studying the origin of polymorphism, structure−property relations in organic crystals, and the industrial control of polymorph selectivity during crystal growth. A particularly well-documented example of the impact of polymorphism in the pharmaceutical industry is ritonavir (an AIDS drug of Abbot), which was found to form
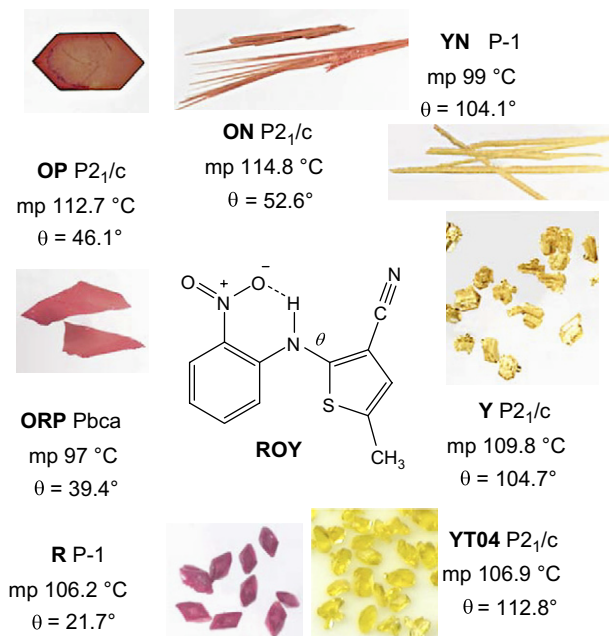
Fig. 8.3. Crystal polymorphs of ROY (clockwise from upper left): OP (orange plates), ON (orange needles), YN (yellow needles), Y (yellow prisms), and YT04 (yellow prisms), R (red prisms), and ORP (orange-red plates).

a new, half-as-soluble polymorph upon storage because the solid-state chemistry of the original form had not been fully studied. The case of "disappearing polymorphs" caused a shortage of this life-saving drug. It is estimated that reformulation of ritonavir to meet FDA requirements costed Abbot $800 million dollars! It is clear that solid-state chemists, who are armed with the skills necessary for understanding structures and physical properties of the solid state, can minimize such mishaps.

A newly recognized mechanism of crystallization in polymorphic systems is cross-nucleation between polymorphs. This mechanism contradicts Ostwald's Law of Stages and other theories of crystallization. By this mechanism, an early nucleating polymorph does not consume the entire liquid or undergo solid-state transformation, but nucleates another polymorph of higher or lower thermodynamic stability and of faster or comparable growth rate. This phenomenon indicates that the pathway of crystallization is not controlled solely by the initial nucleation, but also by the cross-nucleation between polymorphs and the relative growth rates of polymorphs.

Despite the advances, important questions remain about organic polymorphs and solid forms in general. For example:

(1) Are polymorphs predictable? There have been significant efforts to predict polymorphs a priori through computations, largely empirical or semi-empirical. These efforts have been "graded" through a series of "blind tests". While the score cards to date are disappointing, such efforts will likely continue. New advances in computations will fundamentally improve the science and engineering of polymorphs, which can have tremendous impact on pharmaceutical science and on organic solid-state chemistry in general.

(2) Are the relative growth rates of polymorphs predictable from their crystal structures? Recent studies have demonstrated that the initial nucleation does not ensure the polymorph
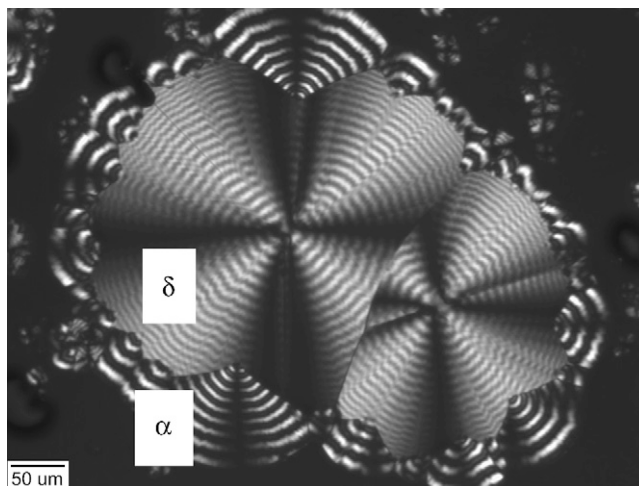
Fig. 8.4. Cross-nucleation between polymorphs. Crystallization of D-mannitol yielded the δ polymorph and then the α polymorph, with α nucleating on δ.

in the final product (Fig. 8.4 [303,304]). The relative growth rates of polymorphs are another key factor. Computational predictions of polymorphs frequently found many more polymorphs than observed experimentally and the cause, again, is thought to be their relative growth rates. Understanding the relative growth rates of different crystal forms provide a kinetic control of crystallization needed to synthesize materials of desired properties. In the case of polymorphs, predicting their relative growth rates are a well defined, likely solvable, problem because their crystal structures are known and they grow from the same liquid.

8.3.3. Amorphous solids

Solid-state chemistry traditionally emphasizes the chemistry of crystals. Amorphous solids have special advantages for many applications, ranging from telecommunication to drug delivery. In pharmaceutical sciences, amorphous solids can be used to improve the solubility and dissolution rate of poorly soluble drugs. Amorphous solids present special challenges to solid-state chemistry. For example, how does crystallization occur in deeply supercooled liquids? Is it controlled by diffusion? How can amorphous solids be stabilized against its natural tendency to crystallize? Here the principles of solid-state chemistry and crystallization can be applied to develop a new class of materials for drug delivery and other applications.

8.4. Role of solid-state chemistry in physics, devices and energy

Crystal growth of inorganic and organic materials is vital to the study of physical properties of solids. The study of the optical, magnetic and electrical behavior on single crystals allows for a fundamental correlation of the structures and physical properties of these materials. Compounds that display signature behavior such as superconductivity and/or heavy fermion behavior, intermediate valence, and large magnetoresistance (MR) can be more

adequately addressed with the growth of high-quality single crystals, especially since the physics of these materials are highly dependent on crystal orientation.

Solid-state chemistry has a strong overlap with condensed matter physics especially in the study of superconductivity and magnetism. The discovery of highly correlated materials involves not only optimizing crystal growth, but also the study of the physics and chemistry of the phases. Magnetic, electrical, and optical properties on single crystals can yield the detail physics of the new phase. From a structural perspective, the chemistry of the compounds can also be correlated to the physics. More advances can be made if there is a stronger interaction with both the condensed matter and solid-state-chemistry community. To impact the condensed matter community, interactions should be strengthened. This synergism can lead to the study of new phenomena.

8.4.1. Strongly correlated systems

Solid-state chemistry continues to have a major impact on condensed matter physics (CMP). In the field of electronic materials, much of the focus is centered on strongly correlated low energy phenomena incorporating many-body interactions among degrees of freedom that are magnetic, electronic, and vibronic. Since the last NSF report on solid-state chemistry, many of the same CMP subjects continue to present challenges that are addressable via novel compounds made by solid-state chemists. These subjects include superconductors, magnetoresistive materials, anomalous thermal expansion materials, novel ferroelectrics, and multifunctional systems. In addition to these subject areas, several ''cross-cutting'' themes continue to drive CMP. These include low-dimensionality, geometrically frustrated lattices, and electronic tuning via ionic substitution. These themes, which are embodied in the theoretical framework of strongly correlated systems, are directly amenable to solid-state chemistry techniques.

8.4.2. Weakly correlated systems

Outside of strongly correlated systems lies semiconductors and organic systems. For the silicon CMOS industry, the roadmap is well defined and we see little impact of solid-state chemistry on this industry. However, the end of the roadmap is insight, and there is presently a receptivity in industry to novel materials' approaches for information processing that lie beyond CMOS. These approaches include molecular electronics, quantum computation, and spintronics. Spintronics is an area in which solid-state chemistry can exert a large impact. Novel magnetic semiconductors are required that would form the substrates of new devices that can transduce both spin and charge. Similar to the development of silicon in the 1950s, there is a great need to understand the materials physics governing transport in these new systems and this will require tight linkage between solid-state chemistry materials development and experiments to understand the role of impurities, grain boundaries, and composition on transport in device configurations. It is presently thought that dilute magnetic semiconductors (DMS) will play a role in spintronics but surrounding the extant experiments is a debate that will be addressed primarily through novel solid-state chemistry. Such systems today are typically II–VI semiconductors with low concentrations of magnetic species that substitute for a native atom in a high-spin state. Intrinsic DMS materials face the limits on ferromagnetic exchange in insulators dictated by the Goodenough–Kanemori rules. A challenge for solid-state chemistry might be to discover systems that circumvent this constraint. Magnetoelectric multiferroics present possibilities for
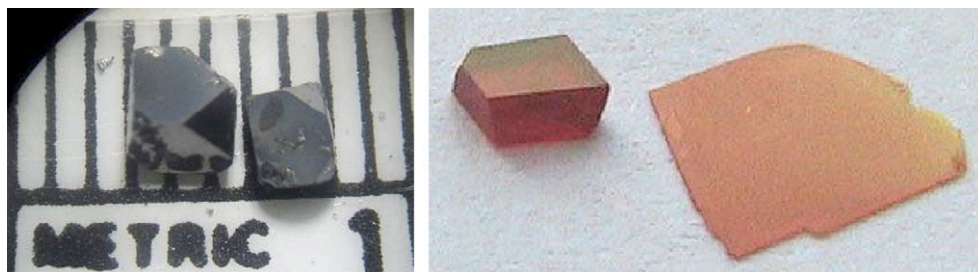
Fig. 8.5. Single crystals of (left) Ln–Co–Al and (right) tetracene, an organic semiconductor.

materials with crossed responses, e.g. magnetic switching with electric perturbation, that afford interesting possibilities for information control using spin degrees of freedom.

8.4.3. Organic semiconductors

The study of organic materials has not traditionally fallen within the solid-state-chemistry community, but the challenges are similar to those encountered in semiconducting systems. Much of the CMP interest in organics in the past centered around charge-transfer salts exhibiting novel low-dimensional spin density and superconducting states. With the growth of plastic electronics targeted primarily for the display industry, their crystalline counterparts are now seen as candidates for semiconductor materials' development. The lack of fundamental understanding of the microscopic transport processes in plastic (e.g., amorphous or polycrystalline) systems has hindered the optimization of basic transport parameters such as mobility. The foundational science for organic electronics will be built on understanding the limiting mobility through computational work, as well as achieving this limit through linked synthesis and experiment. In particular such work will involve synthetic control of the processes of organic crystal growth (Fig. 8.5), the minimization of impurities that act as charge traps, and the development of mechanisms that induce free electron density, i.e. doping. A major challenge for the development of this field is the purity of stock material for crystal growth. Typical concentration of impurities in pentacene (quinone and di-hydra) for example, are in the few-percent range, whereas for inorganics, impurity concentrations are typically several parts per million. The effort required to bring organic materials to purity levels associated with even medium-performance inorganic semiconductors is too large for a single laboratory, suggesting the need for a correlated effort among many laboratories in a program to advanced material purity.

8.4.4. Solid-state chemistry and energy

The interplay between solid-state chemistry and CMP is the pre-competitive research that impacts novel devices of the future. Devices that employ novel materials are mainly either energy related, or information technology related, discussed briefly above. In the realm of energy conservation and production, recent DOE initiatives have focused on solid state lighting using light emitting diodes (LEDs) and solar energy using photovoltaic cells (PCs) as targets for basic research. The development of inorganic materials for such applications is much more mature than organic materials, hence the development of organic-based systems represents a substantial growth opportunity for solid-state chemistry. In state-of-art organic LEDs (luminous efficiency $\sim$100 Lm/W) and PCs (conversion efficiency

∼6%), the performance is limited by some of the same factors that govern the performance of plastic field-effect transistors. Specifically, contact potential barriers, injection efficiency, transport mobility, and emission efficiency govern the overall performance of these devices. In addition, it is necessary to achieve similar performance for both electrons and holes, or suffer energy loss associated with extra buffer layers. Similar to FETs, the basic mechanisms for transport in these devices are not understood. Also important is that current devices employ polycrystalline or polymeric materials where the large density of defects of various types makes the task of identifying individual doping or trapping mechanisms daunting. Similar to FETs discussed above, there is a large role for the study of single crystal-based devices for which solid-state chemistry would play a pivotal role. As for FETs, control of crystallization (size of crystal, polymorphs), reduction of defects, introduction of dopants and light harvesting molecules, and relief of strain are all important activities that would profit from involvement of solid-state chemists. In addition, the growth of heterostructures incorporating all-organic, or hybrid organic–inorganic materials presents different and important challenges. This amounts to no less than the development of a technology to rival molecular beam epitaxy for inorganic heterostructures.

8.5. Role of solid-state chemistry in computer science and electrical engineering

The pace of innovation in information storage technology is torrid even when compared to the semiconductor industries effort to reflect "Moore's Law" doubling of density every 18 months. Market pressures have motivated the storage industry to move at a pace that double areal density every year. This has placed a tremendous strain on the engineering communities that have contributed to the base technology and is rapidly exhausting materials choices with which to design media, heads, supporting electronics and packaging materials. The magnetic storage industry is estimated to be a $40 billion enterprise and sustained innovation will require extensive materials chemistry expertise (Fig. 8.6).

Solid-state chemistry has contributed novel magnetic compositions that have enabled exchange coupled media and perpendicular recording to become realities, but more is needed. Synthesis of intermetallic compounds with extraordinarily high magnetic anisotropy (e.g., FePt, CoPt) point to opportunities to reach stable Terabit encoding but the magnetic field required for write heads to record these ultrasmall bits exceed those achievable by conventional materials, such as permalloy (Fig. 8.7).

Synthesis of families of iron nitrides that may have even higher saturation magnetization pose challenges, as do the formulation of magnetic nanolaminates that comprise the giant magnetoresistive read heads. The magneto-mechanical coupling in these new materials must understood and tamed. Design of materials that can be formed into light, cheap, ultra smooth substrates, which tolerate the centripetal forces experienced during operation is a critical need. This has stimulated the exploration of a host of new non-volatile memory concepts that are targeted at ultra high-density solid-state storage that might compete with hard disk drives on price, performance and reliability.

Pressures on the continued scaling of magnetic storage are spawning many new innovative methods for high-density non-volatile storage. Areas in which solid-state chemistry can impact "customers" in other disciplines by providing materials and interdisciplinary collaborations include the following:

Phase change: phase change memory concepts based of reversible crystallization stretch back 30 years, but materials control and understanding the role of composition, finite size
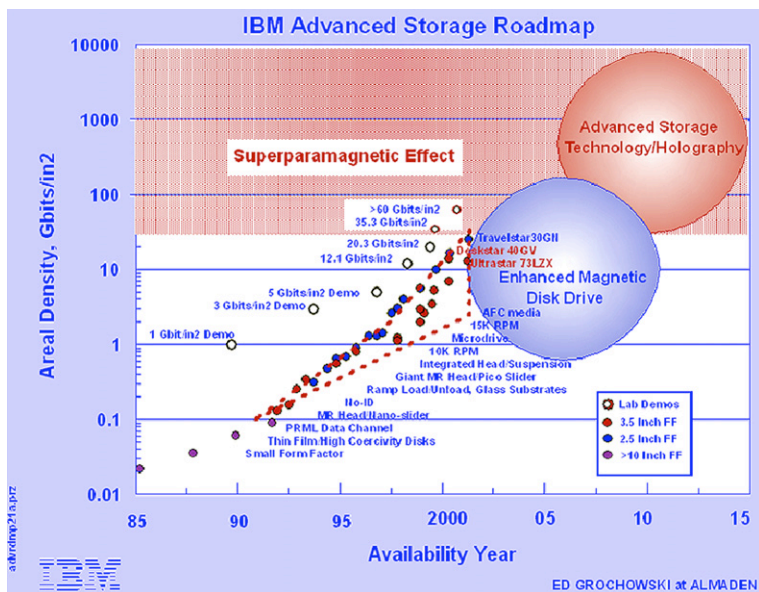
Fig. 8.6. The IBM storage roadmap.

effects, and strain on nucleation and melting require the insights of the solid-state-chemistry community.

Organic thin film memories: the tendency for certain organic films to reversibly trap charge in and manor that modifies the subsequent transport though the films provides that basis for a two terminal, or cross point memory. The materials composition and local structure and the nature of trap states raise basic questions that must be answered for the area to progress.
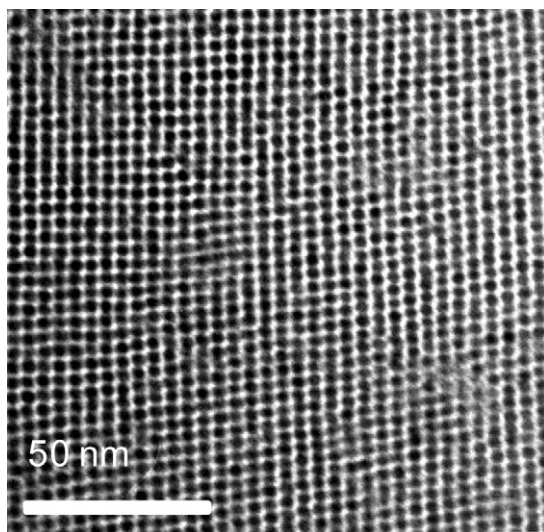

Fig. 8.7. Self-assembled magnetic nanoparticle arrays for Terabit magnetic recording consisting of 4 nm FePt particles.
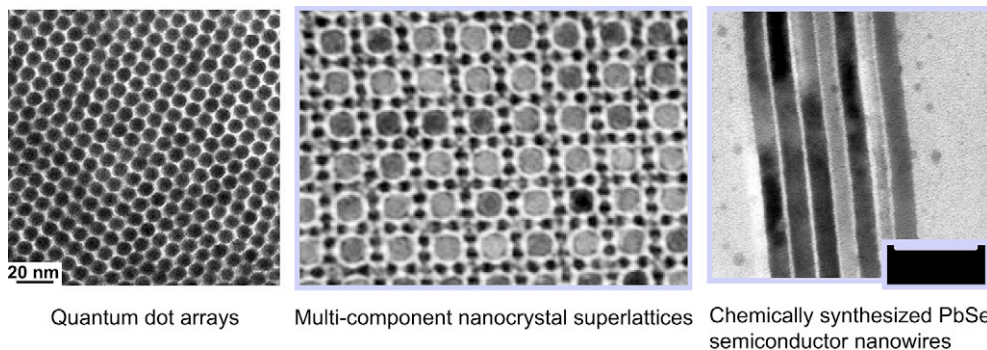
Fig. 8.8. Examples of structures fabricated by bottom-up routes harnessing chemical synthesis and directed self-assembly to provide nanometer scale control.

Ferroelectric materials: degradation of ferroelectric performance upon repeated cycling remains a significant barrier to wider impact from ferroelectric memory concepts. Solid-state chemistry innovations will be essential to address degradation of materials in the vicinity of the electrodes and during processing.

Self-organization as a new manufacturing paradigm: challenges of top-down design of systems containing billions of components motivates the exploration of alternative manufacturing approaches. Self-assembly process in which tailored functional building blocks organize into new extended materials, devices and systems is particularly intriguing (Fig. 8.8). The modular assembly of new multifunctional solids and devices for chemically derived components is impacting a range of low cost electronic applications. This will spawn the synthesis of modular routes to new multifunctional solids (metamaterials), for example, the co-assembly of two different nanocrystal building blocks (Fig. 8.9). Combinations of geometry and balancing van der Waals, electrostatic, hydrophobic, magnetic, dipolar, and other forces can generate periodic arrays with nm-scale dimensions in registry with lithography.

8.6. Role of solid-state chemistry in the mineralogical sciences

Mineralogists are effectively solid-state chemists of Earth materials. Mineralogical research is focused on the formation and behavior of solid minerals under a range of geologic conditions. Significant effort also pertains to the behavior of mineral surfaces under environmental conditions, in contact with a range of solution chemistries. Conditions studied range from crystallization of minerals under ambient conditions through pressures approaching those of the lower mantle of Earth. Mineralogists commonly develop targeted synthesis techniques to probe the formation and growth of minerals, and to provide synthetic analogues for detailed study. Many mineralogists are expert crystallographers, and study the atomic-scale structures of minerals and the hierarchy of such structures. Mineralogists invest in understanding properties of minerals, including their thermochemistry, equations of state, and elasticity as these impact a range of geological processes.

Mineralogists conduct solid-state chemistry by exploring the considerable breadth of natural solid inorganic materials, and historically were often responsible for first discovering important mineral properties that led to technological applications. Mineralogists have developed an understanding of complex geochemical systems that contain many components that change
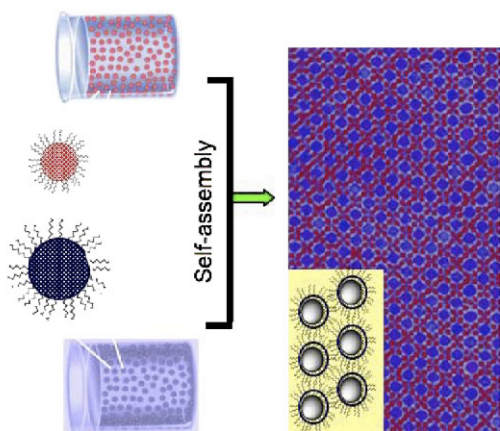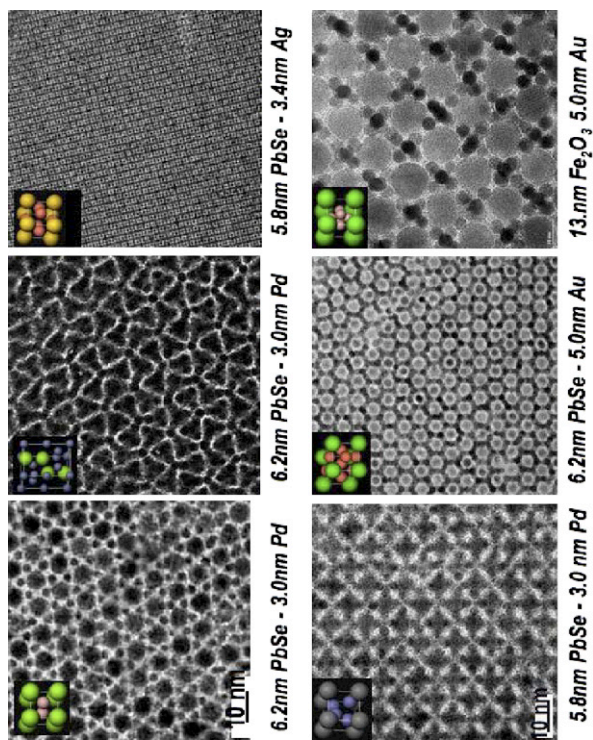
Fig. 8.9. Building binary superlattices with artificial atoms through self-assembly.

through time. Minerals are the subset of inorganic compounds that are sufficiently stable to persist for geological times, and are compatible with the geochemistry provided by element fractionation processes in natural systems. Mineralogists regularly study compounds that formed over time scales that are inaccessible by direct human experience.

Mineralogists and solid-state chemists share many experimental approaches to materials characterization. Both extensively use X-ray and neutron scattering as probes of crystal structure details, and X-ray absorption spectroscopy to derive oxidation state and coordination geometries in solids. Spectroscopic techniques including vibrational, Mössbauer and NMR are common tools of both groups, as are computational techniques for modeling structures and properties of solids.

8.6.1. Potential increased interactions between solid-state chemistry and earth sciences

Several areas are of current and presumably future common interest to solid-state chemistry and earth scientists, including mineralogists and geochemists. Currently, there is little interaction between these scientific communities in most instances. Areas where interaction would be mutually beneficial and could be fostered include

- the details of solid surfaces and how they interact with complex environmental solutions;
- interaction between the surfaces of crystalline solids and organic matter;
- mechanisms of biological precipitation of heavy metals and radionuclides to form crystals (for example in bacterial cell walls);
- aggregation of metals in solution to form nanoscale colloids, and the further aggregation of such colloids into solids;
- development of advanced instrumental techniques for characterization of crystalline and amorphous solids;
- first principles prediction of crystal structures and their stabilities;
- studies of crystalline structures under extremely high pressures;
- the amorphous-to-crystalline transition;
- deformation of crystalline materials over extended timeframes;
- the impact of size on nanoscale materials' properties;
- use of solid-state chemistry to guide understanding of solution complexes of transuranic elements;
- the effects of radiation on crystalline solids.

8.6.2. Solid-state chemistry and nuclear waste disposal

Societal acceptance of an expanded role of nuclear energy in meeting the world's burgeoning energy demands requires a technically defensible solution to managing nuclear waste (Fig. 8.10). Several nations, including the USA, have indicated the intent to dispose of nuclear waste in a geological repository that will isolate the radioactivity well into the future. Developing a case that such a geological repository meets regulatory standards is a hugely complex scientific and engineering problem. Much of this complexity arises from the nature of the material that must be isolated from the environment. These waste forms typically contain highly radioactive fission products and transuranic elements that possess vastly different chemical properties, and many of these radionuclides have long enough half-lives to present a significant risk to the environment should they leak from the repository. Development of solid-state waste forms for the long-term isolation of the radionuclide inventory is essential. Activities in the design of novel waste forms would benefit from attention from the solid-state-chemistry

Fig. 8.10. "Chernobyl lava", which primarily consists of the uranyl peroxide Studdite, a naturally occurring mineral that also forms from uranium decomposition in nuclear waste.

community. Areas of active research include development of ceramic waste forms that will include a range of radionuclides, as well as possessing a resistance to radiation damage, a low solubility in groundwater, and a relatively low cost of production. The mechanisms of alteration of solid state nuclear waste forms in a geological repository, and the fate of the radionuclides contained therein, also presents interesting areas for solid-state chemical research.

8.7. Summary and recommendations

Solid-state chemistry plays a foundational role for fundamental studies by other scientific disciplines, particularly physics, and it is vital for many key technologies. As such, solid-state chemistry should continue to seek actively key collaborations with the "customers" of its materials, and the NSF as well as other agencies should encourage these.

Solid-state chemistry is well poised to influence emerging technologies of vital national importance that ultimately will be reduced to practice by the engineering sector, which will rely on materials synthesized by the solid-state-chemistry community.

Solid-state chemistry also needs to recognize its potentially significant impact on disciplines it may ordinarily regard as outside its purview, particularly in areas of high visibility and societal impact, for example, environmental science, health, and medicine.

The NSF should consider and implement mechanisms for supporting collaborative research between the solid-state-chemistry community and investigators in far-ranging fields, which may require creative funding mechanisms involving other agencies.

Solid-state chemistry has a diversity of expertise and materials within its own boundaries. A more concerted effort to unify its inorganic and organic sectors by striving to identify issues common to both components would likely reveal substantial conceptual overlaps and would strengthen solid-state chemistry overall.

The solid-state chemistry program should consider commissioning a study, possibly by the NRC, that analyzes the impact of solid-state chemistry throughout science and engineering. It is anticipated such a study would find that solid-state chemistry infiltrates numerous disciplines, including many with significant societal impact. This would not only provide guidance for future interdisciplinary activities for solid-state chemistry, but it would expose the ubiquity of solid-state chemistry through science, engineering and technology.

Section 9. International links

Committee and Participants: Miguel A. Alario-Franco, Peter D. Battle, Thomas Bein, Christopher L. Cahill, P. Shiv Halasyamani, Antoine Maignan, Ram Seshadri

9.1. Comparison with the ''United States of Europe;'' international funding within Europe

European nations can seek funding from the European Union, a group of 25 countries that share a common parliament that has limited but growing powers. Other countries (e.g., Norway) that are not members of the EU are able to take part in scientific exchanges and programs organized by the EU. The programs are always international; the EU does not fund citizens of country X to do research in Country X.

There are sometimes criteria that are intended to favor the poorer countries (and the poorer regions in the richer countries).

9.2. Different programs are available

EST—early stage training: thesis students work in different laboratories within the EST partnership. Students gain experience of working in different countries BUT they have to move several times and continuity is difficult to ensure.

RTN—research training network: students or postdocs are funded to go and study/work in a country different from their own. Maximum funding level is 1.5 M€, to be divided between the participating network members. Basically provides the salary and the funding to attend Network meetings every six months, but leaves very little for consumables. It could be said that the focus of this exercise is European cultural exchange rather than scientific research. The associated bureaucracy is complex and time consuming. One assumption of the RTN ideal is that the itinerant students have a ''home laboratory'', that is a laboratory in their own country that will look after them when the Network is finished. This is certainly not true in Britain. On the other hand, postdocs sent out from France are well placed to get CNRS or university positions.

STREP—specifically targeted research european project. This scheme aims to make an impact in a nominated area, e.g. nanotechnologies for electronics. The budget is much higher and covers salaries, equipment, consumables, etc. There are significant benefits once you are funded, but there is a very time-consuming application procedure. Many institutions employ consultants to prepare their application to increase the chances of success. The projects can be difficult to coordinate once they are up and running.

NOE—Network of excellence. These basically fund meetings and associated travel costs for groups working in the same area, e.g. FAME (Functional Advanced Materials for Engineering). They might generate subsequent applications for e.g. RTN. There is no money for actual research, simply for meetings and travel.

The ERA-NET—European Research Area Network. These programs serve to enhance networking and international collaboration. One example is mnt-era.net. MNT ERA-Net is a network of European Micro- and Nanotechnology (MNT) support programs. It is a four-year project under the ERA-NET scheme of the 6th Framework Program of the European Commission. MNT ERA-Net started in January 2004 with a core group of eight European Programs.

After two expansion phases the consortium now comprises 17 countries with 21 funding programs, all represented by their national/regional ministries or by their respective program agencies. The mission is to enhance the competitiveness of European industry through coordination of and cooperation between European support measures for micro- and nanotechnologies and through continuous improvement of excellence of delivery of the support services. The objectives of MNT ERA-Net are

- to exchange information about program design and management;
- to learn from each other through the exchange of good practice;
- to implement joint and coordinated activities;
- to secure mid-term cooperation between the participating programs;
- to expand the project to further countries and regions in Europe.

The NSF might like to consider approaching the EU to set up a joint US/European initiative in solid-state chemistry.

The European Science Foundation receives increasing amounts of funding to sponsor basic research, for example through the EUROCORES program. As a part of a structured approach to EUROCORES development, the ESF invites new and challenging ideas for EUROCORES programs (EUROCORES theme proposals) from the scientific community. Such "bottom-up" EUROCORES theme proposals can be submitted to the ESF once a year. After a selection process of EUROCORES theme proposals, the ESF seeks agreement with interested funding organizations on the scientific scope and participation in each EUROCORES program.

In practice, following an agreement with participating funding organizations, the ESF publishes a call for proposals for each EUROCORES program inviting Collaborative Research Project (CRP) proposals from the scientific community. CRPs consist of a number of individual projects (IPs) based in different European countries. CRP proposals are assessed through a common International Peer Review managed by the ESF.

The evidence provided by the first four EUROCORES Programs, in the fields of Humanities, Materials, Medical and Geosciences, suggests that a EUROCORES Program normally involves 9–23 funding organizations and usually funds 10–20 CRPs (selected out of 50–150 outline proposals) consisting of 40–80 IPs with a total Program budget of 5–12 M€. Participating national funding organizations fund successful CRPs through the IPs. Each CRP is typically funded for three or four years.

9.3. Funding for visits beyond Europe

In addition to the European funding schemes described above, most countries have funding agencies that will fund visits involving countries beyond Europe, either incoming or outgoing. In Britain the Royal Society plays this role, as does the British Council. The CNRS has a long tradition of supporting international collaboration with France. Several schemes have been devised including PICS (Programme International de Cooperation Scientifique) and CNRS laboratories located outside France. In Germany a large number of international schemes exist, each aimed at a particular stage in the career of a scientist, from undergraduate to senior professor. The funding for these schemes comes from a wide range of agencies. The "*Integrated Actions*" program in Spain can be used as an example of this type of scheme. These are international agreements between the governments that provide money for short visits in both senses for up to three months that can be split, with considerable

flexibility, into periods of different length, i.e. one or two weeks for several people or three months for just one person. The number of visits depends also on the money for travel which is somewhat limited. Often the short visit is by a senior member of the group and the long one by a junior member. These agreements, usually signed between two research groups, are filtered by a committee composed of two or three scientists of each country and a couple of members of the diplomatic service. They do not require too long a written proposal (i.e., the level of bureaucracy is lower than that associated with the European programs) and can be renewed at least once, i.e. a total of two periods of three months. They are very useful for starting or keeping alive a collaboration between small groups. As these schemes depend on bilateral agreements that are signed periodically by the governments, they are not always available. For example, the British Council decided some time ago that there are other ways to establish this type of collaboration, and that an agreement between the UK and Spain was no longer needed. Recently, the Spanish ministry and the NSF have reached an agreement and some Integrated Actions have been established, at least in the Materials Science field. Spain also has a very outward-looking program for graduate/PhD students. The national grants and most of the regional/autonomic grants are usually for three or, more commonly, four years. They include usually six, sometimes even up to twelve, months of research in a foreign laboratory. This has been tremendously successful and although staying abroad is not compulsory, most Spanish students do it with great benefit. Very marked differences can be seen, in both scientific and personal development, between those that have and those that have not been abroad as graduate students or postdocs. While abroad students can learn a technique, e.g. HRTEM or EXAFS, do some difficult synthesis, or any of many other possibilities. This program can be, and often is, associated to the European doctorate degree. This provides a title which is recognized in the EU (although not widely advertised). For this degree to be awarded the student must have worked at least three months in another country within the European Union and they must provide a letter of support/recommendation from the supervisor there. Furthermore, part of the oral examination has to be in English, and the exam takes place in front of a jury, at least two out of the five members of which are from a different European country. Very often, however, independently of the European degree, foreign scientists sit on Spanish Ph.D. juries.

9.4. Central facilities

One of the most international aspects of research in Europe is the use of the central facilities where neutron scattering and X-ray scattering are carried out. After the Second World War individual countries developed their own research reactors, for example at Harwell in the UK and CENG in France. By the late 1960s it was clear that a new generation of sources was required and that the investment needed was too great for any one nation to undertake alone. France and Germany therefore agreed to build the Institut Laue Langevin in Grenoble. There was clearly a lot of politics involved in this decision in addition to the scientific considerations, but the end result was a scientific resource so powerful that the UK bought into it as a full partner almost immediately, and several other nations have subsequently joined at a lower level. The habit of building together continued with the ESRF, also in Grenoble, and it is now difficult to imagine a new world-class facility being funded entirely by a single European government (although residual national pride still generates some attempts to do so). There must be scope for collaborative "big science" projects to span the Atlantic, either by ensuring that sources complement one another (difficult to arrange) or by having a mechanism where beamtime can be exchanged.

9.5. Young Americans in Europe

Some comment on the specific difficulties and benefits experienced and gained by young American scientists spending time in Europe is appropriate. Our limited survey suggests that there are few US-based funding sources available, or that they are not well publicised. Most US chemists who post-doc in Europe make direct contact with the potential supervisor and rely on their having funds available. Once abroad, the young researcher usually finds that scientific life in Europe is very similar to that experienced in the US. The next issue is how to get back home, preferably to a faculty position. There seems to be a feeling that it is difficult to get a job in the US unless you are US based. The candidate must be prepared to travel to the US for interview, and once called back they should contact all the schools to which they are applying and try to maximize the number of interviews that they can fit into one trip home. Note that this implicitly assumes that young US researchers do not have a home laboratory where there is a job waiting for them on their return. In this regard the US system is more similar to the British system than to that found in some European countries. One final point that is worth making is that different countries have different expectations with regard to the contents of a letter of recommendation. If a detailed analysis of the candidate is expected whereas the overseas supervisor is used to writing only very brief comments, then the candidate will be disadvantaged.

9.6. International meetings

There appears to be a feeling that the Gordon Research Conference on Solid State Chemistry is the primary meeting in our field. This conference meets every year, alternately in Europe and the US. However, the New Hampshire meeting is usually US-dominated and the European meeting is Europe-dominated. Thus they have not yet become truly international meetings and perhaps they never will be because of travel costs. The European meetings only started in 1997 and they are still developing. It was perhaps unfortunate that the first one was chaired by a German in Germany and the second by a Briton in the UK. The third was scheduled for mid-September 2001 and was cancelled. It therefore took a relatively long time for the Europeans to appreciate the true spirit of GRC, to put aside their national pride and to accept the GRC as a meeting where scientific excellence counted for more than the seniority of the speaker. Producing a more balanced speaker list at both meetings would perhaps be an important step forward, but this will be difficult as long as transatlantic airfares remain higher than those for internal flights.

The Solid State Chemistry session of the MRS meets every two years and draws Europeans to Boston; the European MRS is less significant in the field. There is a feeling in Europe that it is desirable to change the sequence of either GRC or MRS meetings so that two important US meetings no longer happen within six months of each other, with the next year being relatively fallow.

The Elsevier-sponsored Inorganic Materials meeting is growing in status and has perhaps now overtaken the European Solid State Chemistry Conference in significance. This is to be welcomed because it has a more international outlook. We note that many small international meetings exist within Europe, e.g. the Hispano-French Meetings in Solid State Chemistry and Physics. However, it is unlikely that the NSF will want to look towards only one European country if it chooses to increase its international profile. However, it may wish to focus in particular countries for particular sub-topics within the subject if it is perceived that different countries have strengths in different areas.

9.7. Current topics in solid-state chemistry

A survey of the non-American panel members identified the following as the most important topics in the short-term future of solid-state chemistry:

- Advanced synthesis and characterization techniques of materials
- Structure and electronic structure of solids
- Chemistry and physics of glasses
- Novel inorganic materials with electronic, optical, magnetic and other functionalities
- Layered compounds, clathrates, and intercalates
- Ionic conductors
- Porous materials
- Hybrid materials
- Nanostructured systems and morphology control
- Biological solids
- Films and surface chemistry
- Theory and modeling.

 With applications in

- new materials for batteries
- solid oxide fuel cells
- materials for hydrogen storage
- materials for catalysis
- thermoelectric and photovoltaic materials
- materials for the storage of nuclear waste
- multifunctional materials: inorganic/organic hybrids—multiferroic.

9.8. Is the research done in universities or in research institutes?

In considering what international links are possible, it is worth considering and comparing the way research is done in different countries. The following account is intended to be illustrative rather than exhaustive. From a European's point of view, solid-state chemistry research in the USA appears to be carried out mainly in universities, but with some activity in DoE national laboratories, e.g. Argonne. In Britain, a similar system operates. Research in solid-state chemistry is carried out within the chemistry departments of a number of universities, but by no means all of them. There are no national research laboratories specializing in solid-state chemistry, although there is a clear overlap with the activities of those working at the ISIS neutron source at Rutherford Appleton Laboratory. In France a mixed system operates, involving the universities and the CNRS. One laboratory (ICMCB, Bordeaux) is CNRS funded, whereas the remainder are mixed university/CNRS units (UMR). The advantage of this system is that those employed by the CNRS do not have to teach and can therefore make more rapid progress in research. However, there is sometimes friction between the two groups of staff, with those employed as university wishing they were CNRS, and vice versa. The coexistence of the two systems also doubles the amount of administrative work. The system would be more satisfactory if transfer between the two categories was easier.

In Germany, many universities run a chemistry program, but we must also consider the role of the Max Planck Society. The research institutes of the Max Planck Society perform basic research in the interest of the general public in the natural sciences, life sciences, social sciences, and the humanities. In particular, the Max Planck Society takes up new and innovative research areas that German universities are not in a position to accommodate or deal with adequately. These interdisciplinary research areas often do not fit into the university organization, or they require more funds for personnel and equipment than those available at universities. The variety of topics in the natural sciences and the humanities at Max Planck Institutes complement the work done at universities and other research facilities in important research fields. In certain areas, the institutes occupy key positions, while other institutes complement ongoing research. Moreover, some institutes perform service functions for research performed at universities by providing equipment and facilities to a wide range of scientists, such as telescopes, large-scale equipment, specialized libraries, and documentary resources. There are a total of 78 institutes (including, MPI for Solid State Research Stuttgart) and research facilities in Germany (as of 1.1.2006). In addition, there are three institutes and several branches abroad.

Germany also operates Helmholtz Centres. The Helmholtz Association is Germany's largest scientific research community. A total of 24,000 staff work in its 15 scientific−technical and biological−medical research centers. The Association's annual budget runs to more than €2 billion. The Federal and Länder authorities share around 70% of the total budget in a ratio of 90:10. The remaining 30% or so of the budget is acquired by the Helmholtz Centres in the form of contract funding. The Helmholtz Association has been commissioned with performing research, which contributes substantially to answering the grand challenges of science, society and industry. Scientists at Helmholtz concentrate on researching the highly complex systems which determine human life and the environment. For example, ensuring that society remains mobile and has a reliable energy supply that future generations find an intact environment or that treatments are found for previously incurable diseases. To succeed in meeting these responsibilities, the Helmholtz Association concentrates its work in six research fields: Energy, Earth and Environment, Health, Key Technologies, Structure of Matter plus Transport and Space. In 2001 alone, more than 4500 foreign scientists came to the Helmholtz Centres to do research. Helmholtz was the "financing" host for more than half of these scientists. The Deutsches Elektronen-Synchrotron (DESY) is a Helmholtz activity.

9.9. Existing US international collaborations and NSF's MRSEC program

The Division of Materials Research at NSF has been pro-active in stimulating international collaborations. Since around 1999, the larger MRSEC centers have been required to undertake international activities in addition to supporting their research programs, shared facilities, educational outreach, industrial outreach, etc. Many of the major international materials programs in the USA have their origins in MRSEC centers, e.g. the Materials World Network at Northwestern and the International Center for Materials Research(ICMR) at UCSB. The UCSB Materials Research Laboratory held 15 overseas workshops during the period 1995−2003. These bilateral workshops provided the credibility and network for the creation of the ICMR in 2004. This particular center is discussed in more detail below.

The ICMR was created at the UCSB on August 1, 2004 to provide an international forum that convenes scientists and engineers with common interests in the future of materials science. The Center is funded by the Division of Materials Research, the Office of International Science and Engineering at the National Science Foundation, the Materials Research Laboratory, and

UCSB. Its partner institutions include the International Center for Theoretical Physics in Trieste, the Academy of Sciences for the Developing World (TWAS), and the International Center for Young Scientists (Tsukuba). Programs include: workshops in Santa Barbara and overseas, exchange programs, and summer schools.

The goals of ICMR are to stimulate international collaboration through a range of cutting-edge research and educational programs, to provide international experience for young scientists that will prepare them to function in a global scientific environment, and to enhance the capacity of developing countries in the materials science area by engagement and network building.

Sufficient funds exist to send up to 40 US researchers to spend time with overseas collaborators for periods of one week to three months. This is available for researchers throughout the US. Since one of the objectives is to give researchers some international experience, people are not sent to their country of origin. In 2006 funding commenced for an undergraduate exchange program (REU) with Oxford, Stuttgart, Eindhoven, Bangalore, Santiago, Taejon (KAIST), and Dublin.

We believe that the ICMR at Santa Barbara could serve as a model for future international exchange initiatives.

9.9.1. Why are international activities so important?

1. The position that the USA currently holds, close to the forefront in most areas of science and technology, cannot be taken for granted in an increasingly competitive world.
2. Maintaining that position, however, is essential for the success of our knowledge-based economy in the 21st century.
3. In order to remain competitive, it is essential that we are engaged with our peers elsewhere and fully conversant with the latest developments in other countries.
4. It is also essential that our young scientists should gain the international experience that will enable them to function effectively in the global S & T business.
5. The existence of major centers of excellence, such as the MRSECs, is an essential element of the national strategy for remaining competitive in the face of stiff competition from other nations.

In the light of the above discussion we make the following recommendations.

9.10. Recommendations

Increase the number of postdoctoral fellowships for positions abroad. The NSF affiliation will help maintain connections to the US for future employment. Further, travel funds should be made available to facilitate return travel to the US. Despite obvious benefits of international collaboration, postdocs do express a feeling of disadvantage with being removed from the US job market. An appropriately packaged fellowship can address these issues.

Funding for short term (3−4 months) overseas career development 'sabbaticals' for faculty. This will facilitate exposure to new research methods (possibly not widely pursued in the US) through highly—focused immersion in alternative research environments. It may be appropriate to pay an allowance to provide support for the dependents of the scientist.

Funding for travel to international research facilities. Proposals to obtain access (e.g., beam-time) go through a rigorous peer-review process. If beamtime is awarded to an American PI, funds should be awarded for travel to the laboratory and subsistence during the experiment.

Acknowledgements

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