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Pressure Tuning in the Search for New and Improved Solid State Materials

J. V. Badding,* J. F. Meng, and D. A. Polvani

Department of Chemistry, Pennsylvania State University,
University Park, Pennsylvania 16802

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Pressure tuning is a potentially useful tool to increase the rate of discovery of solid-state materials with improved properties. The interaction parameters that determine the properties of a given material define a phase space, which can have one or more dimensions. A single solid-state compound can be represented by a single point in this phase space. The traditional approach to the search for new materials involves an exploration of phase space by sequential synthesis and characterization of new solid-state compounds. Because materials interaction parameters (e.g., orbital overlap, orbital energy, magnetic coupling, etc.) can be tuned with pressure, phase space can also be traversed with pressure, potentially allowing a property of interest to be optimized. The advantages of pressure tuning include the ability to tune rapidly and cleanly, typically without introducing disorder, phase separation, or other complicating factors. Demonstration of the existence of materials that exhibit improved properties at high pressure can provide insight into the structural and electronic parameters necessary for such improved properties to guide the search for such behavior at atmospheric pressure.

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Introduction

Currently there is much interest in alternative strategies in the search for new solid-state materials that have useful properties. The traditional approach to solid-state synthesis in which new compounds are synthesized and characterized sequentially has often proved successful, but can be slow and time consuming because two of the most important problems in chemistry remain largely unsolved: it is generally not possible to predict the structure of a solid given only its composition and it is generally not possible to accurately predict many properties based only on structural information.[1,2] Thin-film combinatorial techniques, in which large numbers of syntheses are pursued in parallel, are being investigated as a tool to help increase the rate of discovery of useful materials.[3−5] The challenges involved in combinatorial syntheses include addressing compositional and materials properties issues related to the fundamental differences between thin-film and bulk synthetic approaches (if one is ultimately interested in bulk materials) and the characterization of a large number of different materials deposited in small amounts in thin-film form.[1] Here we discuss another tool, pressure tuning, that has the potential to increase the rate of discovery of certain types of novel materials.

Pressure tuning involves the use of pressure to change and control a fundamental parameter in solid-state materials, interatomic distance, while probing some appropriate physical property. This tool has long been used, for example, to tune semiconductors and other solid-state materials to better understand their band structures and probe levels that arise from defects or impurities.[6] The results of pressure-tuning studies have provided rigorous tests for solid-state theories; if a theory is correct at ambient pressure, it should also be correct as interatomic distance is varied.[6] Pressure is particularly useful because changes in pressure are typically not associated with large changes in entropy, which can mask the effects of other changes induced by tuning with temperature. Both ambient-pressure phases as well as new phases that form at high pressure can be pressure tuned.

Rapid advances in high-pressure technology have greatly expanded the range of physical properties that can be tuned and probed under pressure.[7,8] With current diamond anvil cell and large volume high-pressure technologies, it is now possible to measure transport properties such as electrical conductivity,[9] magnetoresistance, and thermopower,[7] magnetic properties such as magnetic susceptibility,[10] optical properties,[7] and many other properties as well as determine crystal structures by means of powder[11] or single-crystal[12] diffraction techniques at pressures ranging from <1 GPa to well in excess of 100 GPa.

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How can pressure tuning be useful to the solid-state chemist who is interested in the search for new materials with improved properties? The conventional approach to searching for new materials is to vary the interaction parameters that determine the properties of materials (e.g., orbital overlap, orbital energy, magnetic coupling, etc.) by varying crystal structure, composition, and/or doping levels. Each compound synthesized thus represents a single point in a potentially multidimensional phase space that can be defined to include all of the important interaction parameters. The search for an improved material consists of finding the region of phase space that optimizes the desired property or properties. In the combinatorial approach to materials discovery, many points in this phase space are explored simultaneously. For many materials, the interaction parameters can also be varied considerably with pressures that are readily attainable with current technology. Thus, by varying the pressure, the interaction parameters for a single compound can be tuned continuously over a wide range. Because pressure can be varied much more rapidly than new compounds can be made (at least by traditional bulk solid-state methods), the interaction parameter phase space can be explored more rapidly with pressure. Furthermore, an additional advantage of pressure tuning is that it is cleaner than chemical tuning: difficulties associated with changes in composition or electron count, phase separation, or the introduction of chemical disorder can often be avoided.

Once a material with an enhanced property under pressure has been found, it provides a target for synthetic attempts to reproduce the desired property at ambient pressure. This synthesis could be achieved by chemical techniques such as varying the lattice parameter by substitution of smaller atoms into a structure (effecting a chemical pressure, which can reduce the lattice parameter of an ambient-pressure phase or stabilize a high-pressure phase at ambient pressure) or other chemical or physical means. Often it may be valuable to know, in principle, how large the magnitude of a desired materials property can be. For example, discovery of a material that superconducts above 200 K or, as discussed later, a thermoelectric material with a ZT value of ~ 4 (where Z is the thermoelectric figure of merit and T is temperature) at high pressure would provide a strong impetus for the search for such a material at ambient pressure, as well as useful insights into how to prepare it. To find novel materials with enhanced properties in less time than would be required with chemical techniques alone, an integrated approach that involves a feedback loop between chemical synthesis and pressure tuning efforts is attractive.

Pressure Tuning of Semiconductors

To date the largest amount of effort in pressure-tuning studies on solids has been directed toward semiconductors.[6] Pressure studies at high hydrostatic pressures have played an important role in the study of semiconductors for >40 years. Many semiconductors exhibit phase transitions at high pressures, allowing new crystallographic phases to be probed and understood. Such transitions generally induce large changes in fundamental semiconductor parameters, such as the band gap. Silicon, for example, metallizes at a pressure of 11.3 GPa.[13] This high-pressure metallic phase can be quenched to ambient pressure and has the BC-8 structure, which has a density higher than that of the stable diamond phase of silicon. Many pressure-tuning studies have also focused on providing further information about semiconductor phases that are stable at ambient pressure.

Even modest pressures of 1 to 2 GPa can induce significant changes in the crystal and electronic structures of semiconductors. Early in the study of semiconductors, pressure played an important role in elucidating the differences in the band structure between Si and Ge.[6] It was found that the band gaps of these two materials shifted in different directions with pressure. The gap in Si decreases whereas the gap in Ge increases. This difference allowed a better understanding of key regions of the Brillouin zone. These studies were extended to III−IV and II−VI semiconductors, providing further information about their band structures and various levels within the band gap. Current research is focused on probing deep levels at high pressure and semiconductor heterostructures.[6]

Pressure Tuning of Superconductors

Many compounds and several elements become superconducting under pressure as a result of changes in crystal structure and electronic structure. For example, cesium becomes a superconductor at pressures >10 GPa that correlate with its transformation to a *d*-electron element.[13,14] Sulfur has recently been demonstrated to superconduct at temperatures in the range of 10 to 17 K when compressed to pressures >93 GPa, making it the element with the highest transition temperature reported to date.[10]

Pressure tuning played a role in the discovery of the high T_c superconductors. It was found that compression of $(La_{0.9}Ba_{0.1})_2CuO_{4-\delta}$ increased the transition temperature from 35 K to in excess of 50 K,[15] suggesting the substitution of a smaller ion into the structure could raise the ambient pressure transition temperature (although the resulting YBa_2CuO_3 compound[16] had a different crystal structure). The highest transition temperature reported for any high T_c material is 153 K in $HgBa_2Ca_2Cu_3O_{8+\delta}$ compressed to 15 GPa.[17] The nature of the phase space parameters that are contributing to this rise in transition temperature are still under debate. It has been proposed that the carrier concentration (which strongly affects the transition temperature at ambient pressure) plays a key role, but there has been debate about additional mechanisms for transition temperature enhancement.[17] Efforts are underway to reproduce this high transition temperature at ambient pressure using chemical methods.

Pressure Tuning of Intermediate Valence Thermoelectric Materials

Given the long history of success and the utility of pressure tuning in the areas of semiconductors, superconductors, and other materials, it is reasonable to ask whether there are other classes of materials and problems to which it might be applied. Recently, we have undertaken an effort to pressure tune thermoelectric materials to search for new compounds with enhanced properties. The efficiency of a thermoelectric device for cooling or power generation is determined by the dimensionless product of the thermoelectric figure of merit, Z, of the materials used to construct the device and the temperature, T.[18] The figure of merit is:

$$Z = S^2\sigma/K \tag{1}$$

where S is the thermopower, which is typically measured in units of μV/K, σ is the electrical conductivity, and K is the thermal conductivity.[18] The best current values for ZT are ∼1, which is insufficient for many desired applications. Thus, the key issue in this field is the identification of new materials that exhibit enhanced values of ZT. If materials with larger values of ZT can be found, the range of applications for thermoelectric materials in cooling and power generation devices will be greatly enhanced.[18]

Current thermoelectric devices utilize semiconductors composed of heavy atoms such as Bi_2Te_3.[18,19] These materials can exhibit large thermopowers (on the order of 200 to 300 μV/K), reasonably high electrical conductivities (if doped to appropriate carrier concentrations on the order of 10^{18}/cm^3), and low thermal conductivities because they are composed of heavy atoms, factors which contribute to favorable figures of merit. Metals have generally not been viewed as viable thermoelectric materials because they typically have small thermopowers (on the order of a few μV/K).

However, there is one class of metals, intermediate valence (IV) rare earth compounds, that can have thermopowers in the range of 100 to 125 μV/K, high enough that they have attracted considerable attention for thermoelectric applications.[20,21] In IV compounds, the valence of the rare earth ion can be thought of as fluctuating rapidly between two integral valences to give an average nonintegral valence.[22] The high thermopower arises because of the unusual electronic structure of these materials.[20] According to Boltzmann transport theory,[23] which is applicable to most solids, the thermopower can be expressed as

$$S = \frac{\pi^2 k_B^2 T}{3e}\frac{\mathrm{d}(\ln \sigma(E))}{\mathrm{d}E} \text{ at } E = E_F \tag{2}$$

where $\sigma(E)$ is the electrical conductivity determined as a function of energy and E_F is the Fermi energy. This equation shows that the thermopower is maximized for materials that exhibit a rapid variation in $\sigma(E)$ within a few kT of the Fermi energy.[24] There is a simple physical interpretation of eq 2. For a sample of a material in which a temperature gradient is present, the energies of the conduction electrons differ at the high- and low-temperature sides of the sample. When $\sigma(E)$ varies rapidly with energy near the Fermi energy, the electrons on different sides have different conductivities, favoring the buildup of charge on one side and an increased thermopower. The parameter $\sigma(E)$ is proportional to the density of states at a given energy if the electronic scattering is independent of energy. In some IV compounds, $\sigma(E)$ varies rapidly near the Fermi energy because of a sharp peak, known as a Kondo resonance, in the density of states (Figure 1). The thermopower will be highest in IV materials that have large, sharp Kondo resonances. In contrast, the density of states in most metals varies only slightly near the Fermi energy, resulting in low thermopowers.

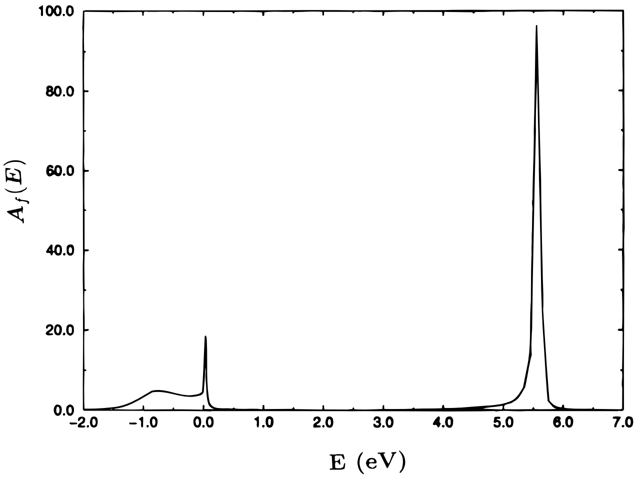

Figure 1. Density of states surrounding a cerium ion in a host metal from simplified Anderson model calculations. The lowest energy and highest energy peaks represent f^1 and f^2 levels. The sharp middle peak is the Kondo resonance, which arises because of a many-body effect involving the cerium valence fluctuation. To obtain maximum thermopower, this peak must be tuned to have maximum height and sharpness. We thank G. Mahan for making available this figure, which is based on unpublished results.

In metals such as the IV compounds, the thermopower plays a primary role in determining ZT and device efficiency. Most metals have a ratio of thermal to electrical conductivities that is not too far from the limiting Wiedemann−Franz value: $K/\sigma = L_0T$, where L_0 has the value 2.45×10^{-8} watt-Ohm/K^2.[25] Thus, for the metallic IV compounds, the figure of merit should be close to (although further work will be necessary to

$$ZT = S^2/L_0 \tag{3}$$

confirm this experimentally[20]) and the key property in determining Z is the thermopower.[20]

The Anderson model can be used to understand the origin of the peak in the density of states in IV compounds.[20,26] According to the Anderson model, two materials parameters determine whether a rare earth compound is intermediate valence: the amount of hybridization between the f-orbitals and other more delocalized orbitals and the energy of the f-levels relative to the Fermi energy. These parameters also influence the height and width of the Kondo resonance and, therefore, the thermopower. They thus represent a two-dimensional phase space. At ambient pressure one compound represents a single point in this phase space, which can be explored with pressure because both the amount of hybridization and the energy of the f-levels relative to the Fermi energy depend on interatomic distance. Pressure tuning thus offers a means to rapidly find new IV compounds as well as optimize the thermopower of existing IV compounds (Figure 2).

Pressure tuning is especially useful for IV materials because IV behavior is rare. Most rare earth compounds

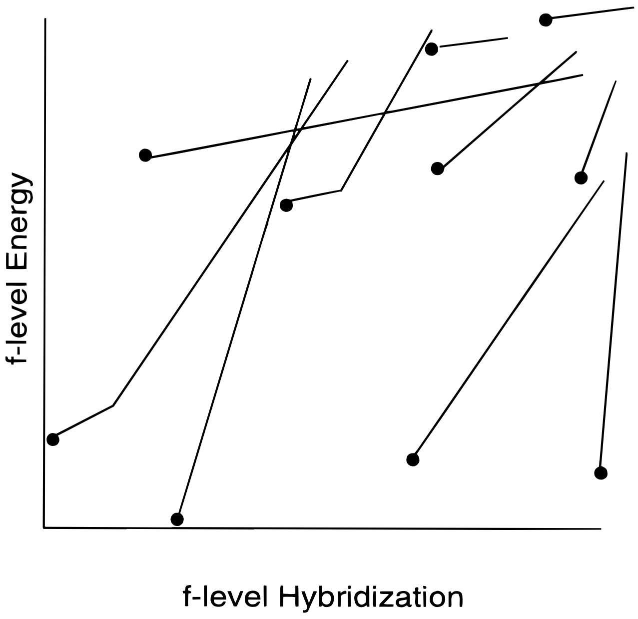

Figure 2. Phase space for IV compounds. Each point represents the phase space parameters for a single compound at ambient pressure. The lines are a schematic representation of paths in phase space that can be explored with pressure. Because pressure can be changed rapidly, a wider range of phase space can be explored more rapidly with pressure to optimize the thermopower and find new examples of IV compounds.

are not in the appropriate region of phase space to exhibit IV and only two or three dozen IV compounds are known at ambient pressure. Furthermore, it is unlikely that in these few compounds, the optimum phase space parameters for maximum thermopowers are achieved. With pressure tuning it is possible to induce IV behavior in compounds that do not exhibit it at ambient pressure.[27,28] An excellent example of a pressure-induced IV transition occurs in samarium sulfide (SmS). At ambient pressure, SmS is a black semiconductor with the rocksalt structure and a Sm valence of +2. At a pressure of 0.7 GPa, SmS collapses into a metallic IV state with an intermediate Sm valence between +2 and +3.[7] Some of the electrons on the divalent Sm are transferred from the Sm *f*-levels to more delocalized levels derived from orbitals of lower angular momentum, resulting in a transition to a metal with a golden luster. A somewhat oversimplified view of the IV transition in SmS is that pressure favors the transformation of Sm ions to higher valence states that are smaller. Many other compounds and several elements, such as cerium, undergo IV transitions upon compression to modest pressures in the range of a few GPa.[13,27,28] Thus, these transitions can be accessed at pressures where complications due the effects of nonhydrostatic stresses or large amounts of band broadening will not be present.

With pressure it should be possible to considerably extend the number of IV compounds that can be investigated for thermoelectric applications. If IV materials with thermopowers in excess of 250 μV/K (about double the thermopower of the best currently known IV compound, $CePd_3$) can be found, ZT, according to eq 3, will increase to the unprecedented value of 2.5. If an ambient pressure material were available with this value of ZT, thermoelectric devices would be considerably more competitive with current technologies. There are several IV materials already known for which the thermopower increases considerably with pressure.[29] After a material that exhibits a high thermopower at ambient pressure is identified there will be a considerable impetus to attempt to find a material that has similar desirable properties at ambient pressure, utilizing the information obtained about the interatomic distances and the electronic structure of the high thermopower material obtained at high pressure. Recent developments in synchrotron radiation techniques make it possible to probe electronic structure at high pressure with X-ray absorption measurements.[30,31] This measurement will allow a detailed understanding of the electronic structure of a high Z IV material. Chemical tuning in the IV materials must be approached carefully, because the IV state is easily destroyed. Nonetheless, with appropriate care, it is possible to chemically tune IV materials such as $CePd_3$.[32]

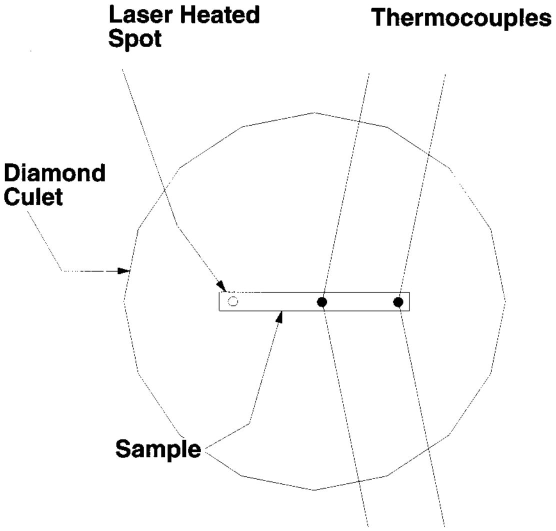

Figure 3. Experimental configuration for the measurement of pressure inside a diamond anvil cell. View is through the top diamond. A small sample on the order of 500 μm long has two thermocouples placed across it. A thermal gradient is induced with an infrared laser. Care must be taken to avoid temperature gradients perpendicular to the long axis of the sample.

To pressure tune thermoelectric materials, it is necessary to perform thermopower measurements at high pressure. Our approach has been to utilize diamond anvil cell technology to perform these measurements. The diamond cell is relatively inexpensive and samples can be rapidly loaded.[8] Sample sizes are small (on the order of a few hundred micrometers), which is a considerable advantage when only small single crystals of an anisotropic material can be obtained, which is often the case for many types of flux or melt-based synthesis techniques. In our experiments, samples are compressed between two diamonds with a CsI pressure transmitting medium contained by a stainless steel gasket with a hole the same size as the diamond culets. A pair of small thermocouples is laid across the sample and a temperature gradient is induced by means of an infrared laser (Figure 3). A pair of Hewlett-Packard nanovoltmeters is interfaced to a Macintosh computer to simultaneously measure the voltages of the thermo-

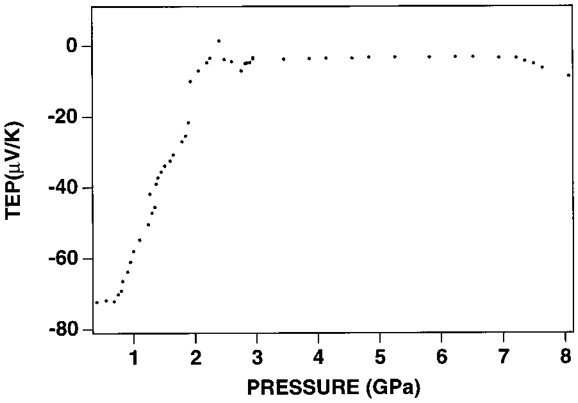

Figure 4. Thermoelectric power of bismuth versus pressure measured inside a diamond anvil cell. The data are in qualitative agreement with earlier data collected by Bridgman anvil high-pressure techniques (the thermopower of bismuth is anisotropic and the sample was not aligned in a particular crystallographic orientation).[33] The phase transitions in bismuth near 2.5 and 7.7 GPa are visible.

couples. It is necessary to perform the measurements simultaneously because small fluctuations in laser power (on the order of 1%) result in fluctuations in the voltages of the thermocouples. These fluctuations are canceled out when simultaneous measurements are made. Figure 4 shows some representative data collected by this technique on a bismuth sample.

Pressure Tuning of Multiple Band Semiconductor Materials

Other classes of thermoelectric materials can be pressure tuned as well. In semiconductors, a rapid variation in $\sigma(E)$ near the Fermi energy (resulting from an asymmetry in the density of states and/or scattering above and below the Fermi energy) and a high thermopower can arise when a band is near the Fermi energy. If multiple bands with different effective masses or scattering rates can be placed near the Fermi energy, the variation in $\sigma(E)$ and the thermopower can be increased. Such multiple band semiconductors have the potential to have higher ZT than the best currently available semiconductors. The challenge is to find a material with multiple bands near the Fermi energy and tune the Fermi level to be within a few kT of these bands. Because typical semiconductor bandwidths are much wider, on the order of 5 to 10 eV, this challenge is difficult.

Bands derived from orbitals with different angular momentum shift in energy at different rates upon application of pressure. Therefore, it should be possible to pressure tune the bands in multiple band semiconductors to be within a few kT of the Fermi level. An additional factor that must be considered with semiconductors is the doping level, which can be systematically varied in conjunction with pressure-tuning studies. Thus, again, for multiple-band semiconductors it is possible to rapidly and to cleanly explore phase space with pressure to optimize the thermopower without the need to prepare a large number of materials. Once promising materials are identified, it should be possible to perform measurements of thermal conductivity with flash diffusivity measurements. Electrical conductivity measurements under pressure are routine, allowing all three materials parameters that determine the figure of merit to be quantified.

Summary

Pressure tuning offers a means to more rapidly search for materials with enhanced properties. It has several advantages over chemical tuning, including speed and the ability to tune more cleanly, without difficulties due to phase separation and compositional inhomogeneities. Although we have emphasized the application of pressure-tuning techniques to the search for novel thermoelectric materials, a similar approach could be utilized to investigate a wide range of other materials where the relevant materials parameters will vary with pressure, such as magnetoresistive materials.

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