

Targeted Crystal Growth of Rare Earth Intermetallics with Synergistic Magnetic and Electrical Properties: Structural Complexity to Simplicity

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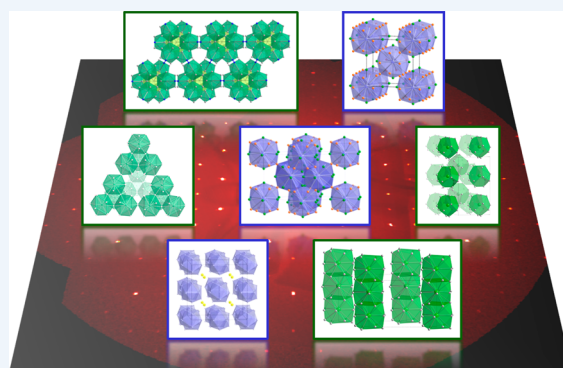
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CONSPECTUS: The single-crystal growth of extended solids is an active area of solid-state chemistry driven by the discovery of new physical phenomena. Although many solid-state compounds have been discovered over the last several decades, single-crystal growth of these materials in particular enables the determination of physical properties with respect to crystallographic orientation and the determination of properties without possible secondary inclusions. The synthesis and discovery of new classes of materials is necessary to drive the science forward, in particular materials properties such as superconductivity, magnetism, thermoelectrics, and magnetocalorics. Our research is focused on structural characterization and determination of physical properties of intermetallics, culminating in an understanding of the structure–property relationships of single-crystalline phases. We have prepared and studied compounds with layered motifs, three-dimensional magnetic compounds exhibiting anisotropic magnetic and transport behavior, and complex crystal structures leading to intrinsically low lattice thermal conductivity.

In this Account, we present the structural characteristics and properties that are important for understanding the magnetic properties of rare earth transition metal intermetallics grown with group 13 and 14 metals. We present phases adopting the HoCoGa_5 structure type and the homologous series. We also discuss the insertion of transition metals into the cuboctahedra of the AuCu_3 structure type, leading to the synthetic strategy of selecting binaries to relate to ternary intermetallics adopting the $\text{Y}_4\text{PdGa}_{12}$ structure type. We provide examples of compounds adopting the ThMn_{12} , NaZn_{13} , SmZn_{11} , $\text{CeCr}_2\text{Al}_{20}$, $\text{Ho}_6\text{Mo}_4\text{Al}_{43}$, $\text{CeRu}_2\text{Al}_{10}$, and $\text{CeRu}_4\text{Al}_{16-x}$ structure types grown with main-group-rich self-flux methods. We also discuss the phase stability of three related crystal structures containing atoms in similar chemical environments: ThMn_{12} , $\text{CaCr}_2\text{Al}_{10}$, and $\text{YbFe}_2\text{Al}_{10}$.

In addition to dimensionality and chemical environment, complexity is also important in materials design. From relatively common and well-studied intermetallic structure types, we present our motivation to work with complex stannides adopting the $\text{Dy}_{117}\text{Co}_{57}\text{Sn}_{112}$ structure type for thermoelectric applications and describe a strategy for the design of new magnetic intermetallics with low lattice thermal conductivity. Our quest to grow single crystals of rare-earth-rich complex stannides possessing low lattice thermal conductivity led us to discover the new structure type $\text{Ln}_{30}\text{Ru}_{4+x}\text{Sn}_{31-y}$ ($\text{Ln} = \text{Gd}, \text{Dy}$), thus allowing the correlation of primitive volumes with lattice thermal conductivities. We highlight the observation that $\text{Ln}_{30}\text{Ru}_{4+x}\text{Sn}_{31-y}$ gives rise to highly anisotropic magnetic and transport behavior, which is unexpected, illustrating the need to measure properties on single crystals.



■ INTRODUCTION

The search for new materials with desired electrical, magnetic, structural, or optical properties motivates the synergism of condensed matter physics, solid-state chemistry, and materials science. Developments on the forefront of scientific endeavor ultimately lead to societal benefits through the concomitant efforts of the pure sciences and engineering for the betterment of technology. Basic research, in particular crystal growth, acts as a playground for the development of new technologies, and at the heart of this effort is the discovery of new compounds with unexpected and often tunable physical properties. While

crystal growth has been respected for advances in fundamental theory and science, it also maintains a lasting vitality that few other areas have demonstrated over the past century. In many cases, when a new material is identified with bolstering potential for application, sufficiently sized single crystals (at least ~ 2 mm on each side), like those shown in Figure 1, must be grown in order that detailed studies can be completed. It has been our focus to join these two with the maxim of a

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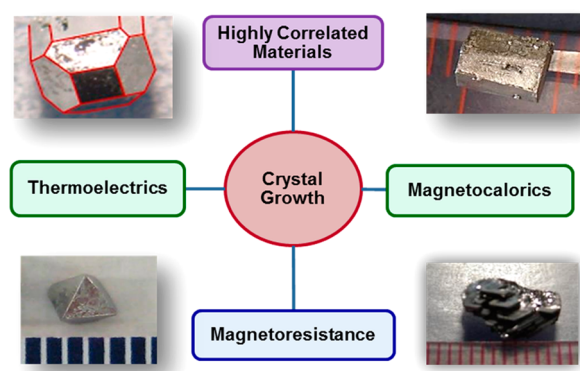


Figure 1. Motivation for crystal growth in our laboratory (tick marks represent 1 mm scale).

properties-driven approach by first growing and subsequently studying single crystals of ternary intermetallics. The direct growth of single crystals via the molten-metal flux-growth technique^{1–3} circumnavigates the need for subsequent recrystallization. The growth of single crystals is a demanding endeavor that is rewarded by not only the beauty of a faceted single crystal but also by the knowledge that the properties measured are almost always intrinsic to the phase, its crystalline quality is naturally high, and it can be oriented to study anisotropic properties.⁴

The discovery of a 100-fold change in linear magnetoresistance in LnSb_2 ($\text{Ln} = \text{magnetic lanthanide}$)⁵ and LaSb_2 ⁶ motivated us to consider incorporating a transition metal into a highly anisotropic intermetallic phase. The incorporation of transition metals such as Fe, Co, and Ni into the LnSb_2 -type structure resulted in the discovery of the CeNiSb_3 structure type.⁷ This structure type can be stabilized for early lanthanides, and CeNiSb_3 is a heavy-fermion compound. The latter lanthanide analogues adopt the HfCu_2Si_2 structure type and exhibit large negative magnetoresistance.⁸ All of the analogues are highly anisotropic, and although transition metals do not carry a magnetic moment, the resistivities are highly dependent on the magnetic field applied. Another example is YbAlB_4 .⁹ The structure of this boride phase features two-dimensional networks of boron in heptagonal and pentagonal units along the ab plane, as in the intermetallic superconductor MgB_2 .¹⁰ β - YbAlB_4 is the first example of a Yb-based heavy-fermion superconductor¹¹ and a unique example of a metal that exhibits quantum criticality. In our quest to understand the magnetism, we found that substitution of Fe into YbAlB_4 led to the destruction of the quantum criticality, likely as a result of antiferromagnetic ordering through Ruderman–Kittel–Kasuya–Yosida (RKKY) coupling.¹² Another example is the layered chalcogenide WTe_2 , which has recently been shown to exhibit up to a 452700% change in magnetoresistance (change in electrical resistivity as a function of magnetic field) at 4.5 K in a field of 14.7 T.¹³ Dimensionality is also important in thermoelectric materials, as was recently demonstrated in a recent report by Kanatzidis and co-workers, who observed ultralow thermal conductivity in SnSe single crystals.¹⁴ The origin of the low lattice thermal conductivity of $2.6 \pm 0.03 \text{ W m}^{-1} \text{ K}^{-1}$ at 973 K and the highly anisotropic electrical behavior would not otherwise have been realized without high-quality crystallographically oriented single crystals. It is evident that precise knowledge of the crystallographic orientation and chemical composition is absolutely essential when determining

a material's physical properties, especially in properties-driven research with earth-abundant materials. In this Account, we present strategies for selecting lanthanide-based intermetallic structures for our study and the motivation for crystal growth of these materials, specifically compounds grown with aluminum, gallium, and tin.

The primary focus of our research is to grow single crystals of rare earth intermetallics with unusual ground states and competing magnetic interactions.¹⁵ This effort is critical to study materials with a fine balance of competing states such as localized versus itinerant electrons (i.e., competition of RKKY and Kondo effects in lanthanide intermetallics).¹⁶ The discovery of compounds with magnetic fluctuations can lead to novel magnetism, such as spin liquid, quantum critical phenomena, and quadrupolar liquid states.^{17,18} This effort is motivated by the fact that quantum fluctuations can further our understanding of superconductivity and unusual magnetism.

To grow ideal single crystals of extended solids, the Ln:M:X ratio ($\text{Ln} = \text{lanthanide}$; $\text{M} = \text{transition metal}$; $\text{X} = \text{main group element}$) is typically tuned to optimize the phase yield. To grow single crystals of a main-group-rich material, we employ the flux-growth (including self-flux) method, which has led to the discovery of many compounds with targeted properties.¹⁵ We vary the synthetic conditions such as ramp rate and dwell temperature systematically. A typical temperature profile involves ramping the temperature up at 50–200 °C/h and then dwelling at temperatures of up to ~950–1150 °C prior to slow cooling to above the melting point of the excess flux. The samples are then removed from the furnace, the flux is removed, and single crystals are retrieved. In this Account, we present two areas for which the preparation of single crystals is advantageous for the elucidation of structure and property relationships. With our properties-driven synthesis, we are discovering that the electrical, magnetic, and thermal properties of the compounds are highly influenced by dimensionality, coordination preferences, and structural subunits.

■ ALUMINIDES AND GALLIDES: DIMENSIONALITY AND COORDINATION ENVIRONMENT

Our research has been focused on synthesizing lanthanide-based ternary intermetallics Ln:M:X . Over the past few years, we have targeted several families of intermetallics with known structure types, and strategic substitutions have led to discoveries of compounds with properties of particular interest.¹⁵ The AuCu_3 -type phase CeIn_3 , for instance, is the first magnetically mediated superconductor with a Néel temperature (T_N) of ~10 K with the application of pressure.¹⁹ Because of the discovery of magnetically mediated superconductivity in $\text{Ce}_n\text{MIn}_{3n+2}$ ($\text{M} = \text{Co, Rh, Ir}$; $n = 1, 2, \infty$),^{20,21} the homologous series of compounds adopting the HoCoGa_5 structure type²² was also chosen for our study. The quest to study layered materials with group 13 elements led to the discovery of the new CePdGa_6 ²³ and $\text{Ce}_2\text{PdGa}_{12}$ ²⁴ related phases. Determination of the mechanism leading to the origin or the dominant magnetic nature of an intermetallic phase, in particular the RKKY and Kondo effects, is possible through the study of several related phases such as CePdGa_6 , CePdGa_{10} , and $\text{Ce}_2\text{PdGa}_{12}$. These new structure types are relatively robust and can accommodate large early lanthanides and other transition metals such as Ni and Cu.^{25,26}

Substitution of one element can also be highly effective in changing the physical properties of the host. The $\text{Ce}_n\text{MIn}_{3n+2}$ homologous series led to our investigation of LnGa_3 and

structurally related $\text{Ln}_4\text{M}\text{Ga}_{12}$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Ni}, \text{Pd}, \text{Pt}, \text{Ag}$)^{27–32} adopting the cubic $\text{Y}_4\text{PdGa}_{12}$ structure type. The AuCu_3 -type subunit is found in both structure types. Our effort to target intermetallics containing the AuCu_3 subunit also led us to grow single crystals of compounds adopting the $\text{Y}_4\text{PdGa}_{12}$ structure type. $\text{Er}_4\text{PtGa}_{12}$ and $\text{Ho}_4\text{PtGa}_{12}$ were found to have unusual electrical properties, with magnetoresistance of 220 and 900%, respectively, as shown in Figure 2.³⁰

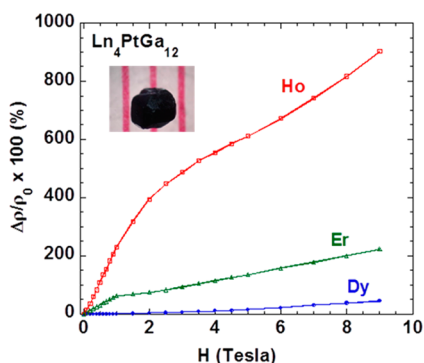


Figure 2. Magnetoresistance in $\text{Ln}_4\text{PtGa}_{12}$.

As part of our effort to study competing magnetic interactions in rare earth and transition metal sublattices, we synthesized a series of $\text{Ln}_4\text{FeGa}_{12}$ compounds ($\text{Ln} = \text{Y}, \text{Tb}–\text{Er}$). The crystal structure consists of iron–gallium octahedra and face-sharing rare-earth cuboctahedra. While the magnetic rare earth analogues order antiferromagnetically, the non-magnetic lanthanide analogue $\text{Y}_4\text{FeGa}_{12}$ is ferromagnetic at 36 K as a result of itinerant contributions from the Fe atoms or sublattice.³¹ $\text{Ln}_4\text{M}\text{Ga}_{12}$ ($\text{M} = \text{transition metal}$) can also be described as LnGa_3 with M occupying one-quarter of the interstitial sites in the body center positions of LnGa_3 unit cells. The “stuffed” AuCu_3 -type LnMn_xGa_3 can be viewed as intermediates between AuCu_3 - and $\text{Y}_4\text{PdGa}_{12}$ -type. LnGa_3 and $\text{Ln}_4\text{M}\text{Ga}_{12}$ have been found to adopt either the AuCu_3 or $\text{Y}_4\text{PdGa}_{12}$ structure type, and structure adoption is highly dependent on the transition metal doping level. We have also grown crystals of LnMn_xGa_3 ($\text{Ln} = \text{Ho}–\text{Tm}; x < 0.15$) from a gallium self-flux (Figure 3).³³ The close structural relationship between the two structure types offers a unique opportunity to study compounds with identical rare earth environments and the role of rare earth hybridization with conduction electrons. The study of binary and related ternary phases can also be useful to target more complex materials from relatively simple binary structure types or structural subunits. Furthermore, we can gain significant insights with electronic structure calculations using density functional theory (DFT)–chemical pressure analysis.³⁴

To study the magnetic properties of other main-group-rich intermetallics, we have grown single crystals of compounds adopting the following structure types: ThMn_{12} ,³⁵ $\text{YbFe}_2\text{Al}_{10}$ and $\text{CaCr}_2\text{Al}_{10}$,^{36,37} $\text{Yb}_6\text{M}_4\text{Al}_{43}$,³⁸ $\text{LnM}_2\text{Al}_{20}$,³⁹ and $\text{Ln}_2\text{Ru}_3\text{Al}_{15}$.⁴⁰ Compounds adopting the ThMn_{12} structure type have been extensively investigated,⁴¹ in particular for permanent magnetic materials such as $\text{RFe}_{12-x}\text{M}_x$.⁴² The impetus of our work related to this structure type was motivated by the change in the magnetic ordering temperatures of $\text{Gd}(\text{Cr}, \text{Mn}, \text{Fe}, \text{Cu}, \text{Al})_{12}$. It is quite unusual to have a phase range in the type of magnetism as a function of composition, from antiferromagnetic at 7 K (GdCr_4Al_8) to ferromagnetic in

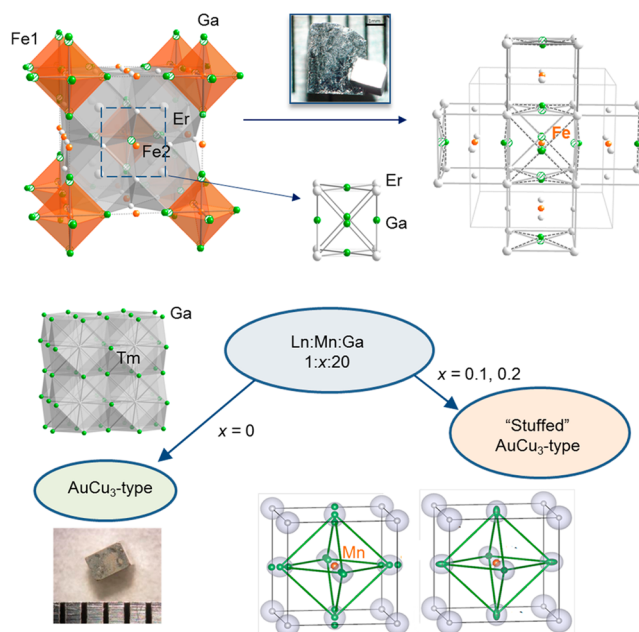


Figure 3. (top left) Crystal structure of $\text{Er}_4\text{Fe}_{0.67}\text{Ga}_{12}$ built from ErGa_3 (AuCu_3 structure type) and FeGa_6 octahedra forming the $\text{Y}_4\text{PdGa}_{12}$ structure type. (top right) Incorporation of Fe into the ErGa_3 . (bottom) “Stuffing” of Mn into the AuCu_3 subunit. Tick marks represent 1 mm scale. Adapted from refs 31 and 33. Copyright 2009 and 2013 American Chemical Society.

GdCr_6Al_6 at 175 K. Even more significant, GdFe_4Al_8 ferrimagnetically orders at 32 K, and a slight change in composition to GdFe_6Al_6 leads to ferromagnetic ordering up to 345 K!⁴³ These structure types were chosen for our study because of the common high-coordination polyhedra and serve as models to study polyhedral packing in magnetically dilute systems. It becomes evident that these cagelike phases can accommodate many different rare earth and transition metals. As shown in Figure 4, we can preferentially grow compounds

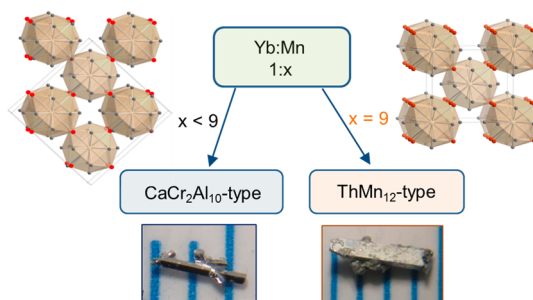


Figure 4. Concentration dependence of $\text{Yb}(\text{Mn}, \text{Al})_{12}$ leading to the adoption of the $\text{CaCr}_2\text{Al}_{10}$ or ThMn_{12} structure type.

adopting the $\text{CaCr}_2\text{Al}_{10}$ or ThMn_{12} structure types by controlling the Yb:Mn ratio.³⁷ It is only with high-quality single crystals that we are able to determine the crystal structure and structural preferences.

■ COMPLEX STANNIDES⁴⁴

One of the most fundamental properties of a material is the ability to transport heat, i.e., thermal conductivity, and this property is linked to the lattice complexity of the material. The initial goal of growing single crystals of complex stannides was

to search for materials with intrinsically low lattice thermal conductivity for potential use in thermoelectric applications. A thermoelectric material's performance is measured by a dimensionless quantity zT known as the thermoelectric figure of merit, defined as $zT = S^2T/(\rho\kappa)$, where S is the Seebeck coefficient, T is the operating temperature, ρ is the electrical resistivity, and κ is the thermal conductivity. Additionally, κ can be subdivided into a lattice contribution, κ_L , and an electronic contribution, κ_e (Figure 5). It is clear from the figure of merit

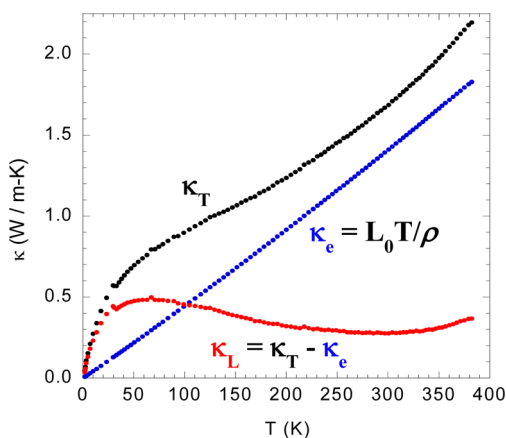


Figure 5. Total (κ_T), lattice (κ_L), and electronic (κ_e) thermal conductivities of $\text{Gd}_{117}\text{Co}_{56}\text{Sn}_{112}$. Adapted from ref 53. Copyright 2012 American Chemical Society.

that thermal conductivity should be considered a parasitic value in thermoelectrics. The typical paradigm for designing thermoelectric materials is to search for materials with high S , followed by optimization of ρ and κ_L . This methodology leads to diminishing returns in overall thermoelectric efficiencies, as the two most common methods used to reduce κ_L are (1) to introduce atomic disorder and (2) to introduce a large number of grain boundaries (nanostructuring); however, both methods tend to increase ρ . In fact, the maximum obtainable zT of thermoelectric materials has only increased by a factor of ~ 3 ⁴⁵ since the 1970s, when the exceptional thermoelectric properties of Bi_2Te_3 ($zT \sim 0.8$)⁴⁶ were first discovered. However, an estimated zT of 4 is necessary for thermoelectrics to be competitive with current technologies,⁴⁷ suggesting that a different design approach is needed to further optimize the technology. Finding materials that exhibit intrinsically low lattice thermal conductivity concomitant with relatively low ρ would change the paradigm to require the optimization of only S and may provide the change necessary to achieve the goal of $zT > 4$.

It has been shown that thermal conductivity can be reduced using materials with large, complex unit cells that contain heavy atoms. A complex unit cell containing many atoms can lower the ratio of phonon vibrational modes that carry heat efficiently as $1/V_p$, where V_p is the volume of the primitive unit cell.^{48,49} $\text{Yb}_{14}\text{MnSb}_{11}$ is a prime example of a heavy-atom-containing, large-unit-cell compound.^{50,51} This high-temperature thermoelectric compound is composed of a tetragonal unit cell ($V_p \sim 3000 \text{ \AA}^3$)⁵⁰ with a remarkably low thermal conductivity of $\sim 0.7 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature and a zT_{max} of ~ 1.0 at $\sim 1200 \text{ K}$.⁵¹ Thus, the following criteria for selecting a system were set: (1) the system should have a large primitive unit cell volume ($V_p > 5000 \text{ \AA}^3$); (2) the system should contain heavy atoms; and (3) the system should not have been fully characterized. In

addition to these requirements, single crystals of the targeted system must be produced in order to ensure measurement of the intrinsic lattice thermal conductivity. The $\text{Dy}_{117}\text{Co}_{57}\text{Sn}_{112}$ structure type⁵² met the aforementioned criteria, and the Gd analogue was selected⁵³ since it had not been previously reported.

A logical step in the synthesis of single-crystalline materials is to employ the flux-growth method using a low-melting and readily available main group element such as Sn as an incorporative flux.^{1,2} Upon examination of high Ln:M and Ln:Sn ratios in the studied compounds, it became readily apparent that in order to stabilize these structures over competing Sn-rich phases, a high concentration of Ln must be utilized. A different flux-growth strategy was necessary that allowed for both a molten flux for rapid diffusion to facilitate single-crystal growth and a higher Ln starting content to stabilize the $\text{Dy}_{117}\text{Co}_{57}\text{Sn}_{112}$ structure type over more Sn-rich phases. Several Ln–M mixtures (Ln = lanthanide; M = Co, Fe, Ru) with eutectic points $< 1000 \text{ }^\circ\text{C}$ occur at an approximate Ln:M ratio of 2:1. To access these high-Ln-concentration phases, a starting Ln:M:Sn molar ratio of approximately 2:1:2 is necessary to provide a molten-growth medium at temperatures accessible using typical high-temperature laboratory furnaces. Thus, in order to grow single crystals of complex materials such as $\text{Gd}_{117}\text{Co}_{56}\text{Sn}_{112}$, it is necessary to consider binary eutectics as fluxes. This strategy has also been successful in producing single crystals of pseudoquaternary phases such as borocarbides.⁵⁴

Single crystals of $\text{Gd}_{117}\text{Co}_{56}\text{Sn}_{112}$, for example, are thought to be stabilized by the use of a eutectic Gd–Co flux, and it is possible that the technique of using Ln–M eutectics may stabilize other Ln–M–X compounds with high Ln:M and Ln:X ratios that were previously unobtainable through conventional flux-growth methods. We have recently grown and characterized single crystals of $\text{Gd}_{117}\text{Co}_{56}\text{Sn}_{112}$ adopting the $\text{Dy}_{117}\text{Co}_{57}\text{Sn}_{112}$ structure type ($Fm\bar{3}m$, $a \sim 30.2 \text{ \AA}$; structure shown in Figure 6).⁵² The structure type can be stabilized for Ln = Ce, Pr, Tb, and Dy as well as for a Nd–Ru–Sn analogue.^{55–58} Our physical property measurements performed on single crystals show that the phase displays semiconductor-like behavior with an exceptionally low lattice thermal

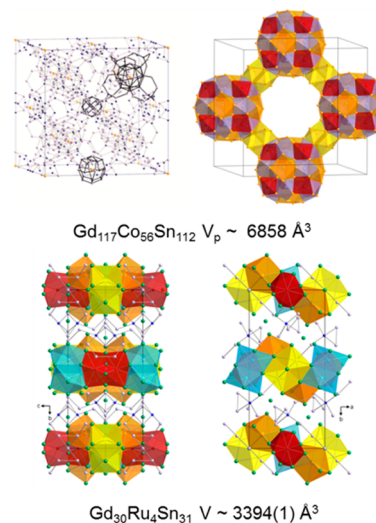


Figure 6. Crystal structures and volumes of two complex stannides. Adapted from refs 53 and 59. Copyright 2012 and 2013 American Chemical Society.

conductivity ($\kappa_L < 0.28 \text{ W m}^{-1} \text{ K}^{-1}$), approaching the theoretical lower limit for a crystalline solid.⁵³

The synthetic growth efforts on the complex stannides brought about the discovery of $\text{Ln}_{30}\text{Ru}_{4+x}\text{Sn}_{31-y}$ ($\text{Ln} = \text{Gd}, \text{Dy}$), which crystallizes in the orthorhombic space group $Pnmm$ with lattice parameters of $a \sim 11.7 \text{ \AA}$, $b \sim 24.5 \text{ \AA}$, and $c \sim 11.6$.⁵⁹ Although $\text{Ln}_{30}\text{Ru}_{4+x}\text{Sn}_{31-y}$ has a V_P approximately half that of $\text{Gd}_{117}\text{Co}_{56}\text{Sn}_{112}$, it contains more overall atomic positions and, in particular, more crystallographically unique Ln atomic sites. Additionally, the structure contains local structural perturbations caused by the presence or absence of a partially occupied Ru atomic sites, which has been modeled in two discrete orientations. The orthorhombic symmetry of the unit cell enables the potential for anisotropic physical properties. Studying the dependence of the physical properties, such as lattice thermal conductivity, on the structural characteristics of these compounds is essential to broaden our fundamental understanding of the structure–property relationships of these phenomena. Hence, we may be able to discover viable high-temperature thermoelectric materials simply by considering lattice volumes, as shown in Figure 7. The effects of complexity

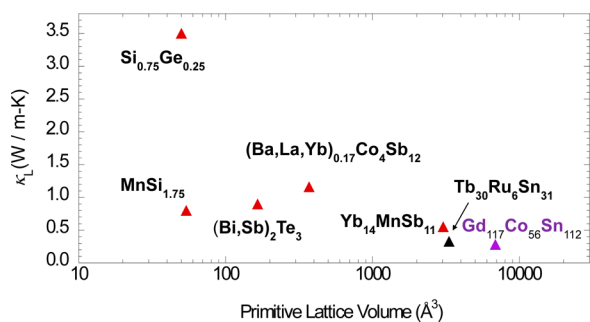


Figure 7. Lattice thermal conductivity as a function of primitive lattice volume of the intermetallic (adapted from ref 44).

on the compounds' electronic properties and whether the $1/V_P$ relationship for lattice thermal conductivity is maintained for highly complex intermetallic compounds with comparable atomic mass elements and bonding characteristics of the stannides are certainly of interest.

Through careful examination of heat capacity and time-dependent magnetization, $\text{Tb}_{30}\text{Ru}_6\text{Sn}_{31}$ was found to exhibit a very large spin-glass component of $>1700 \text{ emu/mol}$ of Tb below $\sim 17 \text{ K}$.⁶⁰ Spin-glass materials have been studied over the past several decades, as they behave as nonequilibrium systems below the glass transition temperature, leading to a multitude of exotic properties including isothermal time-dependent relaxation and frequency-dependent spin dynamics. The slow dynamics of spin-glass systems have precluded them from being used as functional materials. We have found that temperature-specific memory effects of $\text{Tb}_{30}\text{Ru}_6\text{Sn}_{31}$ can be quickly stored through magnetic field pulses as the sample is cooled. Surprisingly, $\text{Ln}_{30}\text{Ru}_{4+x}\text{Sn}_{31-y}$ gives rise to highly anisotropic magnetic and transport phenomena, and we have recently shown that when a magnetic field pulse of a few hundred gauss is applied to the Tb analogue as it is cooling, the system retains a memory of the temperature at which the pulse was applied.⁶⁰ The imprinted memory is then recoverable upon warming with very low imprinted memory degradation over time, creating a potential new application for spin glasses as functional materials. The $\text{Tb}_{30}\text{Ru}_6\text{Sn}_{31}$ structure type is quite unusual. Although they are highly three-dimensional, we have

shown that compounds adopting the structure type exhibit highly *anisotropic* magnetic and electrical behavior. The properties exhibited by the two stannide structure types represent characteristics necessary for potential use in magnetic and energy applications, such as thermoelectrics, and the complex crystal structures represent new classes of materials with intrinsically low lattice thermal conductivity.

CONCLUSIONS AND FUTURE OUTLOOK

Many intermetallics have been discovered in the past decade, leading in turn to other fruitful discoveries. The link to projects presented in this Account is the synthesis of novel materials leading to a perspective that will guide targeted structure types. Considerable effort is spent growing suitable single crystals for the elucidation of intrinsic material properties. This allows us to not only determine the structure of materials but also to think about how dimensionality, coordination environment, and complexity can affect the properties. We have shown that properties can be targeted by considering structures with relatively simple subunits to complex crystal structures with atomic disorder. We also note a recent review of classifying intermetallic compounds on the basis of coloring from considering group–subgroup relationships, specifically, evaluating “aristotypes” of compounds with high space-group symmetry and considering superstructures as a means to describe more complex structures.⁶¹ Another is “Fishing the Fermi Sea”⁶² by selecting a specific structure type with features that can lead to the properties of interest by combining intuition and theory.

Our current research efforts focus on the growth of materials exhibiting superconductivity, unusual magnetism, thermoelectrics, and magnetocalorics, all of which rely heavily on the intimate relationship between structure and physical properties. Likewise, the determination of anisotropic physical properties from high-quality single crystals is vital in probing the intrinsic electrical and magnetic nature of these materials to further our basic experimental and subsequent theoretical understanding, a stepping stone to technological progression. As reported in “Frontiers in Crystalline Matter: From Discovery to Technology” by the National Research Council of the National Academies,⁶³ a grand challenge is to be able to tailor structures to “allow for the creation of a delicate balance between dissimilar ground states, especially in systems supporting strongly correlated or quantum-mechanical interactions among the electrons.” A fundamental understanding of crystal structure and concomitant properties must be attained in order to manipulate the fundamental laws of nature to synthesize, modify, and ultimately control the growth and physical properties of crystalline materials.

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The authors declare no competing financial interest.

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