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# One Ce, Two Ce, Three Ce, Four? An Intermetallic Homologous Series to Explore: $A_{n+1}B_nX_{3n+1}$

Ashley Weiland, Justin B. Felder, Gregory T. McCandless, and Julia Y. Chan*

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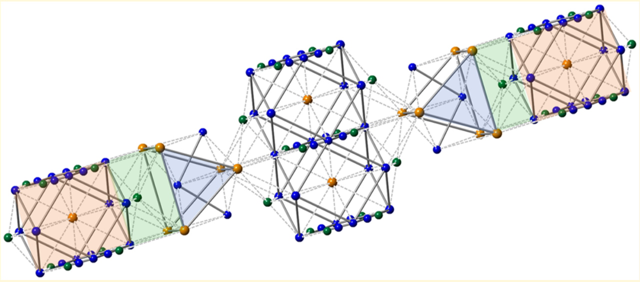
**ABSTRACT:** Low-dimensional solids are highly anisotropic by nature and show promise as new quantum materials, leading to exotic physical properties not realized in three-dimensional materials. To discover correlations in low-dimensional systems, studying robust crystal structures that allow for chemical tuning is critical for optimizing materials properties. In our search for novel quantum intermetallic materials, we discovered a new homologous series, $A_{n+1}B_nX_{3n+1}$ (A = rare earth; B = transition metal; X = tetrels; $n$ = 1−5) which crystallizes in orthorhombic space groups *Cmmm* (for odd "$n$") and *Cmcm* (for even "$n$"). This series, best characterized by the stacking of structural subunits of $AlB_2$, $AuCu_3$, and $BaNiSn_3$, represents a bulk architecture of highly correlated quantum materials. Though not a conventional "low dimensional" material with a van der Waals gap, the lattice parameters of the members of this series have a high aspect ratio ($b/a$) and can systematically be "tuned" as a function of dimensionality. This new homologous series can serve as a robust intermetallic system to study collective phenomena in quantum materials.



## INTRODUCTION

The study of quantum materials represents an exciting area of condensed matter physics and solid-state chemistry.[1] Quantum materials have been of increasing interest in the past decade in part due to the experimental discovery of topological insulators following theoretical predictions.[2−4] The field of quantum materials can be described as a fusion of several areas that share one important characteristic, namely, that their properties cannot be adequately approximated using classical physics and require the invocation of quantum mechanics.[5−9] During the past five years, an area of focus has been exploiting external stimuli, such as temperature or pressure, to tune the quantum properties of these materials to work toward the ultimate goal of properties "on demand".[10,11] The impact of materials discovery has been highlighted recently in the United States Department of Energy's reports of *Basic Research Needs for Synthesis*[12] and *Quantum Materials for Energy Relevant Technology*,[1] driving the field to discover new quantum materials. In this perspective, we introduce a new homologous series with the formula $Ce_{n+1}Co_nGe_{3n+1}$.

To advance the understanding of quantum materials and their optical, electrical, magnetic, and transport properties in a field lacking universal theories, one can study both related systems and new families of compounds. A strategy is to consider targeted structure types, such as the perovskite structure type, to develop overarching rules to guide materials discovery.[13] The perovskite crystal structure, $ABO_3$, one of the most ubiquitous systems, consists of A-site cations where A represents larger cations (commonly alkaline earth or rare earth ions) in a 12-coordinate cuboctahedral $ReO_3$ (or $AuCu_3$) environment and B-site cations typically occupied by smaller cations (commonly transition metals) forming $BO_6$ octahedra. The oxygen sites can also be replaced with main group anions, denoted as X. The list of $ABX_3$ compounds is extensive, adopted by various permutations of A, B, and X site elements.[14,15] This chemical robustness has led to the exploration of an incredible breadth of quantum phenomena, including superconductivity,[16] colossal magnetoresistance,[17] and topological insulators.[18−20] Experimentalists have found many ways to expand the simple perovskite structure to build double,[21,22] triple,[23] and higher-order perovskites[24,25] which have allowed the investigation of complex interplay between $d$ and $f$ electrons.[26,27]

Building upon the perovskite structure-type, the Ruddlesden−Popper (RP) series is an intergrowth of rock-salt structural units between perovskite slabs.[28,29] The RP family of materials form a homologous series described by the general formula $A_{n+1}B_nO_{3n+1}$, where "$n$" is an integer that describes the number of rock-salt intergrowths between perovskite slabs. RP phases have been demonstrated to be exfoliated, highlighting

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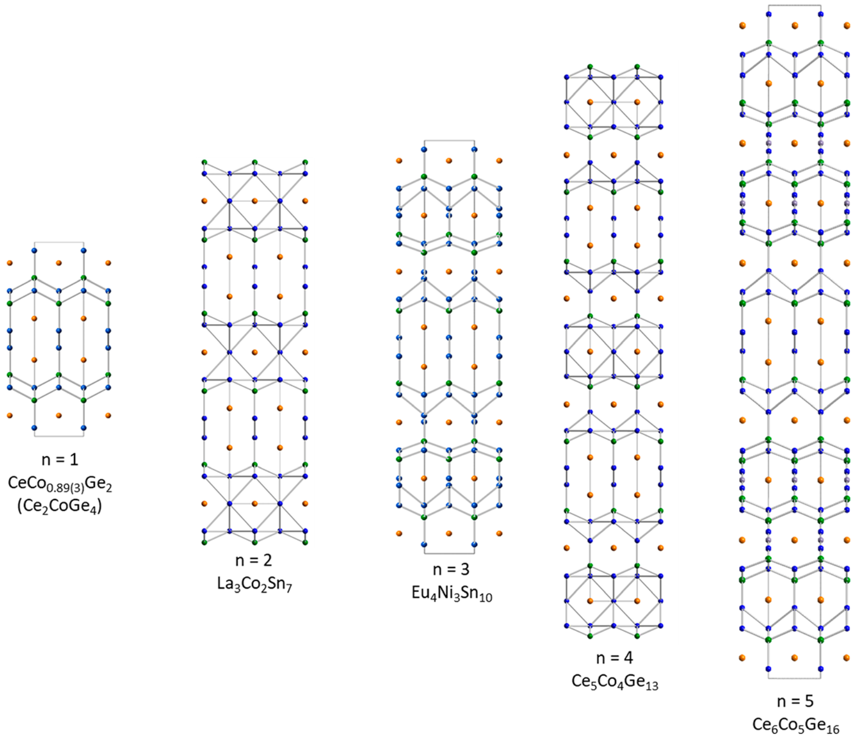

**Figure 1.** Representative members of the $A_{n+1}B_nX_{3n+1}$ series ($n$ = 1−5), where A is orange, B is green, and X is blue/gray.

**Table 1. Summary of Representative $A_{n+1}B_nX_{3n+1}$ Series Members**

| | $n$ = 1 | $n$ = 2[a] | $n$ = 3[a] | $n$ = 4 | $n$ = 5 |
|---|---|---|---|---|---|
| prototype compound | $CeCo_{0.89(3)}Ge_2$ (or $Ce_2CoGe_4$)[37] | $La_3Co_2Sn_7$[38] | $Eu_4Ni_3Sn_{10}$[39] | $Ce_5Co_4Ge_{13}$[40] | $Ce_6Co_5Ge_{16}$[41] |
| no. of unique crystallographic A sites | 1 | 2 | 2 | 3 | 3 |
| space group | *Cmcm* | *Cmmm* | *Cmcm* | *Cmmm* | *Cmcm* |
| $b$ (Å) | 16.74(1) | 27.60(5) | 38.431(8) | 45.175(9) | 55.441(11) |

[a] Ce−Co−Ge analogues have not been reported for these members; therefore, we present the original crystal structures type.

the potential to the tuning of layer dimensions ($n$).[30] An example of the RP series is $Sr_{n+1}Ir_nO_{3n+1}$, where increasing the number of rock salt layers leads to a Mott insulating state from correlated metallic states.[31]

The intermetallic Remeika phases of the $Yb_3Rh_4Sn_{13}$-type have been described as a triple perovskite with "covalent−ionic" interactions.[32] The crystal structure consists of Sn-centered icosahedra and Yb-centered cuboctahedra occupying the A site, Rh trigonal prisms on the B site, and X occupied by Sn. Early work on isostructural $Ce_3Co_4Sn_{13}$ shows complicated semiconducting-like behavior[33] and charge density waves in a three-dimensional structure-type. More recently, several compounds adopting the structure type[34] have been shown to exhibit quantum phase transitions and superconductivity emerging from the semiconducting state.[35,36] For example, $Yb_3Ir_4Ge_{13}$ was demonstrated to be a system to study strong correlation physics in a semimetallic environment.[36] The stannide members are adopted by early lanthanides; however, germanides can be adopted by smaller lanthanides. While determining the stability of Ce cuboctahedral germanides, we discovered a new homologous series.

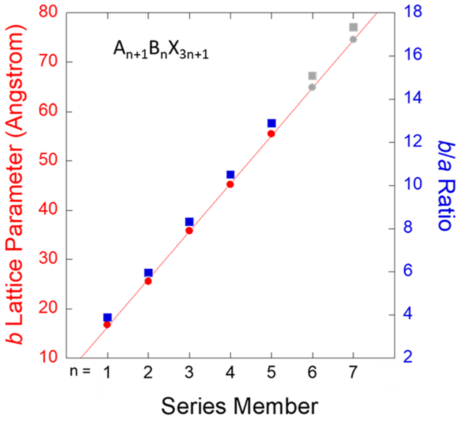

**Figure 2.** $b$ cell dimension as a function of each member of the series $A_{n+1}B_nX_{3n+1}$. Red circles indicate the $b$ lattice parameter, blue squares indicate the $b/a$ ratio, and gray circles and squares represent the theoretical lattice parameter and $b/a$ ratio of possible $n$ = 6 and $n$ = 7 members. The line is a guide for the eye. The $a$ and $c$ parameters are on the order of 4.07 Å−4.33 Å for each member of the series.

## ■ $A_{n+1}B_nX_{3n+1}$, AN INTERMETALLIC HOMOLOGOUS SERIES

Herein, we present a newly realized homologous series following the general formula $A_{n+1}B_nX_{3n+1}$ (A = rare earth; B = transition metal; X = tetrels; $n$ = 1−5), as shown in Figure 1. The formula of this new series is reminiscent of the Ruddlesden−Popper series $A_{n+1}B_nO_{3n+1}$;[28,29] however, the structures are not related. This new intermetallic series, with representative members summarized in Table 1, is comprised

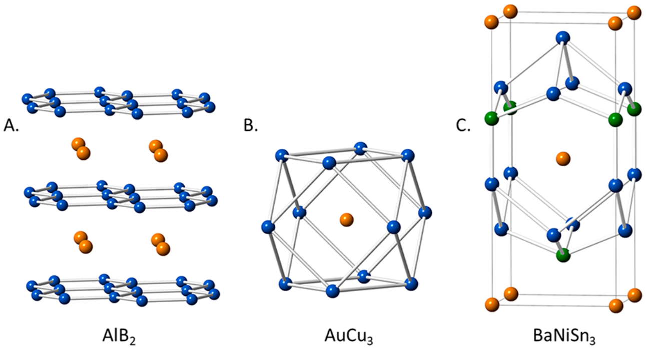

**Figure 3.** Local environment of the A atom in the hexagonal $AlB_2$ (A), cubic $AuCu_3$ (B), and tetragonal $BaNiSn_3$ (C) substructural units that make up the $A_{n+1}B_nX_{3n+1}$ series.

of orthorhombic structures alternating between *Cmcm* (odd "*n*" members) and *Cmmm* (even "*n*" members) space groups with similar *a* and *c* lattice parameters with increasing *b* axis dimensions, as shown in Figure 2.

In our recent work on $n = 2$ ($Pr_3Co_{2+x}Ge_7$ and $Ln_3Co_{2+x}Ge_{7-y}Sn_y$ (Ln = Pr, Nd, Sm))[42] and $n = 5$ ($Ce_6Co_5Ge_{16}$),[41] we noted stacking of common structural prototypes present in the $A_{n+1}B_nX_{3n+1}$ series, including $AlB_2$, $AuCu_3$, and $BaNiSn_3$ (structures shown in Figure 3). Figure 4 highlights the $AlB_2$ subunit which is present in each member of the series. Each member's structure can be thought of as an "atomically scaled" heterostructure of stacked subunits allowing for the study of the interplay of subunit interactions. Figure 5 shows the stacking of substructural units throughout the series. The incorporation of these subunits is fascinating given the discovery of rich magnetic and electrical properties of compounds adopting such structure types. For example, the first Ce-based magnetically mediated superconductor is $CeIn_3$ of the $AuCu_3$ structure-type, where superconductivity is achieved upon the application of pressure.[43] $CeIn_3$ is also a subunit in the homologous series $Ce_nMIn_{3n+2}$ ($n = 1, 2, \infty$; M = Co, Rh, Ir), where the growth of single crystalline Co, Rh, and Ir analogues[44] allowed for the realization of magnetically mediated superconductivity, such as in $CeIn_3$,[43] and the quantum criticality of $CeMIn_5$ (M = Co, Rh, Ir).[45] Additionally, the pressure-induced superconductor, $CeCoGe_3$, adopts the noncentrosymmetric $BaNiSn_3$ structure type,[46] another substructure in this new homologous series. These subunits are a host to exotic properties, and by stacking them in a larger "heterostructure", we can study the emergent phenomena.

## ■ LOOKING FORWARD

Over the last 10 years, the subject of crystal growth has been prominently featured in the discovery of new classes of quantum materials. While our group and others have fruitfully taken advantage of flux growth of intermetallic systems, we have strived to strategically select elements that yield the greatest potential for desired properties.[13,47,48] Due to the similarity of the compositions of each member of the homologous series, the synthesis of homogeneous single crystalline phases has been a challenge. Single crystal and powder X-ray diffraction have been critical in determining the identity of the phase(s) and bulk purity for each synthesis attempt and orienting single crystals for physical property measurements. As we reflect on all the ways crystal growth has impacted and advanced new discoveries, the selection of robust crystal structures is critical for optimizing materials properties. This new homologous series can serve as a robust intermetallic system to study competing magnetic interactions of itinerant electrons leading to potentially rich complex behavior. The determination of Ce hybridization with conduction electrons

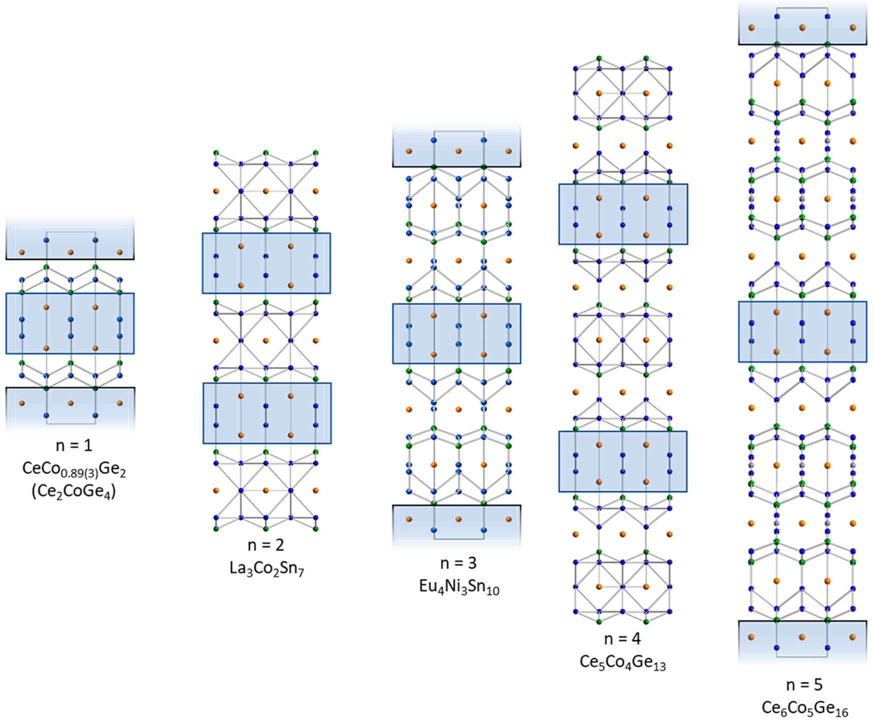

**Figure 4.** $AlB_2$-type subunit (highlighted in blue) in each member of the $A_{n+1}B_nX_{3n+1}$ series. Each structure contains two $AlB_2$ subunits (the odd members have a full $AlB_2$ subunit in the center of the unit cell and one half of the $AlB_2$ subunit at both the top and the bottom of the unit cell).

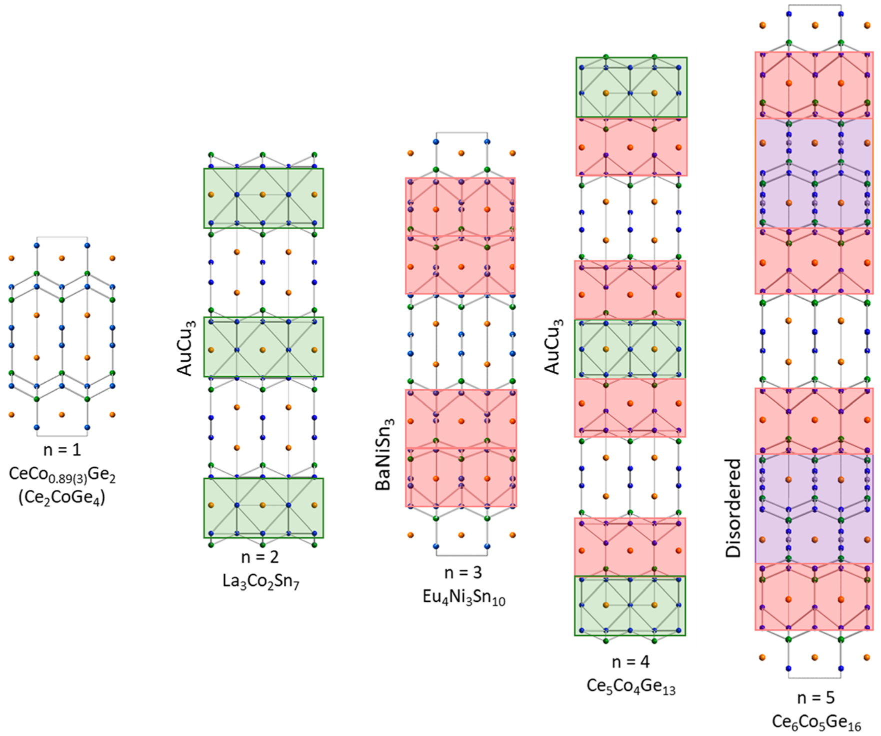

**Figure 5.** Stacking of structural subunits in representative members of the $A_{n+1}B_nX_{3n+1}$ series. $AuCu_3$ is shown in green, $BaNiSn_3$ is shown in red, and purple represents disordered subunits that can be $AuCu_3$ or $BaNiSn_3$.

in the $Ce_{n+1}Co_nX_{3n+1}$ (X = Ge or Sn) series can lead to the systematic study of the coupling of Ce *f*-electrons and conduction electrons, therefore, allowing the systematic investigation of collective phenomena in quantum materials. The strength of our research effort is in the discovery of novel magnetic and electronic properties in low-dimensional materials which has led to the pursuit of hierarchical materials with specific substructures.[48] Here, we have shown that the strategy lies in targeting robust structure types followed by chemical tuning to study the interplay of electronic and magnetic correlations.[1,10,12,49]

Low-dimensional solids are highly anisotropic by nature and show promise in new quantum materials leading to exotic physical properties not realized in three-dimensional materials. We have the opportunity to extend our synthetic strategy of the flux-growth method by designing single crystalline low-dimensional materials in bulk. It is important to consider that the discovery of new layered intergrowth compounds may be possible by using structural subunits as building blocks. We are left with the question, “Can a new homologous series lead to exotic properties that can be tuned solely by chemical substitution of structural subunits?” We envision work on this new homologous series to inspire the “artificial stacking” of new quantum materials.

## ■ AUTHOR INFORMATION

### Corresponding Author

**Julia Y. Chan** − *Department of Chemistry and Biochemistry, University of Texas at Dallas, Richardson, Texas 75080, United States*; orcid.org/0000-0003-4434-2160;
Email: Julia.Chan@utdallas.edu

### Authors

**Ashley Weiland** − *Department of Chemistry and Biochemistry, University of Texas at Dallas, Richardson, Texas 75080, United States*; orcid.org/0000-0001-7198-3559
**Justin B. Felder** − *Department of Chemistry and Biochemistry, University of Texas at Dallas, Richardson, Texas 75080, United States*; orcid.org/0000-0002-2528-1967
**Gregory T. McCandless** − *Department of Chemistry and Biochemistry, University of Texas at Dallas, Richardson, Texas 75080, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.chemmater.9b04743

### Notes

The authors declare no competing financial interest.

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