Chemical Frustration: A Design Principle for the Discovery of New Complex Alloy and Intermetallic Phases, Final Report

1. Project Information

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2. Distribution limitation notices: none.

3. Executive summary

A limiting factor in the design of new metallic materials for energy applications is the inability to predict or control the crystal structures of intermetallic phases. These compounds exhibit an immense structural diversity, which continues to expand with progress in synthetic exploration. In this project, a concept has been developed through experimental and theoretical endeavors to explain and predict how complex structures can arise in these systems: *chemical frustration*. Competing interactions were induced synthetically through the selection of ternary combinations of elements, in which incompatibilities are anticipated to arise between the preferred bonding or packing modes of the binary subsystems. These experiments led to a variety of new compounds which were structurally characterized and interpreted in terms of the chemical frustration concept. Theoretical models based on Density Functional Theory (DFT) and semi-empircal tightbinding calculations were also developed to account for new compounds encountered during these experimental investigations, as well as relevant intermetallic structures in the literature. Examples include the μ_3-acidity model and the reversed approximation Molecular Orbital approach.

This research has contributed to the field by proposing an approach to navigating the structural diversity of intermetallics, which has long been difficult to explain or control, and demonstrating its usefulness in the discovery of new compounds. At the same time, it has provided new tools for explaining structural phenomena in metals and forged deeper connections between the fields of materials and molecular chemistry. In terms of technical effectiveness and economic feasibility, the chemical frustration approach is promising. Several of the compounds discovered illustrate the structural features expected for frustration, and can be prepared simply from the elemental metals as thermodynamically stable phases. The future effectiveness of this approach will require criteria for reliably determining which systems will yield chemically-frustrated phases, and which will result in simple phase segregation. One outcome of the project is the refined guidelines for identifying such systems, which will be tested in future research. In addition to the scientific impacts of this research, there are also long-term benefits to the public: this project has opened routes to compounds based on intergrowths of simple intermetallics. When applied to the intergrowth of intermetallic phases with useful properties, this approach could yield new functional composites whose nanostructuring is extremely resilient as it is dictated by thermodynamics.

4. Comparison of accomplishments with goals and objectives

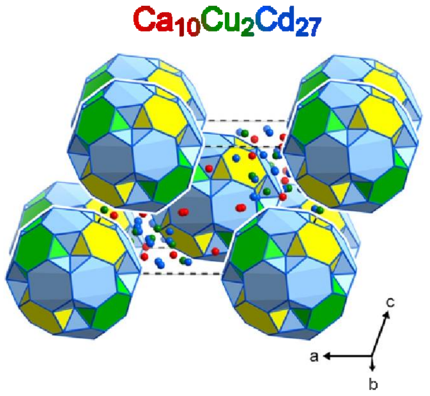
The original goal of this project was the development of chemical frustration into a predictive conceptual framework for the design of complex intermetallic phases. This aim was to be achieved through the pursuit of three research objectives: (1) the synthesis of new phases exhibiting chemical frustration, (2) the development of theoretical tools for analyzing the impact of frustration on electronic structure, and (3) the merging of the experimental and theoretical endeavors into guidelines for creating chemical frustration in intermetallic systems. Over the course of the project, these objectives were refined against our results. A number of new intermetallic phases exhibiting complex structures were obtained in several of the systems proposed, but in other systems no new phases of interest were encountered. For these reasons, our theoretical objective adapted to focus on the driving forces giving rise to chemically-frustrated structures, which would lead more directly to fulfilling objective 3. Models were successfully developed to account for a range of complex structures, including ones synthesized as part of the project. Our combined experimental and theoretical results have successfully resulted in proposed guidelines for the design of chemically frustrated intermetallics. Future work will focus on the validation and improvement of these guidelines.

5. Summary of project activities

The activities of this project were structured around the parallel pursuit of the experimental and theoretical objectives (1 and 2, respectively, in part 4 above) during the first four years of the project, followed by the merging of these endeavors towards objective 3 in the fifth year. In this report, we will discuss the successes of the experimental and theoretical components separately, and highlight how these activities became synergistic without other as we proceed.

Our experimental work began with synthetic surveys of the intermetallic systems suggested in our proposal as being candidates for chemical frustration. Among these systems, the Ca-Cu-Cd, Gd-Fe-C, and Mg-Pd-Ge systems arose as those most promising for extensive investigation. We also branched out from our original systems as we refined our ideas about chemical frustration based on our results. Among these new candidates, we had particular success in the Mn-Si-C system.

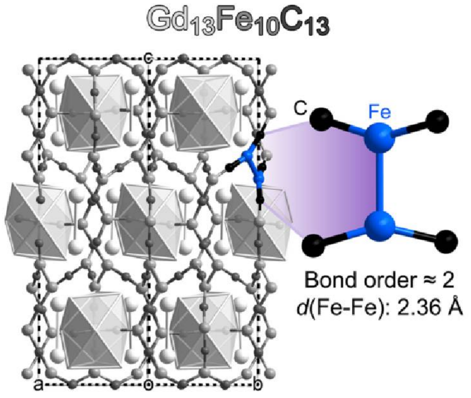
The Ca-Cu-Cd system (*Papers 2 and 9 in part 6a*). In the Ca-Cu-Cd system, we encountered three new compounds which provided insights into the phenomenon of chemical frustration: Ca_5Cu_2Cd, $Ca_2Cu_2Cd_9$, and $Ca_{10}Cu_2Cd_{27}$. The structures of all three compounds shared the remarkable feature that the coordination environments of the minority elements mimicked closely those seen in nearby binary systems. In this way, the crystal structures resembled intergrowths of simpler binary structures (sometimes also with domains of elemental structures) which could be rationalized by the placement of the phase in the ternary phase diagram. For example, $Ca_{10}Cu_2Cd_{27}$ appears in the Ca-Cu-Cd phase diagram almost along a straight line connecting $CaCd_2$ on the Ca-Cd edge and Cu_2Cd_5 on the Cu-Cd edge. The structure of this phase (right) reflects this placement in the diagram, with its major building blocks consisting of Bergman-type icosahedral clusters in which Friauf polyhedral traceable to the $MgZn_2$-type polymorph of $CaCd_2$ enclose Cu-centered icosahedra reminiscent of Cu_2Cd_5.



$Ca_2Cu_2Cd_9$ and Ca_5Cu_2Cd exhibit similar divisions of their structures into fragments of simpler structures, but with different structural results. In $Ca_2Cu_2Cd_9$, the Bergman-type clusters of $Ca_{10}Cu_2Cd_{27}$ are less developed, with the outer Friauf polyhedral being substantially distorted, so as to resemble the one of the Ca coordination environments of $Ca_{14}Cd_{51}$. FCC fragments of Cd also appear in the structure to fill voids left by the Bergman-type clusters. Ca_5Cu_2Cd, on the other hand, is a ternary variant of the Cr_5B_3 structure, derived from the intergrowth of β-Ca, Ca_3Cd_2, and Ca_2Cu.

These structures thus appear to exhibit microscopic phase segregation into small domains of simpler metallic phases. Such segregation is an expected result of frustrated interactions, but in this case, the nature of the frustration is different from that originally anticipated for the system. A deeper theoretical analysis using the DFT-Chemical Pressure (DFT-CP) analysis provided insight into what competing interactions drive the frustration in $Ca_{10}Cu_2Cd_{27}$. In the $MgZn_2$-type $CaCd_2$ phase, the Ca-Cd contacts are overly long relative to their ideal distances due to steric issues elsewhere in the structure. Substitution of Cd atoms with smaller Cu ones (a likely consequence of the addition of Cu to move closer to the $Ca_{10}Cu_2Cd_{27}$ composition), would exacerbate these stresses. This situation leads to an incompatibility of Ca-Cd and Cu-Cd interactions, making their segregation favorable. The result is their core-shell separation in the creation of Bergman clusters. In this phase, then, Bergman clusters emerge in an analogous fashion to that of micelles in amphiphilic systems.

A conceptual issue with this scheme is the question of why the Ca-Cd and Cu-Cd interactions do not simply segregate on a macroscopic scale. One possible answer is found in the CP analysis of the Ca-Cd and Cu-Cd binary phases. The Ca-Cd and Cu-Cd interactions exhibit opposite signs in their CPs. Placing domains of Ca-Cd and Cu-Cd together could offer the opportunity for these opposing CPs to cancel each other out at the interface. Based on these ideas, our strategies for creating chemical frustration became sharpened: desirable systems should exhibit interactions which cannot share the same space, yet are stabilized by being adjacent to each other in a structure. This strategy was further validated by our results in the Mn-Si-C system (*manuscript in preparation*).



The Gd-Fe-C system (*papers 6 and 12 in part 6a*). Our synthetic work in the Gd-Fe-C system resulted in the structures of $Gd_{13}Fe_{10}C_{13}$ (right) and its oxycarbide derivative. These structures are built from complex Fe-C/O polyanionic networks which wrap around Gd^{3+} cations. A bonding analysis (using the reversed approximation Molecular Orbital method developed as part of this project; see below) of $Gd_{13}Fe_{10}C_{13}$ highlights the presence of covalent bonds along the Fe-C contacts. The resulting bonding scheme vividly confirms analogies made by R. B. King, R. Hoffmann, and others between carbometalate phases and organometallic compounds. The Fe atoms achieve filled 18 electron configurations through σ and π bonds to C atoms as well as other Fe atoms in the network. Particularly remarkable are the H-shaped C_2FeFeC_2 units which occur in the polyanionic networks, with extremely short Fe-Fe contacts of 2.36 Å. Our bonding analysis suggests that these short contacts are supported by an Fe-Fe double bond, the π component of which forms part of a delocalized π system including the neighboring C atoms.

The total valence electron count for $Gd_{13}Fe_{10}C_{13}$ is only one electron per formula unit short of that needed to provide filled 18 electron configurations to all of the Fe atoms. This close correspondence helps explain why the Fermi energy for the compounds appears in a deep pseudogap in DFT calculations. The slight deficiency relative to the expected electron count also makes understandable the phase's susceptibility toward oxygen incorporation to form an oxycarbide: for each C atoms substituted with O, two more valence electrons are introduced to the phase.

Lessons for future work in the design of chemical frustration were derived from the role of the 18 electron bonding scheme in stabilizing $Gd_{13}Fe_{10}C_{13}$, and the ability of the reversed approximation Molecular Orbital (raMO) method to uncover these bonding pictures. The favorability of filled 18 electron configurations will be used as one driving force for driving intergrowths between incompatible structures in the next phase of this work.

The Mg-Pd-Ge system (*manuscript in preparation*). A new phase $Mg_{4.5}Pd_5Ge_{1.5}$ was synthesized during our investigations of the Mg-Pd-Ge system. Its structure is based on the intergrowth of slabs of the CsCl type (as adopted by the binary phase MgPd) with layers of the Na_3As type. The complexity of this structure is augumented by disorder: the Na_3As-type layers contain split Pd atom positions in a tricapped-trigonal prismatic coordination. We are in the process now of determining how the addition of Ge to the MgPd phase induces the insertion of Na_3As-type layers, and why the Pd atoms in these layers move off of the high-symmetry positions.

The Mn-Si-C system (*manuscript in preparation*). Intermetallic carbides were of interest to us due to the geometrical incompatibility of the tetrahedral close packed (TCP) geometries observed for many intermetallics with the octahedral or trigonal prismatic coordination preferred by C atoms in carbides. Introducing carbon into TCP intermetallics might lead to segregation between carbide and TCP features. This idea was realized in our discovery of two compounds in the Mn-Si-C system: these phases contain Mn-Si TCP domains reminiscent of the Mn-rich silicides separated by manganese carbide regions, with local environments similar to those in Mn_3C. As such, the phases exhibit a microscopic segregation between fragments of simpler phases close-by in composition space. Chemical pressure calculations on Mn_3C and a hypothetical Cr_3Si-type Mn_3Si (to represent the significantly more complicated TCP phases in the Mn-Si system) reveal that the Mn-C and Mn-Si interactions in these two structures have opposite CP schemes. Just as in the Ca-Cu-Cd system, the opportunity for the cancellation of opposite CPs at an interface appears as a possible mechanism driving the intergrowth of incompatible bonding types.

Additional structural chemistry revealed (*Papers 1 and 13 in part 6a*). In addition to the phases described above, we also characterized two phases less directly related to the chemical frustration concept, $Mg_{11}Cu_6Al_{12}$ and $(Nb/Ta)_4Ga_5$, which nevertheless offer lessons in the factors shaping the structures of intermetallics. We begin with $Mg_{11}Cu_6Al_{12}$. In terms of composition, this phase appears to be derived from the α-Mn-type $Mg_{17}Al_{12}$ phase by simply replacing 6 Mg atoms per formula unit with Cu ones. In fact, the structures of both phases are built from a BCC-type packing of fragments of the $MgCu_2$ type. The major structural difference is that while in $Mg_{17}Al_{12}$ all $MgCu_2$-type clusters have the same orientation, in $Mg_{11}Cu_6Al_{12}$ every other cluster is rotated by 90 degrees. A topological charge stabilization analysis of these structures provides a clear explanation for how the introduction of Cu into the system drives this transformation. In $Mg_{17}Al_{12}$, the outer sites can be seen geometrically as extending either the relatively anionic or cationic networks of the clusters, depending on which contacts are drawn. As such, these outer sites are ambiguous in terms of whether they would prefer an electronegative or electropositive atom. Because they are all occupied by Mg, the majority element in the structure, there is little need to differentiate them from each other. This situation becomes less satisfactory, however, when Cu is substituted onto some of these sites. Cu is significantly more electronegative that Mg, and thus would prefer a site more tailored to an anionic atom. The rotation of every other cluster by 90 degrees provides this differentiation. Following this operation, half of the outer sites become clearly aligned with the cationic network, while the other half locks into the anionic network. These classes of sites are then occupied by Mg and Cu, respectively. One result of this is that while in $Mg_{17}Al_{12}$, relatively polar clusters appear embedded in a nonpolar matrix, in $Mg_{11}Cu_6Al_{12}$, continuous anionic and cationic networks pass through the whole structure.

During syntheses involving Ga in Ta or Nb tubes, we encountered crystals of substituted versions of Ta_4Ga_5 and Nb_4Ga_5 phases as side products. These compounds appear in the Ta-Ga and Nb-Ga phase diagrams, but little structural information was available for them; for Nb_4Ga_5 a unit cell has been determined, while no data was reported for Ta_4Ga_5. We were then able to prepare crystals of the original binary phases and solve their crystal structures. A prominent feature of the structures is a primitive cubic lattice of BCC-type clusters. The voids left by these frameworks are then filled by two different types of motifs: a pseudo-icosahedral cluster, and a dimer of BCC clusters. Throughout this complexity, a division of the structure into Ga- and Ta/Nb-rich domains is evident, making these phases relevant to the theme of chemical frustration. A bonding analysis of Ta_4Ga_5 using the raMO method suggests that this homoatomic clustering helps form a DOS pseudogap at the Fermi energy, enhancing the electronic stability of the phase. The electron count at which the pseudogap occurs is governed by strong Ta-Ta bonding interactions, which are preferentially supported relative to their antibonding counterparts by the placement of Ga at the periphery of the Ta clusters. Similar bonding schemes are expected to arise for transition metal-main group intermetallics when the electron count/transition metal atom drops below 9.

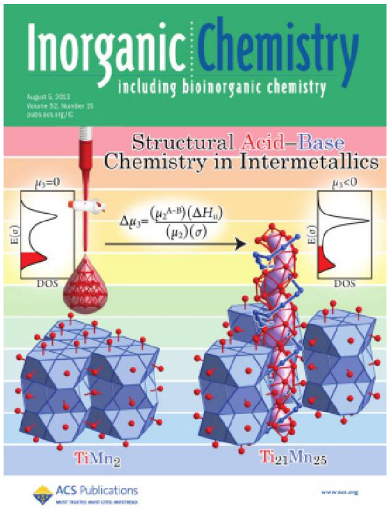
DFT-calibrated Hückel calculations (*Papers 2 and 5 in part 6a*). In examining the chemically frustrated phases using theory, it is important to have a direct connection between local features in a crystal structure and stability. To make these connections, we have made use of the ability of simple Hückel theory, a semi-empirical orthogonal tightbinding method, to quantitatively reproduce the band structures of higher level DFT calculations using a simple orbital-based model, when properly parameterized. As a first step, we developed the *eHtuner* program (freely available on our group website) to streamline the creation of these Hückel models. The program reads in the DFT band structure and projected density of states curves calculated for a phase, and then optimizes Hückel parameters to obtain a best-fit Hückel model. Often, these fits will result in root-mean-squared deviations in the band energies (up to about an eV above the Fermi energy) under a tenth of an eV.

The ability to obtain DFT-calibrated Hückel models quickly has facilitated the development of a number of theoretical methods in our group, some of which were later adapted to DFT calculations. One example is the μ_2-Hückel chemical pressure (CP) method, in which the macroscopic pressure of a phase is spatially resolved to reveal competing desires for expansion and contraction among the interatomic contacts in a phase. The DFT-adaptation of this method then became the center-piece of a new research project. Our application of the DFT-calibrated Hückel approach to a wide range of systems has also led to parameters for much of the period table.

The μ_3-acidity model (*Papers 4, 7, and 11 in part 6a*). Another advantage of using DFT-calibrated Hückel models is that it allows us to bring the accuracy of DFT to a theoretical approach offering a unique connection between geometry and electronic structure: the Method of Moments. The basis of this approach is that the moments (μ_n's) of a phase's density of states (DOS) curve provide all the information necessary to construct that DOS curve, and (due to the simplicity of the Hückel Hamiltonian) can be calculated directly from the local environments in a crystal structure, without the determination of wave functions. As such, the moments provide a clear bridge between the geometrical features we associate with chemical frustration, and the impact these features have on the electronic structure.

Hitherto, the Method of Moments has been used in rationalizing the relative stability of crystal structures as a function of electron count, but its potential as a tool for bonding analysis has been little explored. In this project, we pursued this adaptation of the method of moments to bonding analysis with the creation of the μ_3-acidity model. Through investigations of the optimal values of the moments as a function of electron count, we found that the third moment (μ_3) controls the position of a pseudogap in the DOS curve (for a μ_0-μ_4 model system). For any given electron count, the energy is minimized when the μ_3 value places the Fermi energy into the pseudogap it controls. This relationship can be inverted to given an optimal electron count as a function of μ_3. In applying this idea to the d-only models of transition metal elements, we saw that these elements could be grouped into three classes of metals: those whose electron counts fall below their μ_3 ideal, those that essentially match ideal, and those whose electron counts exceed the ideal. By analogy with the Lewis theory of acids and bases, these metals were assigned as μ_3-acidic, μ_3-neutral, and μ_3-basic, respectively. These assignments closely matched the observed tendencies for transition metals to react with each other to form intermetallics, and align well with the earlier acid/base picture of L. Brewer. The formation of observed intermetallic phases was found to correlate with the reduction of the μ_3-acidity or μ_3-basicity of its component metals, relative to the unreacted elemental phases.

As we examined intermetallic phase formation from this viewpoint, it became clear that the favorability of phase formation and the structure types adopted is a function of the relative strengths of the μ_3-acids and bases combined. For example, in 3d metal systems, the CsCl type has a certain domain of stability corresponding to a closing matching of acid-base structures. The μ_3-acidity picture not only explains why the CsCl type might be less favorable outside this region, but also accounts for the intriguing phases encountered at the edges of the region: TiCu and $Ti_{21}Mn_{25}$.



Consider $Ti_{21}Mn_{25}$ (see journal cover art to the right), formed from the moderate acid Ti and weak base Mn. Due to Ti being relatively strong as an acid, good neutralization is found when mixing 1 Ti with 2 Mn, to form the $MgZn_2$-type $TiMn_2$ phase. If one were then to add additional Ti, however, the high acidity of this extra Ti would provide a driving force for trying to accommodate it in the intermetallic. The structure finds an elegant way to do this (without detracting from the original neutralization of $TiMn_2$) by breaking the $TiMn_2$ structure into columns, and inserting the extra Ti into the interstitial spaces. These inserted Ti atoms make the most of the Mn neighbors available by arranging themselves into a hollow tube to minimize Ti-Ti contacts that would interfere with Ti-Mn bonding, and twisting this tube into a helix to create a concave groove with maximal surface area for bonding to the Mn.

This idea of structural acid-base chemistry can also be extended to intergrowths of tetrahedral close packed (TCP) and simple close packed (SCP) features in intermetallics formed from transition metals. In the Sc-Ir system, a CsCl-type phase appears at the center of the phase diagram, indicative of the good matching of the strong acid Sc with the moderate base Ir. However, on moving to Sc-rich side of the system, a series of increasingly complex structures are found: Sc_2Ir, $Sc_{11}Ir_4$, $Sc_{57}Ir_{13}$, and $Sc_{44}Ir_7$. In the progression across Sc_2Ir, $Sc_{57}Ir_{13}$, and $Sc_{44}Ir_7$, one sees the gradual isolation of Ir-centered icosahedra (TCP) in a SCP matrix of Sc atoms, with one motif to emerge being the Mackay-type cluster of icosahedral quasicrystals. These observations can be understood through calculations which show that TCP geometries tend to maximize the average strength of interatomic interactions, while SCP arrangements minimize those strengths. The adoption of TCP geometries in the Ir environments and SCP character in the Sc sublattice thus serves to maximize the neutralizing power of the available Sc-Ir interactions while minimizing competition with the Sc-Sc contacts.

Following these successes in transition metal-based systems, we are eager to extend the μ_3-acidity model to a wider range of compounds. In our current work, we are beginning this process with phases containing main-group atoms as minority components.

The reversed approximation MO (raMO) analysis (*Paper 10 in part 6a*). Our theoretical work in this project has also led to the reversed approximation MO (raMO) method, a technique for breaking down the electronic structure of materials. In a typical quantum mechanical calculation, one uses a basis set of simple functions in order to approximate the true wave function of a system. The raMO approach reverses this procedure, using the occupied wave functions of a compound as a basis set for the solution of a simple molecular orbital (MO) problem, yielding the best reproductions of the MO diagram possible using these wave functions. Through this approach, the bonding schemes underlying the preferred electron counts of intermetallics can often be quickly extracted from the wave functions of the phases. This potential is illustrated in our analysis of $Gd_{13}Fe_{10}C_{13}$ (see above), where the raMO method revealed the importance of 18 electron configurations on the Fe atoms, and the extensive conjugation in the Fe-C π systems. In other applications, the raMO approach is establishing the generality of an electron counting rule, the 18-n rule, to transition metal-main group intermetallics, and the prominence of multi-center interactions isolobal to transition metal-transition metal bonds in such phases.

6. Products developed/technology transfer activities

a. Publications

1. Berns, V. M.; Stacey, T. E.; Sapiro, M.; Fredrickson, D. C. $Mg_{11}Cu_6Al_{12}$, A New Link in the Structural Chemistry of $MgCu_2$-Type Clusters, *Eur. J. Inorg. Chem.* **2011**, *2011*, 3936-3949.

2. Fredrickson, D. C. Electronic Packing Frustration in Complex Intermetallic Structures: The Role of Chemical Pressure in Ca_2Ag_7, *J. Am. Chem. Soc.* **2011**, *133*, 10070-10073.

3. Harris, N. A.; Hadler, A. B.; Fredrickson, D. C. In Search of Chemical Frustration in the Ca-Cu-Cd System: Chemical Pressure Relief in the Crystal Structures of Ca_5Cu_2Cd and $Ca_2Cu_2Cd_9$, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1961-1974.

4. Stacey, T. E.; Fredrickson, D. C. The μ_3 Model of Acids and Bases: Extending the Lewis Theory to Intermetallics, *Inorg. Chem.* **2012**, *51*, 4250-4264.

5. Stacey, T. E.; Fredrickson, D. C. Perceiving Molecular Themes in the Structures and Bonding of Intermetallic Phases: The Role of Hückel Theory in an ab initio Era, *Dalton Trans.* **2012**, *41*, 7801-7813.

6. Hadler, A. B.; Fredrickson, D. C. $Gd_{13}Fe_{10}C_{13}$: Indications of Fe–Fe Multiple Bonding Emerging from Chemical Frustration, *J. Am. Chem. Soc.* **2012**, *134*, 10361-10364.

7. Stacey, T. E.; Fredrickson, D. C. Structural Acid-Base Chemistry in the Metallic State: How μ_3-Neutralization Drives Interfaces and Helices, $Ti_{21}Mn_{25}$, *Inorg. Chem.* **2013**, *52*, 8349-8359.

8. Fredrickson, D.; Doverbratt, I.; Ponou, S.; Lidin, S. Bonding Schemes for Polar Intermetallics through Molecular Orbital Models: Ca-Supported Pt–Pt Bonds in $Ca_{10}Pt_7Si_3$, *Crystals* **2013**, *3*, 504-516.

9. Hadler, A. B.; Harris, N. A.; Fredrickson, D. C. New Roles for Icosahedral Clusters in Intermetallic Phases: Micelle-like Segregation of Ca-Cd and Cu-Cd Interactions in $Ca_{10}Cd_{27}Cu_2$, *J. Am. Chem. Soc.* **2013**, *135*, 17369-17378.

10. Yannello, V. J.; Kilduff, B. J.; Fredrickson, D. C. Isolobal Analogies in Intermetallics: The Reversed Approximation MO Approach and Applications to $CrGa_4$- and Ir_3Ge_7-Type Phases, *Inorg. Chem.* **2014**, *53*, 2730-2741.

11. Guo, Y.; Stacey, T. E.; Fredrickson, D. C. Acid–Base Chemistry in the Formation of Mackay-Type Icosahedral Clusters: μ_3-Acidity Analysis of Sc-Rich Phases of the Sc–Ir System, *Inorg. Chem.* **2014**, *53*, 5280-5293.

12. Hadler, A. B.; Yannello, V. J.; Bi, W.; Alp, E. E.; Fredrickson, D. C. π-Conjugation in $Gd_{13}Fe_{10}C_{13}$ and Its Oxycarbide: Unexpected Connections between Complex Carbides and Simple Organic Molecules, *J. Am. Chem. Soc.* **2014**, *136*, 12073-12084.

13. Fredrickson, R. T.; Kilduff, B. J.; Fredrickson, D. C. Homoatomic Clustering in T_4Ga_5 (T = Ta, Nb, Ta/Mo): A Story of Reluctant Intermetallics Crystallizing in a New Binary Structure Type, *Inorg. Chem.* **2015**, *54,* 821-831.

b. Internet sites

c. Networks or collaborations fostered

During this project, the PI developed a collaboration with Dr. E. E. Alp at the Advanced Photon Source, Argonne National Laboratory. The expertise of the PI's group was combined with that of Dr. Alp in Mössbauer spectroscopy to experimentally probe the bonding in $Gd_{13}Fe_{10}C_{13}$ (*paper 12 in part 6a*). In the future, this collaboration will expand to include inelastic X-ray nuclear resonant scattering measurements of vibrational properties.

This project also fostered interactions between the PI and Prof. S. Lidin at Lund University, in which the PI helped with the theoretical analysis of a complex phase synthesized in Prof. Lidin's group (*paper 8 in part 6a*).

d. Technologies/techniques

The major techniques developed are theoretical methods for explaining and predicting structural chemistry using the results of density functional theory calculations as input. These techniques developed include the procedure for the optimization of Hückel models to fit DFT results, as is implemented in the eHtuner program (*paper 5 in part 6a*), the μ_3-acidity model (*papers 4, 7, and 11 in part 6a*), the μ_2-Hückel chemical pressure method (*paper 2 in part 6a*), and the reversed approximation Molecular Orbital analysis (*paper 10 in part 6a*).

e. Inventions/patent applications

f. Other products

eHtuner: an open-source program for fitting Hückel or extended Hückel models against the results of density functional theory band structure calculations. This program is freely available at URL: http://chem.wisc.edu/~danny/software/ehtuner/