Communicating Research to the General Public

The WISL Award for Communicating PhD Research to the Public launched in 2010, and since then over 100 Ph.D. degree recipients have successfully included a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance—as well as their excitement for and journey through their area of study—to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere, through the cooperation of PhD candidates, their mentors, and departments. WISL offers awards of $250 for UW-Madison Ph.D. candidates in science and engineering. Candidates from other institutions may participate, but are not eligible for the cash award. WISL strongly encourages other institutions to launch similar programs.

Wisconsin Initiative for
Science Literacy

The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

Contact: Prof. Bassam Z. Shakhashiri

UW-Madison Department of Chemistry

bassam@chem.wisc.edu

www.scifun.org

FAST and Frivolous:

Five Years Studying Chemical Pressures and Soft Atomic Motions in Intermetallic Structural
Transitions

By

Kendall R. Kamp

A dissertation submitted in partial fulfillment of

The requirements for the degree of

Doctor of Philosophy

(Chemistry)

At the

UNIVERSITY OF WISCONSIN-MADISON

2022

Date of final oral examination: 08/08/2022

The dissertation is approved by the following members of the Final Oral Committee:

Daniel C. Fredrickson, Professor, Chemistry, Inorganic Path

Kyoung-Shin Choi, Professor, Chemistry, Materials Path

Song Jin, Professor, Chemistry, Materials Path

Yang Yang, Assistant Professor, Chemistry, Physical Path

Intermetallics and the FAST Principle: Making, Analyzing, Calculating, and Understanding Structural Transitions

By: Kendall Kamp

Advisor: Daniel C. Fredrickson

Preface.

I come from a long line of scientists. In fact, I am not even the first in my family to make a career out of inorganic chemistry—my great-grandfather was an inorganic chemist who worked for Technicolor making dyes and pigments. Since then, my family has had all sorts of scientists: nurses, a radiologist, a dentist, a herpetologist, a microbiologist, a physician assistant, an environmental scientist, a rocket scientist, an accountant (still STEM), and even a budding computer scientist. Even with all these scientific minds in my family, our different specialties still create gaps in the knowledge from person to person— and some of the fields of study are a bit more niche than others, which only widens these gaps. It is for this reason I am writing this chapter: to give my family (and also my lovely STEM friends) an easily digestible way to learn about my research. Communicating research to the public is an often overlooked, but vitally important, part of the scientific process, for there is no use for new scientific findings and technology if they only ever stay in the lab. For helping my research leave the lab, I want to thank the Wisconsin Initiative for Science Literacy (WISL) and all those working behind the scenes to support researchers like me in spreading their hard work and scientific findings to the public—who, after all, fund this research through tax dollars and who spur the need for bigger and better technologies.

Throughout this chapter, I hope I convey the passion I have for my science, and how important this work is to me, as well as in the development of future technologies that I know my family and friends will someday use. I am honored to continue on my family's legacy in the sciences and dedicate this chapter to them, the people that have supported my love and interest in all forms of science since I was a little girl.

Introduction.

You probably don't think much about what elements and materials make up the things you see and touch every day, but if you do stop and take a moment to do so, you might be surprised how interesting these materials are. Some of these materials fall into categories you can easily recognize, like plastics, ceramics, minerals, and so forth, but there are also some types of materials that you probably have never heard of, such as intermetallics, metallic glasses, and alloys. My research focuses on intermetallics, a type of material made up only of metallic elements (such as aluminum, titanium, platinum, etc.).

The need to study intermetallics is increasing, as the needs for greener energy and technology grow. Intermetallics have many applications in improving energy efficiency and technology as superconductors (a material that resists electrical current),[1,2] permanent magnets (a very strong type of magnet),[3,4] catalysts (a material that makes a chemical reaction occur faster),[5,6] thermoelectrics (a material that converts heat to electricity),[7-9] and more (Figure 1), which are applications the world needs to focus on with the growing demands of energy and technology. And we see the application of intermetallic materials all the time, in medicine, where superconductors help power MRI machines; in aviation, where high heat resistant materials keep jet engines from overheating; and in computers, as permanent magnets are used in data storage.
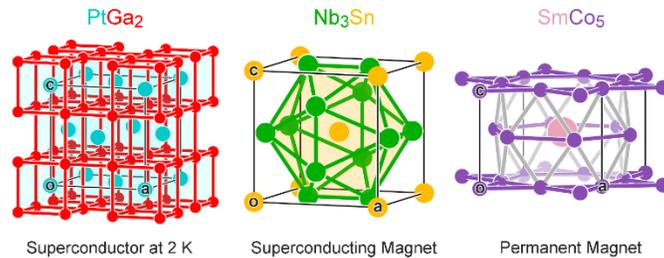
Figure 1. Applications of intermetallic materials. From left to right: $PtGa_2$ (pronounced platinum gallium two) is a superconductor, Nb_3Ge (niobium three germanium) is a high temperature superconducting magnet, and $SmCo_5$ (samarium cobalt five) is a permanent magnet used in MRI machines.

The need to study intermetallics and find all these applications is impeded by how complex intermetallics are. On top of the many combinations of metallic elements that can make an intermetallic, there are also hundreds of structures an intermetallic can form, some having thousands of atoms in them. With so many combinations of elements and so many structures they can form, it makes it hard to see the metals and know what ratio they will form in and what that structure will look like—and even harder to say that this compound will have a certain property.

A major push in modern materials science research is in connecting the structure of a material with its properties, and my research works on part of this connection. My research in the Fredrickson group focuses on the fundamentals of why a compound forms in the structure it does. We study this through a combination of experiments and theoretical analysis. The aim of this chapter is to walk readers through the major steps of a project: making the intermetallic, analyzing the structure of the synthesized crystals, calculating intrinsic features of the compound such as the role of the size of the atoms and the number of electrons, and finally, putting all these pieces together to understand why this compound forms.

Making.

In the Fredrickson Group, we make our intermetallics through solid state synthesis. This means that all of our reactants (the starting materials for our chemical reactions) are solids—which goes against the classical thinking of chemistry as mixing liquids in beakers and flasks. In the next few paragraphs, I will explain the general steps for each of our solid state synthesis.

All of our syntheses start in a glove box. A glove box is just that, a box that has two gloves built into one side of it, you can then put your fingers into the gloves outside the box and push your whole arms through them, allowing your arms and hands to be completely inside the box without having to open the box at all. This is important because the box is full of a different atmosphere than what is outside it, this allows us to work with materials that would decompose in air or react with it. The glove boxes in our labs are full of either Argon (Ar) or Nitrogen (N_2), what we call inert—or unreactive—atmospheres.

Inside one of our glove boxes we keep all of our metals. Many of the metals are powders, looking a lot like gray flour, some others come in small, shaved pieces, and still others come in large chunks that we shave down ourselves. We take the metal powders or small pieces we need and weigh them out on a balance and mix them together with a mortar and pestle (Step 1. in Figure 2). For some syntheses, just mixing the powders is all that is needed, and the sample can move onto the sealing step (but we will get to that in a bit). The next step in many syntheses though, is to press the powders into a pellet (Step 2. in Figure 2). This is done with a machine aptly called the pellet press. The powders to be pressed are placed in a cylindrical vessel and then the pellet press pushes a pin through the cylinder until the sample is placed under pressure of 5,000 lb—about the weight of an adult rhinoceros. The pressed pellet then just pops out of the cylindrical tube and is ready for the next step.

A pressed pellet is then ready to be arc melted (Step 3. in Figure 2). The arc melter is also located in an Argon glove box and heats samples up very hot (~3,000 °F) by taking an electric arc (an electric arc is where there is so much electricity in the air that you can see it, and the electricity moves from where it is generated to a target; lightning is an electric arc, with the sky generating the electricity and the target hopefully being a lightning rod) and placing it directly on the sample. We need to do this in many samples to get them to react. Putting two solids together often doesn't do much (think putting flour and sugar together without putting it in the oven) but putting liquids together or a liquid and a solid together is much more likely to cause a reaction. The metals we use have really high melting points and need the energy from the electric arc to get them to melt. In our group, we like to think of arc melting as hitting our samples with lightning. Though when we do arc melt our samples to melt them, they re-solidify immediately, so even though we hit them with lightning a few times, they come out of the process as little gray spheres.

The next step is to put the samples in reaction vessels. The vessels we use are fused silica tubes that look just like glass tubes that are melted shut on one end. We can put a couple of different things inside these tubes, the first is just the arc melted pellet, we can also put in a pellet that we did not arc melt but just pressed, as well as other smaller containers we call crucibles (Step 4. in Figure 2) The crucibles are made either out of alumina, niobium metal, or stainless steel. We can put the mixed powders from the glove box directly into these crucibles—we do not put the powders just in the tube, as the metal powder can react with the tube and then a product we might not want will be made. The crucibles are loaded with the sample inside the glove box. The crucibles or pellets are then placed inside a fused silica tube and the tube is attached to a vacuum line. The vacuum line removes all of the argon from the tube and creates a

gas-less, vacuum environment within the tube. This environment helps to reduce any unwanted side-reactions that might occur with our samples. Next the tubes are sealed with a flame that melts the side of the tube attached to the vacuum, sealing the tube shut with its vacuum environment. The flame comes from a blow torch of mixed oxygen and natural gas that creates a flame hot enough to melt the tubes. Once sealed, we have our samples in a complete and enclosed vacuum environment and they are ready for the furnaces.

The furnaces we have in our lab are called muffle furnaces and look and are used much like the oven in your kitchen (Step 5. in Figure 2). The muffle furnaces have a door that opens into a chamber that will heat the sample and a control pad that allows us to set the temperature of the furnace and how long the furnace will stay at that temperature. The difference is that our furnaces are a lot hotter than your oven at home, most of our furnaces go up to 1100 °C. We place our samples in the furnace when they are cool and then program them to go up to a certain temperature and hold the sample at this temperature for a while. The program is often two steps, the first—usually hotter and shorter—part is the reaction, where we get our samples hot enough that the metals start to move around and react, the second step is then called the anneal, which is usually much longer (on the order of days or weeks) and a bit cooler (~800 °C) and allows the desired products to grow. Using the furnaces is a lot like baking a cake: you need to heat your ingredients (metal powders or pellets) up to a temperature that they will react with each other to form the cake (reaction), and then you have to leave the oven at this temperature long enough to complete the baking of the cake (annealing), so it comes out right.
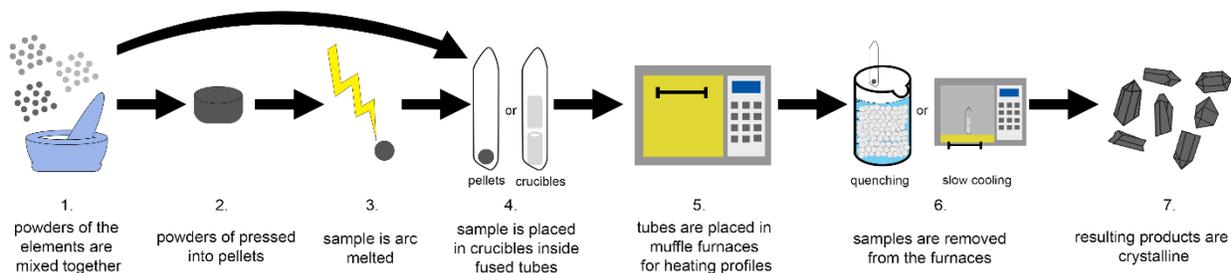
Figure 2. Solid State Syntheses. 1. metal powders are mixed together inside a glove box; 2. the powders are pressed into small pellets; 3. the pellets are arc melted to get the metals to react with each other; 4. the samples are placed inside a crucible inside a tube or directly into a tube and sealed shut under vacuum; 5. samples are placed in a muffle furnace to react and grow product; 6. after the reaction, the samples are removed from the furnaces by either quenching into ice water or slow cooling; 7. final products are crystalline.

We can get the samples out of the furnace in a couple of ways. They are called slow cooling and quenching (Step 6. in Figure 2). Slow cooling is programming the furnace to slowly decrease the temperature of the furnace from the annealing temperature to room temperature. Once at room temperature, the samples can just be taken right out of the furnace. Quenching is when we take the reaction from the hot environment of the furnace and immediately put it into ice water. This is done by taking a very long set of tongs and taking the tube out of the furnace and placing it into a beaker of ice water. We do this to suddenly stop the reaction going on within the sample. Stopping the reaction very quickly allows us to 'trap' a product that is only stable at high temperatures and view and analyze it at room temperature.

We have now completed our synthesis! Our intermetallic samples are crystalline, this means that the product is solid with the atoms organized in a 3-dimensional, repeating pattern. These crystals are often dark gray and shiny and very small and can then be placed in a petri dish for further analysis.

Analyzing.

Once we have our crystalline products, we need to investigate them on the atomic level. This will tell us about the arrangements and identities of the atoms within our crystals—which is very important information for determining what the compound we made is and why it formed. In the Fredrickson group, we do this through three primary ways:

1. Powder X-ray Diffraction

2. Single Crystal X-ray Diffraction

3. Electron Microscopy

Let's begin with powder X-ray diffraction (PXRD). In this type of analysis, we can learn how many different compounds are present in our experimental sample and what they are. This analysis is useful as it tells us if we made the compound we want or not, it will also give us information on how much of each compound made there is relative to each other, we can think of this as a percentage, what percent of the sample is compound 1, and what percent of the sample is compound 2 and so forth. Knowing this information can help us design future experiments.

To do PXRD, you first must have a powder. In this context, a powder sample is a crystalline material broken up and ground down into many tiny crystals. These hundreds or thousands of tiny crystals will then be oriented in just as many directions. When we focus X-rays on all of these different crystals with all of their different orientations, the X-rays will diffract (diffraction is bouncing off a material at a different angle than it originally hit the material) and hit a detector rotating around an axis called two theta (2θ). The data hits the detector in a pattern of rings. Each ring corresponds to a different type of spacing between atoms in a structure, and these are characteristic of a specific atomic composition in a specific

atomic packing arrangement. The data from the detector is transformed into what is called a powder pattern (shown on the far-right side of Figure 3), which is plotted as the spacing between atoms on one axis, and the frequency of that spacing as intensity on the y axis.
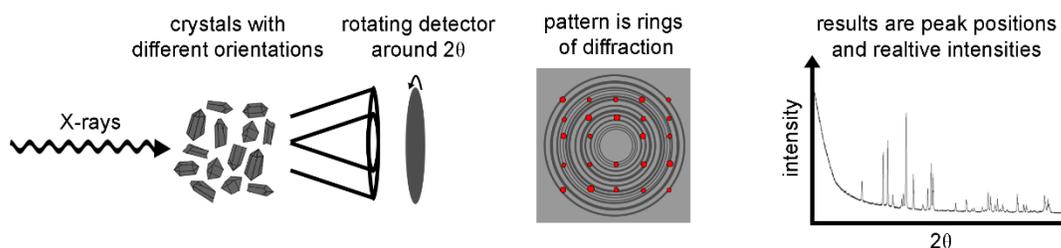

Figure 3. Powder X-ray Diffraction uses many crystals with random orientations to produce diffraction patterns of concentric circles which can then be transformed into a plot of spacings between the atoms (depicted as 2θ) and their intensity which tells us which phases are present in the sample and in what relative amounts.

Since the powder pattern of each compound is very unique, we can then match different patterns known from other phases to our experimental pattern to find out what phases (a phase is a distinct form of a material, in this case, a phase is the crystals of a specific compound) are present in our sample and in what ratios. Matching in this way can also tell us if what is in our sample is a new phase and has not been characterized yet. After we know what phases are present in our sample, we can move on to solving the structure of these phases through single crystal diffraction experiments.

The purpose of a single crystal X-ray diffraction experiment is to get the atomic arrangements (where each atom is located within the crystal) of a compound. Knowing the atomic arrangement of the atoms allows us to determine the details of the structure of a compound, where each atom is, what bonds are in the compound, the exact elemental make   up, and many more details that help us understand what we made and how it relates to other structures. The amount of information we get from a tiny crystal (the biggest are only about ½ a millimeter big) is astounding. In the next few paragraphs, I will tell you

how we get all this information out of a crystal and how we interpret it to solve the structure of the compound.

The first step in a single crystal X-ray diffraction experiment is to find a crystal—which is not always an easy task. The sample is placed in a petri dish and then we look at it under a microscope (Figure 4). While most of the sample can look shiny and metallic, not all of the particles make good candidates for single crystal diffraction experiments. In order to get high quality data of a crystal, the crystal must meet a few criteria: 1. that it be a single crystal, meaning it has only grown in one orientation (think a tree without any branches), 2. it must be well faceted, meaning it must have very clean edges and distinct faces (similar to a cube, where each face is distinct from all the others and the faces are separated by crisp angles), and, 3. that the crystal is the right size for the x-ray beam of the experiment—this will change with the instrument used to collect the data.
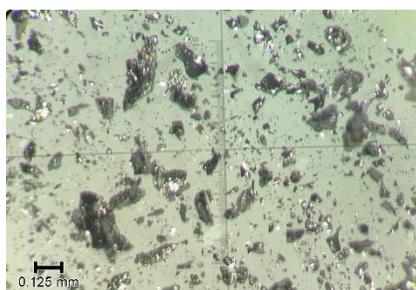

Figure 4. Crystals of a Sc$_2$Ru (scandium two ruthenium) phase synthesized in the lab. The crystals are all nice and metallic looking with sharp faces and angles, the size of the crystal is selected based on the instrument used to take measurements.

Once a good candidate is identified, the crystal is then mounted on the top of a thin glass fiber. This fiber then fits into a pin that fits onto an attachment that fits in the instrument that will collect the data: called the diffractometer. The crystal is then aligned with the x-ray beam so that the x-rays pass right through the crystal. When the x-rays hit the crystal, they will diffract off the atoms within it and exit the

crystal at a different angle than they hit the crystal with. The diffracted x-rays then hit a detector. The

pattern produced by the diffracted x-rays is then a series of spots that form a lattice and the intensity of the

diffraction at the points in the lattice tells of how many diffracted x-rays hit this point.

The data from the detector is first used to determine the space group of the unit cell (smallest

repeating unit) of the crystal. The space group is defined by the symmetry of the crystal. Symmetry is one

of the most important parts of crystallography. Symmetry is all around us and we see it every day,

symmetry elements such as mirror planes (Figure 5a), translations (Figure 5b), rotations (Figure 5c), and

inversion centers (Figure 5d), to name a few, determine where each of the atoms are in the unit cell.
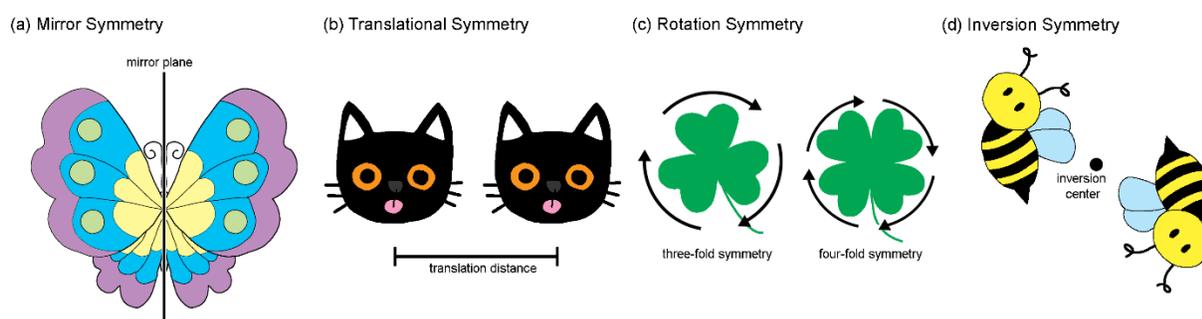

Figure 5. Symmetry elements that can be found in the unit cells of crystals.

Next, the electron density of the crystal has to be solved for. Electron density is the probability of

finding an atom in a certain location and is used to determine what element is in which location. The more

electron density at a spot the heavier the atom is that occupies that site. Once all of the electron density in

the structure has been assigned to an element, we have a completed structural solution. We can think of

the final structural solution like putting the last piece of a puzzle together, where each puzzle piece is an

atom that assembles in a way that gives a clear image of the whole structure. Sometimes these solutions

are quite complicated, with more than one element at one site, splitting the occupation of that site between

the two types of atoms. Other times, there is disorder in how the atoms are arranged and the structure

11

must be described in very large units to describe the pattern of atoms present. This means our puzzle is often very large with thousands of pieces and it is really hard to find the overall image the puzzle represents. Despite the complexities of solving a single crystal's structure, the ultimate results of single crystal diffraction experiments are finding out the precise atomic arrangements and stoichiometry (ratios of one element to another, such as $TiSi_2$ is a stoichiometry with one titanium atom for every two silicon atoms) of the compound we synthesized.
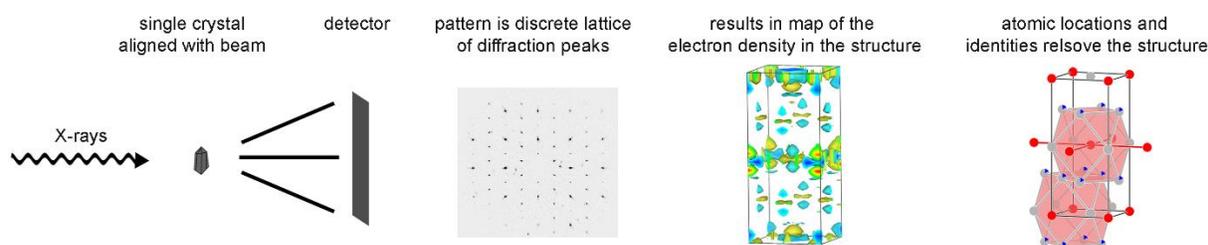

Figure 6. Single crystal X-ray diffraction begins with aligning a single crystal with the x-ray beam, then the x-rays hit and diffract off the crystal to create the spots of a diffraction pattern. From the diffraction pattern, the symmetry, and sites for atomic sites of the compound are found, and elements are assigned to each site through an analysis of the electron density. The result is a structure with known atomic positions and atomic identities.

The last way we characterize our synthetic compounds is through two forms of electron microscopy: energy dispersive X-ray spectroscopy (EDS) and backscattered electron analysis. While these are types of microscopy, we don't use the kind of microscope that most comes to mind (the one you look through to see very small things), instead, an electron microscope shoots a beam of high powered electrons at a sample, when this happens the sample lets off different kinds of energy that can then be looked at by different detectors to tell us different things about the sample. To do accurate electron microscopy, your sample must first be polished to a nice flat surface. We do this by placing pieces of the sample in epoxy and then polishing this surface flat. Once we have our nice flat sample, we can put it in the microscope and shoot an electron beam at it.

One way to look at the sample in the electron microscope is to look at the electrons that backscatter off the sample. Backscattered electrons interact with the sample in that more electrons are backscattered off—or bounce off—of heavy elements/compounds, and the more electrons scattered, the more intense the signal. This means that in a backscattered image, the different phases present in a sample will appear as different shades of gray on the image, with the heaviest phase (comprising the heaviest elements) having the lightest color. These backscattered images are then able to tell us how many phases are present in the sample. A backscattered image is shown on the left side of Figure 7. In this image, the black areas are the epoxy surrounding the sample, the light gray/white is a matrix Sn (tin), and the medium gray is the compound $ZrAl_{2.6}Sn_{0.4}$ (Zirconium Aluminum 2.6, Tin 0.4), which is of intermediate weights compared to the light epoxy and the heavy Sn.
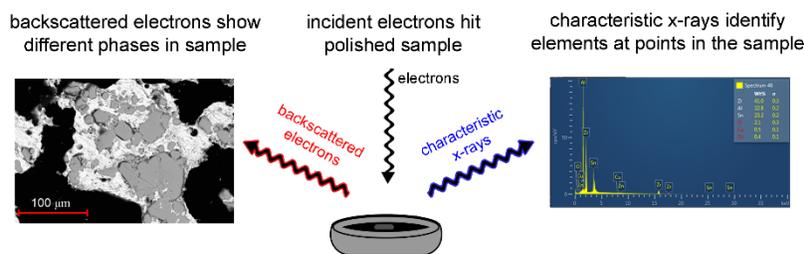

Figure 7. Electron microscopy can tell us how many phases are present and how heavy they are relative to one another by looking at the backscattered electrons and also what the precise composition of the phases are by looking at the characteristic x-ray after they interact with the sample.

Another way we can use electron microscopy to look at our sample is to equip it with a detector that can interpret the characteristic X-rays in a method called energy dispersive X-ray spectroscopy (EDS). In EDS, when a high energy electron beam hits a sample, it interacts with the atoms within, exciting the electrons on the atoms. When the atomic electrons fall back from their excited state, they release energy in the form of X-rays that are of a characteristic energy pertaining to that specific excitation in that atom type. This is fairly similar to how we react when we get excited, first, we get excited and let

13

out an excited scream that calms us down, but the scream is in our own, characteristic voice. The scream in your own voice is then just like the characteristic X-rays let off by an atom. Looking at these characteristic X-rays allows us to know exactly what atoms are present in the sample and in what relative amounts to one another. In this way, EDS provides very accurate data on the composition of a phase.

At this point in the research, we have made an intermetallic compound and then analyzed its physical structure through a variety of methods. However, making a phase is only half the work, the other half is learning about why this phase is stable and formed in the crystal structure it did. To look at why a phase forms, we have to turn to computational and theoretical work, which we will explore next.

Computing.

In the Fredrickson Group, we use a lot of theoretical tools to look at our structures. These tools give us insights into how the atoms pack together, how the elements bond with each other, and how many electrons are in the structure. These features of a structure give us insight into the tensions of a structure and ideas on how to soothe these tensions in a structure. Also, from these computations, we can detect trends and connect structures to one another.

We will start by looking at the tensions that can arise in a structure through its packing of atoms, which depends heavily on the size of the atoms. We can think of atomic size and packing in terms of how the size of two sports balls compare to one another and how they fit together in a box. A soccer ball is much bigger than a baseball, and a golf ball is even smaller than that. If we take a box and pack soccer balls and baseballs in it in a way that maximizes the space available in the box, we will get a particular arrangement of soccer balls and baseballs that best accommodates the relative sizes of the two balls. If we

14

repeat this with soccer balls and golf balls, we will get a different arrangement that will best accommodate the relative sizes of these balls. A crystal structure works this same way: arranging atoms in a way that is efficient in terms of the radius of its atoms, where the radius is a measure of the size of that atom. Figure 8 shows a schematic of how atoms can be put under stress when they pack together: each type of atom and atom pair has a length they would like to be away from one another, then, when we mix the types of atoms and interactions together, we must get some sort of compromise between all the ideal lengths. Despite these compromises, the atoms feel strained, some of them will feel that a certain length is overly long and some lengths overly short. The Fredrickson group has found a way to look at these strains, in a method we call Chemical Pressure (CP).[10-12]
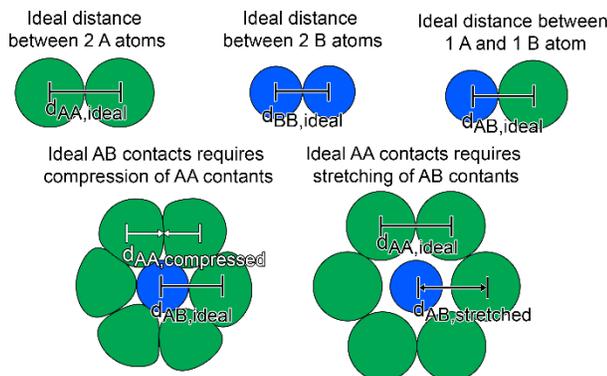

Figure 8. Pairs of atoms prefer an ideal contact distance between one another, but when we combine many of these pairs, compromises have to be made which leads to atomic packing strains, such as compressed contact lengths and stretched contact lengths.

A CP scheme is shown in Figure 9. The chemical pressure of a structure is calculated from looking at the energies of a structure as we increase or decrease its volume, then mapping the pressures onto the atoms within a structure. The resulting CP schemes have two types of lobes: black, which represent negative pressure or a desire to make that contact shorter (like a black hole sucking in), and white, which represent positive pressure, showing the want of that contact to lengthen (like a white star exploding).

From these schemes, we can determine what ways an atom will want to move as it transitions to another structure. They also tell us about what kind of element might be best suited in a certain environment, such as is this current environment too small for this atom? Or too large?
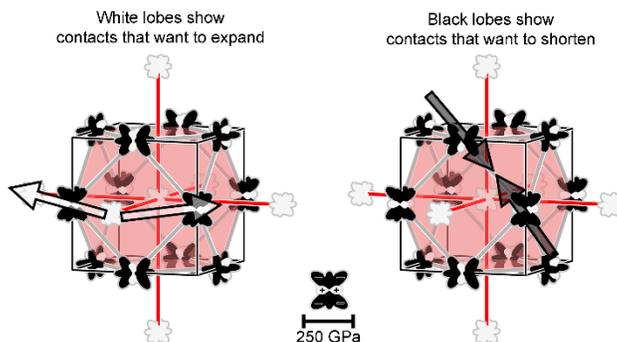

Figure 9. A chemical pressure scheme shows contacts that are overly short and want to expand (shown as white lobes) and overly long contacts that want to get shorter (shown by black lobes).

In addition to atomic size effect (the strains a compound feels due to the arrangement of its atoms and their sizes relative to one another), we also look at the electron concentration. The number of electrons in a structure can be thought of in terms of a glass of water. Here, the water is the electrons, and the glass is a structure; we want to put a certain amount of water into a glass that holds just that amount of water, no more no less. Overfilling the glass of water means   we have too many electrons in the structure, and hints that the structure might not be stable (as spilled water can also be thought of as not ideal). Underfilling the glass is just as bad, think of this as you need the whole glass of water to quench your thirst, if the glass isn't full to start with, you will end up still wanting more water after you drink what was in the glass.

We look at the electronics of a compound through its electronic structure, and specifically a density of states (DOS) distribution. The Fermi Energy (E_F) tells us how many electrons are in the structure (analogous to the amount of water in the glass), everything below the E_F is a filled state and

16

everything above the E_F is an unfilled state. A gap or valley in the distribution is called a pseudogap and represents the ideal number of electrons in the system (the top of the glass). We use DOS distributions to determine if a structure wants more or less electrons, which in turn tells us if we can make the compound more stable by adding electrons or removing electrons.[13] We can add electrons by substituting in an element with more electrons or breaking a bond, and we can remove electrons by forming bonds or substituting in an element with fewer electrons.
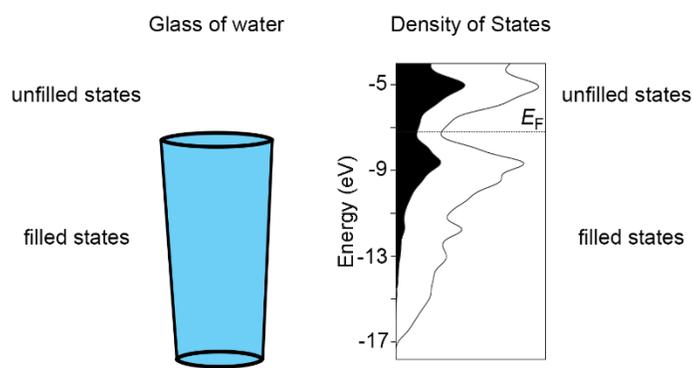

Figure 10. Analogy of a glass of water and the number of electrons in a structure. The ideal number of electrons is like having a perfectly full glass of water and corresponds to the E_F of a structure lying in a valley in the DOS curve.

Understanding.

So far, we have learned a lot about the intermetallic system we are studying: we have synthesized an intermetallic, solved its atomic arrangement, and analyzed its atomic packing and electronic factors. While each of these tells us a lot about the material, to fully understand why this compound crystallizes in the structure that it does, we must add up the results of the experiments and theoretical computations to see the big picture.

Many of the compounds we look at are quite complex—having many atoms in them, atomic mixing at different sites, and some not even describable in 3-dimensions—so it is useful to start the analysis of these complex structures by looking at simpler, but similar, parent structures. We can then take a simple parent structure and look at just a few key elements and determine what makes this structure transform into the more complex structure in what we call a structural transition. We focus on the key factors outlined by Hume-Rothery in the early 1900s, who theorized that the stability of an intermetallic structure is determined by the sizes of the atoms (radius ratio rules), how many electrons are in the structure (valence electron concentration) and how much charge each atom has (electronegativities of the atoms).[14,15]
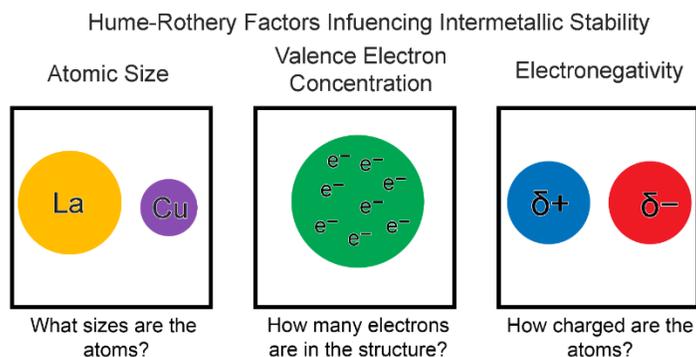

Figure 11. Hume-Rothery's factors for influencing the stability of an intermetallic structure. These factors can be viewed at the size of the atoms, the number of electrons in the structure, and how charged the atoms are.

We can then break a structural transition down to just one or two of these factors through a lens called the Frustrated and Allowed Structural Transitions (FAST) Principle.[16,17] In the FAST principle, we take two of our factors and think of them as agreeing or disagreeing on how the parent structure will transition; this can be through disagreeing on the way to get to a certain structure or disagreeing on what the complex structure looks like. When disagreement between the factors occurs, we call this a frustrated

transition, but when the factors agree on a path and final structure, we call it an allowed transition. A frustrated transition is likely to take some energy input and will occur under fewer conditions, as well as potentially not getting the lowest energy structure. An allowed transition will be easy to accomplish, the final structure will be lower in energy than the parent structure and there will be very few obstacles to cross to get to this structure, making it likely to occur more often.

We can think of these transitions like a path of a ball down through a series of hills trying to get to the lowest point, the frustrated transitions will be harder (or impossible) for the ball to roll down, while an allowed transition makes an easy path for the ball to roll down. In Figure 12, Path A shows a frustrated transition, where we have a disagreement on the hills the ball has to roll along: one being uphill, the next being downhill. This combination of downhill then uphill will require the ball to have more energy to get to the endpoint. Path B also shows a frustrated transition, with the first hill the ball comes across being uphill, and the second downhill. It would be very hard for this ball to move along this path without anyone to push it. Path C though, is an allowed transition. Both of the hills the ball comes across are downhill, an analogy to our factors agreeing, and rolling down two hills is easy for a ball, and this path will take it to the absolute bottom of the hill.

To complete our analogy, the ball rolling down the hill is the parent structure, though when the ball gets to the end of the path, it has transitioned into a new structure. The hills themselves are our factors that influence intermetallic stability, and the height of the hill is how much energy it takes to go over it, going downhill is then lower in energy than going uphill. We can call the first hill in each path in Figure 12 the atomic size component and the second the electronic component. The height of the end of the path is then how low in energy the final, transitioned structure is. The lower in energy a structure is, the more

stable it is. In Path A, the atomic size factor is low in energy and the electronic factor is high in energy. In Path B, the atomic size factor is high in energy and the electronic factor is low in energy. Finally, in Path C, both the atomic size and electronic factors are low in energy, leading to a low energy transition. The final structure at the end of Path C is also lower in energy than the end structures in Paths A or B, meaning that not only was Path C the lowest or easiest to move through, but it also found the lowest energy structure (most stable).
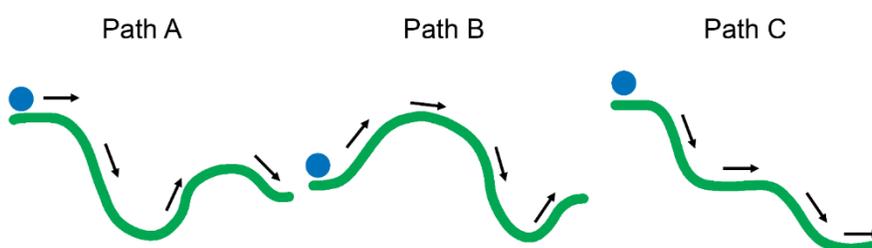

Figure 12. The Frustrated and Allowed Structural Transitions (FAST) principle viewed through the paths a ball can take from one point to another. Having one uphill and one downhill component in the path, like Paths A and B, is like a frustrated transition, and leads to an endpoint that is not the lowest. Having both downhill components like in Path C is an allowed transition and leads to the lowest point out of all the paths. The lowest point is the lowest energy structure, a low energy structure is more stable.

The structure at the end of Path C is the lowest in energy and therefore most likely to be the structure that is experimentally realized in the lab. Comparing the energetics of the electronics and atomic packing of the parent structure to those of the end structure tells us what likely influenced and facilitated the transition from the parent to the synthesized structure—and also how likely this transition is to occur and what conditions it might need to occur under. This is the idea behind the FAST principle: determining how and why a structure transitions through a combination of experimental and theoretical work.

However, while the examples above showed the FAST idea beginning with an experiment, solving a structure, and then looking at it computationally, this is not the only way to look into these transitions.

Another way we in the Fredrickson Group look at transitions is through finding structures, performing computations on them, and then making predictions on what the structure will be before heading into the lab to make it. The ability of the FAST principle to both predict structural transitions before we know about them experimentally, and also take an experimental structure and explain why it transitioned creates a circular path for learning about intermetallics. This enables a complete circle of learning: what we learn from an experiment influences the computations we do, what we learn from computations influences our next experiments and so on and so forth. We like to depict the cycle as an ouroboros—a snake eating its own tail—as it serves as a great example of how we are always hungry to learn more, and we are always positioned to learn more.
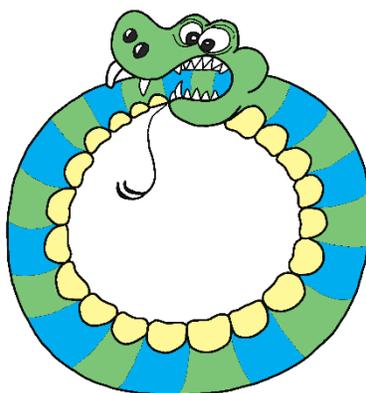

Figure 13. The Ouroboros idea: all learning leads to more learning in an endless cycle.

Conclusions.

The connecting of simple and complex structures together not only helps to create a web that ties structures and their potential properties together, but it has also helped me learn how to look at problems creatively and with a detailed eye. The fundamental work of the Fredrickson Group has taught me that

sometimes the smallest detail from a crystal structure or a computational result can have a huge impact on how we view structural transition. This new view then leads to new questions and ideas that spur on whole new research themes. While the work done here is on the very fundamental side of science, the ideas and methodologies explored here have endless potential to impact other fields of science: looking at the structure of anything, be it a cell, a machine, a molecule, even a community, and thinking about why this structure is the one formed, and what this structure means in terms of its function, is truly a primary goal of science.

Working on the fundamental side of chemistry often makes it hard to summarize the significance of my work—some can say they are actively making medicines to cure diseases, I can't. What I can say is that Rome wasn't built in a day. It was built brick by brick until something amazing came about. My research is those bricks, pieces of a giant puzzle that will one day all tie together and lead to the production of newer, greener, safer technologies that will change the world as we know it. Each brick laid is one more connection between the structure of a material and its properties and is one step closer to being able to design materials with idealized properties with a snap of the finger. While it would be nice to just snap my fingers now, I am happy to help lay the foundation brick by brick.

Beyond the science, my advisor Danny has taught me how important communicating science is—even to other scientists in our field. From this emphasis on communication, I have learned so much about how to think about huge, intricate structures in easily digestible pieces and show these wild structures clearly in figures, whether in a journal article, poster presentation, or a slide show presentation. While challenging, the communication skills I have learned here at UW will be lifelong skills that will benefit my research for years to come.

I hope that through this chapter you have enjoyed learning about intermetallics and all the ways we can investigate and learn about them as much as I have enjoyed the last 5 years doing the same. From here, I am going to stay in the solid state chemistry field (couldn't leave it if I tried), and will continue to work on the fundamental side of structure-property relationships with a postdoctoral fellowship at Northwestern University with Ken Poeppelmeier. There, I will be looking at how the symmetry and packing of molecules in a crystal influences its properties, more specifically, its optical properties.

References.

(1) Xie, W.; Luo, H.; Baroudi, K.; Krizan, J. W.; Phelan, B. F.; Cava, R. J. Fragment-based design of NbRuB as a new metal-rich boride superconductor, *Chem. Mater.* **2015**, *27*, 1149-1152.

(2) Gui, X.; Cava, R. J. LaIr$_3$Ga$_2$: A Superconductor Based on a Kagome Lattice of Ir, *Chem. Mater.* **2022**, *34*, 2824-2832.

(3) Das, B.; Choudhary, R.; Skomski, R.; Balasubramanian, B.; Pathak, A. K.; Paudyal, D.; Sellmyer, D. J. Anisotropy and orbital moment in Sm-Co permanent magnets, *Phys. Rev. B* **2019**, *100*.

(4) Chen, H.; Yang, X.; Sun, L.; Yu, P.; Zhang, X.; Luo, L. Effects of Ag on the magnetic and mechanical properties of sintered NdFeB permanent magnets, *J. Magn. Magn. Mater.* **2019**, *485*, 49-53.

(5) Zhou, C.; Fang, Z. Z.; Ren, C.; Li, J.; Lu, J. Effect of Ti Intermetallic Catalysts on Hydrogen Storage Properties of Magnesium Hydride, *J. Phys. Chem. C.* **2013**, *117*, 12973-12980.

(6) Ye, T.-N.; Lu, Y.; Kobayashi, Y.; Li, J.; Park, S.-W.; Sasase, M.; Kitano, M.; Hosono, H. Efficient Ammonia Synthesis over Phase-Separated Nickel-Based Intermetallic Catalysts, *J. Phys. Chem. C.* **2020**.

(7) Zhang, J.; Song, L.; Sist, M.; Tolborg, K.; Iversen, B. B. Chemical bonding origin of the unexpected isotropic physical properties in thermoelectric Mg$_3$Sb$_2$ and related materials, *Nat. Commun.* **2018**, *9*, 1-10.

(8) Qin, F.; Nikolaev, S. A.; Suwardi, A.; Wood, M.; Zhu, Y.; Tan, X.; Aydemir, U.; Ren, Y.; Yan, Q.; Hu, L.; Snyder, G. J. Crystal Structure and Atomic Vacancy Optimized Thermoelectric Properties in Gadolinium Selenides, *Chem. Mater.* **2020**, *32*, 10130-10139.

(9) Yamada, T.; Yamane, H. Crystal structure and thermoelectric properties of β-MoSi$_2$, *Intermetallics* **2011**, *19*, 908-912.

(10) Engelkemier, J.; Fredrickson, D. C. Chemical Pressure Schemes for the Prediction of Soft Phonon Modes: A Chemist's Guide to the Vibrations of Solid State Materials, *Chem. Mater.* **2016**, *28*, 3171-3183.

(11) Fredrickson, D. C. DFT-Chemical Pressure Analysis: Visualizing the Role of Atomic Size in Shaping the Structures of Inorganic Materials, *J. Am. Chem. Soc.* **2012**, *134*, 5991-5999.

(12) Hilleke, K. P.; Fredrickson, D. C. Discerning Chemical Pressure amidst Weak Potentials: Vibrational Modes and Dumbbell/Atom Substitution in Intermetallic Aluminides, *J. Phys. Chem. A* **2018**, *122*, 8412-8426.

(13) Yannello, V. J.; Fredrickson, D. C. Generality of the 18-*n* Rule: Intermetallic Structural Chemistry Explained through Isolobal Analogies to Transition Metal Complexes, *Inorg. Chem.* **2015**, *54*, 11385-11398.

(14) Hume-Rothery, W. Researches on the nature, properties, and conditions of formation of intermetallic compounds, with special reference to certain compounds of tin I-V, *J. Inst. Met.* **1926**, 55.

(15) Hume-Rothery, W.; Raynor, G. V. *The structure of metals and alloys*; Institute of metals, 1936.

(16) Mitchell Warden, H. E.; Lee, S. B.; Fredrickson, D. C. Frustrated and Allowed Structural Transitions at the Limits of the BaAl$_4$ Type: The (3+2)D Modulated Structure of Dy(Cu$_{0.18}$Ga$_{0.82}$)$_{3.71}$, *Inorg. Chem.* **2020**, *59*, 10208-10222.

(17) Mitchell Warden, H. E.; Fredrickson, D. C. Frustrated and Allowed Structural Transitions: The Theory-Guided Discovery of the Modulated Structure of IrSi, *J. Am. Chem. Soc.* **2019**, *141*, 19424-19435.