Making Ce_2Ge_2Mg: Technical Note

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1 Introduction

A quantum spin liquid is a quantum ground state of magnetic moments where there is no long range magnetic order but rather a superposition of every possible singlet states creating a disordered ground state. This disordered ground state then leads to interesting unconventional excited states. [2, 5] Quantum spin liquids have been a recent area of interest because of how this superposition of states can be used in quantum information. These quantum Spin liquids have been well explored in insulating materials, but have yet to be fully explored in metals because the conductivity of metals often gives rise to a preferred magnetic order due to longer ranged magnetic interactions, as opposed to the more interesting quantum spin liquid state. [2, 5] Previous studies have observed these unconventional magnetic states in the material Yb2Pt2Pb, so in attempt to find these in another material we plan to grow samples of Ce_2Ge_2Mg. [4, 1] We've chosen Ce_2Ge_2Mg as a good candidate to again find these unconventional excited states, because it not only is of the same general form as Yb2Pt2Pb, 2 parts rare earth metal, 2 parts transition metal, and 1 part main group element, but it also shares the same crystal structure, similar magnetic properties, and similar discontinuities in the derivatives of magnetic susceptibility and magnetization. [3]

So, the goal of our project will be to make these crystals of Ce_2Ge_2Mg, to allow for better study and eventual use of quantum spin liquids in metals

2 Flux Method and Procedure

To make our sample we will be using the flux method. Generally the Flux Method works by dissolving particularly proportioned amounts of the elements of the desired material in a solvent, called the flux. The elements are then given time to crystallize into the desired compound as they cool but taken out before they can form a different compound. To find the necessary atomic ratios of elements and manner of heating, we analyze the binary phase diagrams of each pair of elements, as we can see in Fig. 1. Fortunately, Previous groups, overseen by M.S. Kim, analyzed the binary phase diagrams for Ce_2Ge_2Mg and performed multiple trials to find the necessary

atomic proportions of elements, and heating process for making Ce_2Ge_2Mg. They also found that the necessary flux solvent to make Ce_2Ge_2Mg an excess of magnesium itself. Unfortunately, magnesium has a very high vapour pressure thus making it difficult to keep as a liquid to act as solvent for the flux process to take place. To address this, the sample must be contained in a strong material to hold the pressure and liquefy the magnesium. In fact, previous groups in Dr. Gannon's lab have successfully grown Ce_2Ge_2Mg by sealing the measured out Ce Ge Mg in expensive tantalum tubing. In order to efficiently make larger quantities of the crystal, our sample will be sealed in a tube of niobium, a similar strong metal much cheaper than tantalum.

2.1 Sample Preparation

To begin our actual growth of Ce_2Ge_2Mg, we had to first prepare the containers it is to be sealed in: first the niobium tube to hold the pressure of the magnesium, and then a quartz tube filled with argon so that the niobium is unable to react with any elements in the air while in the furnace. We began by cutting a piece of niobium tubing to a rough length of 4-5 in. and closed one end with a simple clamp that kept the shape of the tube for the sample. Since this clamped closed end is still far from airtight, we then had to seal it by arc-melting the clamped end. Generally, the arcmelter works by shorting a current from the pointed tip of a rod called the stinger to s copper plate below creating a very hot arc of current that can weld the clamped niobium giving us an airtight seal. From here, using atomic proportions 8.54:1.06:90.82 of Ce:Ge:Mg, we did some simple calculations to find the necessary mass for each element. We started by measuring out about 1g of Magnesium, then used the actual weighed out mass of magnesium to calculate and measure the required amounts of the other two elements. After measuring out the appropriate amounts of each element in to a crucible, we placed the crucible into the niobium tube then clamped and arcmelted the other end being careful to to keep the sample as upright as possible so that the crucible did not spill. Since the process of arcmelting takes place in a controlled argon atmosphere, we were able to create an essentially inert atmosphere of argon within the niobium tube as we sealed this other end of the niobium tube. In theory this process is very straight forward, but in practice we ran into a few issue arcmelting the tube closed. During my initial attempt arcmelting, the glass walls of the vacuum chamber cracked, delaying our process for a couple days, and during my second attempt accidental contract with the niobium cause it to splatter onto the stinger and and blunt the end, making it much more difficult to use. Despite these troubles, we were eventually able to seal two samples and begin our next steps.

After sealing the sample in the niobium tube. We then needed to seal it in a quartz tube with controlled argon atmosphere so that we can insure that there is no reaction between the niobium and anything in the air. The process of making the quartz tubes has two main components: cutting and necking, both of which are

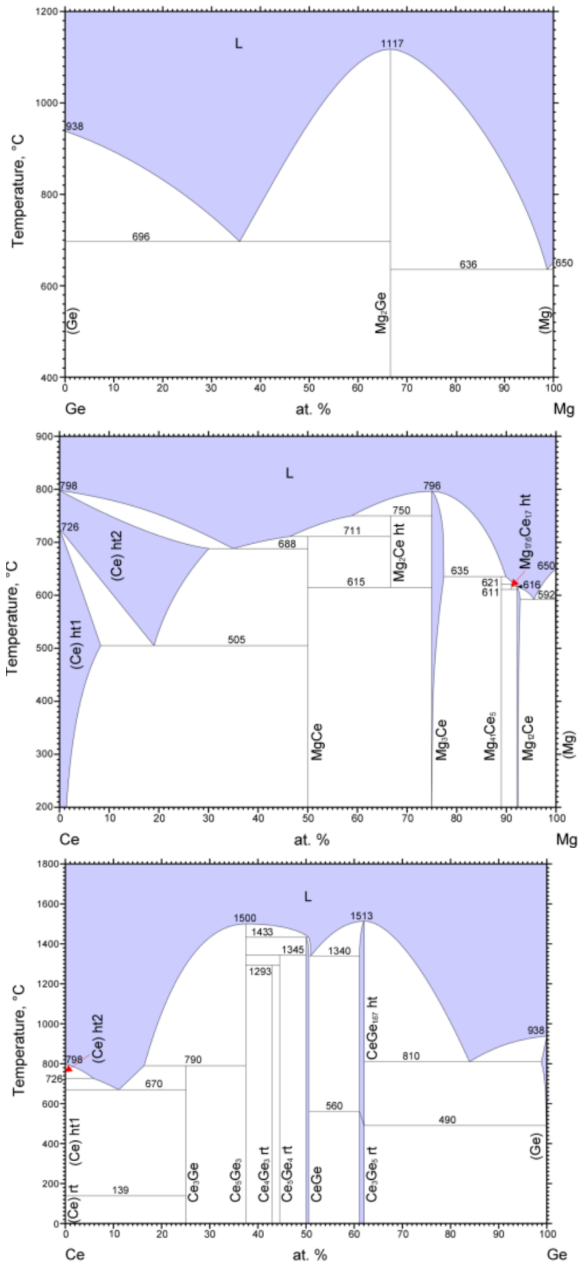


Figure 1: The different binary phase diagram of each combination of cerium germanium and magnesium, top:the binary phase diagram between germanium and magnesium, middle: cerium and magnesium, bottom: cerium and germanium. Previous groups predicted the proper ratio of elements and heating process for making Ce_2Ge_2Mg, by comparing these diagrams and finding achievable temperatures and percentages where all the elements are liquid and do not quickly form binary compounds different from the desired that Ce_2Ge_2Mg. The most precise ratios and temperatures cannot be determined entirely from the diagrams, so,after predicting what could work, these groups performed various trials to find the specific ratios and temperatures that do work.

performed by melting the glass with a hydrogen torch. The goal of cutting is to cut the quartz tube in half while also making sure that both ends of the cut are sealed in the process, creating two tubes that are closed at one end .The necking process occurs after the sample ready to be sealed in the quartz tube and is necessary for us to fill the tube with argon. The goal of necking is to create a long thin section between the side of the tube with the sample in it and the open end so that it can easily be cut while still attached to the system for draining the air and filling the tube with argon. We practiced these processes with small empty tubes, cutting them in half with sealed ends, necking each half, pumping out the atmosphere, refilling with inert argon, and finally cutting the small neck while attached to the vacuum system to seal the new atmosphere inside the tube. Once we were comfortable with the smaller tubes, we started our attempts to seal one of our samples in a larger tube, and were eventually successful.

2.2 Heating Process

After we sealed the sample in both the niobium tube and the quartz tube, it was ready to be put in the furnace. Just as previous groups performed trials and used the phase diagrams pictured in Fig. 1 to find the necessary atomic ratios, they also found the appropriate heating procedure in the same way. Generally our plan for heating the sample to form crystals is to raise the temperature to 1050 C over four hours, let it soak at 1050C for 4 hours, then cool to 750 over 152 hour. Since this was the first heating trial with the sample in the niobium tube, instead of making a whole crystal, it had the purpose of testing the integrity of the niobium tube at the high temperatures and high pressure from magnesium. Because of this, we planned to take out the sample sooner than the 4hr mark. As we were monitoring the furnace with the test sample, we heard small clicking noises. Out of an abundance of caution, we turned off the furnace 40 minutes after it reached 1050° C, let it cool, and opened the furnace once it was around 760 ° C. There were no obvious issues with the sample, and the clicking noises were explained by the convection air currents in the furnace moving the sample tube slightly in the crucible. Since this was our first test trial, we went ahead and freed the sample from the containers, breaking both the quartz and niobium tubes. Upon removal, we found our melted together sample with some interesting indications of a crystalline structure and powder in the niobium tube with interesting red coloring throughout, pictured in Fig. 2.

2.3 EDX Spectroscopy

In order to know if teh niobium contaminated any of the sample, we performed Energy-dispersive X-ray (EDX) Spectroscopy using a scanning electron microscope (SEM) to examine the composition of the heated sample. Since the EDX machine returns the clearest spectrum when scanning a flat surface, we first had to slice our solid sample into flat pieces using a diamond saw. After this we clean the flat

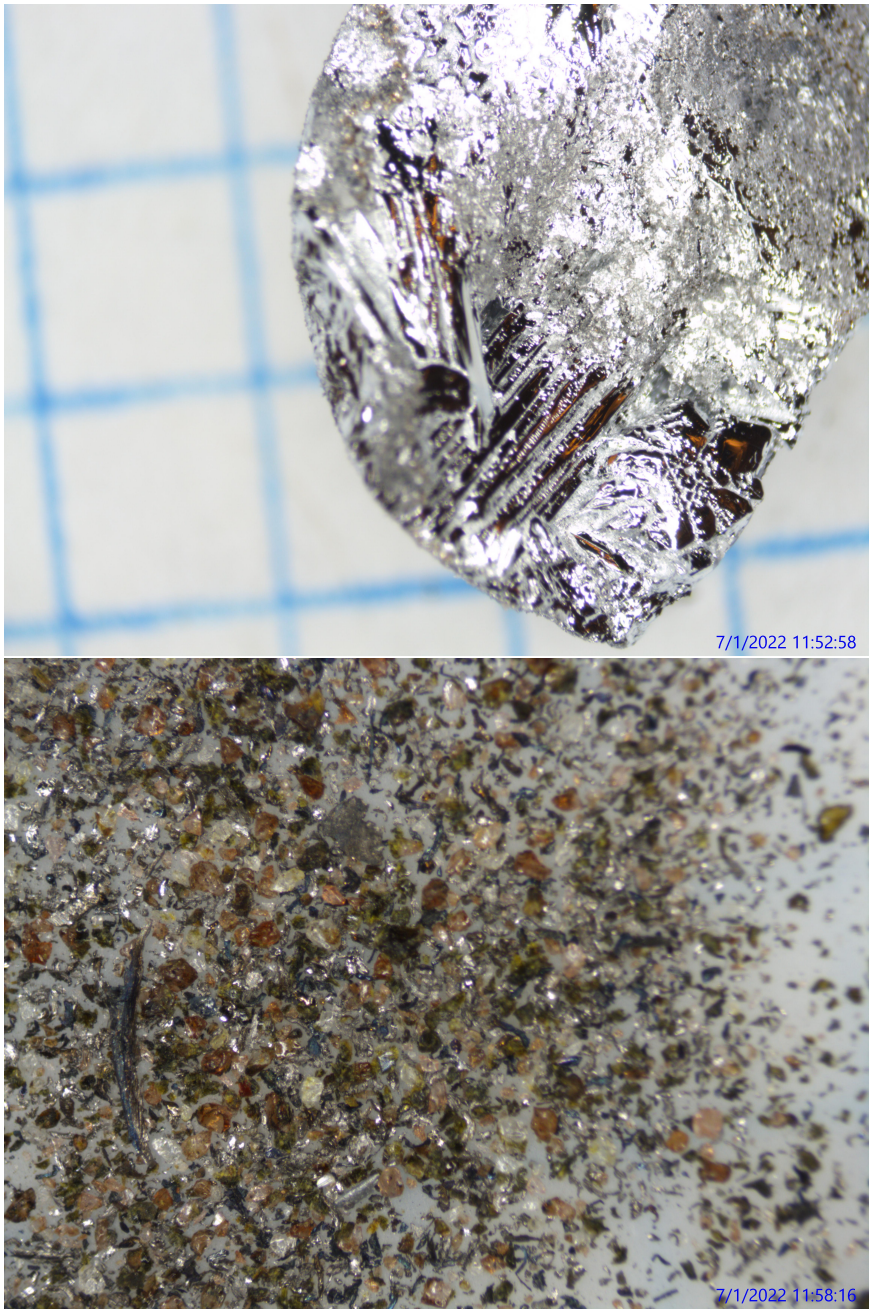
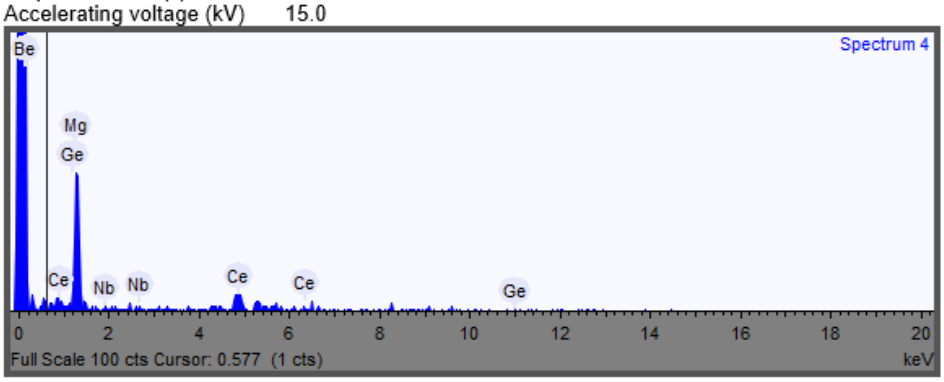


Figure 2: The contents of the niobium tube after removal from the furnace. On the top is pictured the contents of the crucible, the majority of our sample. Since we turned off the furnace early and did not centrifuge the sample to separate any crystals from flux, it is not unexpected that this sample is an undefined mass of the different metals melted together. However, it is interesting that we can already see some kind of crystallization already taking place on the left side of the pictured piece. On the bottom is pictured an unexpected dust from the niobium tube. It's unclear exactly what this dust is due to the different colors among the dust particles, but we can see what appears to be small pieces of niobium that presumably came off during the clamping process.

Acquisition conditions

Acquisition time (s) 45.0 Process time 5
Accelerating voltage (kV) 15.0



Quantification Settings

Quantification method	All elements (normalised)
Coating element	None

Summary results

Element	Weight %	Weight % σ	Atomic %
Magnesium	59.269	6.300	88.195
Germanium	5.365	6.279	2.674
Niobium	0.000	0.000	0.000
Cerium	35.366	5.744	9.131

Figure 3: Pictured here is one EDX spectrum read from a piece of our sample after the furnace. We can see that the atomic percentages of elements are the same as the ratios measured out beforehand within the roughly 2% precision of the EDX machine. This makes sense since we didn't separate any of the material in sample. We can also see that there is no niobium contamination of our sample meaning that this is an effective container for performing this heating process.

pieces with ethanol and mounted them for the SEM. With the EDX machine, we measured spectra from various pieces of the main sample and from the dust also in the niobium tube, as pictured in 3. Overall, We found little to no amounts of niobium in the main sample, and what little amounts seemed to found were well with in the precision error of the EDX machine. In the dust from the tube, we did find pieces of what appeared to be entirely niobium. This is probably due to just pieces of niobium pinching off during the clamping and sealing process of the tube.

3 Conclusions and Next Steps

Since there was no niobium contamination of the sample substance, this test trial was successful. This means that our next steps will be to repeat this heating process on another prepared sample, this time giving the sample the full soaking and cooling time in order to hopefully make a full crystal of Ce_2Ge_2Mg. If we are able to make a crystal, we will then use x-ray diffraction to examine the structure of the crystal.

References

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