

Hf₂Te₂P Single Crystal Synthesis

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ABSTRACT

Hf₂Te₂P was synthesized using the crystal synthesis cycle. It was grown using iodine chemical vapor transport, and studied as a polycrystal precursor powder and single crystal. We took X-ray diffraction measurements of the precursor powder and single crystal to measure the lattice parameter c . We determined $c = 29.170 \pm 0.067$ Å. We also chemically added selenium and measured $c = 28.343$ Å. We used the Magnetic Property Measurement System to measure the magnetization as a function of magnetic field (0 to 7 T) at low temperatures (1.85 K), and observed quantum oscillations starting around 2.5 T. Parallel and future work by STM and ARPES groups, as well as magnetization measurements at more temperatures are the next steps for investigation on this material, which is a candidate for Dirac physics, and behaves like a Fermi liquid at low temperatures.

Keywords: Crystal synthesis, chemical vapor transport, solution growth, Hf₂Te₂P, Fermi liquid, Dirac physics, quantum oscillations

1. Introduction

We are an experimental condensed matter physics laboratory which designs and studies new materials with novel physical properties. In our research we synthesize single crystals, which have clear grain boundaries and defined axes. We use the crystal synthesis cycle (Figure 1) to develop and study new materials. The focus of this paper is the application of the crystal synthesis cycle in growing and studying Hf₂Te₂P. We chose Hf₂Te₂P because its physical properties can help increase understanding of the physical interactions that create the unconventional properties of new materials. It also has quantum oscillations in its magnetization at low temperatures and high fields, which allow research into its Fermi surface [1]. We wanted to see if we could observe the quantum oscillations in the Magnetic Property Measurement System (MPMS), and to see if we could change the lattice parameter c through the chemical addition of selenium.

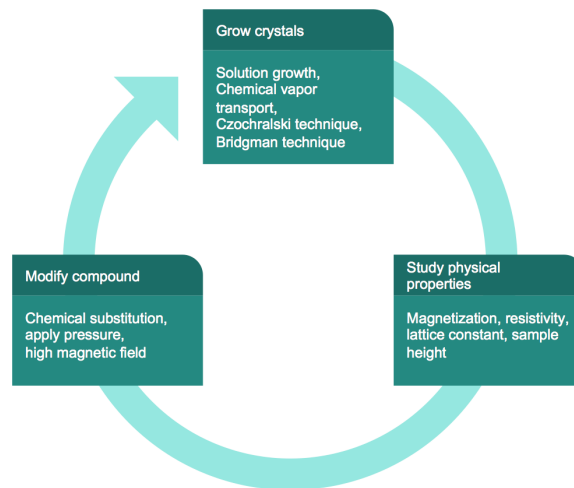


Figure 1. Crystal synthesis cycle (counterclockwise from top: grow crystals, study physical properties, modify compound).

The crystal synthesis cycle is a three step process: growing crystals, studying their physical properties, and modifying the compound. In our lab we use solution growth, chemical vapor transport, the Czochralski technique, and the Bridgman technique to grow crystals. The physical properties that we study are magnetization, resistivity, lattice parameter, and sample height. We also give crystals

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to other labs at UC Davis for analysis, including Eduardo da Silva Neto's Scanning Tunneling Microscopy group and Inna Vishik's Angle-Resolved Photoemission Spectroscopy group. We then modify the compound through chemical substitution, and by applying pressure and high magnetic field. Using the results of studying and modifying the crystals, we then begin the process of synthesizing a new batch.

2. Materials and Methods

2.1. Polycrystal Precursor Powder Procedure

To grow single crystals of $\text{Hf}_2\text{Te}_2\text{P}$ first we synthesized the polycrystal (or precursor) powder. Polycrystal powder is a collection of small grains of the same phase (element ratio). They are easier to grow than single crystals, which are continuous crystal lattices without grain boundaries. However, synthesizing single crystals rather than polycrystal powder allows us to measure their physical properties.

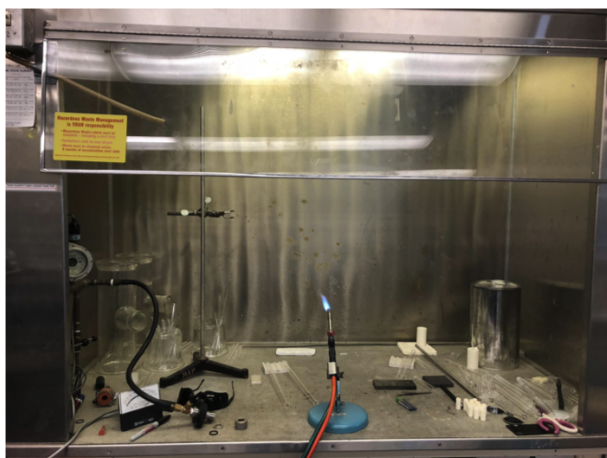


Figure 2. Fume hood and oxygen natural gas torch.

The first step to make the precursor powder is to weigh and pour the elements into the prepared silicon ampoule under the fume hood. Next, we neck the ampoule in the fume hood using the gas-oxygen torch. The torch flame height and strength can be adjusted. Necking is the process of narrowing the ampoule to a diameter of 1-2 mm with the torch. This is done by rotating the ampoule slowly under a hot flame to evenly distribute the flame, and tilting the ampoule so the materials do not slide into the hot region. Once a glowing green ring has formed, it is important to pull on the ends of the ampoule so the two ends do not collapse inwards and create thicker silicon. Once the ampoule is halfway closed, we stopped rotating it, and let it narrow to 1-2mm thickness. The thin neck is important for the next step of the precursor powder synthesis step, sealing under vacuum.



Figure 3. Necking an ampoule.



Figure 4. Necked ampoule. Quartz wool and crucible with unreacted elements to the right, empty ampoule in the left.

We then attached the ampoule to a vacuum pump and argon gas fill setup (Figure 5). The purpose of putting the ampoule under vacuum is to remove any impurities that would interfere with the reaction. We can also control the air pressure of the ampoule by sealing it under vacuum or backfilling it with argon, depending on the temperatures reached during the furnace stage of synthesis. We then sealed the ampoule completely with a focused, lower temperature flame. This was done making sure not to heat the ampoule too much, causing it to cave inwards from the external air pressure.



Figure 5. Sealing an ampoule. The necked ampoule is attached to a vacuum pump and argon gas tank. The ampoule is alternatively put under vacuum and backfilled with argon to purge impurities from the sample and ampoule.

Next, we put the ampoule in a furnace and set and run a temperature profile (Figures 6 and 7). The temperature profile was designed to heat up the elements in the ampoule slowly so as to not increase the air pressure inside too rapidly and cause the ampoule to break. It also had to reach the highest possible temperature to incorporate the hafnium, since its melting point is over 2000°C, but not too high to melt the silicon ampoule (over 1200°C). The temperature profile in Figure 7 shows the steps we took to heat up the $\text{Hf}_2\text{Te}_2\text{P}$ precursor powder. For the first step, from room temperature to 150°C, we dwelled right above the melting point of phosphorus. The next step, at 250°C is just below the boiling point of phosphorus, and the third step, 455°C, is at the melting point of tellurium. Each step and ramp are done slowly to not change the internal pressure of the ampoule too quickly. The final step is just above the boiling point of tellurium, and was as hot as possible to incorporate the hafnium.



Figure 6. Sealed ampoule in a crucible inside furnace.

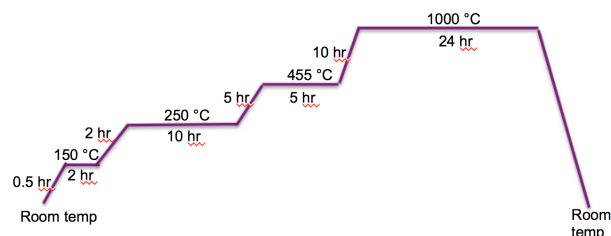


Figure 7. Temperature profile for $\text{Hf}_2\text{Te}_2\text{P}$ precursor powder.

2.2. Chemical Vapor Transport

We used chemical vapor transport to grow single crystals from precursor powder. Typical chemical vapor transport uses a transport agent (in our case iodine) to carry elements from a hotter to cooler region in a two temperature zone furnace using convection. This cycle is normally exothermic, and so the single crystals will form in the cooler temperature region. However, the reaction with $\text{Hf}_2\text{Te}_2\text{P}$ is endothermic, so we used the opposite temperature scheme. First we confirmed that the precursor powder was the correct phase using X-ray diffraction (see results and discussion section). The precursor powder was placed into a new ampoule and sealed with iodine pellets. The ampoule was sealed under vacuum with a length of 10cm. The precursor powder and iodine mixture were placed in the cooler temperature region (800°C) and single crystals grew in the hotter temperature region (900°C). The temperatures were ramped up slowly, and then the furnace was set to dwell for 3+ weeks. We let the crystals cool down slowly to room temperature before removing them from the furnace.

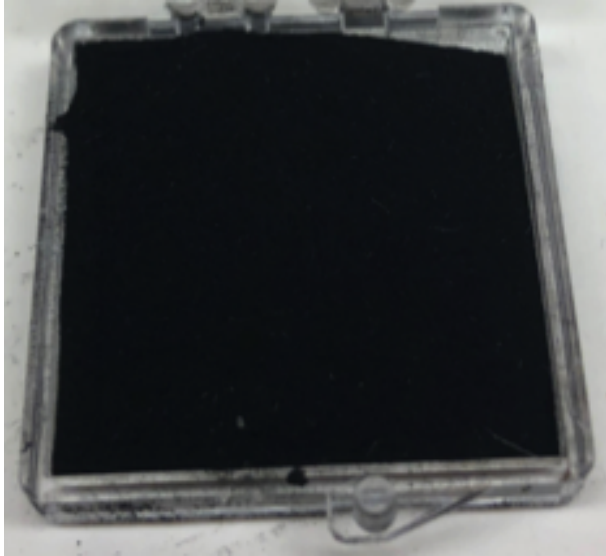


Figure 8. MM142 50% silver precursor powder. After being removed from furnace, but before chemical vapor transport.

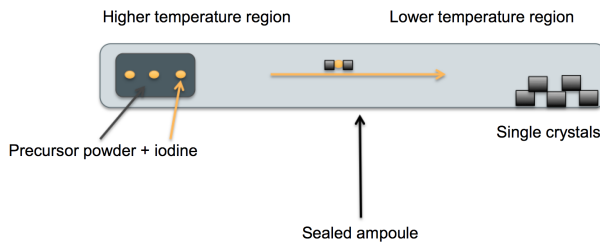


Figure 9. Chemical Vapor Transport diagram. The precursor powder ($\text{Hf}_2\text{Te}_2\text{P}$) and transport agent (iodine) in the lower temperature region (left) are transported via conduction to the hotter temperature region and deposited as single crystals.



Figure 10. MM147 $\text{Hf}_2\text{Te}_2\text{P}$ with selenium in the chemical vapor transport furnace. The temperature increases left to right.

2.3. Measurement Techniques

We used a X-ray diffractometer and Magnetic Property Measurement System (MPMS) to measure the physical properties of the $\text{Hf}_2\text{Te}_2\text{P}$ single crystals. The X-ray diffraction measurements were used to calculate the lattice parameter. It was also used to confirm the phase of the precursor powder. We used the MPMS to measure the magnetization as a function of magnetic field at low temperatures (1.85 K).

The X-ray diffraction measurements were taken by first mounting the sample (precursor powder or flat single crystal) onto a puck with Vaseline. The X-ray diffractome-

ter is a Rigaku model, with a wavelength of 1.54059290 Å and a radius of 150 mm. The X-ray diffraction pattern was used to find the lattice constant c and sample height H using the method developed by Jesche et al [2]. The wavelength times the Miller lattice constant was plotted against the peak locations (two theta in radians) and fit by the equation

$$\lambda * l = 2 * c * \sin((\theta/2) - (S/2) * \cos(\theta/2)) \quad (1)$$

where $S=2H/R$. The X-ray diffraction patterns were matched with known peaks to confirm the phase of the precursor powder and single crystals.

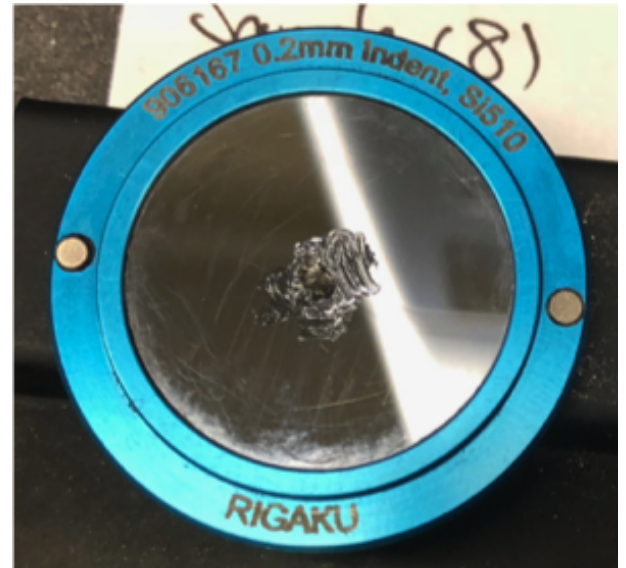


Figure 11. Rigaku X-ray diffractometer puck with a single crystal mounted by Vaseline.

The magnetization measurements were taken of $\text{Hf}_2\text{Te}_2\text{P}$ single crystals in the MPMS (Figure 12). We measured along the c -axis to look for the quantum oscillations, so had to mount the sample perpendicular to the magnetic field. We did this by mounting the sample perpendicularly in a plastic straw, with another straw folded to keep the sample in place (Figure 13). The straw was attached to the MPMS metal probe and moved through the detection coil. This creates a change in the current in the detection circuit. The SQUID detects a change in magnetic flux, and traces a graph of magnetization versus magnetic field at constant temperature (or magnetization versus temperature at constant magnetic field). We took measurements from 0 to 7 Tesla at 1.85 K.



Figure 12. Magnetic Property Measurement System.

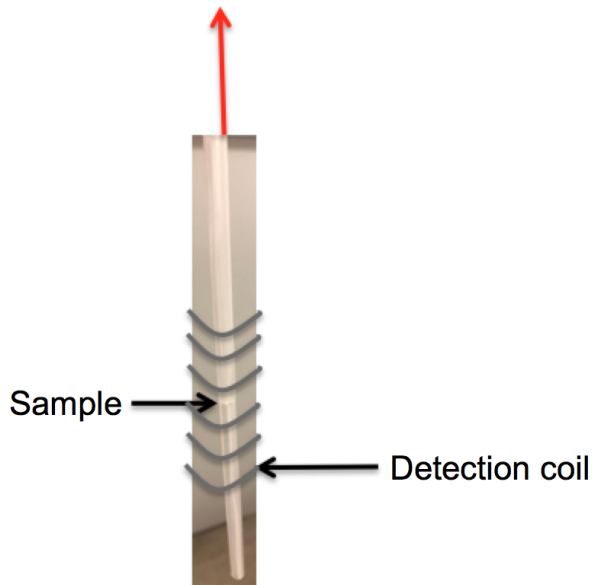


Figure 13. Diagram of sample inside plastic straw and detection coil. The arrow indicates where the straw is connected to the MPMS probe.

3. Results and Discussion

We were able to calculate the lattice parameter for seven $\text{Hf}_2\text{Te}_2\text{P}$ single crystals, and the $\text{Hf}_2\text{Te}_2\text{P}$ plus selenium

precursor powder. We also found quantum oscillations in the magnetization versus magnetic field measurements at 1.85 K.

3.1. $\text{Hf}_2\text{Te}_2\text{P}$ X-Ray Diffraction Results

We found the lattice parameters given in the table below. The average was $c = 29.170 \pm 0.067 \text{ \AA}$, which is well within the value of $29.189(3) \text{ \AA}$ found by Chen et al [1].

Sample	C
Single crystal	29.1855
Single crystal	29.1658
Single crystal	29.2193
Single crystal	29.1588
Single crystal	29.1523
Single crystal	29.1555
Single crystal	29.1544

Table 1. Lattice parameter and sample heights for $\text{Hf}_2\text{Te}_2\text{P}$ single crystals

Figures 14 and 15 are the X-ray diffraction results of the $\text{Hf}_2\text{Te}_2\text{P}$ precursor powder and single crystals. The precursor powder has more peaks than the single crystal because the powder consists of many small grains all aligned differently to the X-ray and so produce many families of peaks. A single crystal only gives one family of peaks; in the case of $\text{Hf}_2\text{Te}_2\text{P}$, the peaks produced were the (003) family (see peaks labeled in Figure 14).

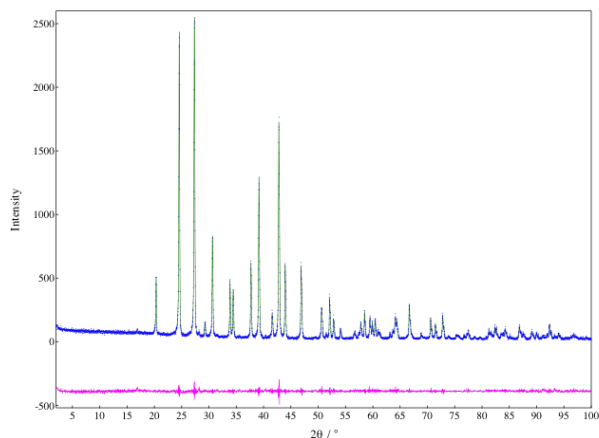


Figure 14. X-ray diffraction results for $\text{Hf}_2\text{Te}_2\text{P}$ precursor powder.

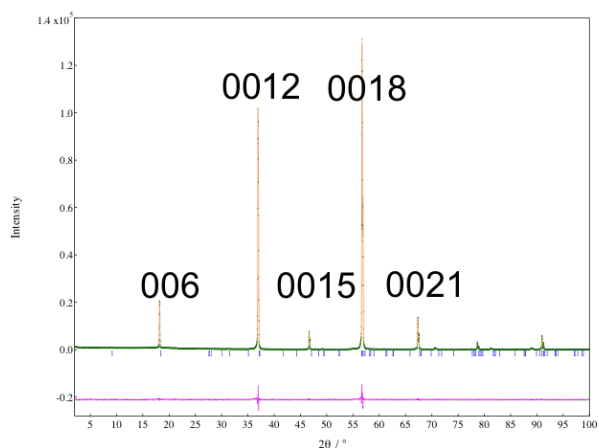


Figure 15. X-ray diffraction results for $\text{Hf}_2\text{Te}_2\text{P}$ single crystals.

3.2. $\text{Hf}_2\text{Te}_2\text{P}$ with Selenium X-Ray Diffraction

We modified $\text{Hf}_2\text{Te}_2\text{P}$ with the chemical addition of selenium. This was done with a molar percentage of 99% selenium and 1% tellurium to introduce impurities into the lattice. We took X-ray diffraction measurements of the precursor powder and compared the results to the unmodified compound. The lattice parameter c that we found was 28.3431 \AA , which falls outside of the error in our unmodified $\text{Hf}_2\text{Te}_2\text{P}$ lattice parameter calculation ($c = 29.1702 \pm 0.067 \text{ \AA}$). Selenium has a smaller atomic radius than tellurium (it is directly above it on the periodic table), and so the new, smaller lattice parameter suggests that the selenium was successfully incorporated into the lattice structure. The X-ray diffraction graphs also show a shifting of the peaks. In Figure 16, the selenium modified sample (red) has peaks shifted to lower theta than the unmodified sample (blue).

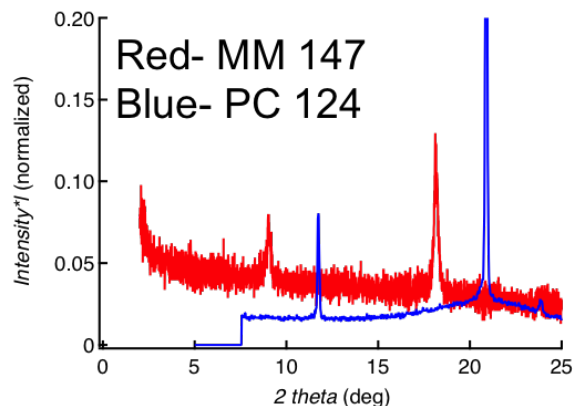


Figure 16. $\text{Hf}_2\text{Te}_2\text{P}$ (PC 124) and $\text{Hf}_2\text{Te}_2\text{P} + \text{Se}$ (MM 147) XRD of 003 and 006 peaks.

3.3. Magnetization Results and Quantum Oscillations

We took magnetization measurements of the unmodified $\text{Hf}_2\text{Te}_2\text{P}$ single crystals at constant temperature 1.85 K . Using the MPMS we swept the magnetic field from 0 to 7 Tesla. The resulting graph is displayed as Figure 17. The quantum oscillations are visible starting around 2.5 T , and are largest over 5.5 T . Quantum oscillations are the Landau quantization of the energy levels of metals. They can be used to map the Fermi surface and measure the masses of the quasiparticles.

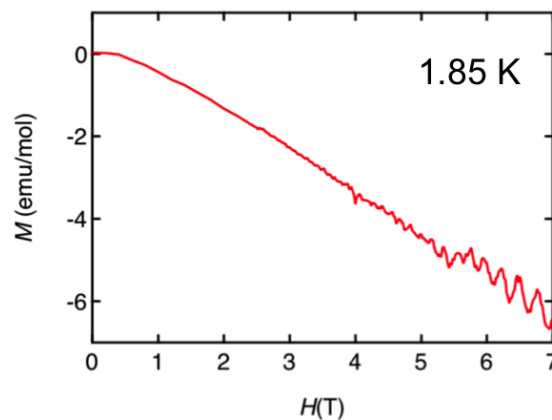


Figure 17. Magnetization vs. magnetic field for $\text{Hf}_2\text{Te}_2\text{P}$ single crystal at 1.85 K .

4. Future and Parallel Work

There are more measurements that our lab can take to further understand the $\text{Hf}_2\text{Te}_2\text{P}$ sample and new physics it exhibits. We can isolate the quantum oscillations by taking MPMS measurements at multiple temperatures. We can also take resistivity measurements with the Physical Property Measurement System (PPMS). This

summer there was also parallel work being conducted by two labs at UC Davis, the Scanning Tunneling Microscopy (STM) lab and Angle-Resolved Photoemission Spectroscopy (ARPES) lab. The STM lab produced Figures 18 and 19, below.

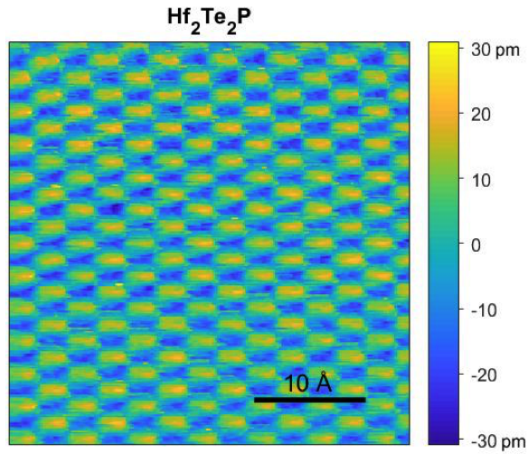


Figure 18. $\text{Hf}_2\text{Te}_2\text{P}$ lattice structure [Boyle, T. and da Silva Neto, E.].

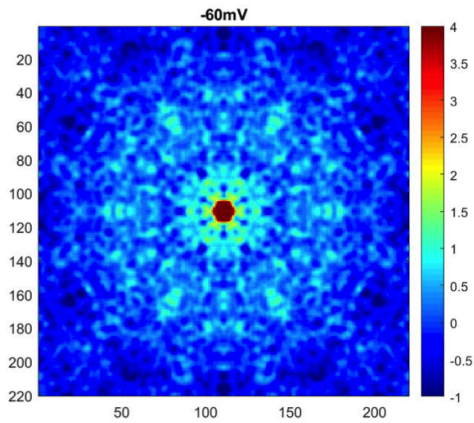


Figure 19. Fourier transform of $\text{Hf}_2\text{Te}_2\text{P}$ quasiparticle interference pattern [Boyle, T. and da Silva Neto, E.].

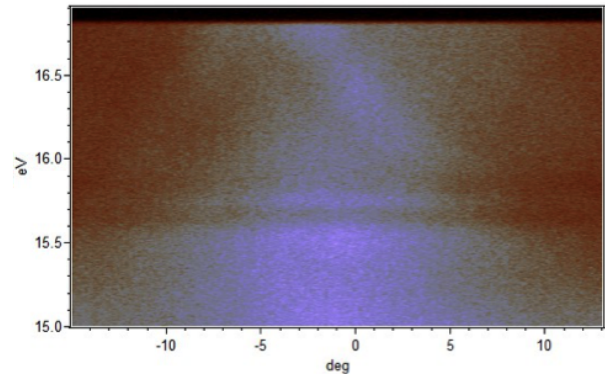


Figure 20. $\text{Hf}_2\text{Te}_2\text{P}$ Band structure (eV vs angle dispersion) [Rossi, A. and Vishik, I.].

The ARPES lab produced Figures 20-22, below. Both labs are doing further investigations into new $\text{Hf}_2\text{Te}_2\text{P}$ samples, including the selenium-added $\text{Hf}_2\text{Te}_2\text{P}$ single crystals.

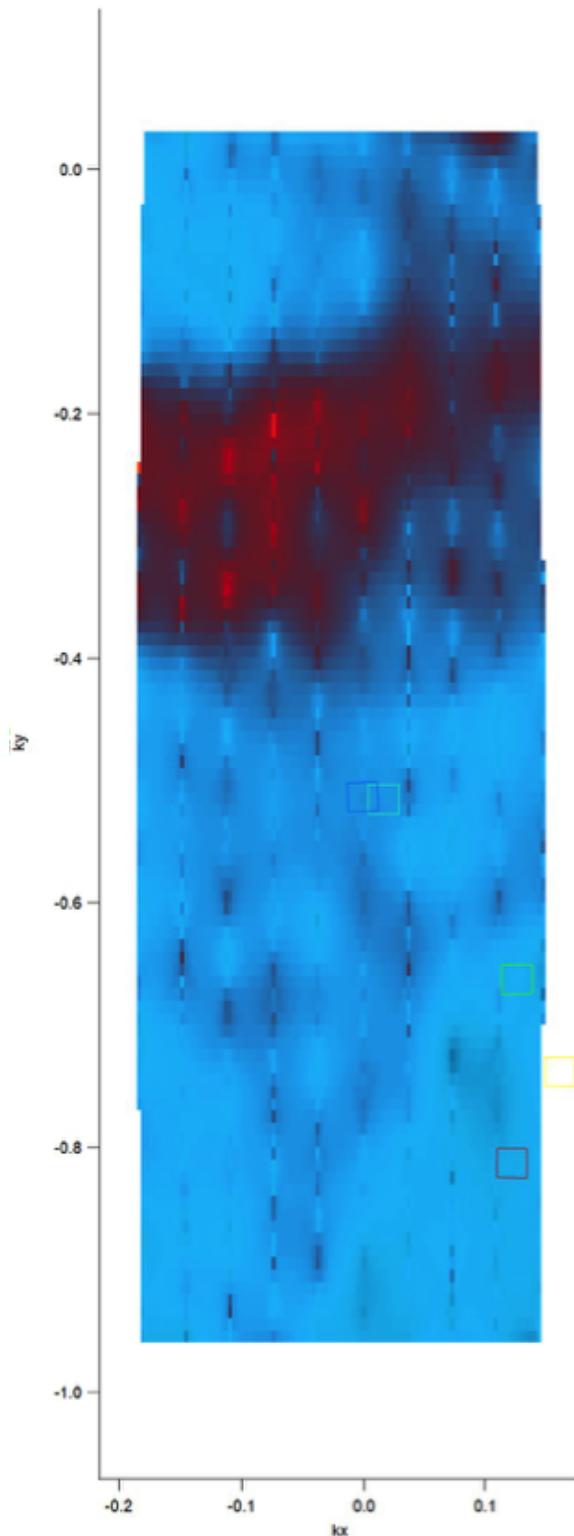


Figure 21. $\text{Hf}_2\text{Te}_2\text{P}$ Fermi surface image (k space, $1/\text{\AA}$) [Rossi, A. and Vishik, I.].

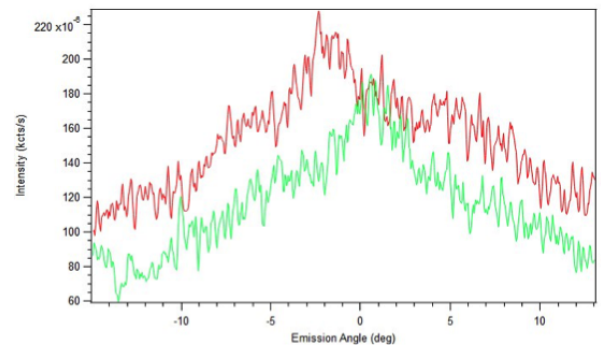


Figure 22. $\text{Hf}_2\text{Te}_2\text{P}$ intensity profile (red at 16.7 eV, green at 16.3 eV). eV refers to the kinetic energy of the electrons coming out of the sample. [Rossi, A. and Vishik, I.].

5. Conclusions

This summer we successfully synthesized $\text{Hf}_2\text{Te}_2\text{P}$ using the crystal synthesis cycle. We synthesized a polycrystal precursor powder and then used chemical vapor transport to grow single crystals. We took X-ray diffraction measurements of the precursor powder and single crystals. With the single crystals we were able to measure the magnetization at low temperature and high magnetic field, and observed quantum oscillations at 1.85 K starting around 2.5 T. We also used chemical addition to add selenium to $\text{Hf}_2\text{Te}_2\text{P}$ and observed a decrease in lattice parameter c which suggest the selenium was incorporated into the lattice. Further study into $\text{Hf}_2\text{Te}_2\text{P}$ could increase knowledge of Fermi liquids and Dirac physics [1].

6. Acknowledgments

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7. References

- [1] Chen, K., et al (2016). *Uncovering the behavior of $\text{Hf}_2\text{Te}_2\text{P}$ and the candidate Dirac metal $\text{Zr}_2\text{Te}_2\text{P}$* . Journal of Physics: Condensed Matter, 28(14). doi:10.1088/0953-8984/28/14/14t01
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