5-2022

Synthesis, Characterization, and Functionality of Novel 2D Material Sn3P2

Cory Stephenson

Synthesis, Characterization, and Functionality of Novel 2D Material Sn_3P_2

An Honors Thesis submitted in partial fulfillment of

the requirements of Honors Studies in Physics

By Cory Stephenson

Spring 2022

Physics

Fulbright College of Arts and Sciences

The University of Arkansas

Acknowledgements

I would like to thank Dr. Jin Hu for serving as my mentor during my undergraduate experience, giving me invaluable opportunities beyond that of lab, and putting up with me for the time I have been in his lab. Along with Dr. Hu, I would like to thank the rest of my research group for their help. I would also like to thank Dr. Julie Stenken for influencing me into pursuing a second major in chemistry and being a great teacher to help my critical thinking. I also thank Dr. Julia Kennefick, Dr. Meagon Clarkson-Guyll, Dr. Delmy Diaz Gonzalez, and Kelly Carter for pushing me to complete honors and giving me the motivation I needed to finish my final year. A final special thanks to all the professors who have agreed to serve on my committee.

Committee Members:

Dr. Jin Hu

Dr. Hugh Churchill

Dr. Julie Stenken

Dr. Susan Marren

Table of Contents

Abstract 3
Introduction and Background 4
I. **Overview of 2D materials** 4
II. **The Sn/P family of 2D materials** 5
Step 1: Synthesis 5
I. **Flux** 5
II. **Chemical Vapor Transport** 6
III. **Single crystal growth for Sn-P system** 7
Step 2: Identification 8
I. **Energy Dispersive X-ray Spectroscopy (EDS)** 8
II. **X-ray Diffraction (XRD)** 8
Step 3: Electronic Transport Properties 9
I. **Resistivity vs. Temperature** 10
Step 4: Magnetotransport Properties: 10
I. **Magnetoresistance (MR)** 10
II. **Hall Effect** 11
Step 4: Thermal Characteristics 11
I. **Heat Capacity (HC)** 11
Discussion and Conclusion 13
I. **Summary** 13
II. **Further Studies** 13
References 14

Abstract

In recent years, two-dimensional (2D) materials have gained a lot of attention due to their potential applications in devices and their promise to revolutionize technology. In our group, we are capable of synthesizing such materials and study their properties. I have discovered a new material of the tin-phosphorus family that displays the 2D layered structure and therefore shows potential to be used in future devices due to this reduced dimensionality from the typical three-dimensional counterpart. This 2D structure may allow for new phenomena to emerge as there is no longer any interatomic interactions along the z- axis. Under this motivation, I studied the crystal growth and properties of this new 2D layered crystal, Sn_3P_2.

Introduction and Background

As society needs better and faster technology, the study of creating and modifying materials for technology applications has vastly expanded. In the realm of material science, we study the materials used in all sorts of electronics and mechanical devices, from things such as the composition of concrete used in construction to the specific molecular structure of a thin film used in a transistor. In my group, we study various materials in bulk or nanoscale, and layered or two-dimensional (2D) materials is the focus of my research.

I. Overview of 2D materials

2D materials arise from the weak van der Waals forces in their crystalline structure. These van der Waals forces are strong enough to lead to a 3D bulk crystal, but also weak enough to enable the mechanical exfoliation of atomically thin layers of the 2D form (shown in Fig. 1). The new 2D can display new and interesting phenomena as it is only confined along a singular plane.[1]

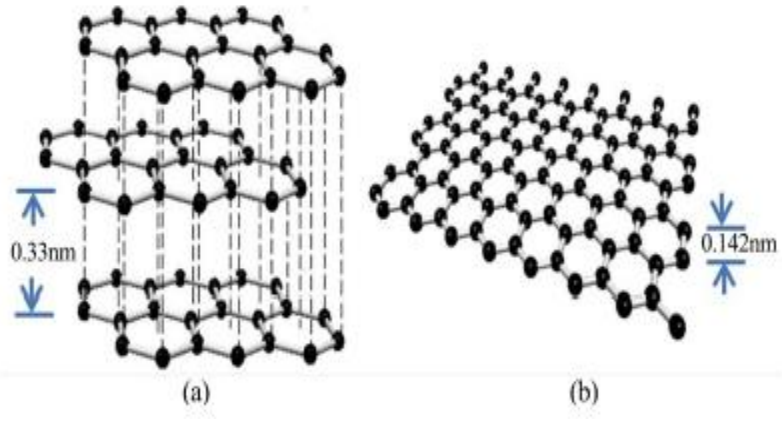


Figure 1. (a) Bulk multilayer form of graphite held together by the van der Waals bonding. (b) single layer of graphene after exfoliation from bulk crystal.[24]

2D materials have gained a lot of attention since the discovery of graphene in 2004 when Professor Andre Geim and Professor Kostya Novoselov used scotch tape to slowly peel away the layers of graphite.[2] From this they obtained the most studied and used 2D material of all time, graphene. Graphene is a sheet of carbon atoms (as shown in Fig. 1) that displays unique properties including: the strongest material known, high thermal conductivity, high electrical conductivity, quantum hall effect, and abnormal superconductivity with bilayer twisting.[2,3] It has numerous applications in optoelectronics, separation membranes, batteries, transistors, etc.[2,4]

With the discovery of graphene, the door was opened to the study of other 2D materials including black phosphorus. Black phosphorus is a 2D semiconductor that has many important applications in optoelectronics and photonics due to its high charge mobility (100-1000 $cm^2V^{-1}s^{-1}$).[3,5,6] Even with black phosphorus being such a useful semiconductor, at the 2D level, it remains unstable when exposed to oxygen or moisture.[6] This leads to the next type of 2D semiconductor discovered known as transition metal dichalcogenides (TMD). The TMD family consists of a transition metal (M) and a chalcogen (X) for the general formula of MX_2 and are all semiconductors.[7,8] The most studied of these is MoS_2 due to its extremely large direct bandgap (1.8eV) and ON/OFF ratio making it great for use in transistors and photoelectric devices.[1,7–10] Outside of this, there are many more 2D materials, such as 2D insulators and even 2D magnetic materials, all with their own respective applications in devices.

II. The Sn/P family of 2D materials

In order to get a better idea of the material that I have been working on, it is important to first look at the family of materials to which it belongs. This family would be that of the tin (Sn) phosphorus (P) family. So far, there have been only a total of 3 different 2D materials consisting of different atomic combinations of Sn and P; these include SnP, Sn_3P_4, and Sn_4P_3.[11] Even though these have been discovered, there has not been too much study on them thus far which leaves a lot of room for study in this family of materials. The atomic structure for each of these compounds can be seen in Fig. 2, where the individual layers and stacking formation can be seen. Each one of these display the desired 2D layered quality that we are interested in studying. The bulk of the experimental research for this Sn/P family has been done on Sn_3P_4, showing that it is a narrow gap semiconductor with high thermoelectric properties. On top of that, Sn_4P_3 has been shown to be a good candidate for the anode of sodium ion batteries.[12]

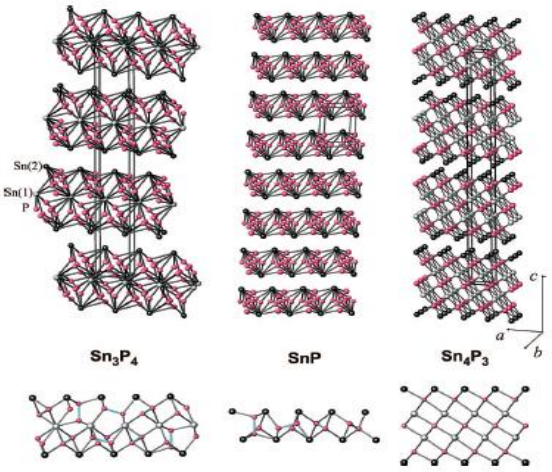


Figure 2. Atomic structure of Sn_3P_4 (left), SnP (middle), Sn_4P_3 (right) with multi-layer representations above. Gray and black atoms being Sn and pink atoms being P.[11]

Recent studies have indicated the possibility of the 2D layers of SnP_3. The van der Waals bonding has been calculated to be weaker than that of graphene and thus easily exfoliable. It also proposes to be a higher carrier mobility semiconductor and flexibility than that of MoS_2 as well as a large optical absorption coefficient; promising for optoelectronics.[13] Though this material has theoretical properties, these properties have not been confirmed in actual experimentation.

As stated before, the Sn/P 2D material family has very little reported information and shows some interesting properties (such as the decreased dimensionality from 3D to 2D) and therefore, potential applications in the use of constructing new devices. With this in mind, I have synthesized a new material in the Sn/P family for 2D material study applications.

Step 1: Synthesis

My lab offers two main types of synthesis capabilities: the flux method and the chemical vapor transport (CVT) method, each having their own unique ways of growing crystals.

I. Flux

In the flux method, the elemental components of the target material are added to a quartz tube. Then, along with the elements being used for crystal synthesis, there is an extra compound added as a solvent (i.e., flux) for which the other components are melted with. The flux is added because it acts as a heat catalysis, allowing for the compounds to be heated at a lower temperature than their own respective melting points. The quartz tube is then put under vacuum, allowing the removal of any chemical interactions from the ambient air. Once the ambient gas in removed, the tube is sealed with a torch and can be placed in a furnace for heating. After heating, the tube can

be removed from the furnace, inverted, quickly put in a centrifuge to remove the solvent from the crystal, and broken to obtain the leftover crystal inside, as illustrated in Fig. 3 below.

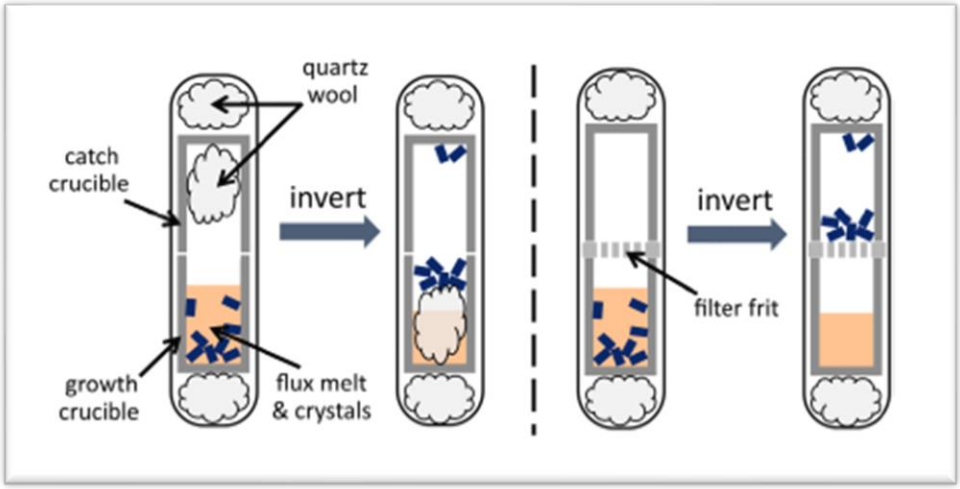


Figure 3. Illustration of flux method and the inversion of the tube. The wool is used as a filter to absorb the leftover solvent in the tube. The crucibles are very helpful, but not mandatory.[14]

II. Chemical Vapor Transport

In the CVT method, the components are added to the tube and sealed in the same way as in the flux method, but without a need for flux solvent. The main difference between the two methods arises in the way the crystals are heated. For flux, the tubes are held vertical, but for CVT, the tubes are held horizontal and a temperature gradient is needed. The premise for CVT is that within the furnace, there are two different heating temperatures: one side is hot and one side is cold (about 50˚C less). With one side being hotter and closer to the sublimation point of the components, the hot side starts to produce mixed vapor that travels to the cold end of the tube where it condenses into the solid, leaving a pristine crystal. This can be seen in Fig. 4 below.

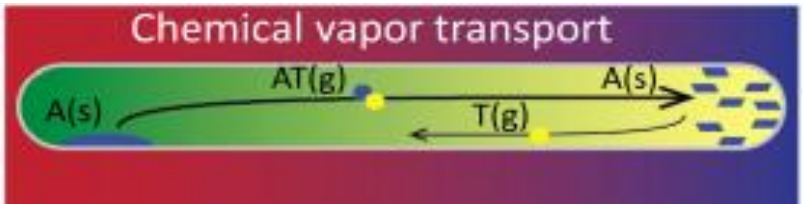
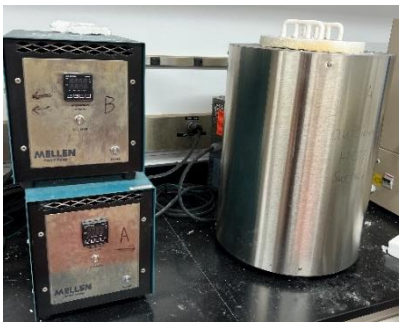


Figure 4. Illustration of CVT. This shows the solid to gas phase transition and then condensation on the right. Here, the heat gradient is hot on the left and cool on the right as shown by the background color display.[14]

III. Single crystal growth for Sn-P system

The method used for my project on Sn-P material system is the flux method where Sn was used as the solvent. This is a very useful element to use for flux since the solvent is also one of the compounds in the chemical makeup of the desired material. This removed the need of centrifuging and the use of crucibles. I added the desired amount of Sn and P to the tube and sealed it under vacuum (Fig. 5). Afterwards, I put it into the furnace (Fig. 6 left) and followed the heating profile that was made shown in Fig. 6. Looking at the graph, it reaches a maximum of 850˚C and takes approximately 12 days to synthesize the crystal. I took the tube out of the furnace and broke the quartz to and obtained the crystal (Fig. 7a). Using tweezers, I separated pieces of the crystal (Fig. 7b) for later use.

Figure 5. Sn pellets and P powder in vacuum sealed quartz tube.



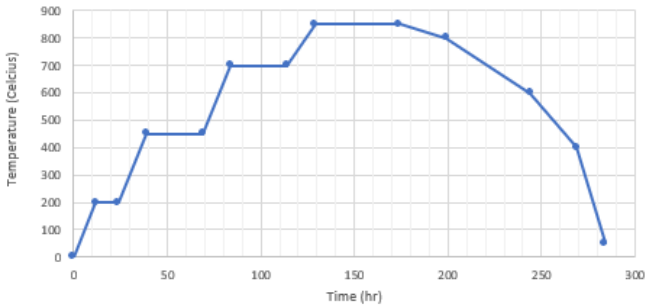
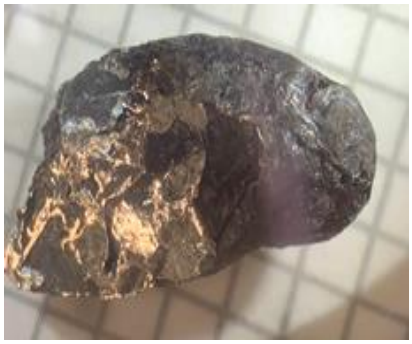


Figure 6. (left) Mellen PS205 Series furnace used to grow crystal residing in the Quantum Materials Synthesis Lab. (right) The temperature profile for synthesizing the crystal using Sn flux method.



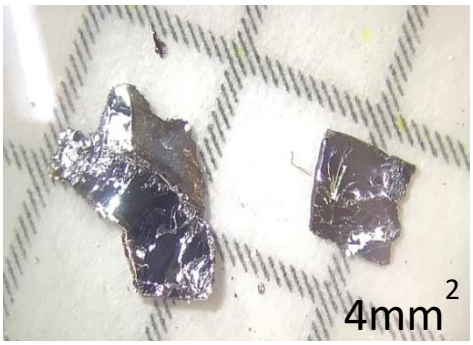


Figure 7. (a) Bulk single crystal on 2mm^2 unit graph paper. (b) Piece of single crystal to be used for later measurements and to display the shininess and visible layering of the material.

Step 2: Identification

There are two primary identification instruments that were used on the crystals obtained. Those two methods include Energy Dispersive X-ray Spectroscopy and X-ray Diffraction. Using these two methods, we can determine the composition of the material and learn more about the atomic structure.

I. Energy Dispersive X-ray Spectroscopy (EDS)

EDS allows for the identification of the chemical composition of a crystal. In this process, there is a beam of electrons that are directed at the crystal that excite the ground state electrons in the atom by absorbing the needed energy. These jumps in energy levels cause holes in the lower-level electron shells that are quickly filled by the excited electrons. This decrease in energy level gives off an X-ray emission that is recorded by the spectrometer. These X-ray emissions are different for every atom and act as a fingerprint. The height of the peaks in the emission spectrum indicates the amount of the components present.[15]

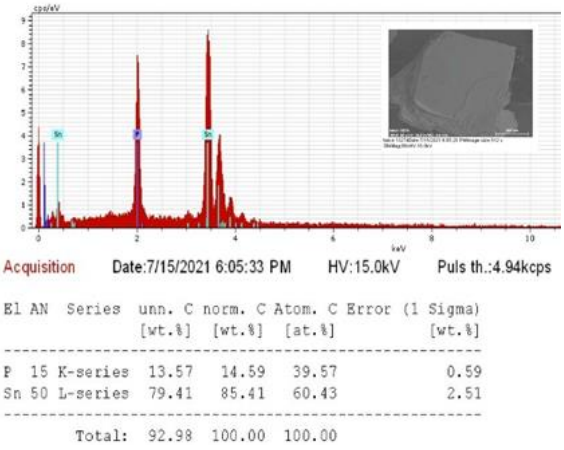


Figure 8. EDS spectrum of Sn/P crystal giving a composition of 3:2 from the atomic concentration. The dark blue peaks are P and the cyan is Sn. The crystal piece used is shown in the top right of the spectrum.

For this crystal, the EDS spectrum is shown to the right in Fig. 8. From the spectrum, it was determined that the composition of the material is Sn_3P_2, a novel material that has not been reported. This presents us with the ability to determine the characteristics of a potentially useful material in device applications.

II. X-ray Diffraction (XRD)

XRD measurements shoot X-rays toward the crystal and they bounce off at different angles and intensities creating a diffraction pattern that is recorded and reveals things such as the electron density. This electron density can then be used to obtain the position of chemical bonds, the atomic structure, and associated disorder in the lattice. This technique can be used on both the single crystal and powdered form of the crystal which were both performed for this Sn/P complex.[16]

The XRD spectrum that we obtained (Fig. 9) displays peaks in both the powder and single crystal form at the same position. As previously mentioned, these XRD spectra can be used to determine the structure of the crystal, which is currently being investigated by one of the collaborators of our group.

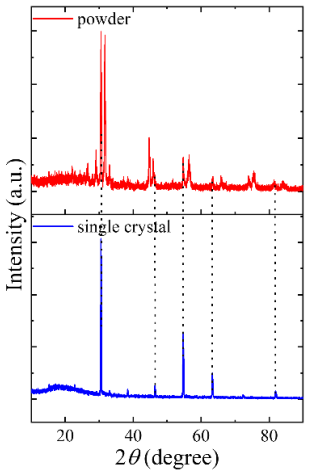


Figure 9. XRD of Sn_3P_2 for both powder (top) and single crystal (bottom)

Step 3: Electronic Transport Properties

To measure the electronic properties of a material, it is easiest to do so using a rectangular piece of crystal since the resistance (R) is dependent on the length (l) and area (A) of the material current is passing through, $R = \rho\left(\frac{l}{A}\right)$. Here, ρ is our resistivity. After cutting the crystal into a rectangular shape, I used silver epoxy to attach 6 contacts to the crystal in the way shown in Fig. 10a with the physical crystal shown in Fig. 10b. Based on the location of contacts with current (I) flowing from one end to the other and voltage (V) read at the middle two contacts on top, the resistance is computed ($V = IR$).

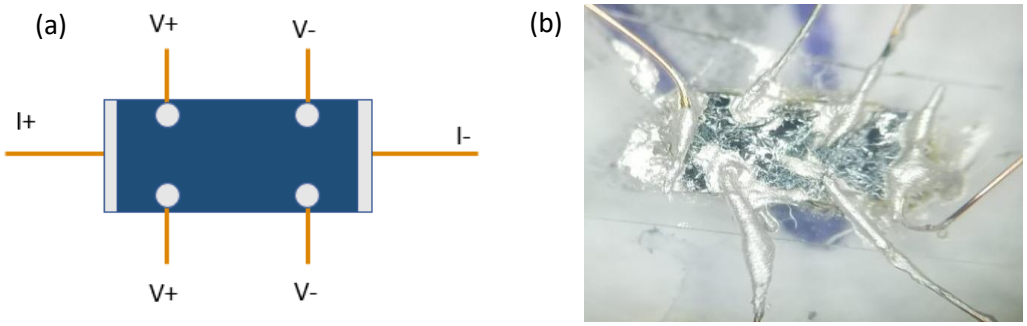


Figure 10. (a) Schematic of crystal (blue) with electric contacts (gold) and silver epoxy (gray). Notice that the contacts for current are across the entire crystal to ensure for uniform current flow. The part used for the length of the crystal is the distance between the top two voltage contacts. (b) Physical crystal with epoxy and copper wires attached.

Figure 11. Physical Properties Measurement System (PPMS) by Quantum Design. This is the mechanism used to obtain the measurements for the physical properties of the crystal.

I. Resistivity vs. Temperature

Using the measurement system device in our lab, Physical Properties Measurement System (PPMS) in Fig. 11 above, that can scan a range of temperatures, magnetic fields, currents, etc. we can plot the resistance of our crystal through a range of temperatures, from 2 K to 300K. After converting resistance to resistivity, the plot can tell us properties such as the type of material it is (e.g., superconductor, semiconductor, metal), the residual resistivity $R(2K)$, and the residual resistivity ratio (RRR). We calculate RRR using the formula $RRR = \frac{R(300K)-R(2K)}{R(2K)}$.

The resistivity plot of Sn_3P_2 given in Fig. 12 displays a direct proportionality between the resistivity and temperature. The positive slope and curve at the end close to temperatures of 2 K tells us that this material is most prominently a metal conductor. This is because at low temperatures for conductors, the crystal lattice and interactions of electrons slows down and the resistance to flowing current this causes at high temperatures will also decrease. If the resistivity ever reached 0mΩ cm, that would mean the material was a superconductor (with absolutely no resistance), but instead it leveled out with a residual $\rho = 0.2$ mΩ cm. The RRR was calculated to be approximately 28 implying good metallicity.

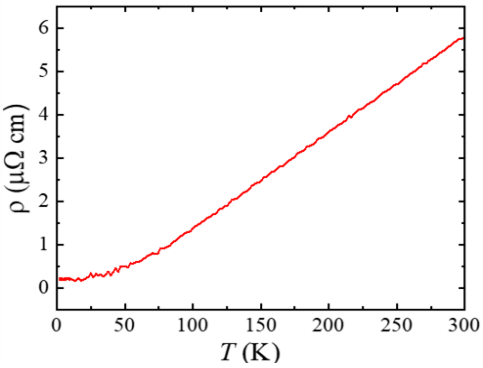


Figure 12. Temperature dependent resistivity for Sn_3P_2

Step 4: Magnetotransport Properties:

Magnetotransport properties can tell us how the material acts in a given magnetic field and can tell us whether or not the material has any magnetic properties. Things seen here can include magnetic tuning of the displayed electronic properties due to interlayer electron coupling. Having tunable electronic properties proves extremely useful in electronic devices.

I. Magnetoresistance (MR)

Again, using PPMS, the MR of the crystal can be plotted and the resistivity ratio of the material based on the applied magnetic field can be found. Based on these results, the higher the MR, the higher dependency and tunability of the resistivity from the magnetic field applied.[17]

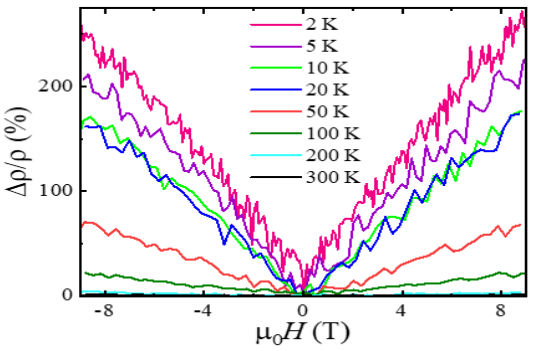


Figure 13. MR of Sn_3P_2 ranging from -9T to 9T, measured at temperature values between 2 K and 300 K.

For Sn_3P_2, the MR measurement gave a couple of abnormalities for a metallic material. The first noticeable abnormality is the linear slope of the line ($\propto B$), having characteristics of an absolute value function rather than the typical quadratic function ($\propto B^2$) .[18] The second abnormality of the MR measurement is seen in the high MR value of 250% at 2 K and 9 T. Both of these qualities are actually seen in the aforementioned black phosphorus.[19] The abnormalities present could be caused by weak antilocalization or other phenomena to be further studied.

II. Hall Effect

The other magnetotransport measurement we performed is the Hall effect measurement where we use the same setup shown in Fig. 8, except this time instead of using voltage contacts on the same side, the contacts are used on opposite sides to get transverse measurements of how the electrons will flow under a magnetic field. The electrons are moving at some velocity (v) and since there is a perpendicular magnetic field (B), the Lorentz force (F) pushes the electrons to the other side of the crystal giving a path from the cross product ($F = v \times B$). The accumulation of electrons at the side of the sample creates an electric field across the transverse direction leading to an electrical force which eventually balances the Lorentz force. The electron path through the material can identify what the charge carrier of the material is, the charge carrier density, and the charge carrier mobility.[20]

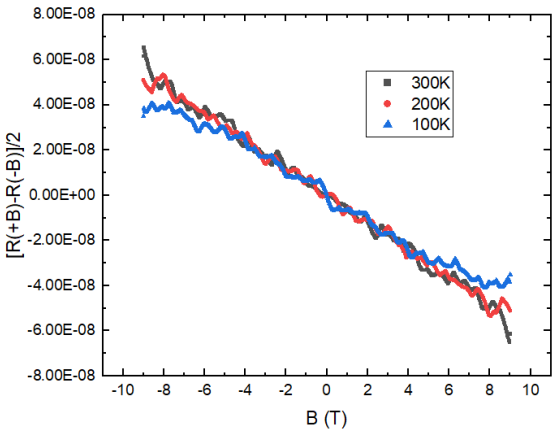


Figure 14. Field dependent Hall resistivity at T = 100 K, 200 K, and 300

By looking at our Hall effect measurement for Sn_3P_2 (Fig. 14), the negative slope tells us that the charge carrier is an electron. The charge carrier density and mobility were calculated from the slope at temperatures of 100K, 200K, and 300K. These values are shown in Table 1, where n_e is the electron density and μ_e is the electron mobility. The values gotten for Sn_3P_2 are low for a normal conducting metal. To put into reference of another metal, the charge carrier density of copper is to the order of magnitude 10^{28}.

Table 1. Calculated values for charge carrier mobility and density

Temperature (K)	n_e (cm^{-3})	μ_e ($cm^2\ V^{-1}s^{-1}$)
100	1.24E+23	34.341
200	1.04E+23	15.293
300	1.01E+23	9.852

Step 4: Thermal Characteristics

I. Heat Capacity (HC)

HC is the amount of heat needed to raise the temperature of a given material by one degree. HC of a material can be found using the PPMS in the relaxation method. This requires a crystal of 2-3 mg in size. It is put on a platform with grease on it as shown in Fig. 15 and then heat is applied to the platform (and thus the crystal) for a given amount of time and the temperature of the crystal is recorded. When the crystal heats up, the atoms are excited and there are more lattice vibrations. After the crystal is heated, it is allowed to cool and the lattice is allowed to "relax" to its standard state. Heat capacity of the sample can be obtained from the fitting of the relaxation process, which is automatically calculated by PPMS.

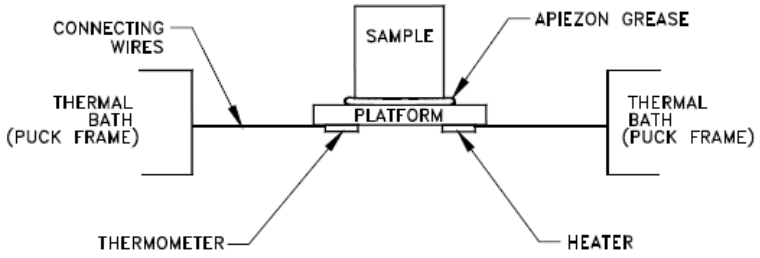


Figure 15. Heat Capacity platform. The heater heats up the platform which heats up the sample. The platform and sample are held at thermal equilibrium by the thermal baths and grease. The temperature is recorded by the thermometer.[21]

There are two parts to the HC measured; there is the electronic contribution (γ) and the phonon contribution (β). The equation for HC is given as $C = \gamma T + \beta T^3$, where T is temperature and C is our HC. In order to simplify the equation, divide by T, $\frac{C}{T} = \gamma + \beta T^2$. This will give the electron contribution as the y-intercept, and the phonon contribution as the slope at low temperatures. Debye temperature (Θ_D) can be calculated from the phonon contribution via $\Theta_D = \left(\frac{12\pi^4 NR}{5\beta}\right)^{\frac{1}{3}}$, where N=number of atoms, R=8.314 J/mol K.[22] The Debye temperature tells us at what temperature the crystal structure has its normal mode of vibration. This also give us indication on the elasticity or hardness of the material. The higher the Debye temperature the harder the material.

The HC graph at low temperatures for Sn_3P_2 shown in Fig. 16 has a y-intercept value (and therefore an electron contribution) of $\gamma = 4.86$ mJ/mol K^2 and a slope (and therefore a phonon contribution of $\beta = 0.432$ mJ/mol K^4. Now, knowing that $N = 5$ for Sn_3P_2, the Debye temperature was determined to be $\Theta_D = 282.3$ K. This is an average Debye temperature for a 2D metal. The original HC graph is shown inset of Fig. 16.

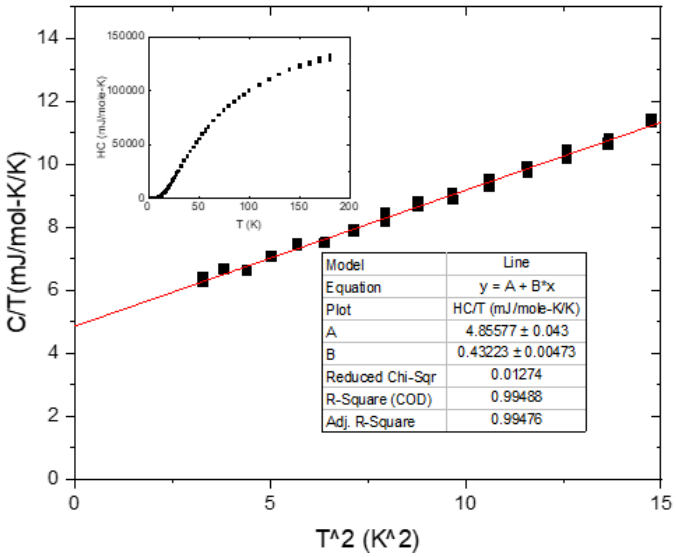


Figure 16. Heat Capacity measurement (C/T vs. T^2) for low temperatures with linear best fit line matched. The slope and y-intercept are displayed representing the corresponding electron and phonon contribution to the heat capacity. (Inset) Original HC measurement showing no transitions ranging from T = 2 K to 200 K.

Discussion and Conclusion

I. Summary

We have recently discovered a new 2D material of the Sn/P family, Sn3P2, that displays abnormalities in both the MR and charge carrier mobility. These abnormalities, along with the metallicity of Sn3P2 present it as a potential material to be used in 2D devices such as sensors. This could also be used to fabricate devices for further 2D analysis. Sn3P2 being a new material also opens many doors to further study of 2D material properties caused by quantum confinement and other phenomena not yet understood.

II. Further Studies

The first thing to further my study of Sn_3P_2 is to determine the atomic structure of the material to gain insight on the actual dimensionality of the crystal and determine the way in which the layers are stacked. This will help in determining the reasons for any abnormalities and other characteristics that the Sn_3P_2 has. Knowing the crystal structure will also help in the process of doping discussed below.

Sn_3P_2 being a 2D layered material gives arise to opportunities of doping the material. Doping is the process of injecting other compounds between the layers to induce new characteristics and properties. This can be done directly during the synthesis process of adding the desired compound to the mixture before heating or it can be done through electrochemical means known as electrochemical intercalation. Intercalating Sn_3P_2 with charge carriers such as Li or Cu could induce superconductivity. Another thing that is commonly induced into 2D materials using intercalation techniques is magnetic properties. By doping the material with ferromagnetic materials (Fe, Co, Ni, etc.), the magnetoelectronic and overall magnetic properties in general can be altered and is something commonly done in my group.[23]

References

1. Zhang, W., Wang, Q., Chen, Y., Wang, Z. & Wee, A. T. S. Van der Waals stacked 2D layered materials for optoelectronics. *2D Materials* vol. 3 (2016).

2. Nguyen Bich, H. & Nguyen Van, H. Promising applications of graphene and graphene-based nanostructures. *Advances in Natural Sciences: Nanoscience and Nanotechnology* vol. 7 (2016).

3. McCreary, A., Kazakova, O., Jariwala, D. & al Balushi, Z. Y. An outlook into the flat land of 2D materials beyond graphene: Synthesis, properties and device applications. *2D Materials* vol. 8 (2021).

4. Chung, C. *et al.* Biomedical applications of graphene and graphene oxide. *Accounts of Chemical Research* **46**, 2211–2224 (2013).

5. Xu, Y., Shi, Z., Shi, X., Zhang, K. & Zhang, H. Recent progress in black phosphorus and black-phosphorus-analogue materials: Properties, synthesis and applications. *Nanoscale* vol. 11 14491–14527 (2019).

6. Ling, X., Wang, H., Huang, S., Xia, F. & Dresselhaus, M. S. The renaissance of black phosphorus. *Proceedings of the National Academy of Sciences of the United States of America* vol. 112 4523–4530 (2015).

7. Li, H., Wu, J., Yin, Z. & Zhang, H. Preparation and applications of mechanically exfoliated single-layer and multilayer MoS2 and WSe2 nanosheets. *Accounts of Chemical Research* **47**, 1067–1075 (2014).

8. Castellanos-Gomez, A. Why all the fuss about 2D semiconductors? *Nature Photonics* vol. 10 202–204 (2016).

9. Li, X. & Zhu, H. Two-dimensional MoS2: Properties, preparation, and applications. *Journal of Materiomics* **1**, 33–44 (2015).

10. Samy, O., Zeng, S., Birowosuto, M. D. & el Moutaouakil, A. A review on MoS2 properties, synthesis, sensing applications and challenges. *Crystals (Basel)* **11**, (2021).

11. Zaikina, J. v. *et al.* Highly disordered crystal structure and thermoelectric properties of Sn3P4. *Chemistry of Materials* **20**, 2476–2483 (2008).

12. Chen, B. *et al.* Sodium-Ion Battery Anode Construction with SnP x Crystal Domain in Amorphous Phosphorus Matrix . *Energy Material Advances* **2021**, 1–11 (2021).

13. Ghosh, B., Puri, S., Agarwal, A. & Bhowmick, S. SnP3: A Previously Unexplored Two-Dimensional Material. *Journal of Physical Chemistry C* **122**, 18185–18191 (2018).

14. May, A. F., Yan, J. & McGuire, M. A. A practical guide for crystal growth of van der Waals layered materials. *Journal of Applied Physics* **128**, (2020).

15. Lewis, B. J., Thompson, W. T. & Iglesias, F. C. 2.20 - Fission Product Chemistry in Oxide Fuels. in *Comprehensive Nuclear Materials* (ed. Konings, R. J. M.) 515–546 (Elsevier, 2012). doi:https://doi.org/10.1016/B978-0-08-056033-5.00042-2.

16. Gonon, M. Case Studies in the X-ray Diffraction of Ceramics. in *Encyclopedia of Materials: Technical Ceramics and Glasses* (ed. Pomeroy, M.) 560–577 (Elsevier, 2021). doi:https://doi.org/10.1016/B978-0-12-818542-1.00005-9.

17. Tsymbal, E. Y. & Pettifor, D. G. *Perspectives of Giant Magnetoresistance*.

18. A.B. Pippard, F. *Magnetoresistance in Metals*. (Cambridge University Press, 1989).

19. Hou, Z. *et al.* Large and Anisotropic Linear Magnetoresistance in Single Crystals of Black Phosphorus Arising from Mobility Fluctuations. *Scientific Reports* **6**, (2016).

20. Offidani, M. & Ferreira, A. Anomalous Hall Effect in 2D Dirac Materials. *Physical Review Letters* **121**, (2018).

21. *Physical Property Measurement System ® Heat Capacity Option User's Manual*.

22. Pandey, K. *et al.* Electronic and magnetic properties of the topological semimetal candidate NdSbTe. *Physical Review B* **101**, (2020).

23. Nabi, M. R. U. *et al.* Giant topological Hall effect in centrosymmetric tetragonal Mn2-xZnxSb. *Physical Review B* **104**, (2021).

24. Adetayo, A. & Runsewe, D. Synthesis and Fabrication of Graphene and Graphene Oxide: A Review. *Open Journal of Composite Materials* **09**, 207–229 (2019).