A Search for Novel Non-centrosymmetric Superconductors

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Solid State and Lithium Intercalation synthesis techniques can both be used to dope materials, the former being much more common. We use these techniques to perform doping studies of and search for novel non-centrosymmetric superconductors in two families of materials: $REBaCuBO_5$ and Li_xTaOCl_2. We succeed in conducting the first doping study of $REBaCuBO_5$, creating a new Lithium intercalated material, and discovering a weakly superconducting signal caused by some material likely in the phase space of Li_xTaOCl_2.

I. INTRODUCTION

During my ten week REU Program at PARADIM I attempted to find new high-temperature non-centrosymmetric superconductors using two different chemical synthesis techniques: Solid State synthesis and Lithium Intercalation. I applied the former to perform a doping study of $REBaCuBO_5$ (RE = Rare-Earth Metal, a family of materials structurally related to the Cuprate Superconductors, known for their high-temperature superconductivity, on which a doping study has never been done, and the latter to $TaOCl_2$ which has a more subtle relationship to the Cuprates but nevertheless is a promising candidate for high-temperature superconductivity.

II. EXPERIMENTAL SETUP

$REBaCuBO_5$ is naturally non-centrosymmetric – it has a lack of inversion symmetry around a central point. It also has a CuO square net layer, which is exactly what is believed to facilitate superconductivity in the Cuprate superconductors. Due to this, $REBaCuBO_5$ seems to be a good candidate for a non-centrosymmetric, high-temperature superconductor. However, the Copper coordination environment introduces some complications that must be corrected to incite superconductivity. Specifically, the in-plane bond lengths between the Copper and Oxygen are unequal. For RE = La, the bond length in the a direction is 2.03 Å while the bond length in the b direction is 1.95 Å. This worsens the connection between the CuO octahedra and inhibits superconductivity, so chemical pressure will need to be added to the system to resolve the issue.

Lithium Intercalation is a technique commonly used in the synthesis of Lithium Ion batteries. It can also be utilized as a technique to dope materials which cannot be doped using traditional solid state methods. But, it is woefully underused. As such, many potential superconductors which have been discarded await a doping study via Lithium intercalation to test their true potential. $TaOCl_2$ is one such material, a naturally dimerized insulating material. But, upon Li intercalation the material suppresses a potential Charge Density Wave (CDW) and becomes undimerized and metallic. This mechanism of suppressing a CDW is also present in the Cuprate superconductors and is not in low-temperature Superconductors, indicating a potential for high-temperature superconductivity in Li_xTaOCl_2.

III. RESULTS AND DISCUSSION

While we tested many doping conditions of the $REBaCuBO_5$, a main focus was doping the Ba site with both K and Sr. The K acted to change the oxidation state on Copper, while the Sr acted to add chemical pressure to the system. Both of these steps are key to evening out the Cu-O in-plane bonds and give the material the best chance it has at being superconducting. X-Ray Diffraction (XRD) data showed that K alone could dope the Ba site up to a concentration of 0.2 without increasing impurity concentration. So, the material is dopable and critically we can change the oxidation state of Cu. However, magnetism measurements, shown in Figure 1, acquired using a Magnetic Properties Measurement System (MPMS) consistently showed very weakly magnetic materials whose magnitudes hardly changed with changing K concentration. XRD data also showed that Sr could dope the Ba site alongside K up to a concentration of 0.2, with K concentration set to 0.1. This shows once again that we can change the oxidation state on the Copper while simultaneously adding chemical pressure to the system. But, magnetism measurements were again underwhelming, showing weakly magnetic signals whose magnitudes changed without any clear pattern. These results indicate that $REBaCuBO_5$ can be doped using tried and true solid state synthesis techniques. While we did not find any superconducting signals, the phase space of possible doping combinations is so large - changing the RE metal alone can completely change the magnetic signal - that a superconductor could easily be lurking nearby. Further research should be focused on a more detailed study of how different dopants change the Cu coordination environment in order to better understand what inhibits superconductivity in this material.

$TaOCl_2$ has a layered structure in which the layers lying in the (002) plane are bonded via Van Der Waals (VDW) interactions. There is a lot of space in between these layers for Li atoms to fit in while performing Li

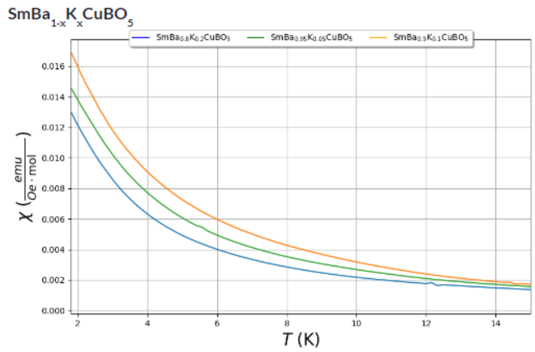

FIG. 1. XRD Measurements of $SmBaCuBO_5$

intercalation. The intercalation process is facilitated by first mixing a solution of Li metal, THF, and Benzophenone. Upon mixing Li takes on a radical, unstable state in this solution and will readily intercalate into a more energetically favorable environment if able to. Adding $TaOCl_2$ to the solution provides this opportunity, and after some amount of time ranging from a few hours to many days (shorter time corresponds to less Li intercalation and vice versa) the solution is filtered and the material is extracted. XRD measurements can be seen in Figure 2 showing peak shifting to the right in the peak corresponding to the (002) plane, as well as the addition of a superstructure peak with roughly twice the d spacing of the (002) peak. This agrees well with expectation. For example, if Li intercalated into one of every two possible spots in the (002) plane, the VDW bonded layers would be pulled closer together, decreasing the unit cell and shifting the (002) to the right. This would also add an extra periodicity to the system, and since in this case one out of every two possible spots for Li are occupied, the d spacing of this new periodicity would be twice that of the (002) plane. This is a great sign that we are creating Li_xTaOCl_2, a new Lithium intercalated material.

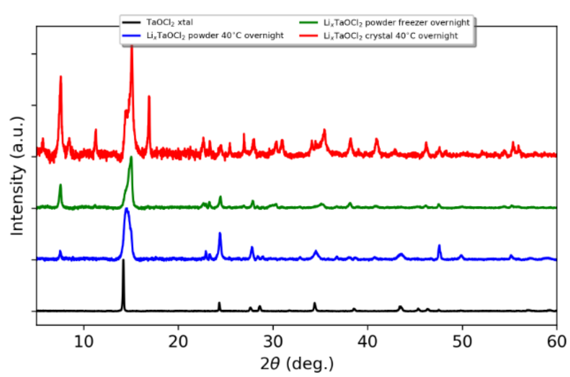

FIG. 2. XRD Measurements of Li_xTaOCl_2

Magnetism measurements on our new material revealed a signal with a superconducting shape and reproducible critical temperatures (TC). These results can be seen in Figure 3. For crystal samples the TC was 6 K and for powder samples there were two TC's at 3.5 K and 6 K indicating the presence of two different superconducting phases. However, the superconducting volume fraction was calculated to be 0.5%. This is so small that whatever material is causing the superconductivity is likely not visible in XRD data. So, Li_xTaOCl_2 likely does not superconduct. Currently our leading theory is that some other binary or ternary in the $TaOCl_2$ phase space superconducts on Li intercalation. One promising candidate is Ta_2O_5, for which preliminary results have shown a potential superconducting signal with similar TC's to our Li_xTaOCl_2 compound. Further research should be focused on isolating this superconducting phase and reproducing the aforementioned TC's in bulk.

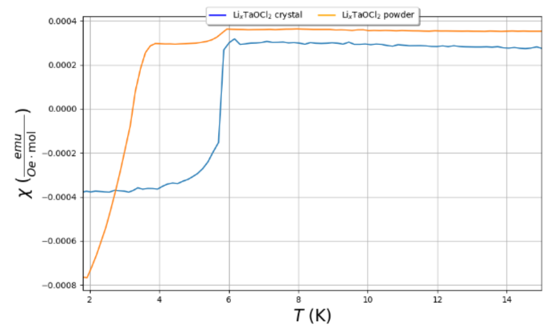

FIG. 3. MPMS Measurements of Li_xTaOCl_2

IV. CONCLUSIONS

The world class facilities of PARADIM were crucial in achieving my goals this Summer. In both lines of my work I had every possible piece of equipment I needed to succeed, and more importantly I was surrounded by extremely knowledgeable people willing to help me with any aspect of my project at any time. In this environment, I was able to conduct a doping study of $REBaCuBO_5$ and show that with further research, superconductivity could be uncovered in this family. I also successfully synthesized a new Li intercalated material, Li_xTaOCl_2, and found a weak superconducting signal that likely belongs to a different binary or ternary living in the phase space of Li_xTaOCl_2. These results are promising for future research, which should involve a more expansive doping study of $ReBaCuBO_5$ and a more precise look at exactly what is causing reproducible superconducting signals with TC's of 3.5 K and 6 K.