

Synthesis and Characterization of LiFeAs and Relatives

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Abstract

After extensive experimentation in the production of LiFeAs both undoped and doped with Co or P, superconductivity was achieved in part of a LiFeAs sample in Sn-24 flux at 8K. Crystal growth results demonstrate that In is not an effective flux for producing large LiFeAs single crystals, and that P doping results in reduced crystal size. Furthermore, excess Li seems to inhibit superconductivity in LiFeAs.

Introduction

In February 2008, Kamihara *et al*[1] discovered superconductivity in $\text{LaFeAs}(\text{O}_{1-x}\text{F}_x)$ at 26 K. This discovery sparked a surge of research on other “iron pnictide” superconductors, so called because they all incorporate Fe and a member of the pnictogen family (P, As, Sb, Bi). The group of superconductors $R\text{FeAsO}$ (R = rare earth element) exhibits the same crystal structure as ZrCuSiAs , often called a “1111” crystalline structure when speaking of iron pnictide superconductors, but superconductivity was later discovered in other iron pnictide crystalline structures as well. Superconductivity was achieved in a ThCr_2Si_2 -type crystal structure, called the “122” structure, by electron-doping or hole-doping $A\text{Fe}_2\text{As}_2$ (A = Ba, Sr, Ca). A third structure, called the “111” structure, was discovered when superconductivity was achieved at 18 K in LiFeAs [2].

In order to advance our understanding of the causes of superconductivity and expand the set of superconducting materials available for use in applications, we must further explore the new realm of iron pnictide superconductors. The focus of this paper in particular is superconductivity in the “111” crystal structure, especially LiFeAs and its close relatives. The ultimate success would be the discovery of a chemical doping strategy in LiFeAs that raised its critical temperature above the current records for iron pnictide superconductors, but the real purpose of my project is to explore possible processes for producing LiFeAs crystals, and to evaluate the success of these processes by measuring the crystals for superconductivity. Then, I extend these methods to the production of LiFeAs with chemical doping and characterize the effects of doping on the superconductivity of LiFeAs . In particular, I look at the effects of Co doping on the Fe site and P doping on the As site.

Synthesizing LiFeAs

First, we needed to develop a method for reliably producing superconducting LiFeAs crystals. Superconductivity in LiFeAs is quite sensitive to the methods of synthesis used in the lab where it was produced. Although LiFeAs is known to superconduct at 18 K, many labs are unable to generate samples with a critical temperature that high. Each lab has its own preferred process, but the basic underlying principles are the same. The component elements need to be dissolved in a medium of molten metal, called the “flux,” through heating. Then, the crystals form during a period of slow cooling. After the sample has cooled to room temperature, the crystals must be extracted mechanically or through heating to melt off the flux. Finally, investigators must prepare the samples for measurement. Because LiFeAs is oxygen-sensitive, labs must take precautions to limit the crystals’ atmospheric exposure. At each step in the process, there are many variables, so optimizing the results is a challenging task.

Choosing a Flux

The first step in producing LiFeAs is choosing a metal flux. In order to work as a flux, a metal must be able to form a solution with an appreciable molar concentration of all the component elements (typically, 5% minimum) at a reasonable temperature (our absolute limit was 1400 °C). To select an appropriate flux for our samples, we looked at binary phase diagrams of Li, Fe, and As with potential candidate metals. Later, we also considered the solubility of Co and P for producing doped crystals.

Tin is the most common metal used as a flux for growing LiFeAs crystals, because it dissolves Li, Fe, and As. Tin is also relatively malleable, and has a melting point of 231.9 °C. Because it melts on a hot plate without dissolving LiFeAs crystals and permits mechanical molding and separation, harvesting crystals grown in tin flux is relatively straightforward. We made our first LiFeAs samples in tin flux.

Another common flux is prereacted FeAs, with which single LiFeAs crystals as large as 6X6X3 mm³ have been reported. Called “self flux” because the crystals are grown in a solution of their own components, this method involves more preparation and poses a more challenging extraction process. To use the self flux method, we compressed iron powder and arsenic flakes into pellets, prereacted them at 1000 °C, and then used the pellets as the flux for sample growth. Heating is not an option for extraction, because it requires prohibitively high temperatures and would simply dissolve the crystals, so the crystals must be mechanically pulled out of the flux, which is much less malleable than tin.

Although we made samples both with tin flux and self flux, we also tried In flux, which has not been reported used with LiFeAs crystals. Indium offers several advantages, because it dissolves all of the component elements, has a melting point of 156.6 °C, and is more malleable than tin. This means that harvesting crystals grown in In flux is even easier than harvesting from tin.

Designing a Temperature Scheme

For each sample, we needed to decide on a temperature scheme, which we programmed into the ovens. The ovens would heat up at 75 °C/hr to a peak temperature where the sample was entirely liquid, hold at that temperature for several hours, and then cool down slowly past the point where the components of LiFeAs would precipitate into solid crystals. At that point, we could cool the ovens at 75 °C/hr and pull out the sample. Each sample demanded slightly different parameters to account for the differing solubility of its components, and we often modified the process by adding dwell periods, decreasing the cooling rate, or adjusting the temperature bounds for the slow cool to promote the growth of larger crystals. Figure 1

illustrates our most successful temperature scheme for LiFeAs growth in Sn-24, featuring a dwell period for soaking at 450 °C and a slow cool at 4 °C/hr from 890 °C to 577 °C.

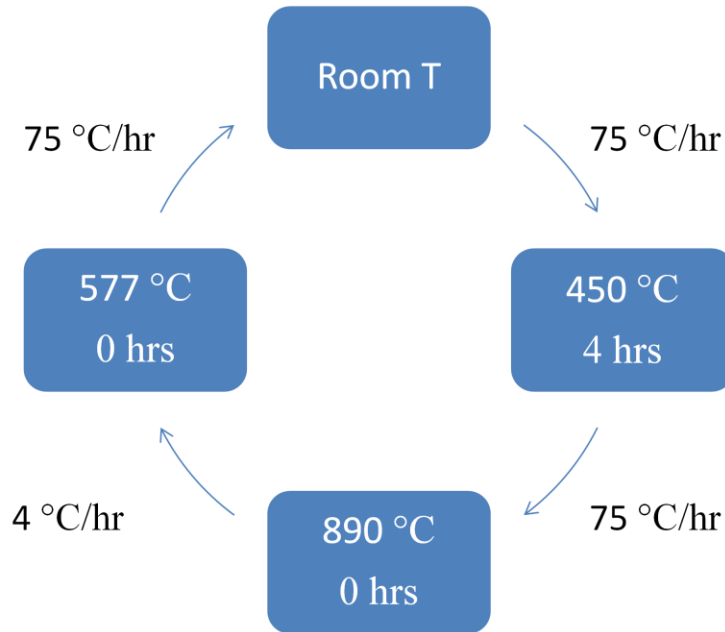


Figure 1. Our temperature scheme for LiFeAs in Sn-24 flux.

Mixing, Sealing, and Baking the Samples

Because the component elements of LiFeAs are oxygen-sensitive, we measured out and mixed all our samples in an argon environment glove box. Basing our stoichiometry on an original mass of Li because it is most difficult to handle, we calculated out and measured the corresponding masses of our other components to make the mixtures shown in Table I.

We mixed earlier samples with a 50% surplus of Li, based on literature indicating that this might lead to a higher critical temperature and more reliable superconductivity. Later, after harvesting these samples, running our own measurements, and finding different literature suggesting lower concentrations of Li yielded better results, we switched to even stoichiometric mixing. In later samples, we also used prereacted FeAs pellets in place of iron powder and arsenic flakes, because labs that used prereacted FeAs seemed to get better results.

After mixing the elements, we poured them into an alumina crucible, a nonreactive material selected for its resistance to extremely high temperatures. We then placed this crucible with a lid into a niobium “bomb,” a cylinder which was then arc-welded shut, all the while maintaining an Ar atmosphere. We slid these bombs on tantalum foil into the center of a tube furnace, which we insulated and sealed. Before turning on the furnace, we started a constant flow of Ar gas through the tube to prevent oxidation at high temperatures. The furnaces ran for several days for each sample, up to almost 2 weeks.

Table I. Synthesized samples. **GREEN** = Crystals large enough to contact individually, **RED** = Small crystals, **BOLD** = Measured as superconducting.

Sn-24 Flux	In-40 Flux	FeAs Self-Flux
Li _{1.5} FeAs	Li _{1.5} FeAs	LiFeAs (FeAs pellets)
Li _{1.5} Fe _{.75} Co _{.25} As	Li _{1.5} Fe _{.75} Co _{.25} As	
Li _{1.5} FeAs _{.75} P _{.25}	Li _{1.5} FeAs _{.75} P _{.25}	
LiFeAs	LiFe _{.75} Co _{.25} As (FeAs pellets)	
LiFe _{.75} Co _{.25} As (FeAs pellets)	LiFeAs _{.75} P _{.25} (FeAs pellets)	
LiFeAs _{.75} P _{.25} (FeAs pellets)		

Harvesting the Crystals

After pulling the Nb bombs out of the furnace, we moved them into the glove box and opened them with a pipe cutter. The size and number of surface crystals we could see determined the qualitative success of our sample. Larger crystals are easier to measure and yield better data, while small crystals are very difficult to work with. Table I breaks down the sample yields.

The first round of samples, made with surplus Li in Sn-24 flux, produced a respectable yield. The undoped sample and the Co-doped sample both held moderately sized crystals measuring about $3 \times 3 \text{ mm}^2$, but the P-doped sample held extremely small crystals, a thin surface layer of mere specks. In two of the samples, we found unreacted pellets of Li, a discovery that would later influence our decision to stop mixing samples with Li surplus. When we returned to Sn-24 flux to make samples without Li surplus, the crystal sizes were consistent with our earlier samples: Undoped and Co-doped held reasonable crystals, while P-doped held very tiny crystals.

The next set of samples, with surplus Li in In-40 flux, yielded only extremely small crystals. Later, when we made the doped samples a second time in In-40 flux with prereacted FeAs and a much slower cooling rate, the sample still had only specks.

When we opened the Nb bomb to look at our self-flux sample, we did not find what we expected. The crucible was blackened and stained green and pink, and small pink crystals had formed on the walls of the bomb. There were crystals in the crucible, but they had a strange red tint to them, different from the crystals we normally worked with. Evidently, when we heated the sample to $1400 \text{ }^\circ\text{C}$, some of the sample (probably lithium) evaporated, and unexpected and unwanted reactions took place.

To retrieve the crystals, we used a hot plate in the glove box to raise the crucibles to the melting point of Sn or In, depending on the sample. Then, we plucked out large crystals individually, and dragged them across a glass slide on the hot plate to clean off what flux we could. If there were only small crystals (as in the case of the In samples), we tried to pull them off in a thin sheet of flux, so that we ended up with a flat cluster of small crystals we called an “alligator skin.” If we could not get a good “alligator skin,” we would transfer the sample to a

vial for centrifuging. We did not harvest the self flux sample because we could not be sure what compounds we would pull out.

Measuring the crystals

Once we harvested the crystals, we selected the best single crystals for resistivity measurements. We contacted the crystals by attaching thin platinum wire to four corners with silver epoxy. It was a delicate procedure in the glove box, and the contacts frequently needed to be repaired. We also contacted alligator skins for samples that had no large single crystals; though the cluster would not be fully superconducting, any transition to a superconducting state by the small crystals would short paths through the flux, which might be noticeable in a resistivity measurement.

Samples without large crystals or alligator skins that went through the centrifuge could be used in the Superconducting Quantum Interference Device (SQUID) magnetometer. The SQUID provides a more precise method of characterizing crystals, but it is often difficult to get time with the machine, and its measurements are much slower. Resistivity measurements are better for our needs, because they provide a relatively quick way to determine if a sample superconducts and at what temperature. For these reasons, and Dr. Kim's suggestion that the centrifuge process could alter the properties of the crystals, we generally favored resistivity measurements.

After contacting the crystals we wanted to measure for resistivity, we soldered them into a probe, sealed the probe, and evacuated it. We then slowly lowered the probe into a dewar filled with liquid helium. We also wired the probe up to a current source and voltmeter for the reference thermometer in the probe, a current source for the heater in the probe and a separate current source and voltmeter to the leads from the crystal. Using the current source and voltmeter, we took a four-point resistivity measurement on the crystal: Current would flow

between two of the contacts, and the potential difference would be measured between the other two. After cooling the sample until it reached an equilibrium at 5 K, we used a computer program to gradually increment current to the heater and to take resistivity measurements from 5 K to 50 K.

In our first rounds of samples, both In-40 flux and Sn-24 flux with surplus Li, none of the crystals demonstrated a superconducting transition. Finally, when we made our undoped LiFeAs sample without Li surplus, we achieved a partial superconducting transition at 8 K, as shown in Figure 2. Although the sample did not fully superconduct, probably because of flux embedded in the sample, and its transition was 10 K lower than the accepted 18 K, this still represents a degree of success in our efforts.

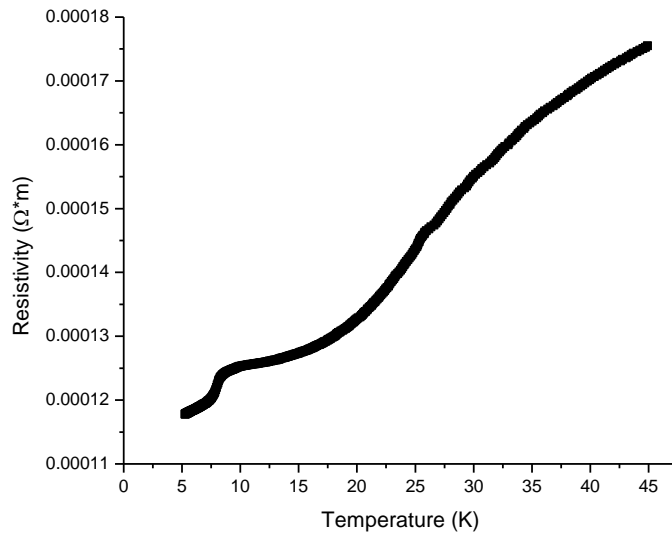


Figure 2. LiFeAs in Sn-24 exhibits a transition to a partially superconducting state at 8 K.

However, when we moved on to measure a Co-doped sample in Sn-24 flux with no surplus Li, we saw no transition, as shown in Figure 3.

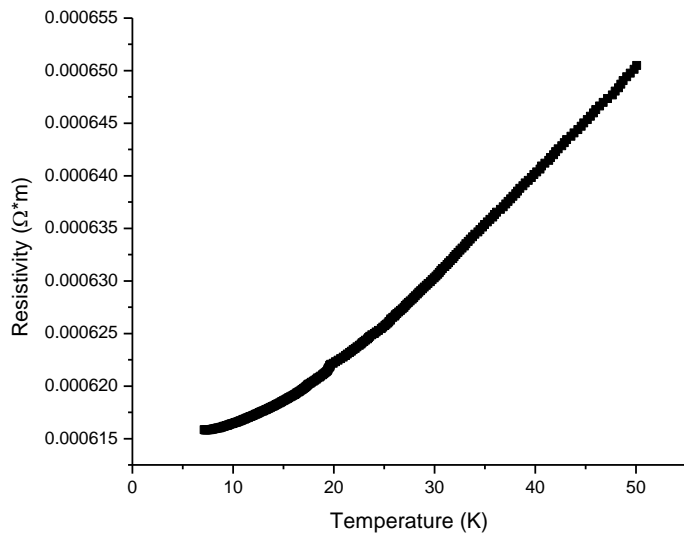


Figure 3. $\text{LiFe}_{0.75}\text{Co}_{0.25}\text{As}$ in Sn-24 shows no transition.

When we ran an alligator skin from a Co-doped sample in In-40 flux, we saw a strange anomaly in the resistivity measurements at about 17 K, as seen in Figure 4. This could possibly be a superconducting transition, and needs to be investigated further.

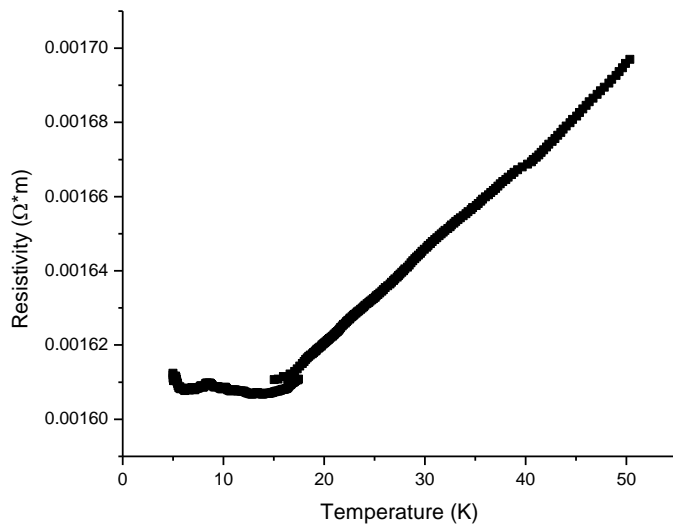


Figure 4. A resistivity anomaly in $\text{LiFe}_{0.75}\text{Co}_{0.25}\text{As}$ at 17 K.

Conclusion

Although almost all of the samples we synthesized failed to superconduct, we did demonstrate some valuable lessons about producing superconducting LiFeAs. Indium is not an effective medium for large single-crystal growth, and when doping LiFeAs with P, only small crystals are produced. Surplus Li also seems to have a negative impact on the superconductivity of the sample.

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References

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