

Searching for new FeAs based superconductors

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Abstract:

LiFeAs is a promising iron-pnictide superconductor of the 111 structure that can help explain high-temperature superconductivity. LiFeAs parent compound as well as Co doped (on the Fe site) and P doped (on the As site) samples underwent resistivity measurements at cryogenic temperatures. Crystals grown in indium, tin and self-flux were examined. LiFeAs crystals grown in Sn flux were found to become partially superconducting at ~8 K. None of the other samples transitioned into the superconducting state. Single crystals grown in In flux were small at the attempted temperature schemes and were not practical for resistivity measurements.

Introduction:

LaOFeP was the first iron-pnictide superconductor discovered by Hosono et al. in 2006 with a transition temperature, T_c , of ~ 4 K [1]. In 2008, Kamihara et al. made the next step by replacing some of the oxygen with fluorine creating $\text{LaFeAsO}_{1-x}\text{F}_x$ with a T_c of 26 K [2]. This structure is now known as the 1111 type superconductor. Other types of FeAs based superconductors include the 122 family (e.g. BaFe_2As_2) and the 11 family (e.g. FeSe) [3]. This paper, however, will focus on the 111 family, primarily LiFeAs and its various doping and flux schemes.

To grow LiFeAs crystals, Li, Fe, and As are combined in the desired molar ratio with another element to act as a solvent, or flux. These elements have to be combined in a crucible made of non-reactive materials in order to keep the crystals unpolluted. Aluminum oxide, or Alumina, crucibles are an acceptable choice but niobium or platinum crucibles can also be used. In the case of LiFeAs, the common flux is tin. Indium fluxes are also examined in this paper, however.

To determine the temperature scheme for crystal growth, binary phase diagrams are used. The diagrams indicate temperatures at which solutes form compounds with the flux. Since the flux is used to facilitate the mixing of the other elements and not as a component of the crystals, these compounds would be undesirable. To avoid these unwanted compounds, the sample is heated to a temperature that is high enough that all elements are dissolved in the flux. Then the sample is slowly cooled so that the crystals can precipitate out of the flux. Slower cooling rates usually tend to yield bigger crystals; however, there is a trade off of time. Finally, the rate of cooling must be increased when the temperature reaches a level at which the non-flux elements tend to form compounds with the flux to prevent the formation of the extraneous compounds.

A possible way to increase T_c of a superconductor is to introduce impurities, or dope the sample. In the case of LiFeAs, one possibility is to replace some of Fe with Co (producing $\text{LiFe}_{1-x}\text{Co}_x\text{As}$) or to replace some of As with P (producing $\text{LiFeAs}_{1-x}\text{P}_x$). Different amounts of doping can produce different transitional temperatures or even prevent superconductivity. Doping elements are usually located close to the ones they are substituting in the periodic table and are usually introduce additional charge carriers (either hole or electron).

Method

Growing Crystals

All samples were prepared in a sealed glovebox in Argon atmosphere. Elements were combined according to the desired molar ratio in an Alumina crucible and sealed in a niobium bomb. The sealed samples then underwent a specific heating and cooling scheme. Phase diagrams of the elements involved were used in order to choose suitable temperatures for the heating scheme. After the samples were removed from the oven, they were opened in the glovebox and the resulting crystals were examined.

Harvesting the Crystals

Grown crystals smaller than a square millimeter were considered too small for resistivity measurements. (It is possible to check for superconductivity in such crystals by centrifuging them and using a susceptometer; however, the goal was to grow larger crystals so this was not done). Larger crystals were mechanically harvested and cleaned from the flux on a hotplate.

Measuring Resistivity

To measure resistivity, the first step is to contact the crystals. Conductive silver epoxy was used to connect four platinum wires (0.0508 mm in diameter) to the crystal such that neither the wires nor the epoxy were touching each other. A contacted crystal can be seen in Figure 1.



Figure 1. Contacted Crystal

The contacted crystal was then taken out of the glovebox and the wires soldered onto a resistivity probe which was sealed and vacuumed. The probe was then placed in a dewar filled with liquid hydrogen. As the probe was cooling down, a current was sent through two of the wires, and the voltage that appeared due to resistance in the crystal was measured across the other two wires.

To determine the resistance of the crystal, Ohm's law was used,

$$V=IR \quad (1)$$

where V is the voltage, I is the current, and R is the resistance. A computer program was used to record temperature and resistance data throughout the cooling and heating of the probe.

Since resistance depends on the geometry of a crystal as well as on its composition, it is a quantity that changes with each crystal. Therefore, resistivity, which is independent of geometry, was calculated from resistance measurements. Resistivity is related to resistance by:

$$\rho=R*A/L \quad (2)$$

where ρ is resistivity, A is the cross sectional area, L is length and R is the resistance. A plot of ρ vs. temperature was used to determine whether the sample became superconductive and if so, T_c was established. It should be noted that the values for resistivity are only approximate. The wires were placed at irregular locations on the crystal and, therefore, the cross sectional area and length values had to be estimated.

Oven Cycle Schemes for Prepared Samples

The LiFeAs , $\text{Li}(\text{Fe}_{.75}\text{Co}_{.25})\text{As}$, and $\text{LiFe}(\text{As}_{.75}\text{P}_{.25})$ samples prepared in Sn flux were heated from room temperature to 450°C at a rate of $75^\circ\text{C}/\text{hour}$ and held at that temperature for 4 h. The temperature was then increased to 890°C at a rate of $75^\circ\text{C}/\text{h}$. It was then lowered to 577°C at $4^\circ\text{C}/\text{h}$ and then dropped back to room temperature at $75^\circ\text{C}/\text{h}$.

The LiFeAs sample prepared in In flux were heated from room temperature to 1000°C at a rate of $75^\circ\text{C}/\text{h}$ and held at that temperature for 5 h. The temperature then fell to 550°C at a rate of $5^\circ\text{C}/\text{h}$. Finally, the temperature dropped to room temperature at $75^\circ\text{C}/\text{h}$. $\text{Li}(\text{Fe}_{.75}\text{Co}_{.25})\text{As}$ and $\text{LiFe}(\text{As}_{.75}\text{P}_{.25})$ went through the same oven cycle and through a cycle in which the cooling from 1000°C to 550°C was at a rate of $2.5^\circ\text{C}/\text{h}$. The purpose of the slower cooling was to grow larger crystals.

The self-flux sample, $\text{Li}(\text{FeAs})_2$, was prepared by heating the oven to 1392°C at a rate of $75^\circ\text{C}/\text{h}$ and held at that temperature for 5 hours. Then, at a rate of $5^\circ\text{C}/\text{h}$ the temperature was lowered to 400°C and, finally, dropped to room temperature at $75^\circ\text{C}/\text{h}$.

Results:

No superconductivity was found in LiFeAs crystals grown in Sn flux with a molar mass ratio of 1.5:1:1:24 (Li:Fe:As:Sn). Similarly, no superconductivity was found in cobalt and phosphorus doped samples grown in Sn flux with ratios of 1.5:0.75:0.25:1 (Li:Fe:Co:As) and 1.5:1:0.75:0.25 (Li:Fe:As:P) respectively. Likewise, superconductivity was not detected in samples with Li amount being 1 rather than 1.5 in the above ratios for the doped samples. The phosphorus doped samples produced crystals that were too small for contacting and, therefore, resistivity was not measured. The next step will be to attempt to grow bigger crystals. The Co doped sample contained bigger crystals and resistivity measurements were done. Figure 2 indicates that there was no transition into the superconducting state in the crystal.

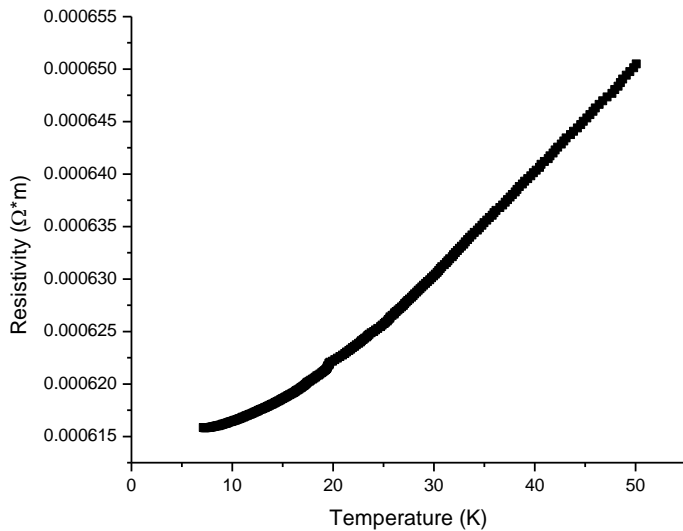


Figure 2. Resistivity vs. Temperature graph of $\text{LiFe}_{0.75}\text{Co}_{0.25}\text{As}$ in Sn flux

However, a transition was observed in crystals with a ratio of 1:1:1:24 (Li:Fe:As:Sn) at ~ 8 K as seen in Figure 3. Although the recorded T_c is ~ 18 K, which is 10 K above the measured T_c , the finding is still a success. While we cannot state that the whole sample became superconductive, the transition indicates that part of the sample did. More measurements will

have to be made on the crystals in order to confirm whether or not the stoichiometry of the sample is as expected. Further attempts can then be made to increase the transition temperature by trying different cooling schemes as well as different molar ratios of elements.

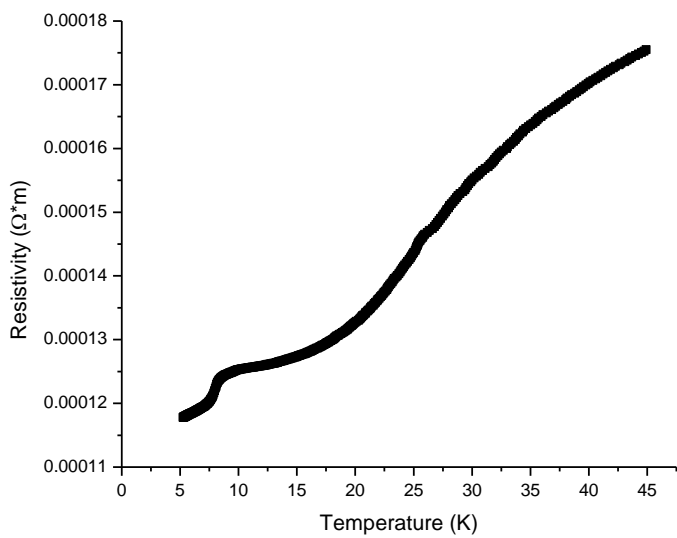


Figure 3. Resistivity vs. Temperature graph of LiFeAs in Sn flux

Crystals grown in In flux with a molar ratio of Li:In being 1:40 were very tiny and could not be contacted individually. However, when the sample was heated on the hotplate, the top layer of crystals could be lifted off as a sheet held together by the flux. This sheet of crystals and flux was contacted and underwent resistivity measurements. Figure 4 shows the resulting graph for the Co doped sample. No superconductivity was detected in this sample.

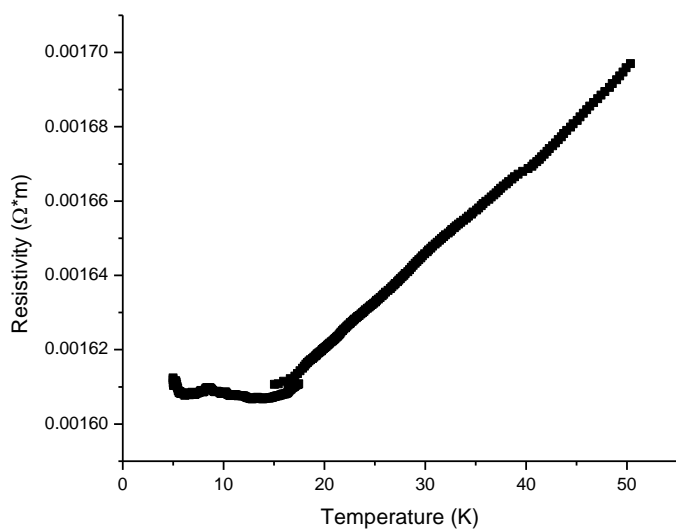


Figure 4. Resistivity vs. Temperature graph of $\text{LiFe}_{0.75}\text{Co}_{0.25}\text{As}$ in In flux

Finally, the crystals grown in self-flux did not undergo resistivity measurements. When the sample was opened, it was observed that some of it had evaporated due to the high temperature to which it was heated. It was not possible to tell if the formed crystals had the desired stoichiometry and until that can be determined the resistivity measurement results would not be useful.

Conclusion:

Crystals grown in Sn flux were of practical sizes while crystals grown in In flux were too small to be contacted. In the future, slower cooling processes will be attempted when In flux is used in order to give crystals more time to form. No superconductivity was found in Co or P doped samples of LiFeAs in either In or Sn flux. Likewise, there was no superconducting transition in LiFeAs crystals grown in In flux. LiFeAs crystals grown in Sn flux did show a transition at ~ 8 K but more measurements need to be taken to make sure that the stoichiometry is

correct. However, the result is still important because it is the first step in achieving full superconductivity in LiFeAs in Dr. Stewart's lab.

Acknowledgments:

I would like to thank the University of Florida REU program and the National Science Foundation for an opportunity to participate in research. I would also like to thank my advisor Prof. Gregory Stewart for all his help as well as Adam Sandwell, Evan Kim, and Jung Soo Kim for their advice and patience. Additionally, I thank Joshua Giles for being a great research partner and his continuous optimism. Finally, I am grateful to Selman Hershfield and Christine Scanlon for their coordination and assistance throughout the program.

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