

## **Test of antimony as metal flux for growth of LiFeAs crystals**

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Homogenous crystals that are free of impurities are necessary for learning more about LiFeAs, but existing growth methods have proven insufficient. Here, antimony was investigated as the flux (solvent) for crystal growth and three crystal extraction techniques were tested. Li, Fe, As, and Sb were heated together in a sealed container to 900°C and then slowly cooled down. Afterward, acid etching, centrifugation, and mechanical separation were attempted. Each had limited to no success in separating crystals from the Sb flux. The magnetic susceptibility of two prospective crystals was measured on a superconducting quantum interference device and the data do not suggest that the tested masses are superconducting crystals. Other materials will need to be tested as the flux for growing these crystals if more is to be learned about LiFeAs.

### **I. Introduction**

LiFeAs is an iron pnictide superconductor, a recently discovered<sup>1</sup> subset of superconductors whose properties and underlying mechanics are not yet fully understood.<sup>1</sup> To effectively characterize and thereby study superconducting materials, high-quality crystals are needed.<sup>2</sup> Being able to consistently and easily yield pure, homogenous crystals of LiFeAs would allow for further research into this unusual<sup>1</sup> superconductor, which could in turn lead to advancements in the study of superconductivity as a whole. Implementation of superconducting materials has already led to MRI machines and high-speed maglev trains;<sup>3</sup> less expensive superconductors with higher critical temperatures<sup>4</sup> would allow for more widespread use and numerous other applications.<sup>5</sup>

LiFeAs has a critical temperature of 18 K and a tetragonal structure that results in crystals with two-dimensional plane surfaces.<sup>1</sup> LiFeAs is one example of an iron pnictide superconductor, a group of superconductors first discovered in 2008.<sup>1</sup> Unlike other type II superconductors,<sup>6</sup> iron pnictide superconductors have nodes<sup>1</sup> (though it appears that LiFeAs does not).<sup>1</sup> Iron pnictides' electrons pair in an unknown manner (perhaps by exchange of spin fluctuations)<sup>1</sup> that is significantly different from conventional superconductors.<sup>1</sup> Additionally, the fact that LiFeAs is non-magnetic yet does not have a phenomenon called nesting may mean that nesting is needed for magnetism.<sup>1</sup> To gain more knowledge and answer these unknowns requires better crystal samples.<sup>1</sup>

The broadness of the temperature range of the transition to superconductivity is an indicator of sample quality that is often used – a high-quality sample will have a very narrow transition.<sup>1,7</sup> LiFeAs crystals grown using self-flux (i.e., the solvent used for crystal growth is FeAs that has already been reacted)<sup>1</sup> and with tin flux have not been of sufficient quality.<sup>7</sup> (FeAs may be being deposited in the lattice structure of the crystal, and the Sn may be doing the same and/or forming pockets of pure tin within the crystal.<sup>1</sup>) Could antimony serve as a more effective flux, resulting in objectively better crystals that can help further our understanding of LiFeAs? After experimenting with acid etching, centrifugation, and mechanical separation to find and separate crystals, and then measuring their magnetic susceptibility, it appears that this is not the case. Additional research, using other elements as the flux, will be needed if satisfactory crystals of LiFeAs are to be obtained.

## II. Methods

## A. Materials and instruments

A glovebox filled with ultra-high-purity argon was the preparation location. A high-precision Sartorius balance was used to determine the mass of each element as it was prepared. Alfa Aesar-sourced lithium granules (99% pure), iron powder spheres (99+% pure), arsenic powder (99.99% pure), and antimony pieces (99.999% pure) were used. These four elements were contained within an alumina crucible, which in turn was contained within a niobium cylinder. An arc welder was used to seal a niobium lid onto the Nb cylinder. A Lindberg furnace was used to thoroughly melt the elements together. Glacial acetic acid, 50-70% nitric acid, 85% *o*-phosphoric acid, and deionized ultra-filtered water (all from Fischer Scientific) were used in testing acid etching, as were a fume hood, lab glassware, and neoprene gloves. Quartz glass tubes were partially filled with quartz wool for centrifugation. They were sealed with an oxyhydrogen torch. The resistivity of crystals was measured by attaching 0.05 mm-thick platinum wires to the crystals with Epoxy Technology H20E-LV two-part epoxy and using lead solder to attach those wires to a probe with a built-in LakeShore thermometer. Liquid nitrogen was used to precool the cryostat in which resistivity measurements were taken, and liquid helium was used to cool the cryostat further. LabVIEW was used to measure and graph the data. To measure magnetic susceptibility, crystals were placed in pill capsules and secured to a probe with non-magnetic tape; the pill capsules were then placed in a Quantum Design MPMS-5S superconducting quantum interference device (SQUID).

## B. Procedures

Working within an ultra-high-purity argon-filled glovebox, lithium, iron, and arsenic were weighed and placed into an alumina crucible. A stoichiometric amount of each was used so that

their molar ratios were 1:1:1. (The actual mass of each was 0.03600 g of Li, 0.28898 g of Fe, and 0.39280 g of As.) Antimony was added so that its molar amount was 15 times that of the other elements (actual mass of 9.43184 g). The alumina crucible was placed within a niobium cylinder that already had a bottom cap arc welded on. The top cap was firmly pushed onto the cylinder before the cylinder was transferred out of the glovebox in a sealed glass jar; the Nb reaction vessel was transferred into the arc welder as soon as possible to minimize exposure to air and the top cap was arc welded on. The cylinder was placed in the furnace. The furnace was programmed to go through the following sequence: from room temperature to 250°C at a rate of 50°C per hour and stay at 250°C for 24 hours; from 250°C to 900°C at 75°C per hour and stay at 900°C for 4 hours (to allow for thorough homogenization of the elements); from 900°C to 500°C at 3.5°C per hour (to allow for slow crystal growth as the mixture cooled through the unknown nucleation temperature); and then to automatically cool down to room temperature at the fastest rate the furnace allows. During the furnace's operation, argon flowed through the furnace to prevent oxidation of the niobium cylinder. After the sequence was complete, the niobium cylinder was removed from the furnace and transferred back into the glovebox, where it was opened using a pipe cutter. A hammer was used to destroy the alumina crucible in order to extract the disc-like block of metal containing the now-solid mixture of flux and other elements. The block was divided into smaller pieces using a wire cutter.

The effectiveness of acid etching was tested by making three different acid mixtures and testing them on pure antimony and/or old LiFeAs crystals. The three acid mixtures were 400:1 distilled water to glacial acetic acid; 16:4:3 distilled water to nitric acid to glacial acetic acid at 40°C, followed by 400:1 distilled water to glacial acetic acid; and 3:3:1:1 phosphoric acid to nitric acid to glacial acetic acid to distilled water at 50°C [8]. While using the necessary personal

protective equipment (acid-proof neoprene gloves), a fume hood, and appropriate glassware, the constituent acids were added to the distilled water. The antimony and crystals were placed in separate glass jars and then the acid mixture being tested at the time was poured into the jars. The antimony and crystals were observed for changes.

For centrifugation, quartz wool was placed within a quartz tube. An appropriately sized piece of the flux/crystal combination was placed into the quartz tube and the tube was sealed with a stopper. The quartz tube was then transferred out of the glovebox. Using an oxyhydrogen flame, the tube was sealed under vacuum and then placed in a furnace at 800°C (a second attempt was performed at 900°C). After several minutes, the tube was placed into a centrifuge at 4,000 revolutions per minute for 5 minutes. The molten Sb flowed through the glass wool to the bottom of the quartz tube while the crystal-like masses stayed on top of the wool. The tube was transferred into the glovebox, where it was broken open with a hammer. All crystal-like masses were picked out and stored in a vial.

Mechanical separation involved dividing the flux block with wire cutters (under a Kimwipe, to prevent pieces from flying and being lost in the glovebox). Crystals that “fell out” without additional effort were set aside (there were none, in this case). Otherwise, the pieces were broken up further until they became too small to contain any sufficiently large crystals.

A crystal was chosen for magnetic susceptibility measurements, its mass was determined, and it was placed in a pill capsule. Quartz wool was added also to minimize the crystal’s movement during measurements. The pill capsule was transferred out of the glovebox and placed into a SQUID. The SQUID took data points in the following manner: once every 0.5 K from 5 K to 10 K, once every 0.1 K from 10.1 K to 20 K, and once every 0.5 K from 20.5 K to 30 K. The

data were then normalized by multiplying the long moment by the molar mass of LiFeAs and dividing by the product of the mass of the sample and the magnetic field used in Gauss.

For resistivity measurements,<sup>9</sup> epoxy was used to attach four platinum wires to a single crystal face: two for measuring current and two for measuring voltage. The wires were soldered onto a probe's pins and then the probe was placed in a cryostat. LabVIEW was used to measure the resistivity as the sample was heated from the temperature of liquid helium (roughly 4.2 K) to 300 K.

### **III. Results**

#### **A. Separation techniques**

Acid etching using both the 16:4:3 distilled water to nitric acid to glacial acetic acid mixture and the 3:3:1:1 phosphoric acid to nitric acid to glacial acetic acid to distilled water mixture destroys LiFeAs crystals. Acid etching with all three mixtures made no noticeable difference on pure antimony.

The first centrifugation yielded some crystal-like masses. The second centrifugation, performed at 900°C rather than 800°C, resulted in no crystal-like masses. Mechanical separation on the remaining half of the flux/crystal block yielded no LiFeAs crystals.

#### **B. Characterization data**

The first crystal that was placed in the SQUID has a mass of 4.55 mg. Its magnetic susceptibility data are represented in Fig. 1.

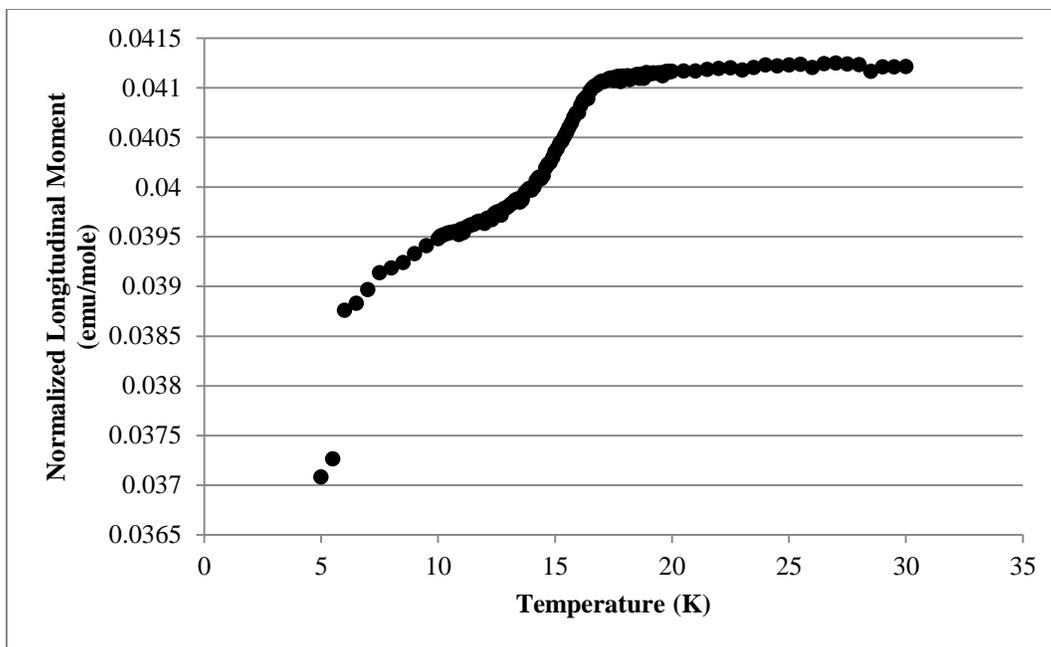


FIG. 1. Plot of longitudinal moment vs. temperature for the first crystal. The longitudinal moment was normalized to take the mass of the crystal into account. Magnetic susceptibility is related to magnetization, which is in turn a measure of magnetic dipole moment per volume.<sup>10</sup>

The second crystal that was placed in the SQUID has a mass of 21.56 mg. Its magnetic susceptibility data are represented in Fig. 2.

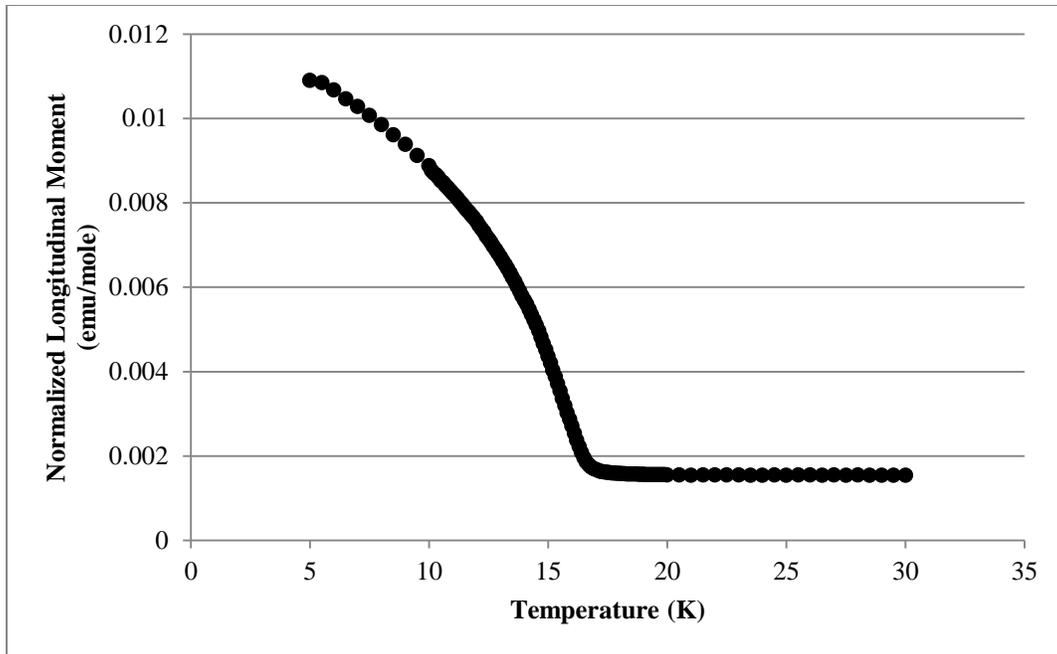


FIG. 2. Plot of longitudinal moment vs. temperature for the second crystal. The longitudinal moment was normalized for this plot as well.

#### IV. Discussion

Antimony is particularly shiny and lustrous and it is thus similar in appearance to LiFeAs crystals. This made visually distinguishing potential crystals from mere flux rather difficult. Since this is a preliminary characterization method, an inability to easily determine what are or are not crystals is a detrimental quality for a flux. The first crystal placed in the SQUID appeared to be a single crystal of LiFeAs in that it was pseudo-two-dimensional (plate-like) and shiny; when the data were judged to be insufficient, a second piece was selected. This second piece was chosen based on its dissimilarities with the first crystal – it was larger and not very plate-like. After the second SQUID measurement was made, the two masses and a piece of pure antimony were examined under a microscope. This revealed a possible explanation for the especially

abnormal data generated while examining the second mass: while the first mass was notably different from the antimony, the second looked virtually identical to antimony.

The goal of acid etching in the context of metal flux growth of crystals is to remove enough of the flux to allow for the collection of crystals. Qualitative observations of pure antimony in the various acid mixtures revealed no changes in the size of the antimony, even after many hours. LiFeAs is very sensitive to air,<sup>2,7</sup> so even if the acids had been effective at removing antimony, etching with acid would be difficult to perform without damaging the crystals. The fact that two of the acid mixtures themselves immediately reacted with LiFeAs crystals is just one more reason to not use acid etching as a separation method.

When a flux is chosen, the solubility of the other elements must be taken into consideration, as should the possibility of competing reactions and the melting temperature of the flux.<sup>2</sup> Additionally, for air-sensitive materials like LiFeAs that must be sealed as they are being heated in a furnace, the vapor pressures of all of the elements is important, particularly because As has a vapor pressure of 1 atm. at 600°C.<sup>2</sup> With these constraints in mind, a 15:1 molar ratio between antimony and Li, Fe, and As was chosen. The size of the crucible limited the total amount of material, resulting in a potential mass of crystals of only 0.718 g (the actual mass was likely lower still). Crystals of LiFeAs are usually between 4 and 20 mg each, so this should not have been a limiting factor.<sup>7</sup>

Because of antimony's high melting point (~631°C [3]), it cannot be melted on a standard hotplate – this would have allowed for crystals to be carefully picked out from the molten flux using only tweezers. Centrifugation is an alternative method that relies on a similar principle, i.e., melting the flux off of the crystals. The fact that some crystal-like masses were obtained in

the first centrifugation but not the second may be because of the difference in the temperature that was used. It is also possible that there simply were no crystals in the piece selected (it was approximately one-fourth the total mass of the flux/crystal block, as was the first piece that was centrifuged).

Based on the data in Figs. 1 and 2, it appears that neither of the tested masses was pure LiFeAs. Although the plot of the first crystal (Fig. 1) has the general shape of LiFeAs,<sup>11</sup> the transition seems to be incomplete – the value for the normalized long moment should have become negative in the lower temperature range.<sup>7</sup> Given the broad transition, it is possible that this was a crystal of LiFeAs, albeit an impure one (perhaps with the same impurities that affect Sn- and self-flux derived LiFeAs discussed above). The plot of the second mass's data (Fig. 2) does not fit the pattern of a superconductor.<sup>7</sup> The second centrifugation was performed after the second SQUID run in an attempt to find better crystals. When neither that nor mechanical separation yielded more crystals, it was decided that further susceptibility measurements would not be made and that no resistivity measurements would be attempted either.

## V. Conclusion

Based on the difficulty in identifying and isolating potential crystals, along with the fact that none of the tested masses had long moment vs. temperature data that indicate a superconductor, it appears that antimony is an unsatisfactory flux for growing crystals of LiFeAs. Tweaking the flux's molar ratio to the other elements and/or the sequence of heating and cooling may each allow for improved LiFeAs crystal growth in Sb. Nonetheless, antimony's other drawbacks make it less than ideal to work with as a flux in this application. If the

properties of LiFeAs are to be further studied and better understood, then experimentation with other fluxes is necessary.

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<sup>1</sup>G. R. Stewart, *Rev. Mod. Phys.* **83**, 1589–1652 (2011).

<sup>2</sup>A. S. Sefat, arXiv:1304.7708.

<sup>3</sup>HyperPhysics from Georgia State University, <http://hyperphysics.phy-astr.gsu.edu/hbase/hph.html>.

<sup>4</sup>The critical temperature is the temperature at which a material begins to superconduct.

<sup>5</sup>Some potential applications include reducing waste in electrical grids by using transmission lines made of superconductors, significantly lighter and smaller generators and motors, and high-capacity surge protectors.<sup>3</sup>

<sup>6</sup>Type II superconductors are usually alloys, while type I superconductors are pure elements. In type I superconductors, the flux enters the material all at once at the upper critical field, while in type II superconductors, it only enters partially [at least until the superconductivity is suppressed at the type II's (higher) critical field].<sup>7</sup>

<sup>7</sup>G. R. Stewart (private communication).

<sup>8</sup>Wet Chemical Etching of Metals and Semiconductors page from Brigham Young University, [http://www.cleanroom.byu.edu/wet\\_etch.phtml](http://www.cleanroom.byu.edu/wet_etch.phtml).

<sup>9</sup>Resistivity was not actually measured for any Sb flux-derived LiFeAs crystals, for reasons explained in the Discussion.

<sup>10</sup>D. J. Griffiths, *Introduction to Electrodynamics* (Prentice-Hall, Inc., New Jersey, 1999), Third Ed., p. 262; (Prentice-Hall, Inc., New Jersey, 1999), Third Ed., p. 274.

<sup>11</sup>G. Li *et al.*, *Phys. Rev. B* **87**, 024512 (2013).