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Anisotropic magnetism, resistivity, London penetration depth and magneto-optical imaging of superconducting K$_{0.80}$Fe$_{1.76}$Se$_2$ single crystals

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Received 9 February 2011, in final form 2 March 2011
Published 31 March 2011
Online at stacks.iop.org/SUST/24/065006

Abstract

Single crystals of K$_{0.80}$Fe$_{1.76}$Se$_2$ were successfully grown from a ternary solution. We show that, although crystals form when cooling a near-stoichiometric melt, crystals are actually growing out of a ternary solution that remains liquid to at least 850°C. We investigated their chemical composition, anisotropic magnetic susceptibility and resistivity, specific heat, thermolectric power, London penetration depth and flux penetration via magneto-optical imaging. Whereas the samples appear to be homogeneously superconducting at low temperatures, there appears to be a broadened transition range close to $T_c \sim 30$ K that may be associated with small variations in stoichiometry.

(Some figures in this article are in colour only in the electronic version)

The iron-based superconductors have attracted intense research attention because of their high transition temperature and their possibly unconventional pairing mechanism, correlated to magnetism [1–4]. Similar to cuprate superconductors, iron-based superconductors have layered structures; the planar Fe layers tetrahedrally coordinated by As or chalcogen anions (Se or Te) are believed to be responsible for superconductivity. Stacking of the FeAs building blocks with alkali, alkaline earth or rare earth oxygen spacer layers forms the basic classes of iron arsenic superconductors in these compounds: 111-type AFeAs [5], 122-type AFe$_2$As$_2$ [6–9], 1111-type ROFeAs [10, 11] and more complex block-containing phases, e.g. Sr$_2$VO$_3$FeAs [12], Sr$_3$Se$_2$Fe$_2$As$_2$O$_5$ [13] and Sr$_3$Se$_2$Fe$_2$As$_2$O$_6$ [14]. The simple binary 11-type iron chalcogenide has no spacer layers and superconductivity can be induced by doping FeTe with S [15] or Se [16]. Different from the other iron-based superconductors, FeSe is a superconductor [17], $T_c \sim 8$ K, with no static magnetic order and its transition temperature can be increased up to 37 K by applying pressure [18] or 15 K in FeSe$_{0.5}$Te$_{0.5}$ [16]. More recently, superconductivity above 30 K has been reported in A$_x$Fe$_{2-x}$Se$_2$ (A = K, Cs, Rb or Tl) [19–22], a compound with the same unit cell structure as the AFe$_2$As$_2$ compounds. These new compounds generally have a width of formation, show strong dependence of electrical transport properties on their stoichiometry/Fe vacancy and are in very close proximity to an insulating state [22, 23]. The growth of single crystals of K$_x$Fe$_{2-x}$Se$_2$ has been reported in a number of publications using various claimed growth methods: self-flux growth [20] and Bridgman method [23]. Due to the off-stoichiometric nature of the K$_x$Fe$_{2-x}$Se$_2$, wide ranges of the values of $x$, $y$ (0.6 $\leq x < 1$ and 0 $\leq y \leq 0.59$) [20–29] have been reported for the superconducting crystals with similar $T_c$ values ($\sim$31–33 K) from several groups. This raises the question what the correlation between superconductivity and stoichiometry is, if there is any, and whether there is a uniformity problem with the single-crystal samples. Thus well-controlled samples are needed and it is desirable to check the homogeneity of the superconducting crystals and understand their growth.

In this work, we will try to clarify the growth details and present elemental analysis, anisotropic magnetization and resistivity data, as well as measurements of heat capacity, thermoelectric power, London penetration depth and flux penetration on K$_{0.80}$Fe$_{1.76}$Se$_2$ single crystals.
Single crystals of $K_xFe_{2−y}Se_2$ were first grown from $K_{0.8}Fe_{2}Se_2$ melt, as described in [20]. First the FeSe precursor was prepared by reacting stoichiometric Fe and Se at 1050°C. Then K and FeSe with a nominal composition of $K_{0.8}Fe_{2}Se_2$ were placed in an alumina crucible that was sealed in an amorphous silica tube. Due to potassium attack on the silica tube, this primary ampoule was sealed into a secondary, larger silica tube to prevent exposure to air if the first ampoule degraded enough to crack. The growth was placed in a furnace in a vented enclosure and heated to 1050 °C, where it was held for a 2 h soak. The furnace temperature was then slowly lowered to 750°C over 50 h; the furnace was then turned off and the sample ‘furnace cooled’ over an additional 10 h. Once the ampoules were opened, large (∼1 × 1 × 0.02 cm$^3$) dark shiny crystals could be mechanically separated from the solidified melt. The crystals are moderately air-sensitive and should be handled under an Ar atmosphere.

The above growth procedure clearly is not simply the cooling of a stoichiometric melt to form a congruently melting line compound. There is clear loss of K from the melt (as seen by the attack of the inner ampoule) and there is a clear mixed-phase resultant sample, consisting of the desired single-crystalline phase separated by fine polycrystalline material. In order to better establish the nature of the growth of $K_xFe_{2−y}Se_2$, the above procedure was repeated for a starting composition of $KFe_2Se_4$. The sample was heated to 1050°C, held for 2 h and slowly cooled to 850°C at which point the remaining solution was decanted. The resulting crystals were about 1/2 the area and thickness of the samples cooled to 750°C, but they were well formed and no longer embedded in solidified flux. This result clearly shows that $K_xFe_{2−y}Se_2$ crystals are grown out of a ternary melt.

Crystals were characterized by powder x-ray diffraction using a Rigaku Miniflex x-ray diffractometer. The actual chemical composition was determined by wavelength dispersive x-ray spectroscopy (WDS) in a JEOL JXA-8200 electron microscope. Magnetic susceptibility was measured in a Quantum Design MPMS, SQUID magnetometer. In-plane ac resistivity $\rho_{ab}$ was measured by a standard four-probe configuration. Measurement of $\rho_c$ was made in the two-probe configuration. Contacts were made by using a silver alloy. For $\rho_c$, contacts were covering the whole $ab$ plane area [30]. Thermoelectrical power measurements were carried out by a dc, alternating temperature gradient (two heaters and two thermometers) technique [31]. Heat capacity data were collected using a Quantum Design PPMS. The in-plane London penetration depth was measured by using a tunnel-diode resonator (TDR) oscillating at 14 MHz and at temperatures down to 0.5 K [32]. Magneto-optical imaging was conducted by utilizing the Faraday effect in bismuth-doped iron garnet indicators with in-plane magnetization [33]. A flow-type liquid $^4$He cryostat with a sample in vacuum was used. The sample was positioned on top of a copper cold finger and an indicator was placed on top of the sample. The cryostat was positioned under a polarized-light reflection microscope and the color images could be recorded on video and high-resolution CCD cameras. When linearly polarized light passes through the indicator and reflects off the mirror sputtered on its bottom, it picks up a double Faraday rotation proportional to the magnetic field intensity at a given location on the sample surface. Observed through the (almost) crossed analyzer, we recover a 2D image [34].

The x-ray diffraction pattern can be indexed using space group $I4/mmm$. The lattice parameters refined by Rietica were $a = 3.8897(8)$ Å and $c = 14.141(3)$ Å. They are in good agreement with the previously reported values in [20] ($a = 3.8912$ Å, $c = 14.139$ Å), but disagree with [19] ($a = 3.9136(1)$ Å, $c = 14.0367(7)$ Å) and [27] ($a = 3.9034$ Å, $c = 14.165$ Å), in lattice constant $c$. It is probably due to the different stoichiometry of the crystals.

Previous reported stoichiometries of $K_xFe_{2−y}Se_2$ crystals were determined by the semi-quantitative energy dispersive x-ray (EDX) spectroscopy [20–29]. Here we performed precise measurement of the stoichiometry using WDS. Twelve measurement spots were spread uniformly across the crystal surfaces of dimensions approximately 3 × 3 mm$^2$. All of the spots showed consistent results. By averaging 12 spots, the stoichiometry was determined to be $K$:$Fe$:Se = 0.80(2):1.76(2):2.00(3) for the crystal grown from solidified melt and $K$:$Fe$:Se = 0.79(2):1.85(4):2.00(4) for the crystal grown from solution, where the atomic numbers of K and Fe are normalized to two Se per formula unit and the standard deviation $\sigma$ is taken as the compositional error and shown in parentheses after the value. The spread in composition, the difference between the maximum and minimum values of the measurements, is 0.07, 0.06 and 0.10 for K, Fe and Se, respectively.

for crystals grown from solidified melt and 0.04, 0.12 and 0.09 for crystals grown from solution, roughly within $3\sigma$ of a normal distribution of random variable. The crystals grown from solution have very similar compositions to the furnace-cooled samples, with only a little higher concentration of Fe.

Basic, temperature-dependent electrical resistivity and magnetization measurements were performed on crystals grown by both the furnace-cooled and decanted methods. The in-plane resistivity of the furnace-cooled sample is very similar to that of earlier reports [20, 23]. There is a broad resistive maxima centered near 160 K followed by a lower temperature drop by nearly a factor of 6 ($\rho$(300 K)/$\rho$(35 K)). There is a sharp transition to a zero resistance state. The inset to figure 1(a) shows the low temperature resistivity as well as the in-plane, magnetic susceptibility ($H = 50$ Oe). The superconducting transition temperature, $T_c = 30.1$ K, can be inferred by the first deviation of the zero-field-cooled curve from normal magnetic susceptibility. It is consistent with the $T_c^{offset} = 30.9$ K inferred from resistivity. The transition is sharp with a width of 0.7 K and $T_c^{onset} = 31.6$ K.

The in-plane resistivity of single crystals grown out of solution (the decanted samples) is shown in figure 1(b). It exhibits a broad maximum around 280 K and becomes superconducting below 30 K. The inset shows the in-plane magnetic susceptibility ($H = 50$ Oe) and resistivity at low temperature. The superconducting transition temperature, $T_c = 29.0$ K can be inferred by the first deviation of the zero-field-cooled curve from normal magnetic susceptibility. It is consistent with the $T_c^{offset} = 29$ K inferred from resistivity. The
transition is sharp with a width of 1 K and \( T_{\text{onset}} = 30.0 \) K. The temperature of the broad resistive peak in figure 1(b) is higher than the one shown in figure 1(a) and the \( T_c \) value is slightly lower. Wang et al showed that the position of the hump is sensitive to Fe deficiency [23]. With decreasing Fe deficiency, the hump shifts to higher temperature. This may imply that our decanted crystal has a slightly higher Fe concentration, reasonable for a crystal grown out of solution with a greater excess of Fe–Se. Even with these slight differences, the WDS analysis and the data shown in figure 1 demonstrate that these are closely related compositions with very similar properties.

Figure 2(a) shows the magnetic susceptibility of \( K_{0.80}\text{Fe}_{1.76}\text{Se}_2 \) for two directions of an applied field of 50 Oe. For a magnetic field along the \( c \) axis, a correction of demagnetization for a thin rectangular sample has been made. For \( H \parallel ab \), the zero-field-cooled (ZFC) curve decreases slowly with temperature and for \( H \parallel c \) the transition becomes sharper. Similar behavior can be seen in \( \text{Tl}_{0.58}\text{Rb}_{0.42}\text{Fe}_{1.72}\text{Se}_2 \) [35]. This temperature dependence of the ZFC curve is similar to an inhomogeneous superconductor with a range of transition temperatures and may be related to the small spread of stoichiometry found in the WDS data. Both of the zero-field-cooled (ZFC) curves in figure 2(a) approach \(-0.6\), consistent with bulk superconductivity, and \( T_c \) inferred from both curves is the same, \( T_c = 30.1 \pm 0.1 \) K, within experimental error.

The magnetic susceptibility \( M/H \) \((H = 50 \) kOe\) as a function of temperature for both field directions is shown in figure 2(b). Similar temperature dependence is observed for both field directions, i.e. \( M/H \) decreases almost linearly with decreasing temperature above 150 K and shows a sudden drop below 30 K associated with superconductivity. \( \chi_{ab} \) is clearly larger than \( \chi_{c} \) over the whole temperature range. The inset to figure 2(b) shows the magnetization as a function of magnetic field at \( T = 40 \) K Magnetization is linear with magnetic field for both directions. It also should be noted that the magnitude of magnetization, even at highest field, is very small, \( 10^{-3} \mu_B/\text{Fe} \). This indicates that there are no ferromagnetic impurities or Curie–Weiss-like, local Fe moments and the system might be deep in an antiferromagnetic state, similar to what was suggested for \( \text{Cs}_{0.8}\text{Fe}_{2}\text{Se}_{1.96} \) [36] and \( K_{0.8}\text{Fe}_{1.6}\text{Se}_2 \) [37], or in a non-magnetic state.

Heat capacity data was collected to verify the bulk thermodynamic nature of the superconducting transition. \( C_P \) versus \( T \) at low temperature is shown in figure 3 on a log–log plot. In the superconducting state, below 15 K, \( C_P \) roughly follows a \( T^3 \) power law. This implies a dominant phonon
contribution and a very small electronic term. $C_p/T$ versus $T$ is plotted in the inset for $T \sim T_c$ and a clear jump of heat capacity associated with the superconducting transition at 31.6 K is seen and $\Delta C_p/T = 7.7$ mJ mol$^{-1}$ K$^{-2}$ can be identified. If we assume the value of the normal state electronic heat capacity coefficient $\gamma_n = 5.8$ mJ mol$^{-1}$ K$^{-2}$ (as in [38]), $\Delta C_p/\gamma_n T = 1.33$ of $K_{0.80}Fe_{1.76}Se_2$ is close to the weak coupling BCS value and is at variance with the strong coupling conclusion in [38]. On the other hand, this more likely implies that a reliable conclusion about the coupling strength cannot be made due to the difficulty of estimating the normal state electronic contribution $\gamma_n$.

Anisotropic resistivity as a function of temperature is shown in figure 4(a). It is clear that there is a broad maximum peak around 160 K for $\rho_{ab}$ and 180 K for $\rho_c$. The difference in maximum positions suggest that they result from a crossover rather than a transition. The temperature range of this broad maxima does not correlate with any anomalies in magnetic susceptibility. The anisotropy is probably due to the layered structure of $K_{0.80}Fe_{1.76}Se_2$. Figure 4(b) shows the anisotropy $\rho_c/\rho_{ab}$, reaches the maximum of 6 around 180 K and decreases to 4 around 300 K. It is comparable to the anisotropy of AFe$_2$As$_2$ [39]. But a much larger resistivity anisotropy of 30–45 was reported in (Tl, K)Fe$_2$Se$_2$ [35], which implies that the specific composition influences carrier tunneling significantly. An expanded view around the superconducting transition is shown in the inset to figure 4(a). For both of the current directions, the transition width is about 0.7 K, but $T_c$ for $\rho_c$ is slightly higher than that of $\rho_{ab}$. The transition temperatures for the two current directions are very close to the one inferred from the heat capacity measurement using an isoentropic construction, as well as resistivity and susceptibility measurements.

The thermoelectrical power (TEP) as a function of temperature is shown in figure 5. We present results for three different samples: for samples A and B silver paste was used for electrical and thermal contact, while for sample C silver wires were soldered to the sample by In–Sn solder and then electrical/thermal contact was established between the wires and the contact pads by silver paste. For all three samples $T_c$ inferred from $S(T) = 0$ is 31.6 K, consistent with all of our previous measurements. The data for the three samples are similar in the whole temperature range. The origin of the local minimum and maximum at 100–200 K is not clear, but is very likely to be associated with the multiband structure of $K_{0.80}Fe_{1.76}Se_2$ and the crossover (metal-like at low temperature) observed in resistivity. The negative sign of thermopower indicates that electron-like carriers are dominant, and thus in agreement with the observation of electron-only pockets at the Fermi surface by ARPES [26]. The large absolute value of $S$ above 50 K is noteworthy and is consistent with high normal state resistivity.

London penetration depth measurements with good reproducibility were performed on several single-crystal samples. In order to compare between the samples, we plot in figure 6 normalized frequency shift, proportional to differential magnetic susceptibility, $\delta f_{\text{norm}} = (f(T) - f(T_c))/(f(T_c) - f(T_{\text{min}}))$, where $f(T_{\text{min}})$ is the resonant frequency at the lowest
Figure 5. Thermoelectric power as a function of temperature. Samples A and B use silver paste as contact (contact resistance $\sim 1$–3 k$\Omega$). Sample C uses silver wires attached by In–Sn solder as contact (contact resistance $\sim 200$ k$\Omega$).

Figure 6. Normalized London penetration depth expressed via resonant frequency shift, $\Delta f_{\text{norm}} = (f(T) - f(T_e))/(f(T_c) - f(T_{\text{min}}))$, proportional to magnetic susceptibility. $f(T_c)$ is the resonant frequency at the lowest temperature $\geq 0.5$ K. $f(T_e)$ is the frequency in the normal state right above $T_e$. Inset shows an upturn, presumably due to paramagnetic ions and/or impurities below 2 K from two samples A and B.

Figure 7. Magneto-optical image of single-crystal K$_{0.80}$Fe$_{1.76}$Se$_2$.

To gain further insight into the homogeneity of the superconducting state and, roughly, estimate the critical current density, we performed magneto-optical imaging. A magneto-optical image of a trapped flux is shown in figure 7. In the experiment the sample was cooled in a 2 kOe magnetic field from 40 to 5 K. We did not observe any noticeable Meissner expulsion, similar to other 122 pnictides [42]. When the magnetic field was turned off, it revealed a typical ‘Bean’ roof, again similar to other pnictide superconductors [43, 44]. As can be seen in figure 7, magnetic flux distribution is quite uniform and is definitely consistent with the bulk superconducting nature of the material. However, some macroscopic variations (upper left corner) might indicate some smooth variation of stoichiometry across the sample and may help to explain the broadened transition curves. In order to quantify the critical state, figure 7 also shows profiles of the magnetic induction taken along two lines (shown in the figure). The remanence reaches about 250 Oe. A simple one-dimensional estimate, using
\[
\frac{4\pi}{c} J_c = \frac{dB}{dx}
\]
gives
\[
J_c = \frac{250 \cdot 10}{0.77 \cdot 4\pi} \approx 2.6 \times 10^3 \text{ A cm}^{-2}.
\]
Of course, this estimate is very crude, but shows that the current samples cannot support large critical current density even at low temperatures. Similar numbers are estimated from the magnetization measurements. Nevertheless, magneto-optical imaging is consistent with the bulk superconducting
nature of $K_{0.80}Fe_{1.76}Se_2$ and shows that it is not filamentary or phase separated, but rather shows smooth variation of the stoichiometry.

In summary, single crystals of $K_{x}Fe_{2-y}Se_2$ have been grown via two related methods. In both cases $T_c \sim 30$ K, with the furnace-cooled crystals having $K_{0.80}Fe_{1.76}Se_2$ composition and $T_c = 30$ K (from magnetization) and decanted crystals having composition $K_{0.83}Fe_{1.86}Se_2.98$ and $T_c = 29$ K (from magnetization). We found moderate anisotropy in both magnetic susceptibility and electrical resistivity with $\chi_{ab}/\chi_c \sim 2$ and $\rho_c/\rho_{ab} \sim 4$ at 300 K. Broadened transitions seen in several measurements imply a small variation of stoichiometry of the crystal, consistent with what was shown by WDS analysis. It has also been shown that the critical current density of the $K_{0.80}Fe_{1.76}Se_2$ is only of the order of $10^3$ A cm$^{-2}$, much smaller than those of FeAs superconductors [45].

Acknowledgments

This work was carried out at Iowa State University and supported by the AFOSR-MURI grant no. FA9550-09-1-0603 (RH and PCC). Part of this work was performed at Ames Laboratory, US DOE, under contract no. DE-AC02-07CH11358 (KC, HK, HH, WES, MAT, RP, SLB and PCC). SLB acknowledges partial support from the State of Iowa through Iowa State University. RP acknowledges support from the Alfred P Sloan Foundation.

Note added. During the preparation of this paper, a preprint was posted on arxiv.org showing similar studies of anisotropy in electrical transport and magnetization of $K_{x}Fe_{2-y}Se_2$ [46]. The results are consistent with ours.

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