Phase relations in $K_{x}Fe_{2−y}Se_{2}$ and the structure of superconducting $K_{x}Fe_{2}Se_{2}$ via high-resolution synchrotron diffraction

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Superconductivity in iron selenides has experienced a rapid growth, but not without major inconsistencies in the reported properties. For alkali-intercalated iron selenides, even the structure of the superconducting phase is a subject of debate, in part because the onset of superconductivity is affected much more delicately by stoichiometry and preparation than in cuprate or pnictide superconductors. If high-quality, pure, superconducting intercalated iron selenides are ever to be made, the intertwined physics and chemistry must be explained by systematic studies of how these materials form and by and identifying the many coexisting phases. To that end, we prepared pure $K_{2}Fe_{3}Se_{5}$ powder and superconductors in the $K_{x}Fe_{2−y}Se_{2}$ system, and examined differences in their structures by high-resolution synchrotron and single-crystal x-ray diffraction. We found four distinct phases: semiconducting $K_{2}Fe_{3}Se_{5}$, a metallic superconducting phase $K_{x}Fe_{2}Se_{2}$ with $x$ ranging from 0.38 to 0.58, an insulator $KFe_{1.6}Se_{2}$ with no vacancy ordering, and an oxidized phase $K_{0.91(5)}Fe_{0.70(2)}Se_{2}$ that forms the PbClIF structure upon exposure to moisture. We find that the vacancy-ordered phase $K_{2}Fe_{3}Se_{5}$ does not become superconducting by doping, but the distinct iron-rich minority phase $K_{2}Fe_{2}Se_{5}$ precipitates from single crystals upon cooling from above the vacancy ordering temperature. This coexistence of metallic and semiconducting phases explains a broad maximum in resistivity around 100 K. Further studies to understand the solubility of excess Fe in the $K_{x}Fe_{2−y}Se_{2}$ structure will shed light on the maximum fraction of superconducting $K_{x}Fe_{2}Se_{2}$ that can be obtained by solid state synthesis.

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INTRODUCTION

The brief history of iron chalcogenide superconductivity has seen a flurry of activity, beginning with the discovery of $T_c = 8$ K in $\beta$-FeSe,[1] and later the announcement that ternary intercalated compounds in the $A_xFe_{2−y}Se_{2}$ system display $T_c \approx 30$ K when $A$ is K, Rb, Cs, or Tl.[2] Much like the superconducting iron arsenides, these compounds form the ThCr$_2$Si$_2$ structure type with layers of tetrahedrally-coordinated Fe and are in the vicinity of antiferromagnetism, but the differing anion charges (formally Se$^{2−}$ versus As$^{3−}$) lead to issues of chemical stability that have a profound effect on the structures and properties. While arsenides are only known to exhibit superconductivity in the fully-occupied ThCr$_2$Si$_2$ structure type without vacancies, the hallmark of the selenides (intercalated and not) is that stoichiometry is never exact for superconducting samples—some disorder is always present, often in conjunction with phase separation.[4–7]

Experimental efforts to understand superconductivity in iron selenides must grapple with the sensitive stoichiometry required to observe $T_c$. Compared to iron pnictides, where a superconducting dome appears from $x = 0.2$ to 1 in Ba$_{1−x}$K$_x$Fe$_2$As$_2$ for example,[8] in $\beta$-FeI$_{3}$Se there is only a window of $\delta = 0.01$ to 0.03 where superconductivity is observed, and there is no such dome versus composition.[9] No dome is present in $A_xFe_{2−y}Se_{2}$ superconductors either, with $T_c$ approximately invariant around 30 K.[10–12] Additionally, the thermal history of the sample plays a key role, as even moderate thermal annealing has an effect on the sharpness of the transition in $A_xFe_{2−y}Se_{2}$.[13] [14]

Divalent Se$^{2−}$ leads to the presence of alkali and iron vacancies that are not found in the iron arsenides. In fact, most attention in the $K_{x}Fe_{2−y}Se_{2}$ system is focused on $K_{0.8}Fe_{1.6}Se_{2}$, shown in Figure[1] This compound is a Mott insulator with $1/5$ ordered Fe vacancies and disordered K, and can be written as $K_{2}Fe_{3}Se_{5}$ with valence-precise Fe$^{2+}$.[15] Due to prevalent vacancies and the ability of Fe to adopt $+2$ or $+3$ formal oxidation states, (as in Fe$^{2+}$Se or KFe$^{3+}$Se$_2$[16]) it may seem that doping either cation in $K_{x}Fe_{2−y}Se_{2}$ would tune $T_c$ as in the arsenides, but this is not the case: the superconducting transition appears and disappears abruptly, and does not shift.[10]

A synthetic route to pure superconducting $K_{x}Fe_{2−y}Se_{2}$ phases is elusive. Microscale phase separation between closely-related structures, mobile Fe/K vacancies, and iron impurities are widespread.[2] [17] [22] As a result, models or measurements that describe properties without accounting for sample heterogeneity are up to now incomplete. For example, photoemission spectroscopy, energy dispersive spectroscopy, and inductively-coupled...
Methods

Samples of $K_xFe_{2-y}Se_2$ were prepared from metallic K, Fe powder, and crushed Se shot (Alrich, 99.5%, 99.99%, and 99.99%, respectively). All manipulations were performed in a $N_2$-filled glovebox. Stoichiometric powders, including pure $K_2Fe_5Se_8$, were prepared by intimately mixing Fe and Se in a mortar and pestle in a $N_2$-filled glovebox with a ratio of $4Fe + 5Se$, then loading in a carbon-coated quartz tube and sealing under vacuum. This tube was heated with a 12 h ramp to 700°C, 2 h hold, and furnace cool back to room temperature. This powder was ground again in a glovebox and loaded with K pieces in a covered alumina crucible in a quartz tube, sealed under vacuum, and heated over the same temperature profile. Finally, the powder was homogenized by grinding and fired with a 1 h ramp to 700°C, 10 h hold, and 1 h cool to room temperature.

Single crystals were prepared by prereaction of K pieces with Fe and Se powder in alumina crucibles sealed under vacuum and heated to 600 or 650°C in 12 h, with a 4 h hold and 4 h cool to room temperature, followed by grinding. Slow-cooled crystal growth was performed in alumina crucibles sealed under Ar in Nb tubes. Flame-melted samples were prepared by melting the prereacted powders in evacuated quartz tubes until the mixture was visibly molten. The nominal composition $K_xFe_{2-y}Se_2$ was varied from 0.8 ≤ $x$ ≤ 0.85 and 0 ≤ $y$ ≤ 0.4. Specific compositions and heat treatments are presented in the Supplemental Material.

High-resolution ($\Delta Q/Q < 2 \times 10^{-4}$) synchrotron powder diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using an average wavelength of 0.413 Å (≈30 keV). A NIST standard Si sample (SRM 640c) was used to calibrate the instrument, where the Si lattice constant determines the wavelength for each detector. Samples were sealed under vacuum in glass capillaries to prevent oxidation. Time-of-flight powder neutron diffraction measurements were conducted at the HIPD instrument at the Lujan Center, Los Alamos National Laboratory with samples sealed under He in vanadium cans. Rietveld refinements to synchrotron x-ray and neutron diffraction data were performed using GSAS.[27]

Laboratory x-ray powder diffraction was performed using a Philips X’Pert diffractometer with Cu-Kα radiation, and Rietveld refinements were performed using the XND code.[28] Single-crystal diffraction data were collected on a STOE 2T image plate diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) and X-Area software, and structures were refined using SHELXTL.[29] Four-probe resistivity, ac magnetic susceptibility, and heat capacity were measured using a Quantum Design PPMS.
RESULTS AND DISCUSSION

Characterization of pure, polycrystalline K$_2$Fe$_4$Se$_5$

The composition-temperature phase space of K$_2$Fe$_{2-y}$Se$_2$ is mostly unknown, so the need for a pure, homogeneous sample that can serve as a reference point is paramount. The most stable phase near pure FeSe with nearly complete vacancy ordering: only 7% of the Fe 4$d$ sites are occupied. Low-angle peaks corresponding to the I4/m cell due to Fe ordering are arrowed. High-Q data are enlarged in the inset to show fit quality. Structural details are given in Supplementary Information.

Fig. 2. (Color online) Rietveld refinement to high-resolution synchrotron diffraction data for powder K$_2$Fe$_4$Se$_5$ shows a pure compound with nearly complete vacancy ordering; only 7% of the Fe 4$d$ sites are occupied. Low-angle peaks corresponding to the I4/m cell due to Fe ordering are arrowed. High-Q data are enlarged in the inset to show fit quality. Structural details are given in Supplementary Information.

This is a simple, reliable method for producing pure K$_2$Fe$_4$Se$_5$. Our magnetometry and resistivity measurements confirmed that K$_2$Fe$_4$Se$_5$ is an antiferromagnetic semiconductor. While this powder synthesis provides great compositional control, we have never observed superconductivity in any powders created by this method, even when changing the stoichiometry in K$_2$Fe$_{2-y}$Se$_2$ where $0.5 < x < 1$ and $1.4 < y < 2$.

This stoichiometric polycrystalline powder sample is crucial because it sets a structural reference point for which all other compositions will be compared. There is no evidence (line broadening, extra peaks, extra phases) in the 11-BM diffraction data for phase separation when pure K$_2$Fe$_4$Se$_5$ is made by this route.

Structural characterization of nominal K$_2$Fe$_4$Se$_5$ crystals

To date, there has been no mention of a superconducting powder of K$_2$Fe$_{2-y}$Se$_2$, nor did we find one despite our efforts. This implies that melting and recrystallization may be required for the formation of the superconducting phase. We prepared single crystals of nominal K$_2$Fe$_4$Se$_5$ composition to determine how stoichiometry is affected by melting. Crystals prepared by melting nominal K$_2$Fe$_4$Se$_5$ formed plates which readily degrade in air, as judged by a change in color from shiny gold to matte brown.

Single crystal diffraction of these nominal K$_2$Fe$_4$Se$_5$ crystals shows superstructure Bragg peaks arising from I4/m K$_2$Fe$_4$Se$_5$. These peaks form an octagon in the (00l) reciprocal-space reconstruction in Figure 3, with the first peak at (1 1 0) arrowed. Extra reflections appear at the (010) position of the I4/mmm K$_{0.8}$Fe$_1.6$Se$_2$ lattice (arrowed in Figure 3) which is forbidden by I-centered symmetry. They do not represent a $\sqrt{2} \times \sqrt{2}$ modification of the K$_2$Fe$_{2-y}$Se$_2$ structure, but instead arise from an oxidized phase that will be discussed in the next section. No other vacancy ordering patterns are observed in these crystals.

High-resolution x-ray diffraction was performed on ground batches of these crystals to search for phase separation in the form of split c-axis reflections, seen often in superconducting samples and to screen for any minor impurities. Both are absent, and the fit from Rietveld refinement is shown in Figure 4.

We found that the lattice constants of nominal K$_2$Fe$_4$Se$_5$ crystals display an expanded a and contracted c-axis compared to the pure powder K$_2$Fe$_4$Se$_5$ (8.74536(8) $\times$ 14.10024(18) Å versus 8.721763(10) $\times$ 14.125178(23) Å for powder K$_2$Fe$_4$Se$_5$). The refined stoichiometry of the crystal was K$_{0.79(1)}$Fe$_{1.56(1)}$Se$_2$, while the ground batch of crystals had a refined composition of K$_{0.84(1)}$Fe$_{1.43(1)}$Se$_2$ from synchrotron powder diffraction. The difference between powder and single-crystal
FIG. 3. (Color online) Reciprocal space reconstruction of single crystal x-ray diffraction data from a nominal $K_2Fe_4Se_5$ crystal. Reflections are labeled with Miller indices of the $I4/mmm$ ThCr$_2$Si$_2$ substructure. The fractional superstructure peaks, including the labeled peak at $(\frac{1}{5}\frac{5}{0})$, arise from vacancy ordering and lowering of symmetry to $I4/m$ The (010) reflection is forbidden by both $I$-centered cells, and represents a new, coherent phase. Subsequent analysis in this manuscript confirms it to be an oxidized phase with $c = 9$ Å.

FIG. 4. (Color online) Rietveld refinement to high-resolution synchrotron diffraction data for a non-superconducting, ground single-crystal sample of nominal $K_2Fe_4Se_5$ composition. This sample displays $I4/m$ vacancy ordering. Measurements likely arise from heterogeneity among the crystals or systematic errors, but in any case both techniques find that $K_2Fe_4Se_5$ becomes Fe deficient after melting and recrystallization, and does not exhibit superconductivity. Still, the presence of an impurity phase in the single crystals merits further investigation, primarily to understand and avoid its conditions for formation.

FIG. 5. (Color online) The reciprocal space reconstruction along the (100) direction of the parent $I4/mmm$ $K_{0.8}Fe_{1.6}Se_2$ lattice shows that the extra reflections, including (010) from Figure 3, lie along an $l$ index that is distinct from $K_{0.8}Fe_{1.6}Se_2$. This distinct spacing is shown with $d = 9$ Å. An intensity linescan along 00$l$ in (b) shows that these spots arise from a phase where the FeSe interlayer spacing is 9 Å, as opposed to $c/2 = 7$ Å for $K_2Fe_4Se_5$.

Forbidden (010) diffraction spots arise from the oxidized phase $K_{0.51(5)}Fe_{0.70(2)}Se$

The extra (010) Bragg reflections in the $K_{0.8}Fe_{1.6}Se_2$ reciprocal space reconstruction in Figure 3 merit further investigation to understand whether they might correspond to a $\sqrt{2} \times \sqrt{2}$ superstructure of the $K_{x}Fe_{2−y}Se_2$ cell. Such a cell has been proposed on the basis of electron diffraction patterns viewed down the ⟨001⟩ direction. No such phase has ever been made in bulk quantities or detected by x-ray diffraction, and the electron diffraction peaks were not shown in the ⟨0kl⟩ or ⟨h0l⟩ directions to confirm registry with the $K_{x}Fe_{2−y}Se_2$ lattice.

In Figure 5 we present the single crystal diffraction pattern from a perpendicular direction, down ⟨100⟩ in the (0kl) plane. From this vantage point the extra reflections form a vertical column with an $l$-spacing that is distinct from the major $K_{0.8}Fe_{1.6}Se_2$ peaks in the diffraction pattern. This column is at a distance $d = 9$ Å$^{-1}$ from $l = 0$, arrowed in Figure 5(a). A line scan along the ⟨00l⟩ direction produced the intensity profile in Fig-
The exposure to moist air shows conversion to the oxidized phase. Results from single-crystal structure solution are given in the Supplemental Material.

TABLE I. Single-crystal refinement results for the oxidized structure type, $K_{0.51(5)}Fe_{0.70(2)}Se$ with the PbClF structure, containing buckled $K^+$ layers and Fe vacancies. Peaks from the oxidized phase and the superconducting minority phase, which we discuss subsequently, should be considered when interpreting angle-resolved photoemission spectroscopy in particular, where a $\sqrt{5} \times \sqrt{5}$ supercell is not seen. [39]

| Atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | Occupancy |
|------|-----|-----|-----|---------|---------|---------|-----------|
| K 2c | 0.75 | 0.75 | 0.428(4) | 0.140(10) | 0.150(20) | 0.51(5) |          |
| Fe 2a | 0.75 | 0.25 | 0 | 0.045(3) | 0.120(8) | 0.698(19) |          |
| Se 2c | 0.25 | 0.25 | 0.1559(6) | 0.061(2) | 0.116(4) | 1 |          |

Superconducting $K_xFe_{2-x}Se_2$: Changes in the $I4/m$ majority phase and evidence for phase separation

We grew superconducting crystals using the same procedure as our nominal $K_2Fe_4Se_5$ crystals, except the nominal stoichiometry was $K_{0.85}Fe_{1.9}Se_2$. These crystals appear visually similar, but excess iron precipitates as metal and often pervades the solidified ingot, with its highest concentration at the top of the ingot. Iron is denser than $K_2Fe_2Se_5$ (7.8 versus 4.3 g/cc) so it was most likely pushed upward by the advancing solidification front and not floating on the selenide melt. The extent of Fe solubility in $K_xFe_{2-x}ySe_2$ melts remains unknown, and may be a key in determining how to control phase separation in these materials.

Reciprocal-space reconstructions of a superconducting crystal from single-crystal x-ray diffraction (Figure 7) show the supercCell reflections from vacancy-ordered $K_xFe_4Se_5$. The single-crystal refined composition is $K_{0.72(2)}Fe_{1.63(1)}Se_2$, but the question of phase separation is crucially important, since a distinct phase that induces superconductivity may be present. [40][43] Our laboratory single-crystal diffractometer could not resolve any new reflections that were not present in nominal, non-superconducting $K_xFe_4Se_5$ crystals, so we performed high-resolution synchrotron powder diffraction to investigate the totality of phases present in these materials.

A comparison of the Bragg peak splitting in superconducting crystals (nominal $K_{0.85}Fe_{1.9}Se_2$) and non-superconducting samples (nominal $K_xFe_2Se_5$ crystals and powder) is shown in Figure 8. The superconduct-
ing crystals display a clear split of the (002) reflection. This splitting is commonly seen when Rb, Cs, and K-containing single crystals are characterized using simple Bragg-Brentano diffraction measurements, and most likely represents the metallic superconducting phase which we discuss in the next section. There is no splitting in Figure 8(a) for the non-superconducting nominal K$_2$Fe$_4$Se$_5$ crystal or powder. This implies that phase separation is not an intrinsic feature of pure K$_2$Fe$_4$Se$_5$. Rather, deviations from that stoichiometry are required to drive phase separation. The (110) peak of the I4/m vacancy-ordered phase is compared in Figure 8(b), and both single crystalline samples are considerably broadened, with a long tail on the high-Q side of the peak, in the direction of β-FeSe which has its (110) peak at $Q = 1.17 \text{ Å}^{-1}$.

Stoichiometric deviation from pure K$_2$Fe$_4$Se$_5$ leads to weakening of antiferromagnetic order. Neutron powder diffraction at 300 K in Figure 8(c) shows a strong (011) magnetic peak at $Q = 0.84 \text{ Å}^{-1}$, indicating strong antiferromagnetic order in pure powder K$_2$Fe$_4$Se$_5$, which has $T_N = 559\text{ K}$.[44] This peak is substantially weakened in the nominal K$_2$Fe$_4$Se$_5$ crystal, and has disappeared in the superconducting crystal. Indeed, subtle changes in stoichiometry disrupt the magnetic ordering in the K$_x$Fe$_{2−y}$Se$_2$ lattice, and antiferromagnetism and superconductivity appear mutually exclusive.

**The superconducting metallic phase K$_x$Fe$_2$Se$_2$**

The 11-BM synchrotron x-ray data resolves splitting in not only the the (002) reflection, but an entirely separate I4/mmm phase that occurs in superconducting samples, shown in the insets of Figure 9(a,b,c). These extra peaks can be modeled using a separate cell with disordered vacancies. For three separate superconducting samples, this phase refines to a composition of K$_x$Fe$_2$Se$_2$ where $x = 0.38(2)$, 0.55(1), and 0.58(2), with weight fractions of 13, 18, and 12%. Rietveld refinement results are summarized in Table 11. Full details are given in the Supplemental Material. Our compositions, along with those determined by a lower-resolution diffraction study,[42] and NMR measurements[23] all find evidence for the metallic minority phase to have nearly full iron occupancy and K deficiency. This phase must not display any K$^+$ vacancy ordering, as any superstructure peaks arising from $\sim 15\%$ of the sample would be clearly visible in the single-crystal diffraction pattern (Figure 7). Recent high-temperature diffraction data have confirmed that this phase is absorbed into K$_2$Fe$_4$Se$_5$ above the vacancy ordering temperature.[43]

All three samples which exhibited phase separated K$_2$Fe$_2$Se$_2$ (3, 4, and 6 in Figure 10) by synchrotron diffraction displayed a diamagnetic response at $T_c$. No semiconducting samples contained this minority
In all our samples, regardless of superconductivity, the $I4/m$ $K_2Fe_2Se_3$ phase is present. We have searched via Rietveld refinement for systematic changes in the $I4/m$ phase that might be associated with the onset of superconductivity.

Lattice parameters for the $I4/m$ phase are given in Figure 10. Sample 1 is a pure powder (non-superconducting) of $K_2Fe_2Se_3$. The cluster of superconducting samples all have an $a$-axis smaller than 8.73 Å and a $c$-axis larger than 14.11 Å, distinct from the non-superconducting crystals and separated by a dashed line. However these lattice parameters are not a structural trigger of superconductivity, since the insulating powder sample falls in the superconducting range. Instead we assert that the superconducting samples contain a majority $I4/m$ component that is near the edge of its compositional range, and so are predisposed to containing the minority $K_xFe_2Se_2$ superconducting phase.

The stoichiometries of all $I4/m$ $K_xFe_{2-y}Se_2$ phases from Rietveld refinements are shown in Figure 11(a). The superconducting samples are tightly clustered in composition space, but there is no distinction between them and the non-superconducting samples. $K$ contents are near nominal values, while Fe tends to be deficient, around $K_xFe_{1.5}Se_2$. An approximate calculation of Fe valence us-

FIG. 9. (Color online) Rietveld refinement to high-resolution synchrotron x-ray diffraction data of a superconducting sample of nominal $K_{0.85}Fe_{1.9}Se_2$ composition displays peak splitting corresponding to a distinct $I4/mmm$ phase at room temperature. Selected regions are expanded in (a,b,c) to show detail on equivalent pairs of reflections. The labeled peaks would be coincident for both phases in the absence of lattice distortions.

TABLE II. Rietveld refinement results for the superconducting metallic phase $K_xFe_2Se_2$ for three different samples. Sample numbers correspond to points in Figure 10 and to the full refinement details and processing conditions given in the Supplemental Material.

| # | $R_{wp}$ | Stoichiometry | wt%a (Å) | c (Å) |
|---|---|---|---|---|
| 3 | $R_{wp}$ $K_{0.58(2)}Fe_{1.84(4)}Se_2$ | 12 | 3.83414(20) | 14.2360(12) |
| 4 | $R_{wp}$ $K_{0.55(1)}Fe_{2.00(2)}Se_2$ | 18 | 3.82803(23) | 14.2634(10) |
| 6 | $R_{wp}$ $K_{0.38(2)}Fe_{2.06(28)}Se_2$ | 13 | 3.82707(26) | 14.2658(15) |

$I4/mmm$ phase. Two samples, (2 and 5 in Figure 10) were superconducting but the diffraction peaks were too broad to resolve the second phase due to quenching. While samples with a small superconducting fraction can be made reliably, creating homogeneous samples is a requirement for understanding the mechanisms of superconductivity in these samples, for example by photoemission spectroscopy or inelastic neutron scattering. To that end, we have begun to map the available phases in the $K_xFe_{2-y}Se_2$ system and probe their stability.

The previous claim that $KFe_2Se_2$ is the superconducting phase seems implausible since this formula requires half to the Fe atoms to be in the 1+ state and tetrahedrally coordinated by Se. Such a state is unlikely to be stable since it requires excessive negative charge on a large fraction of the Fe atoms and is unprecedented in the literature. On the other hand, a $K_xFe_2Se_2$ formulation with $x \sim 0.5$ would require only a quarter of Fe atoms to be in a 1+ state and in this case the extra negative charge may be delocalized over a broad conduction band.
We present preliminary work on this subject in the next section.

A clear division was seen in lattice parameters (Figure 10) for superconducting and non-superconducting samples, but not in the refined stoichiometry (Figure 11). As a result, the lattice parameters may be a more exact probe of the response of the K$_2$Fe$_2$Se$_2$-type I4/m lattice to stoichiometry, and further work should be done to explain how the lattice parameters change with K and Fe content, and their relation to phase separation, which is now believed to be necessary for superconductivity.\textsuperscript{18–20} We present preliminary work on this subject in the next section.

Comparing related phases in the K$_x$Fe$_{2-y}$Se$_2$ series: $\beta$-FeSe, K$_2$Fe$_2$Se$_2$, K$_4$Fe$_2$Se$_5$, and KFe$_{1.6}$(Se$_2$)$_3$

Hypothetically, the K$_x$Fe$_{2-y}$Se$_2$ phase space could contain a plethora of homologous (K$_2$Se)/(FeSe)$_n$ phases containing strictly Fe$_{2+}$, from $n = 3$ K$_2$Fe$_3$Se$_4$, where the K layer is filled, to $n = \infty$ corresponding to $\beta$-FeSe. Our attempts to produce phases with higher $n$ (K$_2$Fe$_5$Se$_6$, K$_2$Fe$_9$Se$_7$, etc.) by solid state reactions simply led to K$_2$Fe$_3$Se$_5$ + $\beta$-FeSe. Reactions with the nominal composition K$_2$Fe$_3$Se$_4$ gave a pure compound, and upon synchrotron x-ray diffraction the refined occupancy was found to be K$_{0.959(4)}$Fe$_{1.606(6)}$Se$_2$, with excess K and Se likely precipitating as amorphous K$_2$Se$_4$.\textsuperscript{15} There are no superstructure peaks in this compound, indicating that the Fe vacancies are truly disordered and the symmetry remains I4/m/mm. The fit from Rietveld refinement is shown in Figure 12 and results are tabulated in the Supplemental Material. The isostructural phase TlFe$_{1.6}$(Se$_2$)$_3$ exhibits multiple magnetic transitions at low temperatures.\textsuperscript{46, 47} so further investigation is warranted. We did not detect any superconducting diamagnetic response in KFe$_{1.6}$Se$_2$ down to 2 K.

The KFe$_{1.6}$Se$_2$ phase represents a third distinct phase in the K$_x$Fe$_{2-y}$Se$_2$ system, in addition to K$_2$Fe$_3$Se$_5$ and K$_4$Fe$_2$Se$_2$. The lattice parameters of all these phases are shown in Figure 13 (with the I4/m phase normalized by $\sqrt{5}$). This diagram provides a full view of known phases in the K$_x$Fe$_{2-y}$Se$_2$ system, from full K occupancy in KFe$_{1.6}$Se$_2$ to empty interlayer space in $\beta$-FeSe. A trend of decreasing $a$ with increasing $c$ is evident, likely driven by
weak van der Waals interlayer forces yielding to stronger ionic bonding as K$^+$ is inserted. Simultaneous carrier donation from K$^+$ into the FeSe layers leads to weaker Fe-Se bonding and an increase in intralayer distances (a lattice parameters). From this plot, the separation between $I4/m$ K$_2$Fe$_4$Se$_5$ phases and the superconducting minority phases is shown to be quite significant. We discuss implications for the synthesis of this phase subsequently. It remains to be seen if there is a solid solution between K$_2$Fe$_4$Se$_5$ and KFe$_{1.6}$Se$_2$.

**Superconducting composite of K$_2$Fe$_4$Se$_5$ and K$_x$Fe$_2$Se$_2$: Magnetometry and heat capacity**

DC magnetometry of a superconducting sample (sample 6) is shown in Figure 14 with $T_c = 28$ K. Such measurements are unfortunately not a viable way to probe the superconducting volume fraction. If the fraction is small but pervades the entire sample, as in a net-like model,[48] then magnetometry would give an inflated view of the volume fraction. For this reason, we performed heat capacity measurements on samples that had already been confirmed to be superconducting by magnetometry.

Heat capacity measurements provide an excellent way to confirm bulk superconductivity, although the precise volume fraction would depend on a known model for the entropy release at $T_c$. Studies on YBa$_2$Cu$_3$O$_{7-\delta}$ and $\beta$-FeSe have shown clear signatures of entropy release ($\Delta C_p \approx 6.9$ and 3 mJ/gK, respectively) across $T_c$.[9][39] We measured a single crystal (sample 6) with a strong zoom across $T_c$ and the measurement is seen in Figure 15. The inset in Figure 15(b) shows the difference between heat capacity measured at zero field and $H = 1$ T. The anomaly at $T = 31$ K is approximately 2 mJ/gK, which is comparable to $\beta$-FeSe, even though the fraction of K$_x$Fe$_2$Se$_2$ phase is only $\sim$15% by weight. The small peak in this data confirms the minor phase fraction of superconducting K$_x$Fe$_2$Se$_2$ seen in powder diffraction patterns and magnetic susceptibility. Further evidence for this two-phase coexistence is seen in resistivity measurements.

**Resistivity: Metal-insulator crossover implies two-phase coexistence**

Resistivity ($\rho$) measurements from superconducting and non-superconducting crystals are shown in Figure 16. The $\rho$ drops to zero at $T_c = 31$ K, in agreement with our magnetization and heat capacity measurements.
There is a hump in the resistivity around 100 K, which was seen in many studies, including the initial report by Guo, et al [2 10 50] and attributed to a metal-insulator transition. [20] However, given the phase separation between K$_2$Fe$_4$Se$_5$ and K$_x$Fe$_2$Se$_2$, it is more likely that the metallic and insulating phases are always present. Thus the full resistivity range can be fit using a model of two percolating phases that act as resistors in parallel, one with metallic Bloch-Grüneisen temperature dependence $\rho_{metal}$ and the other with Boltzmann-type insulating temperature dependence $\rho_{ins}$:

$$\frac{1}{\rho_{total}} = \frac{1}{\rho_{metal}} + \frac{1}{\rho_{semi}}$$  \hspace{1cm} (1)

$$\rho_{metal}(T) = \rho(0) + AT^n$$  \hspace{1cm} (2)

$$\rho_{semi}(T) = \rho_0 e^{E_g/RT}$$  \hspace{1cm} (3)

Where $\rho(0)$, $A$, and $\rho_0$ are all constants that depend on phase fractions and geometry in this case. This fit (dashed in Figure 16) is excellent and gives $n = 2.78$, and insulator activation energy of $E_g = 83$ meV. Changes in the position of the hump can be accomplished by simply changing the relative volume fractions of these two phases. The metallic phase is not iron since it is present in such small amounts (≤ 2% by weight by synchrotron powder diffraction). Furthermore, muon spin rotation and scanning probe measurements indicate that the superconducting phase is metallic above $T_c$. [18 24 61]

This resistivity maximum provides further confirmation that the minority $I4/mmm$ phase is the cause of superconductivity, and further work should be conducted to optimize its synthesis.

**Implications for synthesis**

Pure, bulk superconducting samples of K$_x$Fe$_2$Se$_2$ remain elusive, but careful structural studies can explain why this phase is difficult to synthesize. First, it is surprising that K$_x$Fe$_2$Se$_2$ forms from solid state reactions because all known alkali iron chalcogenides have Fe valence nearly 2+ or 3+. We attempted to intercalate K into β-FeSe by vapor transport in a sealed tube at 300°C. However this reaction only resulted in the formation of K$_2$Se and metallic Fe, and no increase in $T_c$ above 8 K. Why then does Fe-rich phase K$_x$Fe$_2$Se$_2$ form during heat treatment of K$_x$Fe$_2$Se$_2$?

We propose that the metallic superconducting fraction precipitates upon cooling through the Fe vacancy ordering temperature at ~540 K [43] but only in cases where the crystal size is large enough for lattice strain to prevent escape of supersaturated Fe from the K$_x$Fe$_2$Se$_2$ structure. Formation of a coherent intergrowth of this I4/mmm phase is supported by recent evidence from electron microscopy and muon spin rotation. [17 24] We have not observed superconductivity in polycrystalline powder samples, indicating lattice strain may be a key factor. If $T_c$ is eventually observed in powders, it would mean that the Fe supersaturation in the K$_x$Fe$_2$−ySe$_2$ structure at high temperatures is the only prerequisite for formation of K$_x$Fe$_2$Se$_2$.

Only a small amount of Fe excess can be incorporated in the K$_x$Fe$_2$−ySe$_2$ structure at high temperatures. This places a limit on the volume of minority I4/mmm phase that will precipitate when cooling through the vacancy ordering temperature. The separation between the maximum Fe solubility at high temperatures and 80% Fe occupancy (in K$_2$Fe$_4$Se$_5$) determines the amount of K$_x$Fe$_2$Se$_2$ that can form. This explains why superconducting samples show I4/m lattice parameters on the edge of the K$_2$Fe$_4$Se$_5$ stability region in Figure 10 and why the heat capacity measurements and powder diffraction both find a small volume fraction of superconducting phase.

Solid-state routes toward single-phase, superconducting K$_x$Fe$_2$Se$_2$ will require an understanding of, and control over, the delicate temperature-composition space in the region between K$_2$Fe$_4$Se$_5$ and β-FeSe. In-situ experiments (diffraction, calorimetry, or vibrational spectroscopy) that investigate the limit of Fe solubility in K$_x$Fe$_2$−ySe$_2$ around and above the vacancy ordering temperature may prove invaluable. Quenching from above this temperature has shown to increase the sharpness of the superconducting transition, [13 14] and understanding the kinetics of this transition may provide insight into stabilizing Fe-rich phases. Topotactic reactions at low temperatures, such as those conducted in liquid ammonia, seem to have the ability to intercalate β-FeSe without significant expulsion of Fe, [52 54] while oxidative deintercalation as was performed on KNi$_2$Se$_2$ may approach K$_x$Fe$_2$Se$_2$ by removal of Fe$^+$. [55]

Expanding the available I4/mmm composition space by doping may provide new routes to stabilize phases similar to K$_x$Fe$_2$Se$_2$. The response of ThCr$_2$Si$_2$ structures with substitution of Se$^{2−}$ for As$^{3−}$ has not been systematically investigated. Only the solid solution K$_x$Fe$_2$−y(Se$_2$)S$_2$ has been investigated (albeit without a description of subtle phase separation). [26] Even simple phase equilibria studies, such as the evolution of phases across nominal K$_x$Fe$_2$Se$_2$ (0 ≤ x ≤ 1) from room temperature to ~1250 K remain unknown.

**CONCLUSIONS**

The stable phase close to superconducting stoichiometry, vacancy-ordered K$_2$Fe$_4$Se$_5$ phase can be made pure by a solid state powder reaction. We find no evidence that this I4/m phase can be doped or substituted to become superconducting. As a result, high-resolution
diffraction experiments are needed to detect the presence of additional phases.

The metallic minority phase $K_xFe_2Se_2$ with $I4/mmm$ symmetry appears only in samples that exhibit superconductivity, as judged by a diamagnetic response around $T_c = 30$ K. This phase does not exhibit any vacancy ordering. It only occurs in large crystals of $K_xFe_{2-y}Se_2$ grown from the melt, so the excess Fe is likely trapped by lattice strain, forming a coherent intergrowth with a volume fraction that is limited by the solubility of excess Fe above the vacancy ordering temperature of $K_2Fe_2Se_5$. This model of phase separation is supported by our resistivity measurements, which indicate a percolative composite of an insulator and metal, which is supported by local NMR and muon spin resonance probes and electron microscopy studies. [13][23][24][13]

We identified an oxidized phase $K_{0.51(5)}Fe_{0.70(2)}Se$ as the cause of $(010)$ reflections in the single-crystal diffraction pattern that are forbidden by $I$-centered symmetry. This phase has a FeSe interlayer spacing of 9 Å, which is highly expanded versus the 7 Å spacing of $K_2Fe_2Se_5$, due to buckling of the K layer after oxidation of Fe and loss of Se. This phase forms in the PbClF structure, similar to NaFeAs. It is not relevant to superconducting behavior, as judged by a diamagnetic response around $T_c$. Yet another phase, $KFe_4Se_3$, was identified to form with disordered vacancies ($I4/mmm$) and pure polycrystalline powders were obtained by solid state reaction. This phase was produced when we attempted to synthesize the hypothetical ordered compound $K_2Fe_3Se_4$ in the homologous series ($K_2Se)(FeSe)_n$. The response of the $K_xFe_{2-y}Se_2$ lattice to stoichiometry is varied from $KFe_1.6Se_2$ to $K_xFe_2Se_3$, $K_xFe_2Se_2$, and $β$-FeSe may prove to be a valuable probe of phase equilibria and electrical response in these systems, especially because the Rietveld-refined K/Fe stoichiometry does not provide a definitive picture of the divide between superconducting and non-superconducting samples.

Further investigations of superconducting $K_xFe_2Se_2$ must embrace the fact that these phases are unstable and heterogeneous. More informed synthesis should be pursued by investigating the high-temperature phase relations in these systems, and by understanding the kinetic processes occurring when the superconducting minority phase separates from related $K_2Fe_4Se_5$.

Finally, the insights obtained from this work call for detailed transmission electron microscopy studies to understand the superconducting/semiconducting interface and assess the nature of strain and defects associated with it. Clearly, bulk phase separation can form such composite structures. Phase separation can proceed by nucleation and growth or spinodal decomposition. The dividing line between them depends critically on the strain that develops in the system during phase separation. According to our studies, $K_2Fe_4Se_5$ and $K_xFe_{2}Se_2$ have a lattice mismatch of 1-2%, leading to considerable strains. Our present results call for first principles studies of the thermodynamics of incoherent and coherent phase separation in the $K_2Fe_4Se_5/K_xFe_{2}Se_2$ systems to calculate strain energies and mixing energies.

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