Direct observation of nanoscale interface phase in the superconducting chalcogenide $K_xFe_{2-y}Se_2$ with intrinsic phase separation

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We have used scanning micro x-ray diffraction to characterize different phases in superconducting $K_xFe_{2-y}Se_2$ as a function of temperature, unveiling the thermal evolution across the superconducting transition temperature ($T_c \sim 32$ K), phase separation temperature ($T_{ps} \sim 520$ K) and iron-vacancy order temperature ($T_{vo} \sim 580$ K). In addition to the iron-vacancy ordered tetragonal magnetic phase and orthorhombic metallic minority filamentary phase, we have found a clear evidence of the interface phase with tetragonal symmetry. The metallic phase is surrounded by this interface phase below $\sim 300$ K, and is embedded in the insulating texture. The spatial distribution of coexisting phases as a function of temperature provides a clear evidence of the formation of protected metallic percolative paths in the majority texture with large magnetic moment, required for the electronic coherence for the superconductivity. Furthermore, a clear reorganization of iron-vacancy order around the $T_{ps}$ and $T_{vo}$ is found with the interface phase being mostly associated with a different iron-vacancy configuration, that may be important for protecting the percolative superconductivity in $K_xFe_{2-y}Se_2$.

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INTRODUCTION

The observation of superconductivity in the iron-based pnictides [1] and chalcogenides [2] has opened new frontiers in the field of layered materials with interesting interplay of atomic defects, magnetism, and superconductivity [3, 4]. In particular, defects in the iron-based chalcogenides are known to be important for the suppression of long-range magnetic order and appearance of the superconductivity [2, 3, 5]. Among these materials, the intercalated layered iron-chalcogenide system with chemical formula of $A_xFe_{2-y}Se_2$ (A = K, Rb, Cs) [6, 9] is a good example in which a large magnetic moment is associated with the iron vacancy order [10]. The $A_xFe_{2-y}Se_2$ system also shows an intrinsic phase separation [11, 12] and a delicate balance between an insulating magnetic phase associated with the iron vacancy order and a metallic phase considered to be superconducting below a transition temperature $T_c$ of $\sim 32$ K. Indeed, $A_xFe_{2-y}Se_2$ manifests peculiar microstructure, including iron vacancy order in the ab-plane, an antiferromagnetic order in the c-direction [10, 13] along with an intrinsic phase separation [11, 19] in which the majority phase with block antiferromagnetism has a stoichiometry of $A_{0.8}Fe_{1.6}Se_2$ (245) while the minority metallic phase is $A_xFe_{2}Se_2$ (122). Incidentally, suppression of iron-vacancy order by high pressure produces a new phase with a $T_c$ of $\sim 56$ K [20]. A variety of experimental techniques have been used to study the intrinsic phase separation [6, 9, 19, 21, 23], revealing a wealth of information on the peculiar microstructure of these materials.

While most of the studies on $A_xFe_{2-y}Se_2$ have been focused either on the iron-vacancy ordering or the phase separation, there are limited efforts to address the relationship between the peculiar microstructure and the multi-band electronic structure sustaining the superconductivity. Very recently, an orbital selective Mott phase (OSMP) has been proposed to have an important role in $A_xFe_{2-y}Se_2$ [23]. This phase has been observed around 100-300 K in the multi-band metallic phase by angle resolved photoemission spectroscopy (ARPES) [24]. In addition, a recent high pressure study [27] has underlined the importance of the OSMP phase as an intermediate phase between the iron-vacancy ordered insulating texture and the minority metallic phase. Also a recent high energy x-ray emission (XES) study has found anomalous evolution of the magnetic phase below 300 K that can
be assigned to the OSMP phase \[28\]. These new findings suggest that a space resolved characterization of different phases is of utmost importance.

Space resolved diffraction is emerging as one of the key experimental tools to study the distribution of phases in intrinsically inhomogeneous materials, and has been efficiently exploited to obtain useful information on the structure-function relationship in a variety of systems \[29\][35\]. Earlier, we have used this space resolved micro x-ray diffraction (µXRD) to explore intrinsic nanoscale phase separation in \( \text{K}_y\text{Fe}_2-y\text{Se}_2 \) \[11\]. The temperature dependent study revealed the phase separation below \( \sim 520 \text{ K} \) and a \( \sqrt{5} \times \sqrt{5} \) superstructure due to iron-vacancy order below \( \sim 580 \text{ K} \). The study also revealed spatial distribution of different phases, i.e.: i) the majority phase (\( \sim 70-90\% \)) with \( \sqrt{5} \times \sqrt{5} \) superstructure due to iron vacancy order and; ii) the minority phase (\( \sim 10-30\% \)) with a compressed in-plane lattice. In this work, we have further exploited the technique and focused on finding different coexisting phases and found that, in addition to the tetragonal majority antiferromagnetic insulating (AFM) phase and orthorhombic minority paramagnetic metallic filamentary (PAR) phase, there exists a phase having tetragonal symmetry, that appears below a temperature of \( \sim 300 \text{ K} \) and distributes at the interface of the two main phases. The space resolved diffraction across the superconducting transition temperature \( T_c \) provides a clear evidence of percolative paths protected by the interface phase, required for the coherent electronic state for the superconductivity. The results also reveal reorganization of an iron-vacancy ordered phase around \( T_c \), suggesting that the interface phase should be associated with a different iron-vacancy configuration and that may have an important role in the percolative superconductivity of \( \text{K}_y\text{Fe}_2-y\text{Se}_2 \).

**RESULTS AND DISCUSSIONS**

Here, we start with the already known intrinsic phase separation \[10\][11\] in superconducting \( \text{K}_y\text{Fe}_2-y\text{Se}_2 \). Unlike the earlier studies, we have performed µXRD measurements in a wide temperature range using a coherent x-ray source. Figure 1 (a) shows the temperature evolution of the (004) Bragg peak in the ac-plane, measured on a single crystal sample of superconducting \( \text{K}_x\text{Fe}_2-y\text{Se}_2 \). At \( 540 \text{ K} \), a sharp and highly symmetric peak appears due to a tetragonal structure \( (a=b=4.01 \text{ Å}, c=13.84 \text{ Å}, \text{space group } 4/mmm) \). Once the sample is cooled across the phase separation temperature of \( \sim 520 \text{ K} \) \[11\][12\], the peak splits in two, and a new tetragonal phase with elongated c-axis (see e.g. in Fig. 1, the (004) peak at \( 517 \text{ K} \)) appears, coexisting with the main phase. Thus, \( \text{K}_x\text{Fe}_2-y\text{Se}_2 \) phase separates containing a majority phase with \( \sqrt{5} \times \sqrt{5} \) superstructure due to ordered iron vacancies and associated block antiferromagnetism \[10\][11\] (AFM phase). The phase separation occurs due to thermal contraction affecting the iron vacancy ordering configuration with coupled magnetism in the main phase. Further cooling hardly affects the main phase, while the peak associated with the new phase (with elongated c-axis) reveals reduction in the crystallographic symmetry. Indeed, the peak splits diagonally indicating orthorhombic symmetry (see e.g. in Fig. 1, the profile at \( 450 \text{ K} \)). This minority phase is known to be free from any
FIG. 1: (a) Temperature evolution of the (004) Bragg peak of superconducting K$_{x}$Fe$_{2-y}$Se$_{2}$ single crystal showing intrinsic phase separation at 520 K and a tetragonal to orthorhombic structural transition of the minority metallic phase below 500 K. (b) Temperature dependence of the lattice parameters for different phases. Color shades are used to show superconducting and tetragonal non-magnetic regions in (b).

iron-vacancy order [10], and is metallic (PAR phase). If the sample is cooled further, the AFM and PAR phases are hardly affected, however a new peak appears, reflecting the appearance of a third phase characterized by an elongated $c$-axis. We will come back to show that this third phase appears at the interface between the majority tetragonal AFM phase and minority orthorhombic PAR phase. This new phase, having average tetragonal symmetry is called, the interface (INT) phase.

The temperature evolution of the lattice parameters of different phases in K$_{x}$Fe$_{2-y}$Se$_{2}$ is shown in Fig. 1(b). The phase separation appears below $\sim$ 520 K in the AFM and PAR phases, however, the symmetry of the PAR phase changes by further cooling down to $\sim$ 500 K. In addition, the INT phase appears below $\sim$ 300 K, with $c$-axis similar to the PAR phase. Therefore, three phases coexist at low temperature. The average lattice parameters measured here are consistent with earlier studies on superconducting the K$_{x}$Fe$_{2-y}$Se$_{2}$ system [7 10 12 24].

The relative weights of coexisting phases have been estimated by the intensity of the (004) Bragg peak corresponding to the different crystallographic phases. Figure 2 shows the normalized intensity of the (004) diffraction peak for different phases plotted as a function of temperature. As expected, the majority AFM phase decreases sharply across the phase separation temperature ($\sim$520 K) due to the appearance of the minority PAR phase. The majority AFM phase contributes $\sim$85-90% while the remaining $\sim$10-15% is the PAR phase at $T \leq$ 520 K. This is consistent with earlier studies, estimating relative weights of the two phases at $\sim$80-90% and $\sim$10-20% respectively [10 19 23 28]. While cooling across $\sim$300 K, the majority AFM phase suffers a further decrease to about $\sim$78% with the appearance of a third (INT) phase having maximum weight of $\sim$6%. The PAR phase also appears to gain, reaching a value $\sim$16%. Therefore, at low temperature ($T \leq$ 300 K), there are three phases in K$_{x}$Fe$_{2-y}$Se$_{2}$ with different relative weights.
FIG. 2: Normalized intensity of (004) peak of K$_x$Fe$_{2-y}$Se$_2$ for different phases as a function of temperature, representing the evolution of their relative weights. The majority phase decreases sharply (red) due to the appearance of the new phase (blue) below the phase separation temperature ($T_{ps}$ $\sim$ 520 K). Further cooling results in the appearance of an interface phase (green) at $\sim$300 K.

Let us focus on the majority AFM phase that is characterized by the iron vacancy order and the associated antiferromagnetic order [10]. To further explore the iron-vacancy order we have followed the temperature dependence of the $\sqrt{5} \times \sqrt{5}$ superstructure peak normalized with respect to the corresponding (004) peak. This quantity is shown as a function of temperature in Fig. 3, revealing the degree of the vacancy order in the majority phase. The superstructure peak shows up below the iron-vacancy ordering temperature, apparent from the sharp jump at $\sim$580 K. The normalized intensity shows a small deviation from the order parameter-like behavior at $\sim$520 K, expected due to change in the microstructure and associated iron-vacancy order configuration across the phase separation. Upon cooling further, a small upturn can be seen at $\sim$350 K followed by a gradual decrease before a rapid decrease around $\sim$150 K due to evolving iron vacancy order configurations. This anomalous change is followed by a sharper (albeit small) decrease at $T_c$ $\sim$32 K with an upturn at lower temperature. The anomalous evolution of the iron-vacancy ordered phase is apparent from the zoom over the low temperature range shown as the inset in Fig. 3. Such a thermal evolution suggests that iron-vacancy order is anomalously affected by cooling and should be related with the symmetry of different phases at local scale. Also, the anomaly around $T_c$ $\sim$32 K indicates that the superconductivity should be affected by the iron-vacancy order in this system.

Let us recall the known phase separation [11, 17, 18, 21–24]. It is established that the superconducting K$_x$Fe$_{2-y}$Se$_2$ contains: (i) a majority insulating 245-phase and; (ii) a minority metallic 122-phase [11, 24]. The 245 and the 122 phases have tetragonal and orthorhombic structures with the latter being slightly compressed in the plane and expanded in the out of plane [11, 12]. Here, it is clear that, in addition to the majority 245 and minority 122 phase, an interface phase appears as a third phase at low temperature that may be important for the superconductivity. While such a phase has been proposed on the basis of recent high pressure measurements on A$_x$Fe$_{2-y}$Se$_2$ [27], we have observed it directly [see, e.g. Figure 4(a)]. This interface phase is characterized by a tetragonal symmetry with the $c$-axis longer than the one of the AFM phase (however, almost similar to the $c$-axis of the PAR phase).

To get further information on the INT phase and its spatial distribution, we have performed a limited area space resolved $\mu$XRD map as a function of temperature. The spatial distribution of different phases at 15 K is shown in Figure 4B. The minority PAR phase appears below the phase separation temperature, revealing the degree of the vacancy order in the majority phase. The superstructure peak shows up below the iron-vacancy ordering temperature, apparent from the sharp jump at $\sim$580 K. The normalized intensity shows a small deviation from the order parameter-like behavior at $\sim$520 K, expected due to change in the microstructure and associated iron-vacancy order configuration across the phase separation. Upon cooling further, a small upturn can be seen at $\sim$350 K followed by a gradual decrease before a rapid decrease around $\sim$150 K due to evolving iron vacancy order configurations. This anomalous change is followed by a sharper (albeit small) decrease at $T_c$ $\sim$32 K with an upturn at lower temperature. The anomalous evolution of the iron-vacancy ordered phase is apparent from the zoom over the low temperature range shown as the inset in Fig. 3. Such a thermal evolution suggests that iron-vacancy order is anomalously affected by cooling and should be related with the symmetry of different phases at local scale. Also, the anomaly around $T_c$ $\sim$32 K indicates that the superconductivity should be affected by the iron-vacancy order in this system.
temperature and increases with cooling, developing in percolative paths (blue). These paths are protected by the INT phase (green) below \( \sim 300 \) K. Therefore, the INT phase indeed evolves below 300 K consistent with the recent XES study \[28\]. The INT phase is likely to be the OSMP indicated in the ARPES study \[26\] where the Fe 3d \( xy \) electrons are localized and magnetic. On the other hand, the phase separation in the majority insulating AFM phase and the minority metallic PAR phase is known to occur below \( \sim 520 \) K, while the INT phase appears below \( \sim 300 \) K. In this temperature range a resistivity hump also appears \[7, 24\]. Therefore, it is clear that the PAR phase (embedded in the majority AFM phase) is not enough for a metallic conductivity in the system, and hence the INT phase is required for the same and for the superconductivity on cooling across \( T_c \). Furthermore, the results clearly show that the AFM phase is reduced by the metallic INT phase in establishing percolative paths. Thus, the reported spatial distribution of coexisting phases as a function of temperature is a clear evidence of the formation of protected metallic percolative paths in the majority AFM texture with large magnetic moment. This protection by the INT phase may help in realizing the superconducting coherent quantum state in the metallic filamentary phase for the percolative superconductivity in \( \text{K}_x\text{Fe}_{2-y}\text{Se}_2 \).

CONCLUSIONS

In summary, we have used space resolved micro x-ray diffraction measurements on superconducting \( \text{K}_x\text{Fe}_{2-y}\text{Se}_2 \) as a function of temperature. We find that, the phase separation at low temperature is characterized by the coexistence of the majority tetragonal magnetic phase, orthorhombic minority metallic phase, and an interface tetragonal phase appearing below \( \sim 300 \) K. The results reveal an anomalous behavior of the iron-vacancy ordering, affected by phase separation and superconductivity. Spatial distribution of different coexisting phases measured by space resolved micro diffraction provides a clear evidence of the formation of percolative paths with decreasing temperature, having protection by the interface phase required for the electronic coherence for the superconductivity. The results suggest that the interface phase should be associated with different iron-vacancy configuration and likely to have an important role in the percolative superconductivity of \( \text{K}_x\text{Fe}_{2-y}\text{Se}_2 \).

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