Microstructure and ordering of iron vacancies in the superconductor system $K_xFe_ySe_z$ as seen via transmission electron microscopy


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Structural investigations by means of transmission electron microscopy (TEM) on $K_{0.8}Fe_2Se_2$ and $KFeSe_2$, with $1.5 \leq x \leq 1.8$, have revealed a rich variety of microstructure phenomena. Materials with $1.5 \leq x \leq 1.6$ often show a superstructure modulation along the [310] zone-axis direction, and this modulation can be well interpreted by the Fe-vacancy order, which likely yields a superstructure phase of $K_2Fe_4Se_5$. The superconducting $K_{0.8}Fe_2Se_2$ and $KFeSe_2$ ($1.7 \leq x \leq 1.8$) materials contain clear phase separation, in particular, along the c-axis direction, recognizable as visible parallel lamellae in the crystals; this fact suggests that the superconducting phase could have the Fe-vacancy disordered state.

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Since the discovery of high-temperature superconductivity in the quaternary $ZrCuSiAsS$-type (so-called the 1111-phase) Fe-based oxypnictide LaFeAsO (F doped) with critical temperature ($T_c = 26$ K) in 2008,1 superconductivity in the PbO-type $\alpha$-FeSe$_x$ and related materials has been extensively investigated.2 More recently, the superconductivity with $T_c \sim 33$ K has been found in the FeSe-layered compounds $K_{0.8}Fe_1.7Se_2$ and $C_{90.8}(FeSe_{0.99})_2$,3–5 which inspires wide interests in the study of this kind of superconducting material. Experimental studies revealed no structural phase transition occurring over the temperature ranging from 60 to 300 K.6 The effect of varying Fe content on transport properties of this paper, we performed a transmission-electron-microscopy (TEM) study on the Fe-Se layers stacking along the c-axis direction, as discussed for TiFe$_2S_2$ and TiFe$_2Se_2$,7,8 and they all have an antiferromagnetic structure at low temperatures. Experimental measurements of Mössbauer spectroscopy and neutron diffraction revealed the presence of Fe vacancies and a visibly antiferromagnetic order in this system,9,10 and the Fe deficiency and related ordered states are considered as playing a critical role for understanding the microstructure and physical properties. In this paper, we performed a transmission-electron-microscopy (TEM) study on $K_{0.8}Fe_2Se_2$ and $KFeSe_2$ with $1.5 \leq x \leq 1.8$. The microstructure features and superstructures corresponding to different Fe-vacancy orders are reported.

Both single-crystal and polycrystalline samples were used in this study. Fe$_{1+x}$Se$_2$ was first synthesized as a precursor by reacting Fe powder with Se powder at 750 °C for 20 hours. K pieces and Fe$_{1-x}$Se$_2$ powder were put into an alumina crucible with nominal compositions as KFe$_x$Se$_2$ (1.5 \leq x \leq 2.0). The single crystals used in this study were synthesized by the method as reported in previous publications.3 Specimens for TEM observations were prepared by gently crushing the single crystals into fine fragments in the glove box. We also prepared a few TEM samples by Ar-ion milling at liquid-N$_2$ temperature with the voltage of 100 V for 30 minutes. Microstructure investigations were performed on a FEI Tecnai-F20 TEM equipped with double-tilt cooling holder. Image simulations were performed by using the MACTEMPS software.

The structural and physical properties of all $K_{0.8}Fe_2Se_2$ and $KFeSe_2$ samples used for our TEM study were well characterized. The x-ray-diffraction measurements demonstrate that these samples, in general, have a tetragonal basic structure with lattice parameters $a = b = 3.913$ Å, $c = 14.10$ Å, and the space group of $I4/mmm$ (No. 139). It is similar to the crystal structure of the 122 phase in the known Fe-based superconducting systems, such as KFe$_2As_2$, BaFe$_2As_2$, and SrFe$_2As_2$.17–19 In order to understand the microstructure features in correlation with the Fe deficiency in this system, we performed an extensive structural investigation by means of selected-area electron diffraction and high-resolution TEM observations.

We first focus our study on the $K_{0.8}Fe_2Se_2$ ($1.5 \leq x \leq 1.6$), which shows a semiconductortlike resistivity from room temperature down to 4 K. Figures 1(a)–1(d) show a series of electron diffraction patterns from different areas taken along the relevant [001], [100], [1–30], and [001] zone-axis directions. The main diffraction spots with relatively strong intensity can be well indexed by the known tetragonal structure in consistency with the x-ray-diffraction results.3 On the other hand, the most striking structural phenomenon revealed in our TEM observations is the appearance of a series of superlattice spots following with the main diffraction spots, as clearly illustrated in Figs. 1(a), 1(c), and 1(d). Careful examination reveals that these satellite spots, in general, are clearly visible in the $ab$ plane of reciprocal space and can be characterized by a unique modulation wave vector $q_1 = (3/5, 1/5, 0)$ as also confirmed by the observations along the [1–30] zone-axis direction as illustrated in Fig. 1(e). We herein interpret this superstructure by the Fe-vacancy ordering in the Fe-Se layer, and the Fe content is therefore estimated to be 2(1–1/5) = 1.6. A careful analysis of chemical composition for this superstructure phase suggests the presence of an Fe-deficient $K_2Fe_4Se_5$ phase (i.e., $K_{0.8}Fe_2Se_2$) with the lattice parameters of $a_1 = b_2 = 8.70$ Å and $c_1 = 14.13$ Å, which are consistent with neutron diffraction.13,16 The Fe valence state in this
superstructure phase is Fe$^{2+}$. Occasionally, other kinds of superstructures can be also observed in certain areas, as discussed in the following context.

Sometimes, two sets of superstructure reflections appear around each basic Bragg spot, as shown in Fig. 1(d), in which two sets of superstructure reflections are indicated by $q_1$ and $q_2$. These two sets of superstructure spots are considered to originate from the domains where the superstructure vectors are twinning related with respect to one another. This kind of twin domain was previously observed and reported in a variety of superstructure systems,$^{20,21}$ and the $q_1$ and $q_2$ could appear in different areas or in different layers in a crystal.

Figure 2(a) shows the high-resolution TEM image taken from a K$_{0.8}$Fe$_{1.6}$Se$_2$ single-crystalline sample, indicating a well-defined 122-type layered structure.$^{22}$ This image taken along the [100] zone-axis direction was obtained from a relative thicker region of a crystal. The K-atom positions are therefore recognizable as bright dots. The Se and Fe atoms with a distance of 1.56 Å are not resolvable in this image, but yield bright contrast between K layers.

We now go on to discuss the superstructure, as illustrated in Fig. 1, in correlation with the Fe deficiency in this superconducting system. According to previous neutron diffraction study for TlFe$_x$Se$_2$ ($1.5 < x < 2$) (Ref. 13) and careful analysis of our TEM data, we herein interpret this superstructure phase by a Fe-vacancy order along the [310] zone-axis direction. To directly observe the ordered arrangement of the Fe vacancies in the crystals, we carried out the high-resolution TEM investigation on the superstructure along several relevant directions. Figure 2(b) shows a high-resolution TEM image taken from thin crystal, in which the ordered behavior as visible periodic features within the $a$-$b$ plane can be clearly read out. Image calculations based on the proposed superstructure model as shown in Fig. 2(b) were performed by varying the crystal thickness from 5 to 10 nm and the defocus value from $-40$ to $-100$ nm. A calculated image with a defocus value of $57$ nm and a thickness of $9$ nm is superimposed onto the image, and it appears to be in good agreement with the experimental image.

It is also noted that the superstructure with lattice parameter $2 \times 2 d_{110}$ as discussed for KFe$_{1.5}$Se$_2$ in previous literature$^{23}$ appears frequently in certain areas. Figure 3(a) shows a high-resolution image revealing this kind of superstructure as observed in a crystal. This TEM image is taken along the [001] zone-axis direction in an area with a thickness estimated to be 8 nm, clearly displaying a KFe$_{1.5}$Se$_2$ crystal with visible superstructure features. Careful examinations suggest that the ordered state of the Fe vacancies adopts a well-defined $2 \times 2$ supercell corresponding with the structural model of Fig. 3(b). Our study on this superlattice suggests the appearance of another phase of K$_2$Fe$_3$Se$_4$ (i.e., KFe$_{1.5}$Se$_2$). Further investigation on the structural and physical properties of this phase is in progress.

It is remarkable to note that the increase of the Fe concentration could result in the appearance of superconductivity in this system, e.g., the KFe$_{1.8}$Se$_2$ shows clear superconducting...
transition at $T_c \sim 33$ K. Actually, experimental studies show that the Fe concentration visibly affects the electrical transport and structural properties of this layered system. For instance, a clear insulator-metal transition often appears in samples with $1.6 \leq x \leq 1.8$ and disappears for high Fe concentration. This fact suggests that the Fe vacancy and the ordered states could play a critical role for understanding the physical properties in KFe$_1$Se$_2$.

For a better understanding of the microstructure properties in the superconducting phase, we have focused our attention on the superconducting samples with nominal composition of K$_{0.8}$Fe$_x$Se$_2$ and KFe$_{1.8}$Se$_2$ ($1.7 \leq x \leq 1.8$), which, in general, show sharp superconducting transitions at around 33 K, and the alteration of K content could slightly affect the width of superconducting transition. TEM observations indicated that all samples with the nominal compositions of K$_{0.8}$Fe$_{1.8}$Se$_2$ and KFe$_{1.8}$Se$_2$ apparently have inhomogeneous microstructure and clear phase separation, in particular along the $c$-axis direction.

Figure 4 shows the high-resolution TEM images obtained from a superconducting sample. It is clearly recognizable that the superconducting crystals, in general, have the same tetragonal basic structure and a clear superstructure within the $a$-$b$ plane as discussed in the above context. However, clear changes of microstructure and superstructure properties can be commonly observed. Figure 4(a) shows a high-resolution TEM image revealing the presence of complex microstructures. Careful analysis on the structural properties in a relatively large domain size (>100 nm) suggests a similar superstructure as discussed in the KFe$_{1.8}$Se$_2$ sample with $q_1 = (3/4, 1/4, 0)$, but the structural inhomogeneity and changes of ordered behaviors occur visibly along the $q_1$ direction, as shown in Fig. 4(b), in which a layer without the Fe-vacancy order is indicated by an arrow.

Figure 4(c) shows a high-resolution TEM image illustrating the phase separation along the $c$-axis direction in the superconducting sample. It is clearly recognizable that the additional Fe ions could result in the appearance of Fe disordered layers in the superconducting crystals and yield the intergrowth of structural lamellae with the Fe-vacancy order state (OS) and disorder state (DOS) along the $c$-axis direction.

Our observations suggest that the superconducting phase in this system could have the Fe-vacancy disordered state, as illustrated in Fig. 4(c). Moreover, in the superconducting sample KFe$_{1.8}$Se$_2$, we can also see a superstructure with periodicity of $q_1 = (3/4, 1/4, 0)$ coexisting with $q_1 = (3/5, 1/5, 0)$ in certain crystals. This fact suggests that the alteration of Fe concentration in KFe$_x$Se$_2$ materials could yield not only superconductivity, but also clear microstructure changes.

In conclusion, microstructure analysis of K$_{0.8}$Fe$_x$Se$_2$ and KFe$_x$Se$_2$ with $1.5 \leq x \leq 1.8$ reveals a rich variety of structural phenomena in correlation with the presence of Fe deficiency in this layered system. A clear superstructure has been commonly observed with a modulation wave vector of $q_1 = (3/5, 1/5, 0)$. This superstructure can be well interpreted by the Fe-vacancy order within the $a$-$b$ plane and suggests the presence of a K$_2$Fe$_2$Se$_5$ phase in this system. The increase of Fe concentration in the K$_{0.8}$Fe$_x$Se$_2$ and KFe$_x$Se$_2$ materials could result in clear alternations of microstructure properties in superconducting materials. Structural phase separation and the complex superstructures commonly appear in the superconducting samples as observed by high-resolution TEM investigations; these facts suggest that the superconducting phase could have the Fe-vacancy disordered state.
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