Role of the extra Fe in $K_{2-x}Fe_{4+y}Se_5$ superconductors

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The exact superconducting phase of $K_{2-x}Fe_{4+y}Se_5$ has so far not been conclusively decided since its discovery due to its intrinsic multiphase in early material. In an attempt to resolve this mystery, we have carried out systematic structural studies on a set of well-controlled samples with each chemical stoichiometry $K_{2-x}Fe_{4+y}Se_5$ ($x = 0−0.3$) that are heat-treated at different temperatures. Using high-resolution synchrotron radiation X-ray diffraction, our investigations have determined the superconducting transition by focusing on the detailed temperature evolution of the crystalline phases. Our results show that superconductivity appears only in those samples that have been treated at high enough temperature and then quenched to room temperature. The volume fraction of superconducting transition strongly depends on the annealing temperature used. The most striking result is the observation of a clear contrast in crystalline phase between the nonsuperconducting parent compound $K_2FeSe_5$ and the superconducting $K_{2-x}Fe_{4+y}Se_5$ samples. The X-ray diffraction pattern can be well indexed with the phase $I4/m$ symmetry in all temperatures investigated. However, we need two phases with similar $I4/m$ symmetry but different parameters to best fit the data at a temperature below the Fe vacancy order temperature. The results strongly suggest that superconductivity in $K_{2-x}Fe_{4+y}Se_5$ critically depends on the occupation of Fe atoms on the originally empty 4d site.

Cuprates and Fe-based high Tc superconductors turn superconducting when their parent compounds are properly doped. The similarity of these superconductors, in which superconductivity emerges with the suppression of competing phases, has created the possibility for a unified picture of high-temperature superconductivity (1, 2). Iron-based superconductors all have FeAs or FeSe layers, just as the CuO$_2$ layers are the crucial ingredients for superconductivity (3−5). It is generally believed that the quasi-2D characteristics of these active layers and the proximity to magnetically ordered states induce superconductivity via unconventional pairing in these high Tc materials. However, the parent compounds of the Fe-pnictide superconductors are metallic with spin-density wave antiferromagnetism. Later studies indicate that there exists a parent compound (18), which in contrast to having excess Fe is actually Fe deficient and is a Mott insulator. This Fe-deficiency material becomes superconducting after being properly annealed at high temperature (19).

An important development in Fe-based superconductors is the discovery of the relatively higher Tc in alkaline-metal (A) intercalated FeSe with nominal composition $A_{10}Fe_2Se_2$ (20). The nominal $A_{10}Fe_2Se_2$ sample was considered to crystallize in the tetragonal $ThCr_2Si_2$-type structure, which is isostructural to the BaFe$_2As_2$ system. Researchers have long debated the exact superconducting phase in this material. One group claimed the superconducting composition is identified as $K_{0.83(2)}Fe_{1.44(1)}Se_2$ with enlarged $\sqrt{5}/2 \times \sqrt{5}/2 \times 1$ crystallographic unit cell due to Fe vacancy order (21). The ideal Fe vacancy order phase has a chemical stoichiometry of $K_{0.8}Fe_{1.2}Se_2$ ($K_2FeSe_2$, referred to simply as “$245$” in the following), which orders antiferromagnetically below 559 K. The second group proposed that the stoichiometric $K_2FeSe_2$ phase (which was indexed from X-ray diffraction to exist with about 13% in volume) is the superconducting phase in the matrix of the insulating AF 245 phase (22−24). The third group suggested that superconductivity arises due to the interface between the iron vacancy ordered and free phase (25, 26). Bao et al. (21, 27, 28) have argued that the antiferromagnetic order phase is the origin for superconducting phase, and slightly excess Fe is critical to the stability of the superconducting phase. It was noted that the Fe content of the superconducting samples $K_{0.6}Fe_{1.8}Se_2$ is slightly off-stoichiometry compared with the parent compound 245 (29−33), which seems to play a significant role in the onset of superconductivity.

In our earlier study (34), we identified the ideally Fe vacancy order 245 phase to be a Mott insulator with a block checkerboard...

Significance

This paper presents the results of a detailed structural study using synchrotron X-ray diffraction at various temperatures up to 850 °C on $K_{2-x}Fe_{4+y}Se_5$ superconductors. The results confirm that extra Fe atoms begin to fill the empty 4d site and stabilize the structural-phase $I4/m$ symmetry so that the lattice size remains the same even above the order−disorder temperature. The results demonstrate that the addition of extra Fe suppresses the Fe vacancy long-range order and the accompanied magnetic order so that superconductivity emerges. The significance of this research is that it provides unambiguously the structural origin for superconductivity in the $K_{2-x}Fe_{4+y}Se_5$ superconducting system.

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antiferromagnetic (AFM) ordered below 559 K (21, 35). We also reported that superconductivity could be induced with adding small amount of Fe to fill the vacant site plus strong disorder of the Fe vacancy. We noted that the processing temperature has decisive effects on the properties of the samples. Superconducting transition only appears in those samples that have been annealed at high temperature and then quenched. Annealing the superconducting sample at low temperature (<400 °C) gradually suppressed superconductivity. The results showed that superconducting to nonsuperconducting state can switch back and forth in the same sample by changing the heat treatment process. We concluded that the observed facts strongly indicate superconductivity emerges as Fe vacancy becomes disordered.

To understand the effect of annealing conditions to superconductivity better, we carried out a detailed systematic study on a series of samples with stoichiometry K$_{2-x}$Fe$_{4+y}$Se$_5$, subject to various annealing temperatures. We also took advantage of the high-resolution X-ray diffraction in the National Synchrotron Radiation Center (NSRRC) with in situ high-temperature measurements. Our results revealed that the superconducting volume fraction, even with the same chemical stoichiometry, depends strongly on the annealing (and quench) temperature. There is a critical anneal temperature. Below that temperature, the superconducting volume fraction is close to zero. The results of the high-temperature in situ X-ray diffraction provide further evidence that the random occupation of the original vacant site is the key to superconductivity.

**Experimental Procedures**

We synthesized polycrystalline bulk samples using an approach described elsewhere in detail (34). DC magnetic susceptibility measurements were performed in a Quantum Design superconducting quantum interference device vibrating sample magnetometer. The synchrotron X-ray diffraction of samples was performed at the BL01C2 BL17A and TP509A beamline of the NSRRC. The ring of NSRRC was operated at energy 1.5 GeV with a typical current of 360 mA. The wavelengths of the incident X-rays were 0.61993, 1.3216, and 0.77491 Å, delivered from the 5-T Superconducting Wavelength Shifter and a Si(111) triangular crystal monochromator. Two pairs of slits and one collimator were set up inside the experimental hutch to provide a collimated beam with dimensions of typical 0.5 mm × 0.5 mm (horizontal × vertical) at the sample position. The diffraction pattern was recorded with a Mar345 imaging plate detector ~400 mm from the sample, with a typical exposure duration of 1 min. The pixel size of Mar345 was 100 μm. The 1D powder diffraction profile was converted with program GSAS II and cell-type integration. The diffraction angles were calibrated according to Bragg positions of LaB$_6$ standards.

**Results and Discussion**

Fig. 1A shows the X-ray diffraction pattern of three K$_{2-x}$Fe$_{4+y}$Se$_5$ samples with $x$ ranging from 0.1 to 0.2. The Inset displays the relevant magnetic susceptibility of the samples. The magnetic data indicate that the superconducting diamagnetic signal diminishes with reducing K content, with almost no diamagnetic signal in K$_{1.8}$Fe$_{4.2}$Se$_5$. Meanwhile the X-ray diffraction patterns show no additional peaks, which have been associated with the extra K$_{2-x}$Fe$_{4+y}$Se$_5$ phase by other groups (22), in this nonsuperconducting K$_{1.8}$Fe$_{4.2}$Se$_5$ sample. Based on this observation, one would consider that superconductivity might originate from this extra K$_{2-x}$Fe$_{4+y}$Se$_5$ phase. However, close examination of the X-ray and magnetic data of two K$_{1.9}$Fe$_{4.2}$Se$_5$ samples, as shown in Fig. 1B, which are prepared under different annealing and quenching temperatures, one at 650 °C and the other at 790 °C, shows a high-volume superconducting signal in the sample prepared at 790 °C, but no diamagnetic signal in sample prepared at 650 °C. The X-ray diffraction patterns for both samples are almost identical, showing the presence of the extra peaks associated with K$_{2-x}$Fe$_{4+y}$Se$_5$ phase. The above contradictory observations suggest that there are more subtleties regarding the correlation between crystal structure and superconductivity in this intriguing superconducting system.

Subsequently, we carried out detailed X-ray diffractions at different temperatures up to 750 °C for the K$_2$Fe$_5$Se$_5$ (2(4)5) and excess-Fe K$_{1.9}$Fe$_{4.2}$Se$_5$ (1.9(4.2)5) samples. Both the warming and cooling cycles exhibit no difference in the diffraction patterns, as shown in Fig. 2. Fig. 2A illustrates the significant shifts in diffraction peaks (008) and (051) at 275 °C in warming, which are the indication of the transition from the Fe vacancy order to disorder state. A large hysteresis shows the transition temperature, the material exhibits clearly the Fe vacancy order of 14/m symmetry with $\sqrt{5} \times \sqrt{5}$ superlattice; and above the order temperature, the crystal symmetry seems to fit well to 14/mmm symmetry. In addition, the superstructural peaks related to the vacancy order state completely disappear above the ordering temperature. However, since the chemical stoichiometry of the...
Fig. 2. Evolution of the temperature-dependent X-ray powder diffraction pattern of (A) K$_2$Fe$_4$Se$_5$ (245) and (B) K$_{1.9}$Fe$_{4.2}$Se$_5$ (2(4.2)5). The color red indicates increasing temperature; blue indicates decreasing temperature. Refined lattice parameters of K$_2$Fe$_4$Se$_5$ and K$_{1.9}$Fe$_{4.2}$Se$_5$ samples are displayed in C and E, respectively. All data are refined using the I4/m unit cell. A cell with compressed c axis and expanded ab plane is observed above vacancy disorder temperature in 245 sample; two cells with different lattice parameters (one for vacancy-ordered cell and the other for vacancy-disordered) are found to best fit the data for 2(4.2)5 sample below Fe vacancy disorder temperature. D illustrates the I4/m unit cell. The Left cell is Fe vacancy-ordered phase, and the Right cell is disordered phase. In the Fe vacancy order phase, the mirror image of Fe2 (16i) layers is according to magnetic moment orientation (21). The disordered phase shows that the c axis is compressed, and ab plane is expanded. F shows the schematic of mix structure, which includes both ordered and disordered phases. The black boxes outline the I4/m unit cell. The iron vacancy site (4d) is marked by the hollow symbol, and the Fe(16i) site is marked by the khaki (black) color. K and Se atoms are not shown in the plot.
sample was exactly 245, it was a puzzle to us: how could the high-
temperature phase belong to the high-symmetry I4/mmm group as
there is 20% Fe deficiency? Thus, we tried to fit the diffraction
pattern with I4/m symmetry considering that the high-temperature
phase Fe could occupy both 16i (fully occupied) and 4d site
(originally empty site). The fitting was almost perfect and the
resulted lattice parameters are shown in Table 1, which is almost
identical to those values obtained by fitting with I4/mmm. This
result indicates the crystal structure of 245 could be well described
by single phase with I4/m symmetry even above 285 °C (28).

We were surprised when we first saw the temperature-
dependent diffraction patterns of the excess-Fe sample that ex-
hibits bulk superconductivity, as shown in Fig. 2B, which show
essentially no shift in all diffraction peak positions throughout
the whole temperature range. We carefully examined the dif-
fraction patterns, as shown in Figs. 2B and 3, and we found
additional peaks below the vacancy-order temperature at 270 °C
during warming. The data for 2(4.2)5 sample are found to best fit
with two different sets of parameters (shown in Table 2), one
with Fe vacancy ordered and the other disordered Fe vacancy,
under the same I4/m symmetry. Fig. 2 C and E) plot the lattice
parameters of 245 and 2(4.2)5 samples, respectively, below (both
fit with I4/m symmetry) and above the Fe vacancy order tem-
perature. Fig. 2 D and F are the schematic atomic arrangements
for the two samples based on the refined results.

Fig. 3 A and B displays the diffraction patterns for 245 and
2(4.2)5 samples plotting with diffraction angles and d spacing,
respectively. There are two phases coexisting in excess-Fe sample
shown in Fig. 3A. The Inset shows the superlattice (110) profile.
The intensity of diffraction peak in the excess-Fe sample is not
only decreased but also shifted to a higher angle. It suggests the
Fe vacancy ordered phase of the excess-Fe sample, which has a-
axis parameters significantly smaller than 245. From Fig. 3B,
those additional features can be associated with the Miller index
(002), (130), (132), (134), (136) … Fe-layers, based on I4/m
symmetry. Fig. 3C shows the schematic atomic arrangement of
the plane (132) in the vacancy ordered and disordered states.
The d spacing for the disordered state is about 2% larger than
that of the ordered state. These planes are all crossing the Fe-4d
site, as exemplified by the schematic plot in Fig. 3D. This result
indicates that the presence of excess-Fe atoms shall begin to fill
the original empty 4d sites (construct the disorder phase). Thus,
additional planes with the same Miller index show up. Our
analysis shows that the difference in d-spacing of these new
features with the original peaks is at most 2%, as displayed in
Fig. 3B. These additional features disappear above the vacancy
order-disorder transition temperature, but keep the diffraction
peak positions unchanged. This observation suggests that the
added excess-Fe atoms play a critical role in maintaining the
crystal lattice (high temperature phase) with the I4/m symmetry
as that of the vacancy ordered state. Above the vacancy order
temperature, the lattice remains with the I4/m symmetry but with
disorder occupation of the Fe-atom to all possible Fe site so that
the additional features disappear.

It is known that for tetragonal symmetry the peak of (hkl) and
(hkl) are at the same diffraction angle because a = b, whereas for
orthorhombic symmetry the peak of (hkl) and (hkl) could be at
different diffraction angle because a ≠ b. Thus, we have also
tried to fit the observed diffraction patterns by considering
whether the data fit with orthorhombic symmetry. Detailed
analysis of the data suggests that a monoclinic 245 structure with
II12/m symmetry, using the lattice parameters: a = 8.6 Å, b = 8.72 Å,
c = 14.2 Å, and γ = 90°, could generate most of the
diffraction peaks observed (as shown in SI Appendix). Although
the diffraction peaks seem to fit well with the observed results,
the overall refinement was relatively poor regarding the peak
intensity, which is known to depend on the number, position, and
specie of atoms.

Table 1. The structural information for K$_2$Fe$_4$Se$_2$ (275 °C) as Rietveld refinement from the synchrotron
diffraction data

| Fe vacancy disorder phase (86.3 %) | Fe vacancy order phase (13.7 %) |
|----------------------------------|---------------------------------|
| a (Å) = 8.717743                | a (Å) = 8.582171                |
| c (Å) = 14.125174               | c (Å) = 14.235626               |
| α = β = γ = 90°                 | α = β = γ = 90°                 |
| x x                           | x x                           |
| y y                           | y y                           |
| z z                           | z z                           |
| Mut. Occ.                     | Mut. Occ.                     |
| K$_1$ (2b)                     | K$_1$ (2b)                     |
| 0 0 0.5                      | 0 0 0.5                      |
| 2 2.0359                    | 2 2.0359                    |
| K$_2$ (8h)                    | K$_2$ (8h)                    |
| 0.808077                    | 0.732769                    |
| 0.392152                    | 0.398093                    |
| 0.5 0.8074                  | 0.5 0.8074                  |
| Fe$_1$ (4d)                   | Fe$_1$ (4d)                   |
| 0 0.5 0.25                   | 0 0.5 0.25                   |
| 4 4.2214                     | 4 4.0000                     |
| Fe$_2$ (16i)                  | Fe$_2$ (16i)                  |
| 0.295179 0.406466 0.250104 | 0.293777 0.403941 0.252191 |
| 16 16.0083                   | 16 16.0315                   |
| Se$_1$ (4e)                   | Se$_1$ (4e)                   |
| 0 0 0.137406                 | 0 0 0.144785                 |
| 4 4.0564                    | 4 4.0324                     |
| Se$_2$ (16i)                  | Se$_2$ (16i)                  |
| 0.110745 0.292429 0.353529 | 0.101194 0.302082 0.357016 |
| 16 16.0878                   | 16 16.9602                   |

Rwp = 2.94%, Rp = 2.19%, χ² = 0.05283. Space group: I4/m.
Based on the above observations, one might expect even in the stoichiometry 245 sample to observe that Fe atoms occupied the empty 4d site if the sample has been treated at high-enough temperature so that Fe atoms could hop around. Indeed, the high-resolution X-ray diffraction patterns of the 245 sample quenched from 800 °C, as shown in Fig. 4, display extra peaks similar to those observed in excess-Fe samples. Meanwhile, the magnetic susceptibility data shown in the Inset of Fig. 4 exhibits clearly diamagnetic signal indicating the presence of superconductivity, although its volume fraction is rather small. These results demonstrate that the occupation of the 4d site, which maintains the crystal lattice (size), plays a key role for the emergence of superconductivity. It is noted that there is a significant temperature hysteresis in the vacancy order–disorder transition as on cooling the additional features do not appear until below 240 °C, suggesting this transition is first-order thermodynamically.

To clarify further the role of the extra Fe atom to the crystal lattice, two more samples were prepared for detailed studies: K$_{0.5}$Fe$_{4.25}$Se$_5$ and K$_{0.5}$Fe$_{4.25}$Se$_5$. As shown in Fig. 5, the changes in diffraction peak positions of (0 0 8) and (0 5 1) for the K$_{0.5}$Fe$_{4.25}$Se$_5$ sample clearly are less significant compared with that of the 245 sample. For the K$_{0.5}$Fe$_{4.25}$Se$_5$ sample, essentially the same as the K$_{0.5}$Fe$_{4.25}$Se$_5$ sample, the peak positions do not change with temperature. These results further confirm that extra-Fe atoms begin to fill the empty 4d site and stabilize the structural phase I4/m symmetry so that the lattice size remains the same above the order–disorder temperature. By comparing with the parent compound, the extra-Fe sample exhibits much weaker superstructural peaks such as the (222) peak, which almost disappears at room temperature. This demonstrates that the addition of extra Fe suppresses the Fe vacancy long-range order. Consequently, this modification suppresses the magnetic order, which accompanies with the vacancy order, to favor the emergence of superconductivity.

Our experimental observations further confirm that superconductivity in K$_{2-x}$Fe$_{4+y}$Se$_5$ is not due to the impurity phase (K$_{0.5}$Fe$_{2}$Se$_2$), which has been suggested based on the X-ray diffraction features. Our results unambiguously demonstrate that the random occupation of Fe atom in the lattice is key for superconductivity. Nevertheless, the exact origin for superconductivity...
remains to be resolved. Several questions remain to be answered, such as, why does the superconducting volume fraction in the excess-Fe sample depend on the annealing and quenching temperature? We are currently working on a detailed refinement of the X-ray diffraction data, collected with a wide temperature range. A preliminary result indicates that a more subtle high-temperature structural distortion might be closely related to the appearance of superconductivity. Details of these results will be published in the near future.

**Summary**

In summary, in this detailed X-ray diffraction experiment over a wide range of temperature, we have shown that the superconducting K$_{2-x}$Fe$_{4+y}$Se$_2$ samples with excess Fe atoms exhibit the same structure with 14/m symmetry throughout the whole temperature range studied. The observation of extra features, which have been considered by others as the presence of impurity phase associated with the 14/mmm symmetry, actually were the signatures of the original empty Fe-4d sites occupied by the excess Fe atoms. The occupation of the Fe-4d site and an eventual more random distribution of the Fe atom are critical to the emergence of superconductivity. Therefore, the main conclusion of this study further confirms that superconductivity in K$_{2-x}$Fe$_{4+y}$Se$_2$, very much similar to that observed in high Tc cuprates, is derived from the doping (adding extra Fe) to the parent Mott insulator K$_2$Fe$_3$Se$_5$. More disorder of the Fe occupation in the 14/m lattice leads to higher volume fraction of superconductivity. We are investigating a more detailed refinement of the high-temperature diffraction data to unravel the exact origin for the appearance of superconductivity in this intriguing FeSe-based superconductor.

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1. Johnston DC (2010) The puzzle of high temperature superconductivity in layered iron pnictides and chalcogenides. Adv Phys 59:803–1061.
2. Paglione J, Greene RL (2010) High-temperature superconductivity in iron-based materials. Nat Phys 6:465–658.
3. Dagotto E (2013) Colloquium: The unexpected properties of alkali metal iron selenide superconductors. Rev Mod Phys 85:849–867.
4. Hirschfeld PJ, Korshunov MM, Mazin II (2011) Gap symmetry and structure of Fe-based superconductors. Rev Prog Phys 74:124508.
5. Stewart GR (2011) Superconductivity in iron compounds. Rev Mod Phys 83:1589.
6. Li W, et al. (2012) KFe$_2$Se$_3$: The parent compound of K-doped iron selenide superconductor. Phys Rev Lett 109:057003.
7. Bao W, et al. (2011) A novel large moment antiferromagnetic order in K$_{0.8}$Fe$_{1.6}$Se$_2$ superconductor. Chin Phys Lett 28:086104.
8. Wang MJ, et al. (2009) Crystal orientation and thickness dependence of the superconducting KFe$_2$Se$_3$ thin films. Phys Rev Lett 103:057002.
9. McQueen TM, et al. (2009) Extreme sensitivity of superconductivity to stoichiometry in Fe$_{1-x}$Se. Phys Rev B Condens Matter Phys 79:014522.
10. Wang MJ, et al. (2009) Crystal orientation and thickness dependence of the superconducting transition temperature of tetragonal FeSe$_{1+y}$ thin films. Phys Rev Lett 103:117002.
11. McQueen TM, et al. (2009) Tetragonal-to-orthorhombic structural phase transition at 90 K in the superconductor Fe$_{1+y}$Se. Phys Rev Lett 103:257002.
12. Imai T, Aihara K, Ning FL, McQueen TM, Cava RJ (2009) Why does undoped FeSe become a high-Tc superconductor under pressure? Phys Rev Lett 102:177005.
13. Stewart GR (2011) Superconductivity in iron compounds. Rev Mod Phys 83:1589.
14. Liu Y, et al. (2016) Formation mechanism of superconducting K$_{0.6}$Fe$_{1.4}$Se$_2$ superconductors. J Phys Chem C 116:17847.
15. Peng F, Liu WP, Lin CT (2013) Study of thermal behavior and single crystal growth of A$_{x}$Fe$_{1-y}$Se$_2$ (A = K, Rb, and Cs). J Supercond Nov Magn 26:1205–1211.
16. Wang ZW, et al. (2012) Structural phase separation in K$_{0.6}$Fe$_{1.4}$Se$_2$ superconductors. J Phys Chem C 116:17847.
17. Chen TK, et al. (2014) Fe-vacancy order and superconductivity in tetragonal KFe$_2$Se$_3$. Proc Natl Acad Sci USA 111:63–68.
18. Wang C-H, et al. (2015) Disordered Fe vacancies and superconductivity in potassium-intercalated iron selenide (K$_x$Fe$_{2−x}$Se$_2$). Europhys Lett 111:27004.