Superconductivity and Magnetism in (Tl, K, Rb)Fe<sub>x</sub>Se<sub>2</sub>

Minghu Fang<sup>1</sup>, Hangdong Wang<sup>1,2</sup>, Chiheng Dong<sup>1</sup>, Q. Huang<sup>3</sup>

1Department of Physics, Zhejiang University, Hangzhou 310027, China
2Department of Physics, Hangzhou Normal University, Hangzhou 310036, China
3NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

E-mail: mhfang@zju.edu.cn

Abstract. The iron selenide superconductors AFe<sub>x</sub>Se<sub>2</sub> (A=Tl, K, Rb and Cs) discovered at the end of 2010 has attracted great interest because they display a variety of properties unprecedented for the cuprates and iron pnictides. Here, we present the motivation for our discovery on the superconductivity in (Tl,K,Rb)Fe<sub>x</sub>Se<sub>2</sub> system, in which the onset superconducting transition temperature is as high as 40 K. We found that the compound with more Fe vacancies is an AFM insulator, which has been confirmed to be associated with the Fe-vacancy ordering in the crystals. Our discovery represents the first Fe-based superconductivity at the verge of an AFM insulator. A review on the recent results of Fe-vacancy super-lattice, AFM ordering, superconductivity and phase separation in (Tl,K,Rb)Fe<sub>x</sub>Se<sub>2</sub> system is presented.

1. Introduction

Cuprates [1] and Fe-based compounds [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13] are two families with highest superconducting (SC) transition temperature. A common feature in both families is that superconductivity emerges as antiferromagnetic (AFM) long range order is suppressed. While the parent compound of cuprates is a Mott insulator where the electron repulsion is strong, the parent compound of Fe-based materials is metallic implying weak or moderate electron correlation. A key strategy to develop a unified picture for the Fe- and Cu-based high temperature superconductivity (HTSC) is to explore the possibility to tune the Fe-based compound into an insulator. But this has not been successful albeit the worldwide efforts before the reports on the superconductivity and magnetism in (Tl,K,Rb)Fe<sub>x</sub>Se<sub>2</sub> system at the end of 2010 [14, 15, 16, 17].

As we know, all the iron-based superconductors share a common layered structure based on a square planar Fe<sup>2+</sup> layer, as shown in Fig. 1(b), tetrahedrally coordinated pnictogen [18, 19, 20] (P, As) or chalcogen [12, 13, 21, 22] (S, Se, Te) anions. It is now widely believed that the common Fe<sup>2+</sup> layers are responsible to the observed superconductivity, similar to the common CuO<sub>2</sub> layer in the cuprates. The crystal structure [23] of stoichiometric TlFe<sub>2</sub>Se<sub>2</sub>, which is shown in Fig. 1(a), is the same as that of the BaFe<sub>2</sub>As<sub>2</sub> with the ThCr<sub>2</sub>Si<sub>2</sub>-type. However, Tl has a monovalence in the TlFe<sub>2</sub>Se<sub>2</sub> compound and there are always vacancies on the Fe-square lattice sites [24], similar to the situation in the TlFe<sub>2</sub>S<sub>2</sub> compound [23, 25]. Therefore, the actual chemical formula should be TlFe<sub>x</sub>Se<sub>2</sub> with 1.3 ≤ x < 2.0. There are evidences that Fe-ions in TlFe<sub>x</sub>Se<sub>2</sub> with x = 1.5 exhibit long-range AFM orderings. Based on the Mössbauer
and neutron diffraction studies, Haggstrom et al. [24] and Sabrowsky et al.[26] argued that the AFM order in TlFe\textsubscript{x}Se\textsubscript{2} and TlFe\textsubscript{x}S\textsubscript{2} compounds is associated with the crystallization of the Fe-vacancies, as shown in Fig. 1(c) and 1(d) for x = 1.5 and 1.6, respectively. From this viewpoint, we expect the AFM order is suppressed as Fe-content increases. At x = 2.0, Fe-ions occupy all the square lattice sites as shown in Fig. 1(b). The possible emergence of the superconductivity in this new 122-type iron-chalcogenide motivated us to grow TlFe\textsubscript{x}Se\textsubscript{2} single crystals with a relatively high Fe-content.

At the end 2010, we first found that the increase of Fe content in TlFe\textsubscript{x}Se\textsubscript{2} indeed lead to an emergence of superconductivity, and the addition of the (K, Rb) elements can result in the increase of the Fe content in the grown crystals, the maximum Fe-content can reach to 1.88. Superconductivity above 30K, the onset superconducting transition temperature as high as 40K, emerges in the (Tl,K,Rb)Fe\textsubscript{x}Se\textsubscript{2} system. The compounds with less Fe content is an AFM insulator, which represents the first Fe-based HTSC at the verge of an AFM insulator. A review on the recent results of Fe-vacancy super-lattice, block AFM ordering, superconductivity and phase separation in (Tl,K,Rb)Fe\textsubscript{x}Se\textsubscript{2} system is presented.

2. From an insulator to a superconductor in (Tl,K,Rb)Fe\textsubscript{x}Se\textsubscript{2} system

First, we discuss the resistivity and superconductivity of the TlFe\textsubscript{x}Se\textsubscript{2} compounds. At the beginning, in order to get the crystals with more Fe content, we tried to grow TlFe\textsubscript{x}Se\textsubscript{2} single crystals using various nominal compositions as the staring materials, i.e. Tl\textsubscript{0.4}Fe\textsubscript{1.6}Se\textsubscript{2}, Tl\textsubscript{0.5}Fe\textsubscript{1.5}Se\textsubscript{2}, Tl\textsubscript{1}Fe\textsubscript{1}Se\textsubscript{2}, Tl\textsubscript{1.5}Fe\textsubscript{0.5}Se\textsubscript{2}, Tl\textsubscript{2}Fe\textsubscript{0}Se\textsubscript{2}. We have obtained a series of TlFe\textsubscript{x}Se\textsubscript{2} (1.30 \leq x \leq 1.70) single crystals. Their compositions were determined by an Energy Dispersive X-ray Spectrometer (EDXS). The Tl and Se contents are almost of 1.0 and 2.0, respectively, but the Fe content is always less than 2.0. The temperature dependence of resistivity for the crystals with less Fe content exhibits a thermally activated semiconducting behavior with an activation energy of 80.2 meV and 57.7 meV, as shown by the fitting line in the inset in Fig 2(a) and (b), for x = 1.30 and 1.47, respectively. Superconductivity with a transition temperature T\textsubscript{c,mid}=22.4 K and zero resistivity at T\textsubscript{c,zero}=20 K is indeed first observed in the TlFe\textsubscript{1.70}Se\textsubscript{2} crystal, as shown in Fig. 2(e), but the magnetic susceptibility measurement show its superconducting volume fraction being very small (< 1 %), see Fig 2(d). It was first found that the evolution from an insulator to a SC in TlFe\textsubscript{x}Se\textsubscript{2} system with increasing Fe content. At the same time, we found that it is difficult to grow a TlFe\textsubscript{x}Se\textsubscript{2} single crystal with x > 1.70.
The above results indicate that, in order to get bulk superconductivity in this system, it is necessary to further increase the Fe content. We tried to grow Tl$_{1-x}$K$_x$Fe$_x$Se$_2$ single crystals by adding K in the starting materials and choosing three groups nominal composition as the starting material, i.e. Tl$_{0.5}$K$_{0.5}$Fe$_2$Se$_2$ (0.15 ≤ z ≤ 0.45), Tl$_{0.4}$K$_{0.5}$Fe$_2$Se$_2$ (0.2 ≤ z ≤ 0.5) and Tl$_{0.8-z}$K$_z$Fe$_2$Se$_2$ (0.1 ≤ z ≤ 0.4). We have obtained a series of Tl$_{1-x}$K$_x$Fe$_x$Se$_2$ (1.50 ≤ x ≤ 1.88, 0.14 ≤ z ≤ 0.57) crystals. Figure 3(d) shows the photos of a crystal Tl$_{0.48}$K$_{0.52}$Fe$_{1.50}$Se$_2$ (before being cleaved) and a crystal Tl$_{0.64}$K$_{0.36}$Fe$_{1.83}$Se$_2$. Figure 3(a), 3(b) and 3(c) show the single crystal and powder x-ray diffraction (XRD) patterns for the Tl$_{0.64}$K$_{0.36}$Fe$_{1.83}$Se$_2$ and Tl$_{0.48}$K$_{0.52}$Fe$_{1.50}$Se$_2$. All the peaks in the powder XRD pattern can be well indexed with a ThCr$_2$Si$_2$-type structure (space group: I4/mmm). By fitting the XRD data, we obtain the lattice parameters $a = 3.88$ Å and $c = 14.05$ Å for Tl$_{0.64}$K$_{0.36}$Fe$_{1.83}$Se$_2$, and $a = 3.90$ Å, and $c = 13.99$ Å for Tl$_{0.48}$K$_{0.52}$Fe$_{1.50}$Se$_2$. Broader peaks in the powder XRD patterns might indicate the existence of some disorder in the crystals, and it is difficult to observe super-lattice peaks of Fe vacancy order. Only (00l) peaks were observed in the single crystal XRD patterns, indicating that the crystallographic c axis is perpendicular to the plane of the single crystal.

Figure 4(a) and 4(b) show the in-plane resistivity as a function of temperature, $\rho(T)$, for the (Tl,K)Fe$_x$Se$_2$ (1.50 ≤ x ≤ 1.85) crystals. We first discuss x = 1.50 and 1.64 samples, which are
insulators. As shown in Fig. 4(a), the ρ at 300K is about 27.8 mΩ cm for x=1.50 and 27.2 mΩ cm for x=1.64. As T decreases, ρ(T) increases rapidly and shows thermally activated behavior: ρ = ρ₀ exp(E_a/k_BT), where k_B is the Boltzmann constant. From the fitting, the activation energy E_a was estimated to be 36 meV for x = 1.50, as shown by the red line in Fig. 4(c), and 24 meV for x = 1.64. The ρ(T) for both crystals exhibits a typical semiconducting behavior.

We now discuss the superconductivity in the (Tl,K)Fe_xSe_2 crystals with higher Fe-contents. With the x value further increasing, ρ at lower T decreases rapidly. For example, at T=40K, ρ = 18.6 Ω cm for x=1.64 crystal, and drops to 0.46 Ω cm for x = 1.69 crystal. The preliminary indication of SC transitions were observed at 25.8 K and 27.6 K for x = 1.69 and 1.76 crystal, respectively. However, no zero resistivity is observed above 2 K in these Fe-content crystals, as shown in Fig. 4(a). In the x = 1.78 crystal, a sharp SC transition occurs at T_c^mid = 28.4 K, and reach to zero resistivity at T_c^zero = 27.4 K, confirmed by the existence of diamagnetism below T_c, as shown in Fig. 4(d).

The SC transitions in ρ(T) for the (Tl,K)Fe_xSe_2 crystals with various x values are shown in Fig. 5. As we can see, there is only one sharp transition at T_c = 28.4 K for x = 1.78, but two transitions for x = 1.84, with one at T_c = 29.8 K and the other at 33.0 K. For Tl_0.75K_0.25Fe_1.88Se_2 crystal with the highest Fe-content in our study, three transitions are observed at T_c = 30.4, 34.1, and 40.4 K. The existence of SC phase with T_c = 40 K in the crystals with higher Fe contents is confirmed in the measurements of ρ(T) at various fields for the Tl_0.64K_0.36Fe_1.83Se_2 crystal, as shown in Fig. 3(d). all the SC transitions at magnetic field B = 0, 4 and 9 Tesla start at T = 40 K for x = 1.83. The multi-transition in ρ(T) was observed in all the crystals with x ≥ 1.83, regardless of the K content. This indicates that the domains with various Fe-content, corresponding to different carrier concentration, likely exist in the crystals. In the majority domain, SC with T_c = 30 K emerges. The volume fraction of the domains with higher T_c value and higher Fe content may be small because no diamagnetic signal appears at higher temperature. To our knowledge, this phase separation behavior is first observed in Fe-based SCs. Bulk SC with T_c = 40 K may emerges in the crystal with an optimal Fe-content, but it is difficult to realize in this system due to the Fe^{2+} valence limitation. SC with T_c = 40 K
emergence in the (Tl,K)Fe$_2$Se$_2$ crystals is reminiscent of the highest $T_c = 38$ K in the optimal doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ compound [8].

At the same time, we also tried to grow (Tl,Rb)Fe$_2$Se$_2$ single crystals by adding Rb in the starting materials. We have also obtained a series of (Tl,Rb)Fe$_2$Se$_2$ (1.30 $\leq x \leq 1.72$) crystals. Figure 6(a), (b) and (c) show their in-plane resistivity as a function of temperature, $\rho(T)$. We first discuss $x = 1.30$ sample, which is an insulator. As shown in Fig. 6(a), the $\rho$ at 300K is about 18.1 m$\Omega$ cm. As T decreases, $\rho(T)$ increases rapidly and shows thermally activated behavior with an activation energy $E_a$ of 51.7 meV (see the red fitting line in Fig 6(c)). With increasing Fe content, the bulk superconductivity with $T_c = 32$ K emerges in the crystals, which is evidenced by the susceptibility measurements as shown in Fig. 6(d). The evolution from an insulator to a superconductor with increase in Fe content has also been found in the (Tl, Rb)Fe$_2$Se$_2$ system.

Bulk superconductivity with $T_c = 30$ K emerges in TlFe$_2$Se$_2$ ($x$>1.7), (Tl,K)Fe$_2$Se$_2$ ($x$>1.72) and (Tl,Rb)Fe$_2$Se$_2$ ($x$>1.42) crystals. It raises a question: why the Fe content of the crystals bulk SC starting to appear is different for three systems. Nowadays, we can understand this by a phase separation discussed as follow. Two phases always coexist in the SC crystals below AFM transition temperature, $T_N$. In one phase, Fe sites are fully occupied, which should be responsible for bulk SC, while in another phase, Fe vacancies order into the $\sqrt{5} \times \sqrt{5}$ super-lattice, which should be an AFM insulator. Due to the difference in the ionic radius of K and Rb, the Fe content of the crystals a phase separation starting to appear is different. We indeed observed this phenomenon in the single crystal XRD experiments.

3. The Fe-vacancy super-lattice and AFM order in (Tl,K,Rb)Fe$_2$Se$_2$ system

As discussed above, we suggested [16] that there are two kinds of Fe-vacancy order in (Tl,K,Rb)Fe$_2$Se$_2$ system. One with the formula of (Tl,K,Rb)Fe$_{1.5}$Se$_2$, the iron atoms have two or three iron neighbors. Another with the formula of (Tl,K,Rb)Fe$_{1.6}$Se$_2$ (now called as the A$_2$Fe$_3$Se$_5$ phase), each iron atom has three iron neighbors. We pointed out [16] that the insulating phase mentioned above should be associated with these Fe-vacancy order. With these two kinds of Fe-vacancy order, the band structure calculations indicate a band gap with the value of about 0.3-0.5 eV for TlFe$_{1.5}$Se$_2$ [27] and 60 meV for TlFe$_{1.6}$Se$_2$ [28]. Of course, it is very important to determine which kind of the Fe vacancy and AFM order exists most likely in this system.

Based on the neutron diffraction experiments, Bao et al. [29, 30] concluded that the dominating phase had a composition of A$_{0.82}$Fe$_{1.62}$Se$_2$ (A=K, Tl/K and Tl/Rb) and Fe vacancies...
order into the $\sqrt{5} \times \sqrt{5}$ super-lattice between 460-580 K, corresponding to the second Fe-vacancy ordered structure suggested by us. At or slightly below this temperature, the spins align along the tetragonal $c$ axis in a block-checkerboard antiferromagnetic structure (BCAF-$c$, where $c$ indicates the alignment of the spin). The four nearby Fe ions, with a spin 3.31 $\mu_B$/Fe, form a square block with the spins aligned ferromagnetically. The total magnetic moment of the 4-iron-block is 13.4 $\mu_B$. This magnetic structure was later proved by another group at ORNL [31]. They concluded that this is a common crystalline and magnetic structure of superconducting $A_2Fe_4Se_5$ ($A=Tl, K, Rb$ and Cs)[30]. The transmission electron microscopy experiments [32] have also confirmed this kind of Fe-vacancy order.

Very recently, A. F. May et al. [33] reexamined the Fe vacancy order and AFM structure by means of single crystal neutron diffraction, nuclear forward scattering, and transmission electron microscopy for TlFe$_{1.6}$Se$_2$ crystal with complete chemical/vacancy order. They confirmed the existence of $\sqrt{5} \times \sqrt{5}$ Fe-vacancy super-lattice, and found that the Fe moment orientation changes from parallel to $c$ axis above 100K to perpendicular to $c$ below 100K. And there may be two types of magnetic structure below 100K, one is a non-collinear, another is an in-plane, block-checker antiferromagnetic structure. They argued that, although the BCAF-$c$ structure is the main magnetic structure observed in the alkali-metal compounds, the TlFe$_{2.5}$Se$_2$ has a limited compositional window and the Tl sites is always fully occupied, there may be additional magnetic phase transitions in the lower temperatures, which is consistent with our susceptibility data [16] and the results reported in [34].

Another, recently, J. Zhao et al. [35] re-checked also the Fe vacancy super-lattice and magnetic structure in both the insulating ($E_a=500$ meV) and semiconducting ($E_a=40$ meV) K$_y$Fe$_2$Se$_2$ crystals. They found that there is only a $\sqrt{5} \times \sqrt{5}$ Fe-vacancy super-lattice, corresponding to the BCAF-$c$ magnetic structure, in the insulating K$_{0.8}$Fe$_{1.6}$Se$_2$ crystal. But in the semiconducting K$_y$Fe$_2$Se$_2$ crystals, in addition to the $\sqrt{5} \times \sqrt{5}$ Fe-vacancy structure, another a $\sqrt{2} \times \sqrt{2}$ Fe vacancy super-lattice was also found, which corresponds to the first one discussed above, in which the iron atoms have two or three iron neighbors, with the formula of TlFe$_{1.5}$Se$_2$ [16]. According to the Zhao’s neutron diffraction experiments, the magnetic structure in this Fe vacancy super-lattice has a stripe type magnetic order with Néel temperature 280 K, which is the same as that in other iron pnictides. They concluded that this AFM semiconductor is a parent compound of the superconducting AFe$_2$Se$_2$ compounds, interpolating between the antiferromagnetic Mott insulator of the cuprates and the antiferromagnetic semimetal of the iron pnictides. It is important that this indicates the correlation physics playing an important role in the magnetism for this system, which is consistent with that suspected in our work [16]. Of course, now there are debates about which antiferromagnetic order being a parent of superconductivity emerging in this system.
Table 1. The fraction of $I4/m$ and $I4/mmm$ phases obtained by fitting to ND data measured at different temperatures for superconducting Tl$_{0.374}$Rb$_{0.374}$Fe$_{1.764}$Se$_2$ crystals.

| Temperature | $I4/m$ | $I4/mmm$ |
|-------------|--------|----------|
| 30K        | 70.8%  | 20.8%    |
| 300K       | 70.9%  | 21.5%    |
| 400K       | 70.0%  | 21.8%    |
| 550K       | 0%     | 91.56%   |

4. The phase separation in (Tl,K,Rb)Fe$_2$Se$_2$ system

Another important issue is the coexistence of magnetism and superconductivity at temperature up to ~30K in (Tl,K,Rb)$_x$Fe$_2$Se$_2$ system. A lot of techniques have been employed to understand this interesting property of these materials. Now, the coexistence of superconductivity and magnetism is believed to be due to fine-scale phase separation, with each property being associated with a different composition and/or degree of order.[36, 37, 38, 39, 40, 41] All observations by transmission electron microscopy (TEM) [32, 42, 38], nano-focused x-ray diffraction [36] and Mössbauer spectroscopy [37, 43, 44] have confirmed the existence of the phase separation over length scales of 10-100 nm in the superconducting samples. Although superconducting samples with single phase (structural and chemically homogenous) have not produced up to now, it is not so difficult to grow the insulating single phase crystals with BCAF-c magnetic structure.

Figure 7. Temperature dependence of the intensity of (110) peak, corresponding to $\sqrt{3} \times \sqrt{3}$ super-lattice, and the intensity of (101) peak, corresponding to BCAF-c lattice, in the powder neutron diffraction pattern. (Left) for the superconducting Tl$_{0.4}$Rb$_{0.6}$Fe$_{1.72}$Se$_2$ crystals. (Right) for the insulator Tl$_{0.4}$Rb$_{0.6}$Fe$_{1.36}$Se$_2$ crystals.

We chose two kinds of (Tl,Rb)Fe$_2$Se$_2$ crystals to determine their crystal and magnetic structure by neutron diffraction experiments. The first one is an insulator as shown in Fig.6(c), i.e. Tl$_{0.4}$Rb$_{0.6}$Fe$_{1.36}$Se$_2$. Above 510 K, the powder neutron diffraction (ND) data can be well fitted by a pure 122 structure phase with $I4/mmm$, and the composition with Tl$_{0.452}$Rb$_{0.452}$Fe$_{1.578}$Se$_2$. Below 510 K, the ND data can be well fitted by a pure 245 block phase with $I4/m$. At 495K, a BCAF-c magnetic structural transition occurs. The temperature dependence of the intensity of (110) peak, corresponding to $\sqrt{3} \times \sqrt{3}$ super-lattice, and the intensity of (101) peak, corresponding to BCAF-c lattice, in the powder neutron diffraction experiments, are shown in Fig.7(Right).

The second is a superconductor as shown in Fig. 6(b), i.e. Tl$_{0.4}$Rb$_{0.6}$Fe$_{1.72}$Se$_2$ crystals. Above 495 K, the powder neutron diffraction (ND) data can also be well fitted by a pure 122 phase with $I4/mmm$, with a composition Tl$_{0.374}$Rb$_{0.374}$Fe$_{1.764}$Se$_2$. But below 495 K, two phases emerge in these crystals. One is (Tl,Rb)$_{0.818}$Fe$_{1.563}$Se$_2$ with $I4/m$, which becomes BCAF-c below 480K shown in Fig.7 (Left), its volume fraction is about 70%, its refined structure parameters from ND data below $T_N$ is shown in Table 3; Another is (Tl,Rb)$_{0.532}$Fe$_2$Se$_2$, with $I4/mmm$, its refined structure parameters from ND data below $T_N$ is shown in Table 2, no magnetic order was discovered in this phase, its volume fraction is about 22%. Little change was found in the relative ratio of two phases between 490K and 30K, as listed in Table 1. We believed that (Tl,Rb)$_{0.534}$Fe$_2$Se$_2$ phase is responsible for the superconductivity in this compound.
Table 2. Refined structure parameters for the $I4/mmm$ phase, obtained by fitting to ND data measured at 30, 300, 400 and 550 K for superconducting Tl$_{0.374}$Rb$_{0.374}$Fe$_{1.764}$Se$_2$. At 550K, Tl/Rb at 2a (0 0 0), Fe 4d (0 1/2 1/4) and Se at 4e (0 0 z) sites. 3.66% Fe and 4.78% FeSe as impurity were taken into account in the refinement.

|                 | 30K   | 300K  | 400K  | 550K  |
|-----------------|-------|-------|-------|-------|
| $a$(Å)          | 3.8264(3) | 3.8423(3) | 3.8550(4) | 3.9226(1) |
| $c$(Å)          | 14.589(3) | 14.820(2) | 14.894(4) | 14.4414(9) |
| Rb/Tl n         | 0.268(9)  | 0.267(8)  | 0.26(1)   | 0.374(5)  |
| Fe n            | 1      | 1      | 1      | 0.88(1)  |
| Se n            | 1      | 1      | 1      | 1       |
| $z$             | 0.3503(5) | 0.3515(4) | 0.3543(7) | 0.3532(2) |

Table 3. Refined structure parameters for the $I4/m$ phase obtained by fitting to ND data measured at below $T_N$ for superconducting Tl$_{0.374}$Rb$_{0.374}$Fe$_{1.764}$Se$_2$.

|                 | 30K   | 300K  | 400K  | 500K  |
|-----------------|-------|-------|-------|-------|
| $a$(Å)          | 8.6685(4) | 8.7067(4) | 8.7303(5) | 8.7487(5) |
| $c$(Å)          | 14.235(1) | 14.335(1) | 14.355(2) | 14.405(2) |
| Rb1/Tl1 n       | 0.408(6)  | 0.409(5)  | 0.37   | 0.37  |
| Rb2/Tl2 n       | 0.408(6)  | 0.409(5)  | 0.37   | 0.37  |
| x               | 0.399(2)  | 0.396(1)  | 0.394(2) | 0.396(3) |
| y               | 0.190(2)  | 0.194(2)  | 0.181(2) | 0.184(3) |
| Fe1 n           | 0.15(2)   | 0.10(1)   | 0.06(2)  | 0.22(2) |
| Fe2 n           | 0.92(1)   | 0.943(8)  | 1      | 1     |
| x               | 0.1992(8) | 0.1996(6) | 0.1955(9) | 0.198(1) |
| y               | 0.0909(6) | 0.0895(4) | 0.0910(7) | 0.0930(8) |
| z               | 0.2491(9) | 0.2477(9) | 0.252(1) | 0.252(1) |
| Se1 n           | 1       | 1       | 1      | 1     |
| z               | 0.1291(9) | 0.1333(8) | 0.132(1) | 0.133(2) |
| Se2 n           | 1       | 1       | 1      | 1     |
| x               | 0.1077(9) | 0.1080(7) | 0.107(1) | 0.111(1) |
| y               | 0.288(1)  | 0.2946(10) | 0.294(1) | 0.298(2) |
| z               | 0.1480(3) | 0.1483(2) | 0.1490(4) | 0.1498(4) |
| $R_P$(%)        | 5.50    | 5.45    | 6.08   | 7.23  |
| $R_{wp}$(%)     | 7.01    | 6.75    | 7.67   | 9.32  |
| $\chi^2$       | 2.399   | 1.785   | 1.384  | 1.985 |

5. Summary and conclusions
In this article, we summarized our discovery about the evolution from an insulator to a superconductor with increasing Fe content in the (Tl,K,Rb)Fe$_x$Se$_2$ system. We first suggested that the AFM insulator in these systems is associated with the Fe-vacancy ordering in the crystals, which was confirmed by many experiments and the band calculations later. Superconductivity above 30K in (Tl,K,Rb)Fe$_x$Se$_2$ system was discovered, in which the onset superconducting transition temperature is as high as 40K. These results represent the first Fe-based superconductivity at the verge of an AFM insulator. But due to either chemical or electronic reason, the superconducting phase always coexists with the BCAF-c insulating phase in this system. The superconducting samples with single phase (structural and chemically
homogenous) have not produced up to now. Whether BCAF-c insulator or other AFM insulating or semiconducting phase can be regarded as the parent compound of superconductivity in this system, remains unclear.

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