The effect of the Wyckoff position of the K atom on the crystal structure and electronic properties of the compound KFe$_2$Se$_2$

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Abstract

By means of first-principles electronic structure calculations, we study the effect of the Wyckoff position of the K atom on the crystal and electronic structures of the compound KFe$_2$Se$_2$. When the K atoms take up the Wyckoff positions 2a, 2b and 4c (the related structures of KFe$_2$Se$_2$ are referred to as Struc-2a, Struc-2b and Struc-4c), the calculated lattice constants $c$ lie in the ranges 13.5–14.5, 15.5–16.7 or 18.6–19.1 Å respectively. Three concentric cylinder-like Fermi surfaces emerge around $\Gamma-Z$ in the Brillouin zone for Struc-2b in the nonmagnetic state, unlike the cases for Struc-2a and Struc-4c. The Fe–Se–Fe angles are 107.8°, 108.8° and 110.7° respectively in the collinear antiferromagnetic state, and the superexchange interactions $J_2$ between two next neighbor Fe moments are 13.08 meV $\sqrt{\text{Å}^2}$, 20.75 meV $\sqrt{\text{Å}^2}$ and 11.86 meV $\sqrt{\text{Å}^2}$ for the Struc-2a, Struc-2b and Struc-4c structures respectively. Struc-2b and Struc-4c have good correspondence with the newly discovered superconducting phases with $T_c$ = 40 and 30 K in KFe$_2$Se$_2$. Our findings suggest a reasonable approach for achieving an understanding of the existence of multiple superconducting phases in alkali metal intercalated FeSe superconductor.

(Some figures may appear in colour only in the online journal)

1. Introduction

The recent observation of superconductivity at about 30 K in the layered iron selenide compound K$_{0.8}$Fe$_2$Se$_2$ [1] initiated extensive research on the iron selenide superconductors, which were formed by intercalating alkali metal between FeSe layers and had the ThCr$_2$Si$_2$-type structure (figure 1(a)). In contrast to the iron arsenide superconductors, the compounds A$_x$Fe$_{2-x}$Se$_2$ (A = K, Rb, Cs or Tl) form a new class of iron based superconductors. Their electronic structures are very different from those occurring in the iron arsenide compounds—that is, only electron Fermi surfaces are presented around the zone corners and there is no hole Fermi surface near the zone center, as is confirmed by the experimental measurement [2] and the previous first-principles calculations [3].

The crystal structures of A$_x$Fe$_{2-x}$Se$_2$ are complex, since for different $x$ values there are different Fe vacancy arrangement schemes. The X-ray, transmission electron microscopy, and neutron scattering measurements indicate that the composition of K intercalated FeSe superconductors is close to K$_y$Fe$_{1.6}$Se$_2$ with a fivefold expansion of the parent ThCr$_2$Si$_2$ unit cell in the $ab$ plane, namely a $\sqrt{5} \times$
\[\sqrt{5}\] Fe vacancy superstructure [4, 5]. Another experiment shows that there exists a rhombic Fe vacancy pattern related to K\(_{1}\)Fe\(_{1.5}\)Se\(_{2}\) [6]. However it is reported that in the same sample there exist two distinct phases: the insulating phase with a well-defined \(\sqrt{5} \times \sqrt{5}\) Fe vacancy superstructure and another KFe\(_{2}\)Se\(_{2}\) phase containing no Fe vacancies, the latter being suggested to be responsible for the superconductivity [7]. The composition and structure responsible for the superconductivity are still under debate.

Most recently, an Li, Na, Ca, Ba, Yb, or Eu layer has been inserted between adjacent FeSe layers to optimize the superconducting properties of the iron selenide layers [8]. It is a surprising phenomenon that two superconducting phases were observed in K\(_{0.8}\)Fe\(_{2}\)Se\(_{2}\), one with the \(T_c\) of 30 K and another with the \(T_c\) of 40 K. In addition, two kinds of crystal unit cells with unexpectedly long lattice constants \(c = 16.14\) Å and \(c = 20.48\) Å were found to correspond to the two superconducting phases, and the \(c = 20.48\) Å unit cell disappeared after an hour’s exposure to air, accompanying the \(T_c\) change from 40 to 30 K. In the other reports, two superconducting phases were also observed in K\(_{1}\)Fe\(_{2.5}\)Se\(_{2}\) [9–11]. However, theoretical studies on the difference in crystal and electronic structures between these superconducting phases, and the reason for the higher \(T_c\) for the new superconducting phase, are rare.

The Wyckoff position of the K atoms has a great influence on the \(c\) axis length of the crystal unit cell and the character of the Fermi surface in KFe\(_{2}\)Se\(_{2}\). In experiments the occupations of different Wyckoff positions by alkali metal atoms are observed [12]. Meanwhile, the fact that no clear peak due to N–H vibrations is detected in infrared spectroscopy measurements [8] excludes the possibility of the existence of NH\(_3\) in KFe\(_{2}\)Se\(_{2}\) synthesized by the liquid ammonia method. So we can deduce that the three superconducting phases of KFe\(_{2}\)Se\(_{2}\) with different lattice parameters \(c\) should correspond to the different Wyckoff positions occupied by the K atoms. In this paper, we focus on the effect of different Wyckoff positioning of the K atom in the space group \(I4/mmm\) on the crystal structure and electronic properties of KFe\(_{2}\)Se\(_{2}\), with the K atom sited in 2a, 2b and 4c Wyckoff positions. The paper is organized as follows. Firstly, we optimize the crystal structure and obtain reasonable lattice constants for KFe\(_{2}\)Se\(_{2}\), in agreement with the experimental values of \(c = 14.04\) Å, \(c = 16.16\) Å, and \(c = 20.48\) Å for the three superconducting phases. Secondly, the electronic structures of Struc-4c are found to be similar to those of Struc-2a, implying they have similar superconducting behaviors. The Fermi surface of Struc-2b exhibits a different character—that is, concentric cylinder-like Fermi surfaces are present around \(\Gamma–Z\), which should necessarily be connected to the superconductivity with the higher \(T_c\) of 40 K. Lastly, from the three aspects of the Fe–Se–Fe angle, electronic structure and next neighbor superexchange interaction \(J_2\), we demonstrate that the Struc-2b structure is closely related to the superconducting phase with \(T_c = 40\) K, while Struc-4c is closely related to the superconducting phase with \(T_c = 30\) K in KFe\(_{2}\)Se\(_{2}\) synthesized by the ammonothermal method.

2. The method and details

In our calculations the plane wave basis method was used [13]. We adopted the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof formula [14] for the exchange–correlation potentials. Ultrasoft pseudopotentials [15] were used to model the electron–ion interactions. After full convergency testing, the kinetic energy cutoff and the charge density cutoff of the plane wave basis were chosen to be 800 eV and 6400 eV, respectively. The Gaussian

\[\begin{align*}
\text{Figure 1. Schematic structure of the tetragonal unit cell of K}_{1}\text{Fe}_{1.5}\text{Se}_{2} \text{ containing two formula units: (a) the K atom is situated in a 2a Wyckoff position, (b) the K atom is situated in a 2b Wyckoff position, (c) the K atom is situated in a 4c Wyckoff position and only two of the four 4c positions are occupied; } \alpha \text{ and } H_{\text{Se}} \text{ indicate the Fe–Se–Fe bond angle and the Se height above the Fe plane.}
\end{align*}\]
Table 1. The lattice parameters $c$, the Fe–Se–Fe bond angle $\alpha$ and the Se height $H_{Se}$ above the Fe plane of KFe$_2$Se$_2$ in several magnetic orderings for the Struc-2a, Struc-2b and Struc-4c phases. In 'Bicoll-AFM' (bi-collinear antiferromagnetic) order the lattice constants $a$ shrinking leads to a decrease of $c$ along the FM direction, and the distortion of the Fe layer leads to the fluctuation of $H_{Se}$, shown in brackets. For Struc-2b the Bicoll-AFM state is not stable. ('Nonmag', ‘Neel-AFM’, and ‘Coll-AFM’ stand for nonmagnetic, Neél AFM, and collinear AFM respectively.)

| Structure | Magnetic phase | $c$ (Å) | $H_{Se}$ (Å) | $\alpha$ (deg) |
|-----------|----------------|--------|-------------|---------------|
| Struc-2a  | Nonmag         | 13.30  | 1.29        | 112.3         |
|           | FM             | 14.04  | 1.62        | 98.7          |
|           | Neel-AFM       | 13.67  | 1.37        | 109.5         |
|           | Coll-AFM       | 13.79  | 1.42        | 107.8         |
|           | Bicoll-AFM     | 14.45  | 1.45        | 107.0         |
|           |                |        | (1.64)      | (97.2)        |
| Exper. [1]|                 | 14.04  |             |               |
| Struc-2b  | Nonmag         | 18.60  | 1.31        | 110.6         |
|           | FM             | 19.04  | 1.59        | 99.5          |
|           | Neel-AFM       | 18.97  | 1.39        | 108.1         |
|           | Coll-AFM       | 18.84  | 1.40        | 108.8         |
|           | Bicoll-AFM     |        |             |               |
|           |                |        | (—)         | (—)           |
| Exper. [8]|                 | 20.48  |             |               |
| Struc-4c  | Nonmag         | 15.46  | 1.30        | 113.9         |
|           | FM             | 16.70  | 1.57        | 102.1         |
|           | Neel-AFM       | 15.75  | 1.35        | 111.2         |
|           | Coll-AFM       | 15.79  | 1.38        | 110.7         |
|           | Bicoll-AFM     | 16.24  | 1.42        | 109.2         |
|           |                |        | (1.64)      | (96.7)        |
| Exper. [8]|                 | 16.16  |             |               |

3. Results and discussion

First, we study the structural properties of KFe$_2$Se$_2$ including the lattice parameter, the Se height above the Fe plane $H_{Se}$ and the Fe–Se–Fe bond angle $\alpha$ in the FeSe layer. Alkali metal intercalated iron selenides have the tetragonal crystal structure with the space group $I4/mmm$. The Fe atom and Se atom are sited at the 4d and 4e Wyckoff positions in this space group respectively, constructing a stable FeSe layer in the compound KFe$_2$Se$_2$. In the previous studies, KFe$_2$Se$_2$ was thought to have the ThCr$_2$Si$_2$-type structure with the K atom located at the 2a Wyckoff position, similarly to the Ba atom in BaFe$_2$As$_2$, as shown in figure 1(a). The 2a position is at the body center of the Se tetragonal formed by eight Se atoms between two neighboring Fe layers, while the 2b and 4c positions are at the middle point of the side edge and the center of the side face in the Se tetragonal body; see figures 1(b) and (c).

We perform structure optimizations of KFe$_2$Se$_2$ in which the K atoms are sited in 2a, 2b and 4c Wyckoff positions in the space group $I4/mmm$ respectively. The calculated results are shown in table 1 and the optimized lattice parameters $c$ are compared with the measured ones. When the K atom takes up the 2a position, the relaxed lattice constant $c$ is about 13.3–14.5 Å for the different magnetic phases, which is consistent with the measured value 14.04 Å obtained following synthesis by high temperature routes. In the case of K occupying the 2b and 4c positions, the optimized parameters $c$ are about 18.6–19.0 Å and 15.5–16.7 Å respectively for different magnetic orderings, with good agreement with the observed lattice $c$ values of 20.48 Å and 16.16 Å obtained following synthesis using the ammonothermal method.

The $T_c$ dependence of the As height above the Fe plane and the Fe–As–Fe angle in iron arsenide superconductor have been investigated extensively and neutron diffraction measurements reveal that $T_c$ becomes maximum when the Fe–As–Fe angle is close to 109.4°, corresponding to the perfect FeAs$_4$ tetrahedron [16]. The calculated Se heights above the Fe plane $H_{Se}$ and the Fe–As–Fe angles $\alpha$ for the three structure phases of KFe$_2$Se$_2$ are presented in table 1. In general, the Se heights within the given antiferromagnetic orders for the three structure phases are in the range of 1.35–1.45 Å and the discrepancy in the Fe–As–Fe angle between our calculation and the ideal value of 109.4° is less than 2.4° (except for the angles along the ferromagnetic direction of the Bicoll-AFM order in Struc-2a and Struc-4c).

Since the Coll-AFM magnetic phase is the lowest or second-lowest energy state for the three structure phases of Struc-2a, Struc-2b and Struc-4c. Table 2 shows the energy per Fe atom, magnetic moment around the Fe atom and the nearest and next nearest neighbor superexchange coupling of the KFe$_2$Se$_2$ system in different magnetic orderings for the Struc-2a, Struc-2b and Struc-4c structures. The nonmagnetic energy of Struc-2a is set to zero. For Struc-2b, the Bicoll-AFM state is not stable. For Struc-2b, the Bicoll-AFM state is not stable. ('Nonmag', ‘Neel-AFM’, and ‘Coll-AFM’ stand for nonmagnetic, Neél AFM, and collinear AFM respectively.)
The two structure phases have a great resemblance in band structure and topological character of the Fermi surface, including the two Fermi surface sheets at the Brillouin-zone corner and a Fermi surface pocket around the \( Z \) point. They also share the critical feature that no Fermi surface appears near the \( \Gamma \) point, obviously in contrast to the iron arsenide superconductors. According to this resemblance, we expect that the Struc-2a and Struc-4c structures should show similar superconducting behaviors and the \( T_c \) should be approximately equal to each other, associated with the fact that \( T_c \) is about 30 K for both the \( c = 16.16 \) and 14.04 Å superconducting phases in the compound KFe\(_2\)Se\(_2\).

From figures 3(b) and (e) we can see that there are three bands crossing the Fermi level for Struc-2b and the Fermi surfaces present two-dimensionality character better than that of Struc-2a phase. The most surprising thing is that there exist three cylinder shape Fermi surfaces centered around \( \Gamma-Z \); the innermost is of hole type, derived from the band marked 1 in figure 3(b), and the other two are of electron type, derived from energy band 2. The concentric cylinder Fermi surface sheets along \( \Gamma-Z \) are typical features of iron arsenide superconductors, so the electronic structure of the Struc-2b phase of KFe\(_2\)Se\(_2\) is very similar to the electronic structures of iron arsenide superconductors such as LaFeAsO and BaFe\(_2\)As\(_2\). In the Struc-2b phase, it is the emergence of a cylinder Fermi surface around \( \Gamma-Z \) that is expected to bring about the stronger superconducting electron pairing as compared with those in the Struc-2a and Struc-4c phases. The experimental \( T_c = 40 \) K superconducting phase should correspond to the Struc-2b phase in the compound KFe\(_2\)Se\(_2\).

Thirdly, we discuss the magnetic interaction between Fe moments and its connection to the superconducting temperature \( T_c \). The magnetic moments around each Fe atom were found to be about 2.8 \( \mu_B \) in the alkali metal intercalated iron selenide superconductors [5], much larger than the moments in the iron arsenide superconducting materials, so the magnetic interactions among Fe atoms play an important role in the determination of structural and electronic properties of AFe\(_2\)Se\(_2\) (\( A = K, Rb, Cs \) and \( Tl \)).

To quantify the magnetic interactions, we can assume that the energy differences among these magnetic orders mainly originate from the interactions between each pair of two Fe moments with spin \( \vec{S} \). Then the frustrated Heisenberg model with the couplings of nearest, next nearest and next next nearest neighbors \( J_1, J_2 \) and \( J_3 \) can be used to describe the interactions in the KFe\(_2\)Se\(_2\) system, namely,

\[
H = J_1 \sum_{\langle i, j \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle \langle i, j \rangle \rangle} \vec{S}_i \cdot \vec{S}_j + J_3 \sum_{\langle \langle \langle i, j \rangle \rangle \rangle} \vec{S}_i \cdot \vec{S}_j,
\]
where $\langle ij \rangle$, $\langle\langle ij \rangle\rangle$ and $\langle\langle\langle ij \rangle\rangle\rangle$ denote the summations over the nearest, next nearest, and next next nearest neighbors, respectively. From the energy data in table 2, the superexchange coupling parameters $J_1$ and $J_2$ were derived and these are shown in the rightmost column in table 2 (for the detailed calculation, refer to the appendix of [17]).

Comparing these exchange coupling values, we notice that the Struc-2a and Struc-4c phases have similar features as regards the magnetic interactions, but the Struc-2b phase is somewhat different from them. Here we should pay close attention to the next neighbor superexchange interaction $J_2$ in the three structures. Theoretically, the two-band model $t$–$J_1$–$J_2$ indicates that the $T_c$ for iron based superconductor is proportional to the $J_2$ [18], and we also have drawn the same conclusion in previous first-principles studies on the iron based materials [19, 20]. From this point of view, we can obtain the results that the Struc-2b phase has a higher superconducting transition temperature $T_c$ than Struc-2a and Struc-4c, and the latter two structures have similar $T_c$ values, because the next neighbor superexchange interaction $J_2 = 20.74$ meV S$^{-2}$ in Struc-2b is larger than the $J_2 = 13.08$ meV S$^{-2}$ for Struc-2a and $J_2 = 11.86$ meV S$^{-2}$ for Struc-4c. The suggestion that the higher $T_c$ superconducting phase occurs in the Struc-2b structure is consistent with our analysis of both the Fermi surface features and the Fe–Se–Fe angle. The consistency is easy to understand because the superexchange interaction $J_2$ between two next nearest neighbor Fe atoms is bridged by an Se atom and has a direct connection to the Fe–Se–Fe angle.

In addition, we give some discussion as regards the issue of why the K atom can locate in the 2b or 4c Wyckoff position. Fixing the lattice parameters to the experimental values, we optimize the K positions with the initial K position sited in the 2a, 2b and 4c positions respectively. The K positions do not change from the initial 2a or 4c to the 2b position with the fixed $c$ axis at 20.48 Å, or from the initial 2a or 2b to 4c with the fixed $c$ axis at 16.16 Å. The K atom can locate at the 4c or 2b position in the above calculations. As to the formation of the Struc-2b and Struc-4c phases, we can assume that the process happened as follows. At first, the NH$_3$ molecules and K atoms enter in between FeSe layers together, and K atoms site in 2b or 4c Wyckoff positions, leading to the large length of lattice, $c$. Then, NH$_3$ escapes from the compounds and the K atoms still site in a 2b or 4c position. We also investigate the energy change with the lattice parameter $c$ increasing for Struc-2a, Struc-2b and Struc-4c. The lattice parameter $a$ is fixed at the experimental value 3.79 Å and we perform the nonmagnetic calculations. The energies for the three structural phases with different lattice constant $c$ are listed in table 3. When the length of the lattice parameter $c$ becomes larger than 18.58 Å, the energy of Struc-4c begins to become less than that of the Struc-2a phase. When the parameter $c$ becomes larger than 20.85 Å, the Struc-2b energy becomes the lowest one among those of the three structure phases. These results mean that with large lattice parameter $c$, the K atom prefers to occupy the 4c or 2b Wyckoff position.

In summary, we have investigated the effect of different Wyckoff positions of the K atom on the crystal structure

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|------------------|-------------------|
| Figure 3. The energy band structures of KFe$_2$Se$_2$ for the Struc-2a, Struc-2b and Struc-4c structure phases shown in (a)–(c), and the corresponding Fermi surfaces shown in (d), (e) and (f) respectively. The bands crossing the Fermi energy are denoted as lines 1, 2 and 3 in (b). The Fermi level is set to zero. |

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of KFe$_2$Se$_2$ by means of first-principles calculations. We conclude that the occupations of Wyckoff positions 2b and 4c by the K atom correspond to the $T_c = 40$ K and $T_c = 30$ K superconducting phases in experiments, respectively, as demonstrated by the calculated lattice parameters, Fe–Se–Fe angles, electronic structures and superexchange couplings $J_2$. Our results show good agreement with the experiments and suggest a reasonable approach for achieving an understanding of the new superconducting phases in KFe$_2$Se$_2$.

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