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Phase transition, superstructure and physical properties of $\text{K}_2\text{Fe}_4\text{Se}_5$


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Image: Ornamental multiplication of space-time figures of temperature transformation rules (adapted from T. S. Bíró and P. Ván 2010 EPL 89 30001; artistic impression by Frédérique Swist).
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Phase transition, superstructure and physical properties of $K_2Fe_4Se_5$

Y. J. Song$^1$, Z. Wang$^1$, Z.W. Wang$^1$, H. L. Shi$^1$, Z. Chen$^1$, H. F. Tian$^1$, G. F. Chen$^2$, H. X. Yang$^1$ and J. Q. Li$^1$[$^a$]

$^1$ Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences Beijing 100190, PRC

$^2$ Department of Physics, Renmin University of China - Beijing 100872, PRC

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Abstract – The structural features and physical properties of the antiferromagnetic $K_{0.8}Fe_{1.6}Se_2$ (so-called $K_2Fe_5Se_5$ phase) have been studied in the temperature range from 300 K up to 600 K. Resistivity measurements on both single crystal and polycrystalline samples reveal a semiconducting behavior. Structural investigations of $K_2Fe_5Se_5$ by means of transmission electron microscopy (TEM) and powder X-ray diffraction (XRD) demonstrate the presence of a well-defined superstructure within the $a$-$b$ plane originating from a Fe-vacancy order along the $[1\bar{1}0]$ direction (indexed based on the supercell with space group of $I4/m$). Moreover, in situ heating structural analysis shows that $K_{0.8}Fe_{1.6}Se_2$ undergoes a transition of the Fe-vacancy order to disorder at about 600 K. The phase separation and the Fe-vacancy ordering in the superconducting materials of $K_xFe_{2-y}Se_2$ ($0.2 \leq y \leq 0.3$) has been briefly discussed.

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The newly discovered superconductivity in potassium-intercalated FeSe [1] and other iron chalcogenide systems [2–4] has triggered a great interest for the investigation of this kind of layered materials and superconducting mechanism [5,6]. Recent studies on these materials reveal some novel phenomena: large moments of Fe-ions in antiferromagnetic (AFM) state [7] and the hump-like anomaly in resistivity which is sensitive to the Fe-content [8] and pressure [9]. Measurements of neutron diffraction and NMR [10] have focused on the coexistence of magnetic order with superconductivity. Optical investigation of $K_xFe_{2-y}Se_2$ superconducting samples demonstrated the existence of a small energy gap in the superconducting state [11]. It is also noted that these compounds often show a rich variety of structural features [12] and physical properties [13]. $K_{0.8}Fe_{1.6}Se_2$ (i.e. the $K_2Fe_5Se_5$ phase) contains the Fe-vacancy order in association with an AFM structure with $T_N \sim 559$ K [7,14,15]. Theoretical analysis on this semiconducting phase shows the presence of an energy gap of 594 meV in $K_2Fe_5Se_5$ [16]. In order to directly reveal the structural changes associated with the phase transition, we carried out a series of in situ transmission electron microscopy (TEM) observations and X-ray diffraction on $K_{0.8}Fe_{1.6}Se_2$ samples from room temperature up to 600 K. We also characterize the superstructure in correlation with the Fe-vacancy order by using powder X-ray diffraction.

Both single-crystal and polycrystalline samples of $K_{0.8}Fe_{1.6}Se_2$ were used in our study. The polycrystalline samples were prepared in a two-step solid reaction method: Fe, Se powders and K pieces were firstly placed in a small alumina crucible, and then sealed in a silica tube, each tube filled with $1/3$ argon gas. The tube was then preheated at 200 °C for 24 h and then hold at 500 °C for 24 h. The obtained products were then reground, pelleted, and heated at 750 °C for 48 h. The single crystals used in present study were synthesized by Bridgeman method as reported in ref. [8]. The chemical composition of $K_{0.8}Fe_{1.6}Se_2$ single crystals has been determined by inductively coupled plasma (ICP) analysis and SEM-EDX analysis. Powder X-ray diffraction is performed on a Bruker AXS D8 Advance diffractometer equipped with TTX 450 holder working in the temperature range of 80 K–700 K. The temperature dependences of resistivity were measured by a standard four-probe method.

[$^a$]E-mail: LJQ@iphy.ac.cn
The inset of fig. 1(b) shows that the logarithmic form of resistivity to 40K, and the inset displays the logarithmic form of resistivity for semiconductors: roughly following the known thermally activated nature of resistivity.

Fig. 1: (Colour on-line) Temperature dependence of resistivity for a KFe$_{4}$Se$_{5}$ single crystal with current going along the c-axis direction and within the a-b plane (black) and within the a-b plane (red), respectively.

Specimens for TEM observations were prepared by peeling off a very thin sheet of a thickness around several tens of micrometers from the single crystal and milling by Ar ion under low temperatures. Microstructure and phase transition investigations were performed on a FEI Tecnai-F20 TEM equipped with a double-tilt heating holder.

As an AFM semiconductor, the K$_{0.8}$Fe$_{1.6}$Se$_{2}$ often shows a large resistivity at low temperatures and the temperature dependence of resistivity almost exhibits a thermally activated behavior. In fig. 1(a), we show the temperature dependence of resistivity of a polycrystalline K$_{2}$Fe$_{4}$Se$_{5}$ measured at temperature from 290K down to 40K, and the inset displays the logarithmic form of the ρ(T) curve. It is recognizable that the resistivity increases gradually with the decrease of temperature roughly following the known thermally activated nature for semiconductors: ρ = ρ$_{0}$ exp(E$_{a}$/k$_{B}$T), where E$_{a}$ is the activation energy. Figure 1(b) shows the resistivity curve of a K$_{2}$Fe$_{4}$Se$_{5}$ single crystal with current going along the c-axis direction and within the a-b plane, respectively. The inset of fig. 1(b) shows that the logarithmic form of ρ(T) curves is fundamentally in agreement with what observed in the polycrystalline sample. In addition, as for the single-crystal sample, the in-plane resistivity is a somewhat larger than that along the c-axis direction. This fact suggests the presence of anisotropic transport properties in the present system, as similarly discussed in previous literature [3].

In order to understand the fundamental properties of the crystal structure, in particular, the Fe-vacancy ordering in the K$_{2}$Fe$_{4}$Se$_{5}$, we have performed a series of structural investigations by means of the X-ray diffraction and TEM observations. The experimental results demonstrate that the polycrystalline samples and the single crystals have the same average structure, and all main reflection peaks can be indexed with lattice parameters a = b = 8.701 Å and c = 14.036 Å with a space group of I4/m (No. 87). Moreover, the superstructure reflections can be clearly observed in the powder X-ray diffraction pattern taken from the polycrystalline samples. Figure 2 shows an X-ray diffraction pattern obtained from a well-characterized sample at room temperature, the superstructure reflection peaks corresponding to the Fe-vacancy order are indicated by asterisks, these superstructure features are in good agreement with the calculated data of K$_{2}$Fe$_{4}$Se$_{5}$ as reported by Guo et al. [1], the four interlayer Fe-Fe bond lengths are not equal. This fact suggests that visible local structural distortions appear in the K$_{2}$Fe$_{4}$Se$_{5}$ crystal resulting from the Fe deficiency. This structural data are fundamentally in agreement with the results obtained by the neutron diffraction [7] which
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Table 1: The structural data for $\text{K}_2\text{Fe}_4\text{Se}_5$ as obtained from the X-ray diffraction.

<table>
<thead>
<tr>
<th>Formula</th>
<th>$\text{K}_2\text{Fe}_4\text{Se}_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>297</td>
</tr>
<tr>
<td>Space group</td>
<td>$I4/m$ (87)</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>8.7235(5)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>14.1285(0)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>1075.183</td>
</tr>
<tr>
<td>$z$</td>
<td>4</td>
</tr>
<tr>
<td>$R_p$</td>
<td>2.06%</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>2.98%</td>
</tr>
<tr>
<td>$R_{exp}$</td>
<td>1.39%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atomic parameters</th>
<th>occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>2a (0, 0, 0)</td>
</tr>
<tr>
<td>K2</td>
<td>8h (0.3708(8), 0.1619(5), 0)</td>
</tr>
<tr>
<td>Fe1</td>
<td>4d (0, 1/2, 1/4)</td>
</tr>
<tr>
<td>Fe2</td>
<td>16i (0.2045(8), 0.0936(6), 0.2530(1))</td>
</tr>
<tr>
<td>Se1</td>
<td>4e (1/2, 1/2, 0.1379(2))</td>
</tr>
<tr>
<td>Se2</td>
<td>16i (0.1157(3), 0.2923(6), 0.1455(3))</td>
</tr>
</tbody>
</table>

also suggests a quasi–two-dimensional antiferromagnetic structure in association with Fe-vacancy ordering in $\text{K}_2\text{Fe}_4\text{Se}_5$.

TEM observations on the microstructure feature in the K-Fe-Se superconducting system reveal a rich variety of structural phenomena, such as the Fe-vacancy ordering and phase separation. On the other hand, our TEM investigations on the $\text{K}_2\text{Fe}_4\text{Se}_5$ sample in general show a well-defined superstructure. Figure 3(a) shows the high-resolution TEM image taken from a $\text{K}_2\text{Fe}_4\text{Se}_5$ single-crystalline sample, indicating a tetragonal basic structure of the $a$-$b$ plane. This image taken along the [001] zone-axis direction was obtained from a relative thin region of a crystal. The Fe-vacancies positions are clearly recognizable as bright dots and their arrangement and the distance between neighbor bright dots are in conformity with the $\text{K}_2\text{Fe}_4\text{Se}_5$ structure as demonstrated in our previous publications [12]. The inset of fig. 3(a) displays a selected-area electron diffraction pattern along the [001] zone-axis direction showing superstructure feature in the $a$-$b$-plane of the $\text{K}_2\text{Fe}_4\text{Se}_5$ phase in consistence with our X-ray diffraction data as discussed in the above text. Figure 3(c) shows a high-resolution TEM image taken along the [1–10] zone-axis for the supercell, illustrating the layered structural feature modulated by the Fe-vacancy ordering along the [110] direction. The inset shows the electron diffraction pattern with sharp superstructure spots. This image in contrast with what we observed in the superconducting samples does not show visible phase separation and structural inhomogeneity which were commonly seen in the superconducting materials as discussed in our previous publications [12].

Very recently, experimental investigations on the $\text{K}_x\text{Fe}_{2−y}\text{Se}_2$ superconducting materials suggest that this system undergoes an antiferomagnetic transition just above 550K, and resistivity anomalies related to Fe-vacancy ordering also appears at almost the same temperature. Figure 4(a) (upper part) shows schematically the evident changes of resistivity and magnetic susceptibility for a typical $\text{K}_x\text{Fe}_{2−y}\text{Se}_2$ sample. In order to observe the microstructure alternations in the high-temperature range, we have made a careful examination by means of in situ heating TEM observation on a well-characterized $\text{K}_2\text{Fe}_4\text{Se}_5$ sample in the high-temperature range of 300K to 600K. Figure 4(b) shows a series of electron diffraction patterns taken along the [001]
zone-axis in the same region on a K$_{0.8}$Fe$_{1.6}$Se$_2$ crystal, illustrating the visible changes of the superstructure with the increase of temperature. A diffraction pattern taken around 300 K (upper part in fig. 4(b)) displays a typical pattern of the $a^*\cdot b^*$ reciprocal plane for the K$_2$Fe$_5$Se$_5$ superstructure. Careful examinations of the diffraction patterns at high temperatures reveal clear changes on both the intensity and sharpness of the superstructure reflection spots. The intensity change for the superstructure reflection is illustrated in the bottom panel of fig. 4(a), showing a clear correlation between physical properties and superstructure. This high-temperature superconductivity of K$_2$Fe$_{5}$Se$_{5}$ shows the anomalies around 550 K.

In fig. 4(c) we show a series of data taken from a powder X-ray diffraction in the temperature range of 300 K up to 600 K for a K$_{0.8}$Fe$_{1.6}$Se$_2$ sample; the most striking feature revealed in our X-ray diffraction is the disappearance of the superstructure peaks marked by asterisks at about 600 K in agreement with our TEM observations. Moreover, the K$_2$Fe$_5$Se$_5$ phase is found to be unstable at 600 K in the Ar environment, the two small peaks marked by arrows belong to the known FeSe$_{1−x}$ phase [19] with $a = 3.784$ Å, $c = 5.532$ Å, and space group $P4/nmm$.

Actually, the Fe ions in the antiferromagnetic K$_2$Fe$_5$Se$_5$ has a Fe$^{2+}$ valence state; recent theoretical and experimental investigations on the K$_2$Fe$_{2−y}$Se$_2$ superconducting system suggest that charge carrier doping can be successfully produced by varying the Fe-concentration in K$_2$Fe$_{2−y}$Se$_2$. Moreover, the Fe-vacancy order and the related antiferromagnetic structure play a critical role for alternation of the superconductivity in the present system. Experimental study on well-characterized samples with chemical composition deviating from K$_2$Fe$_5$Se$_5$ by varying either K or Fe concentration could result in the appearance of superconductivity in this system. For instance, clear superconductivity with critical transitions between 27 K and 33 K often appears in K$_{0.8}$Fe$_{2−y}$Se$_2$ samples with 0.2 $\leq y \leq 0.3$ and disappears for high Fe concentration [8]. In addition to the influence on physical properties, the variation of Fe concentration could also yield clear changes in microstructure such as phase separation and local structural distortions [20]. Actually, in order to understand the correlation between Fe-vacancy order and superconductivity, we have performed a series of TEM investigations on K$_x$Fe$_{2−y}$Se$_2$ samples with different chemical composition. In contrast with the well-defined ordered state within the $a$-$c$ superstructure plane as shown in fig. 3(c), complex phase separation and structural inhomogeneity appear commonly in the superconducting K$_2$Fe$_{2−y}$Se$_2$ (0.2 $\leq y \leq 0.3$). In fig. 5, we show a TEM image taken on a single crystal with a sharper superconducting transition, in which the Fe-vacancy order is invisible in a large fraction of the crystal. Further study on this kind of domain structure shows a clear change with the temperature rise as similarly discussed in the above text for the in situ heating TEM observations. Moreover, It is possible that there is an interesting similarity between ordering of Fe-vacancies in the present system and the ordering of oxygen interstitials in the inhomogeneous phase of oxygen-doped La$_2$CuO$_4$ [21].

In summary, the K$_2$Fe$_{2−y}$Se$_2$ compounds show a rich variety of structural phenomena in correlation with the Fe-vacancy ordering and the inhomogeneous structure. The K$_2$Fe$_5$Se$_5$, as an important phase for the structural characterization of the K$_x$Fe$_{2−y}$Se$_2$ superconducting phase, is found to be unstable at 600 K in the Ar environment, the two small peaks marked by arrows belong to the known FeSe$_{1−x}$ phase [19] with $a = 3.784$ Å, $c = 5.532$ Å, and space group $P4/nmm$.

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system, has been intensively studied by powder X-ray diffraction and TEM observations in a large temperature range. It is found that the $K_2Fe_4Se_5$ phase undergoes a phase transition from the well-defined superstructure, via an intermediate phase with short-range order state (500–550 K), towards a Fe-vacancy disorder phase (above 570 K). Structural inhomogeneity and phase separation in the superconducting materials have been discussed briefly.

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REFERENCES


Fig. 5: (Colour on-line) A high-resolution TEM image taken along the [1–10] zone-axis direction on a $K_2Fe_4Se_5$ single crystal with a sharper superconducting transition, in which both Fe-vacancy ordered state (OS) and disordered state (DOS) are observed.