Large local disorder in superconducting $K_{0.8}Fe_{1.6}Se_2$ studied by extended x-ray absorption fine structure

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Received 21 January 2012
Published 21 February 2012
Online at stacks.iop.org/JPhysCM/24/115701

Abstract
We have measured the local structure of superconducting $K_{0.8}Fe_{1.6}Se_2$ chalcogenide ($T_c = 31.8$ K) by temperature dependent polarized extended x-ray absorption fine structure (EXAFS) at the Fe and Se K-edges. We find that the system is characterized by a large local disorder. The Fe–Se and Fe–Fe distances are found to be shorter than the distances measured by diffraction, while the corresponding mean square relative displacements reveal large Fe-site disorder and relatively large $c$-axis disorder. The local force constant for the Fe–Se bondlength ($k \sim 5.8$ eV Å$^{-2}$) is similar to the one found in the binary FeSe superconductor, however, the Fe–Fe bondlength appears to be flexible ($k \sim 2.1$ eV Å$^{-2}$) in comparison to the binary FeSe ($k \sim 3.5$ eV Å$^{-2}$), an indication of partly relaxed Fe–Fe networks in $K_{0.8}Fe_{1.6}Se_2$. The results suggest a glassy nature for the title system, with the superconductivity being similar to that in the granular materials.

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

1. Introduction
The discovery of superconductivity in the iron-based ‘1111’ pnictides [1] boosted a renewal of research activities in the field, resulting a number of iron containing superconductors with different transition temperatures, the maximum being about 55 K for the SmFeAsO system [2, 3]. Among these, FeSe (the 11-type chalcogenide) shows the lowest superconducting transition temperature ($T_c \sim 8$ K), however, it could be considered a model system to address basic characteristics of these materials [3]. The FeSe structure contains simple stacking of tetrahedrally coordinated FeSe$_4$ layers without spacer layers that are known to have a substantial effect on the electronic properties [4, 5]. Substitution by Te in the FeSe leads to a marginal increase in $T_c$ ($\sim 15$ K); however, the system gets phase separated and the nanoscale structure is characterized by different iron–chalcogen bondlengths [8]. On the other hand, the superconducting transition temperature of the FeSe shows a large enhancement up to $\sim 37$ K under hydrostatic pressure [6, 7]. The large pressure sensitivity of FeSe indicates chemical pressure to be a potential alternative parameter for raising its $T_c$. Indeed, superconductivity at a $T_c$ as high as 32 K has been observed recently in a K-intercalated FeSe [9], triggering new studies on the iron-based chalcogenides. Later, similar $T_c$ was observed in the Rb$_x$Fe$_{2-y}$Se$_2$ [10, 11], (Tl, K) Fe$_{2-y}$Se$_2$ [12] and Cs$_x$Fe$_{2-y}$Se$_2$ [13] compounds.

There appears to be substantial charge transfer between the active FeSe blocks and the intercalated spacer layers in the $K_xFe_{2-y}Se_2$, with electrons from the $K^+$ ions filling the hole bands at the zone centre. Thus, the Fermi surface of $K_xFe_{2-y}Se_2$ is made by only the electron pockets around
the M points [15, 14], and hence the scenario based on the nesting between electron and hole pockets, usually put forward for understanding the iron pnictides, loses its grounding [16]. On the other hand, although isostructural to the 122-type BaFe$_2$As$_2$ pnictides, K$_x$Fe$_2$−$_x$Se$_2$ has a distinct microstructure, characterized by an iron-vacancy order and a phase separation [17–20]. The magnetic order co-exists with bulk superconductivity and a remarkably large iron magnetic moment [21, 22]. In addition, there are experimental indications on the relation between the superconductivity and the iron-vacancy disorder, with a completely ordered state being an insulator. These facts point out that a complete knowledge of the nanoscale structure is needed to describe the fundamental electronic structure of these materials.

Extended x-ray absorption fine structure (EXAFS), an atomic site-specific experimental probe [23], has been widely used to study the local structure of different materials, including the copper oxide superconductors and related systems [24]. EXAFS has also been exploited to study the new iron-based superconductors, revealing important information about the atomic correlations between different layers [4, 5] and temperature dependent local structural anomalies across the superconducting transition [25, 26]. More recently, we have applied EXAFS to study the local structure of FeSe$_{1−x}$Te$_x$ chalcogenides, providing direct evidence of phase separation in the ternary systems, characterized by different Fe–Se and Fe–Te distances [8]. In the present study, we have used polarized EXAFS to explore the local structure of K$_0.8$Fe$_{1.6}$Se$_2$ superconductor. The results of polarized EXAFS at the Fe and Se K-edges reveal large local disorder similar to the amorphous/glass materials. The local structure of K$_0.8$Fe$_{1.6}$Se$_2$ is significantly different from the local structure of the binary FeSe [8] superconductor. While the local force constant of the Fe–Se bondlength ($k \sim 5.8$ eV Å$^{-2}$) is similar in the two systems, the one for the Fe–Fe bondlength appears to sustain substantial changes due to K-intercalation ($k \sim 3.5$ eV Å$^{-2}$ and $k \sim 2.1$ eV Å$^{-2}$, respectively, for FeSe and K$_0.8$Fe$_{1.6}$Se$_2$ systems), consistent with a partial relaxation of the Fe–Fe networks in due to K-intercalation. The experimental results suggest that glass physics should have a distinct role in the understanding of these superconductors.

2. Experimental details

X-ray absorption measurements were performed at the beamline BM23 in the European synchrotron radiation facility (ESRF), Grenoble on a well characterized single crystal of the K$_0.8$Fe$_{1.6}$Se$_2$ system. The single crystal was grown by melting a precursor of FeSe and K placed in an alumina crucible, that itself was sealed into an arc-welded stainless steel tube. Details on the crystal growth and characterization for superconducting, structural and transport properties are described elsewhere [27]. A platelike and dark-shining as-grown single crystal with $T_c = 31.8$ K was selected and a detailed synchrotron x-ray diffraction study [17] was performed prior to the x-ray absorption measurements. The synchrotron radiation emitted by a bending magnet source at the 6 GeV ESRF storage ring was monochromatized by a double crystal Si(311) monochromator. The polarized EXAFS measurements at the Fe and Se K-edges were acquired at normal incidence (with polarization parallel to the ab-plane and hereafter called $E \parallel ab$ polarization) and in grazing incidence geometry ($10^\circ$ off the E $\parallel c$ and hereafter called $E \parallel c$ polarization). Fluorescence mode was used (exploiting a multi-element Ge-detector system) for the measurements. The samples were mounted in a continuous flow He cryostat and the temperature was controlled and monitored within an accuracy of ±1 K. Several spectral scans were acquired at each temperature to ensure the reproducibility of the measurements. Standard procedure was used to extract the EXAFS signal from the absorption spectrum [23] and corrected for the fluorescence self-absorption before the analysis [28].

3. Results and discussion

Figure 1 shows the Fourier transform (FT) magnitudes of the polarized EXAFS oscillations, measured at the Se
and Fe K-edges on $K_{0.8}Fe_{1.6}Se_2$ single crystal. The FT magnitudes provide partial atomic distribution around the Se and Fe in the direction of x-ray beam polarization. Se K-edge EXAFS, measured in the $E \parallel ab$ polarization shows only the contribution from the nearest neighbour Fe atoms at a distance of $\sim$2.4 Å (main FT peak at $\sim$2 Å). The next nearest neighbours of Se in the $E \parallel ab$ geometry are K ($R = 3.45$ Å), Se ($R = 3.91$ and 4.02 Å) and Fe ($R = 4.62$ Å) atoms, and their contributions are expected to appear at $\sim$3.0–4.5 Å (upper panel). On the other hand, the F-site nearest neighbours are Se (at a distance $\sim$2.4 Å) and Fe (at a distance $\sim$2.7 Å) in the $E \parallel ab$ polarization (lower panel). The contribution of Fe–Fe is not expected in the $E \parallel c$ polarization and the main FT peak in this geometry should be merely due to Fe–Se bonds (middle panel). Contributions of Fe next nearest neighbours are expected to appear at longer distances ($R_{Fe-Fe} = 3.91$ Å, $R_{Fe-K} = 4.02$ Å and $R_{Fe-Se} = 4.62$ Å). Therefore, the main FT peak of the Fe K-edge EXAFS in the $E \parallel ab$ geometry contains information on the Fe–Se and Fe–Fe bonds (lower panel) while that in the $E \parallel c$ geometry only has a contribution from Fe–Se bonds (middle panel), similar to the main FT peak of the Se K-edge EXAFS (upper panel). As a matter of fact, apart from the nearest neighbours, the contribution expected from the farther atoms is apparently absent (or within the noise level). This is a characteristic feature of highly disordered systems and amorphous materials [29]. We will come back to discuss this, but before that let us make a comparison between the local structure of FeSe and $K_{0.8}Fe_{1.6}Se_2$.

Figure 2 compares Fourier transforms of the Fe and Se K-edge EXAFS signals ($T = 60$ K) measured on the polycrystalline FeSe sample [8] and the $K_{0.8}Fe_{1.6}Se_2$ crystal in the $E \parallel ab$ geometry. The Fe nearest neighbours in the FeSe are Se at a distance of $\sim$2.4 Å and Fe atoms at a distance of $\sim$2.7 Å (two peak structure at $\sim$1.5–3.0 Å), similar to the case of $K_{0.8}Fe_{1.6}Se_2$. Significantly intense features between 3 and 6 Å are due to longer Fe–Fe ($\sim$3.8 Å) and Fe–Se distances, and the multiple scatterings involving different near neighbours of the Fe atoms. Similarly, in the Se K-edge EXAFS of the FeSe we expect a contribution from four Fe nearest neighbours at a distance $\sim$2.4 Å (as in the $K_{0.8}Fe_{1.6}Se_2$). The next nearest neighbours are Se and Fe atoms and contributions of these distant shells clearly appear as a multiple structured peak at $\sim$3.0–4.5 Å.

The comparison underlines significant differences in the local structure of the FeSe and the $K_{0.8}Fe_{1.6}Se_2$ systems. In particular, the FT of $K_{0.8}Fe_{1.6}Se_2$ shows only a single peak at $\sim$2 Å that contains a contribution from the Fe–Se distances ($\sim$2.4 Å) in the Se K-edge EXAFS and Fe–Se and Fe–Fe contributions in the Fe K-edge EXAFS. The longer distance contributions are apparently absent in the $K_{0.8}Fe_{1.6}Se_2$ system. Also, the FT magnitude due to similar nearest neighbours is much weaker in $K_{0.8}Fe_{1.6}Se_2$. In addition, the contribution from the Fe–Fe distances in the Fe K-edge EXAFS is strongly damped, indicating a large Fe-site disorder. Apparently the EXAFS data reveal large overall local disorder in the $K_{0.8}Fe_{1.6}Se_2$ system, commonly seen in the local structure of amorphous systems [29]. On the other hand, the measured $K_{0.8}Fe_{1.6}Se_2$ sample is a very good single crystal, evident from sharp diffraction peaks [17], and such a large disorder in the local structure indicates that the system should be some kind of glass.

Coming back, it is clear that only the nearest neighbour (i.e. Fe–Se and Fe–Fe bondlengths) contributions are visible in both Fe and Se K-edge EXAFS. Therefore our focus should be limited to these bondlengths. In the single-scattering approximation, the EXAFS amplitude is described by the following general equation [23]:

$$\chi(k) = \sum_i N_i S_i^2 \frac{2e^{i k R_i}}{k R_i^2} f_i(k, R_i) e^{-2\sigma_i^2 k^2} \sin[2k R_i + \delta_i(k)]$$  \(1\)

where $N_i = 3 \cos^2 \theta_i$ is the number of neighbouring atoms at a distance $R_i$ at an angle $\theta_i$ with respect to the x-ray beam polarization, $S_i^2$ is the passive electrons reduction factor, $f_i(k, R_i)$ is the backscattering amplitude, $\lambda$ is the photoelectron mean free path, $\delta_i$ is the phase shift, and $\sigma_i^2$ is the correlated Debye–Waller factor (DWF) measuring the mean square relative displacements (MSRDs) of the photoabsorber–backscatterer pairs. EXCURVE 9.275 code (with calculated backscattering amplitudes and phase shift functions) is used for the EXAFS model fits [30]. Similar results were obtained with the WINXAS package [31] in which the backscattering amplitudes and phase shifts were calculated using FEFF [32]. The $E_0$, $N_i$ and $S_i^2$ were fixed after a number of trials on different EXAFS scans with structural input from diffraction studies [17–20, 33]. Only the radial distances $R_i$ and the corresponding $\sigma_i^2$, were allowed to vary in the least squares model fits for the temperature dependent study. A single shell (i.e. Fe–Se) was used to model the $E \parallel ab$ polarized Se K-edge EXAFS and $E \parallel c$ polarized
Figure 3. Fe–Se and Fe–Fe distances in K$_{0.8}$Fe$_{1.6}$Se$_2$ as a function of temperature extracted from the polarized EXAFS spectra measured at Se and Fe K-edges. The Fe–Se bondlengths are similar irrespective of the selected absorbing atom and polarization, and slightly smaller than the average Fe–Se distance measured by diffraction. The open circles are from the Se K-edge while the open diamonds represent the data from the E $\parallel$ c polarized Fe K-edge EXAFS. The closed circles are from the E $\parallel$ ab polarized Fe K-edge EXAFS. The error bars represent maximum uncertainty, determined using correlation maps between different parameters.

Fe K-edge EXAFS. On the other hand, two shells (i.e. Fe–Se and Fe–Fe) were necessary to model the E $\parallel$ ab polarized Fe K-edge EXAFS. The number of independent data points, $N_{\text{ind}} \sim (2\Delta k\Delta R)/\pi$ [23] were about 17–18 ($\Delta k = 11–12$ Å$^{-1}$ and $\Delta R = 2.4$ Å), in the two parameter (four parameter) fits for the E $\parallel$ ab Se K-edge and E $\parallel$ c Fe K-edge EXAFS (E $\parallel$ ab Fe K-edge EXAFS). The model fits are shown as insets to the figure 1.

Figure 3 shows the temperature dependence of the local bondlengths determined by Fe K and Se K-edge EXAFS analysis. The Fe–Se distances determined by EXAFS data in different polarizations on two edges are similar within experimental uncertainties (upper panel). However, both Fe–Se and Fe–Fe distances (lower panel) appear slightly shorter than the average bondlengths determined by diffraction studies [18–20, 17, 33]. This may be due to the largely disordered structure, as seen in the glasses [34, 35]. The Fe–Se bondlength hardly shows any change with temperature unlike the Fe–Fe distance (describing the in-plane lattice parameter) that varies with temperature, showing the relative flexibility of the latter.

Figure 4 shows the correlated Debye–Waller factors ($\sigma^2$), i.e. the MSRDs of the Fe–Se and the Fe–Fe pairs as a function of temperature for the K$_{0.8}$Fe$_{1.6}$Se$_2$ system determined by polarized EXAFS measured at Se and Fe K-edges. The empty (filled) circles are from E $\parallel$ ab polarized Se K-edge (Fe K-edge) EXAFS while the open diamonds represent the data from the E $\parallel$ c polarized Fe K-edge. The filled squares are the data obtained for the binary FeSe system [8]. The solid lines represent the correlated Einstein model fit to the data. The Einstein temperatures, $\theta_E$, are $\sim$318 K for the K$_{0.8}$Fe$_{1.6}$Se$_2$, similar to the Fe–Se bonds in the binary FeSe system (the maximum uncertainty is about ±20 K). The $\sigma^2_0$ in the E $\parallel$ ab polarization is smaller ($\sim$0.0002) compared to that in E $\parallel$ c ($\sim$0.002), consistent with large static disorder in the c-direction. While the $\theta_E$ for Fe–Se remains similar to the binary FeSe system, the $\theta_E$ for Fe–Fe is significantly different, suggesting a large change in these bonds due to K-intercalation.
On the other hand, the temperature dependent $\sigma^2(T)$ is well described by the correlated Einstein model [23, 24], an appropriate approximation for local mode vibrations. The Einstein equation is given as

$$\sigma^2(T) = \frac{\hbar^2}{2\mu k_B\theta_E^2} \coth \frac{\theta_E}{2T}. \quad (2)$$

The Einstein temperature ($\theta_E$, i.e. the Einstein frequency $\omega_E = k_B\theta_E/h$) for the Fe–Se pairs remains similar to that in the binary FeSe system ($\theta_E \sim 318$ K), indicating that the local force constant ($k = \mu\omega_E^2$, where $k$ is the effective force constant and $\mu$ is reduced mass of the Fe–Se pair) for the Fe–Se bonds is not very sensitive to the K-intercalation between the FeSe layers. The local force constant for the Fe–Se bondlength is found to be $k \sim 5.8$ eV Å$^{-2}$, similar to that in the binary FeSe superconductor. On the other hand, there is a substantial effect of intercalation on the Einstein temperature (local force constant) of the Fe–Fe pairs, estimated to be $\sim 208$ K ($k \sim 2.1$ eV Å$^{-2}$) and $\sim 268$ K ($k \sim 3.5$ eV Å$^{-2}$), respectively, for the K$_{0.8}$Fe$_{1.6}$Se$_2$ and the binary FeSe. Therefore, it appears plausible to think of an Fe–Fe bondlength that is relatively relaxed in the K$_{0.8}$Fe$_{1.6}$Se$_2$ system, consistent with a glassy nature of this system.

Considering the fact that the system has a well defined crystal ordering, the glassy local structure could be due to freezing of iron-vacancy order coupled with some other degrees of freedom. Several measurements have underlined that the magnetic ordering in this system co-exists with the superconductivity with a large iron moment (3.3 $\mu_B$/Fe) ordered antiferromagnetically along the $c$-axis [21, 22]. Present measurements reveal that there is: (i) a large static disorder along the $c$-axis and (ii) a large Fe-site disorder. In addition, the Fe–Fe network (in-plane lattice parameter) is relaxed. Therefore it appears plausible to think that a frozen state of $c$-axis disorder (associated with local strain fields due to K-intercalation and iron-vacancy order) coupled with magnetic order is realized. This results in a magnetic texture with large frozen magnetic moment and a relaxed Fe–Fe network. Thus, it is likely that the strain fields locally compress the FeSe-block and hence the $T_c$ reaches to a value as high as 32 K, as happens for FeSe under external pressure. Indeed, single-crystal x-ray diffraction has shown clear evidence of nanoscale phase separation between a majority magnetic phase with iron-vacancy ordering, co-existing with a minority compressed phase [17]. This situation is similar to granular superconductors in which a nanoscale superconducting phase coexists in an insulating texture. Therefore, the physics of the K$_{0.8}$Fe$_{1.6}$Se$_2$ system should be quite similar to the physics of glasses and granular superconductors. It should be recalled that the thermodynamic and kinetic fragility of a glass is related to the number of potential energy minima in the phase space and the heights of the activation energy barriers separating these minima. The fact that the superconductivity in the K$_{0.8}$Fe$_{1.6}$Se$_2$ system is strongly dependent on its thermal history [36], a characteristic feature of glasses, further underlines the glassy nature of this system. The observation of a glassy nature puts the K$_{0.8}$Fe$_{1.6}$Se$_2$ in the category of granular superconductors, consistent with the superconductivity in A15 systems [37] and recently observed fractal distribution enhanced superconductivity in superoxygennated La$_2$CuO$_4$ [38].

### 4. Summary

In summary, we have studied the local structure of the superconducting K$_{0.8}$Fe$_{1.6}$Se$_2$ chalcogenide by polarized Fe and Se K-edge EXAFS. The EXAFS data provide clear evidence of large local disorder in this system. Indeed the local structure of K$_{0.8}$Fe$_{1.6}$Se$_2$ is similar to that of amorphous materials indicating the glassy nature of the system. The local bondlengths are found to be slightly shorter than the average diffraction distances, a characteristic feature of glasses. The mean square relative displacements (MSRD) of Fe–Se and Fe–Fe bondlengths are well described by the correlated Einstein model with similar Einstein temperatures in all polarizations, albeit the static component along the $c$-axis is much larger, likely due to substitutional disorder in the K layer. While the Fe–Se bondlengths remain highly covalent in K$_{0.8}$Fe$_{1.6}$Se$_2$, similar to the situation found in the binary FeSe superconductor, the Fe–Fe bondlength is characterized by much smaller force constant compared to the binary FeSe. Such a local relaxation of the Fe–Fe bondlength results in a compression of the FeSe unit, as happens under external pressure, and hence the superconductivity at high $T_c$ in the title system should be due to a locally compressed nanoscale minority phase, co-existing with the normal magnetic phase, similar to the case of granular superconductors.

### Acknowledgment

The authors wish to thank the staff at ESRF for their help and support during the experimental runs.

*Note added.* After finishing this paper we came across a very recent publication by Tyson et al [39] reporting similar kinds of measurements on the K$_{0.8}$Fe$_{1.6}$Se$_2$ system finding a large disorder, similar to the one reported in this paper. However, Tyson et al have compared the data with those obtained on 1111-iron pnictide, unlike the present study in which a direct comparison with binary FeSe has allowed us to clearly identify the effect on the local structure due to K-intercalation. Therefore, the glassy nature revealed in these measurements should provide further insight into our understanding of these superconductors.

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