FAST TRACK COMMUNICATION

Local structural studies of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ using atomic pair distribution function analysis

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Abstract
Systematic local structural studies of the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ system are undertaken at room temperature using atomic pair distribution function analysis. The local structure of the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ is found to be well described by the long-range structure extracted from diffraction experiments, but with anisotropic atomic vibrations of the constituent atoms ($U_{11} = U_{22} \neq U_{33}$). The crystal unit cell parameters, the FeAs$_4$ tetrahedral angle and the pnictogen height above the Fe-plane are seen to show systematic evolution with K doping, underlining the importance of the structural changes, in addition to the charge doping, in determining the properties of Ba$_{1-x}$K$_x$Fe$_2$As$_2$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The appearance of the iron-based superconductors [1] has given a further boost to efforts to understand the role of lattice elastic effects and disorder in layered structures [2] showing intriguing phenomena such as high temperature superconductivity, colossal magneto-resistance etc. The importance of local structural information in these complex systems is well recognized and is the key driving force behind the development of experimental and theoretical tools associated with the total scattering techniques [3, 4]. Several local structural studies in cuprates [5–7], manganites [8, 9], cobaltites [10], etc, have underlined the importance of the local order in the functional properties of complex materials with heterostructures. Polarized extended x-ray absorption fine structure (EXAFS) studies on La$_{1.85}$Sr$_{0.15}$CuO$_4$ crystal have established two different conformations of the CuO$_6$ octahedra below 100 K [5]. In the Nd$_{2−x}$Ce$_x$CuO$_{4−y}$ system, atomic pair distribution function (PDF) studies showed that the CuO$_2$ planes are not flat but are buckled and distorted by oxygen displacements of magnitude $\geq 0.1$ Å [7]. PDF studies indicated that on the local scale, the SmFeAsO$_{1−x}$F$_x$ compounds have a lower symmetry than the symmetry expected from the diffraction data describing the long-range (average) structure [11]. EXAFS studies on the same system indicated the presence of anomalies in the Fe–As bond correlation in the superconducting sample, with no such anomalies being observed for the parent compound [12]. Even for the simplest systems among the new Fe-based superconductors, i.e. the doped iron-chalcogenides, a lower symmetry is observed at the local scale [13], with the presence of two distinct Fe–chalcogen bond lengths [14, 15]. To further understand the role of local structural inhomogeneities in the superconducting and magnetic properties, here we have undertaken PDF studies of the Ba$_{1−x}$K$_x$Fe$_2$As$_2$ system. Unlike the case for the SmFeAsO$_{1−x}$F$_x$ [11] and the FeSe$_{1−x}$Te$_x$ [13, 14]
systems, the present results indicate that the local structure of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ is well described by the long-range structure revealed by the diffraction experiments. However, the results of the PDF refinement suggest the atomic vibrations to be anisotropic, with the thermal fluctuations of the constituent atoms along the $a$–$b$ plane not being equal to the $c$ direction ($U_{11}=U_{22} \neq U_{33}$). The crystal unit cell parameters, the FeAs$_4$ tetrahedral angle and the pnictogen height above the Fe-plane are seen to show systematic evolution with K doping, underlining the importance of the structural changes, in addition to the carrier supply, in determining the doping dependent properties of Ba$_{1-x}$K$_x$Fe$_2$As$_2$.

2. Experimental methods

Ba$_{1-x}$K$_x$Fe$_2$As$_2$ ($x=0.0, 0.1, 0.2$ and $0.34$) samples prepared via solid state reactions are used for the present study. The synthesis, structural and transport properties of these samples are reported in [16–18]. X-ray total scattering measurements were carried out at the ID-31 beamline of the European synchrotron radiation facility, Grenoble (France). Finely powdered samples tightly packed in a 6 mm quartz capillary are used for the measurements. The measurements are conducted at temperature $T=297$ K, using photons of wavelength 0.4008 Å ($\sim$30 keV). As required for the PDF analysis [3], data are collected with sufficient statistics to high $Q$ values by measuring large angular range (2$\theta$ range 0°–110°). Data from an empty container are also collected to take care of the container contributions. The corrected total scattering structure function, $S(Q)$ is obtained using the standard corrections [3] utilizing the PDFgetX2 program. From the $S(Q)$, the PDF data $G(r)$ are obtained by the Fourier transformation according to $G(r) = 2/\pi \int S(Q) \sin(Qr) dQ$, where $Q$ is the magnitude of the scattering vector. Modeling of the PDF data is carried out using the PDFgui and PDFfit2 packages [19].

3. Results and discussions

Figure 1 presents the room temperature PDF data of the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ ($x=0.0, 0.1, 0.2$ and $0.34$) system. At room temperature the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ system has a tetragonal symmetry, with the unit cell parameters of the parent compound ($x=0.0$) being $a=b \approx 3.96$ Å and $c \approx 13.0$ Å. With increasing $x$, $a(b)$ decreases and $c$ increases, with the latter having a larger effect, leading to an overall expansion of the unit cell volume. However, the changes in the unit cell volume are not so significant due to the similar ionic radii of Ba$^{2+}$ (1.42 Å) and K$^+$ (1.51 Å) for the same coordination. The overall PDF structures for all the samples studied are found to be similar (figure 1(a)). However, changes can be observed by a careful comparison of the spectra corresponding to different $x$ values. For example, the peak around 9 Å becomes broader and shows a splitting with increase in K doping. To obtain quantitative information, refinement of the structure using the PDF data is undertaken. It is found that the average structure obtained from the diffraction results gives a reasonable description of the PDF data. Anisotropic, rather than isotropic, thermal factors for the constituent atoms (according to the crystal symmetry constraints) are found to result in a substantial improvement in the refinement. Refinement results in such a case, for the $x=0.0$ and 0.34 compounds, are also shown in figure 1(b).

In figure 2, left panels, we show the evolution of the lattice parameters, $a(b)$ and $c$, with K doping at room temperature obtained from the PDF refinements. The data from the PDF refinement have a similar trend to the diffraction data [18]. The left upper inset in figure 2 presents the changes in the $z$ position of the As atom with K doping at room temperature. The $z$-position of the As seems to be more or less constant (showing a small decrease with increasing K doping). It is interesting to follow the changes occurring in the active layer, Fe–As, in particular the FeAs$_4$ tetrahedra with the K doping. The Fe–As distance shows only small changes with K doping (figure 2, upper right panel), whereas the Fe–Fe distance is seen to show around 1% decrease for the highest doped sample compared to the undoped. These changes
result in an increase in the Fe–As–Fe angle from around 110.82 to around 109.48 (figure 2, inset in the upper right panel). These changes result in an increase in the pnictogen height above the Fe-plane with K doping. In iron-based superconductors, the anion height above the Fe-plane [20] is identified as a key parameter. Local structural studies on the REFeAsO (RE = La, Pr, Nd and Sm) system showed that the Fe–As bond length does not vary significantly with the change in the rare-earth (RE) ionic size, but the Fe–Fe bond length decreases with decreasing RE ionic size, thus affecting the arsenic height above the Fe-plane [21]. Several theoretical calculations reveal that the anion height above the Fe-plane is the controlling parameter of the magnetic interactions [22, 23]. Theoretical calculations indicate that even a small change in the As height above the Fe-plane influences the density of states close to the Fermi level [22] and thus the magnetic and superconducting properties of the system. Substantial changes in the magnetic and superconducting properties from BaFe2As2 to Ba0.66K0.34Fe2As2 are in accordance with this.

As mentioned previously, the PDF refinements are carried out considering anisotropic thermal factors for the constituent atoms with \( U_{11} = U_{22} \neq U_{33} \). In figure 3(a), we present the \( U_{11} (U_{22}) \) thermal factors for the constituent atoms. For the Ba site, the in-plane thermal factors seem to increase with increasing K doping. This can be understood as the K doping induced disorder in the Ba site, due to the slight differences in the ionic radii of the two. A similar increase is also seen for the Fe thermal factors. But the As thermal factors seem to be more or less insensitive to the K doping. The thermal factors of the constituent atoms along the c direction are given in figure 3(b). Compared to the \( ab \) plane thermal factors (\( U_{11} = U_{22} \)), the \( U_{33} \) for the Ba and Fe have larger magnitudes. However, the \( U_{33} \) for
the As is lower in magnitude than the ab plane thermal factor \((U_{11} = U_{22})\). In both cases (along the ab plane and along c), the As thermal factors are found to be lowest compared to the Ba/K and Fe.

In conclusion, we have carried out systematic local structural studies of the Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) system at room temperature using atomic PDF analysis. The local structure refinements indicate that the Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) system does not show any significant structural symmetry deviation at the local scale. However, for a better description of the local structure, the assumption of anisotropic atomic vibrations of the constituent members is necessary, with the thermal fluctuations along the ab plane and along c having different magnitudes. Results also show a systematic evolution of the AsFe\(_4\) tetrahedra, with changing pnictogen height above the Fe-plane with K doping, underlining the importance of the structural changes, in addition to the charge doping, in determining the properties of Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\).

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