Temperature dependent local atomic displacements in Ru substituted SmFe$_{1-x}$Ru$_x$AsO$_{0.85}$F$_{0.15}$ superconductors

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Abstract

The local structure of SmFe$_{1-x}$Ru$_x$AsO$_{0.85}$F$_{0.15}$ ($x=0.0, 0.05, 0.25$ and $0.5$) superconductors has been investigated by temperature dependent As K-edge extended x-ray absorption fine structure analysis. The effect of Ru substitution remains confined to the iron–arsenide layer but neither the static disorder nor the Fe–As bond strength suffers any change for $x \leq 0.25$. With further Ru substitution the static disorder increases while the Fe–As bond strength remains unchanged. Also, the Ru–As distance ($\sim 2.42$ Å), different from the Fe–As distance ($\sim 2.39$ Å), does not show any change in its force constant with Ru substitution. These observations suggest that the SmFe$_{1-x}$Ru$_x$AsO$_{0.85}$F$_{0.15}$ system breaks down into coexisting local electronic phases on isoelectric substitution in the active FeAs layer.

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

1. Introduction

The newly discovered iron-based high $T_c$ superconductors [1–3] have a particular layered structure with electronically active FePn/Ch (Pn = pnictogen; Ch = chalcogen) layers alternated by spacer layers. The superconductivity and magnetism in these materials are strongly dependent on the thickness of the active layers (e.g., the height of Pn/Ch atoms from the Fe plane) [3]. Among the iron-based superconductors, REFeAsO (RE = rare earth), the so-called 1111-system with well defined iron–arsenide active layers stacked together with spacer layers shows the highest $T_c$ [2, 3]. Generally, atomic substitution in either of the stacking layers is used to control and manipulate the superconductivity and other transport properties (e.g., a partial substitution of O by F) [3]. In addition to the control over superconductivity, atomic substitution in the active layer also permits an understanding of the transport phenomena [4, 5] and the development of new structures through detailed information on the role of the different layers. In particular, it is important to have knowledge of local atomic correlations and the modifications introduced by the substituted atoms in the layered structure topology.

X-ray absorption spectroscopy is an atomic site-specific experimental probe [6] that does not require any long range crystal symmetry, and hence permits direct access to local atomic correlations. Indeed, x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) measurements have been widely exploited to study layered high $T_c$ superconductors [7–10], including iron-based...
superconductors [11–19]. In earlier work, we have explored the effect of different spacer layers (REs of different size) in the 1111-system [13, 14], and found that interlayer atomic order/disorder is important in these materials. We have also studied the effect of charge density varied by atomic order/disorder is important in these materials. We have focused on the effect of isovalent Ru (atomic radius 1.34 Å) substitution directly revealing key information on interlayer atomic correlations and dynamics [16]. Recently we have focused on the effect of partial substitution in the REO spacer layers (O by F), have also studied the effect of charge density varied by atomic order/disorder is important in these materials. We have explored the effect of different spacer layers (REs of different size) of SmFeAsO layers [11–19]. In earlier work, we have explored the effect of isovalent Ru (atomic radius 1.26 Å) substitution directly in the FeAs layer in place of Fe (atomic radius 1.26 Å) for optimally doped SmFe1−xRu0.85AsO0.15 [19]. The results have revealed that the local disorder induced by Ru substitution is mainly confined to the FeAs layers, which become thinner and decoupled from the SmO spacer layers. This work is dedicated to distinctly identifying the random static disorder and bondlength fluctuations induced by isoelectric substitution in the iron–arsenide active layer. For this purpose, we have performed temperature dependent As K-edge EXAFS measurements on a series of SmFe1−xRu0.85AsO0.15 (x = 0.0, 0.05, 0.25 and 0.5) samples. Consistent with earlier work [19], the Ru substituted system is found to be characterized by different Fe–As and Ru–As distances. Incidentally, the force constants for these distances remain unchanged with increasing Ru substitution, indicating distinct local electronic phases coexisting in the system. It appears that the system breaks down into coexisting nanoscale electronic phases due to isoelectric substitution, having a direct influence on the fundamental electronic properties of these materials.

2. Experimental details

The As K-edge (E = 11 868 eV) x-ray absorption measurements on powder samples of SmFe1−xRu0.85AsO0.15 (x = 0.0, 0.25 and 0.5) were performed in transmission mode at the beamline BM26A [20] of the European Synchrotron Radiation Facility (ESRF), Grenoble. Measurements on the x = 0.05 sample were carried out at the XAFS beamline of the ELETTTRA, Trieste using a similar experimental approach. Temperature dependent measurements were carried out between 10 and 300 K. Several scans were acquired at each temperature to ensure spectral reproducibility. The EXAFS oscillations were extracted using a standard procedure based on spline fitting to the pre-edge subtracted absorption spectrum [6]. The superconducting transition temperatures (Tc), determined by resistivity measurements, are 51 K, 43 K, 14 K and 8 K for the samples with x = 0.0, 0.05, 0.25 and 0.5, respectively. Details on sample preparation and characterization for transport and structural properties are described elsewhere [21–24].

3. Results and discussions

Figure 1 shows k^2 weighted arsenic K-edge EXAFS measurements for SmFe1−xRu0.85AsO0.15 (x = 0.0, 0.05, 0.25 and 0.5) at several temperatures. The effect of temperature and Ru substitution is evident from the EXAFS oscillations. For example, temperature dependent damping of the EXAFS signal can be seen for all the samples. Similarly, the effect of Ru substitution can be seen in the EXAFS oscillations (see, e.g., k ≥ 6 Å⁻¹). These effects can be better appreciated in the Fourier transforms (FTs) of the EXAFS, providing real space information on the partial atomic distribution around the As atoms.

Figure 2 shows the FT magnitudes, obtained using a Gaussian window (k-range of EXAFS is 3–18 Å⁻¹). There are four Fe/Ru near neighbours of arsenic at a distance ~2.4 Å (the main peak at ~2 Å). The next nearest neighbours of arsenic are Sm atoms at ~3.3 Å and O/F atoms at ~3.5 Å, followed by the As atoms at ~3.9 Å (the two peaks between 3 and 4 Å), mixed with the multiple scattering contribution due to Fe/Ru (~4.6 Å), appearing as a FT peak at ~4.2 Å (see, e.g., top panel). It can be seen that the main FT peak changes with Ru substitution while the other FT peaks due to next nearest neighbour atoms suffer much smaller (or negligible) changes. Indeed, the main peak decreases substantially with Ru and appears as a clear doublet structure in the x = 0.5 sample. Similarly, the multiple scattering Fe/Ru peak at ~4.2 Å sustains a large change, having negligible weight in...
Figure 2. Fourier transform magnitudes for arsenic K-edge EXAFS at low and high temperatures (symbols) together with As–Fe/As–Ru shell model fits (solid lines) for the SmFe$_1-x$Ru$_x$AsO$_{0.85}$F$_{0.15}$ system. Insets show the filtered EXAFS oscillations (symbols) and the corresponding model fits (solid lines).

The $x = 0.5$ sample. All these data suggest that the atomic disorder due to Ru substitution is mainly confined to the active layer, consistent with an earlier study [19]. On the other hand, the temperature dependent damping of the FT peaks appears almost similar in all the samples.

In the single-scattering approximation, the EXAFS is described by the following general equation [6]:

$$\chi(k) = \sum N_i S_i^2 f_i(k, R_i) e^{-2r_i^{\text{2}}} \frac{\sigma^2}{\bar{E}} e^{-2k^2\sigma^2} \sin[2kR_i + \delta_i(k)] \quad (1)$$

where $N_i$ is the number of neighbouring atoms at a distance $R_i$ from the photoabsorbing atom. Here, $S_i^2$ is the passive electrons’ amplitude 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 $\sigma^2$ is the correlated Debye–Waller factor measuring the mean square relative displacement (MSRD) of the photoabsorber–backscatter pairs.

For As K-edge EXAFS in SmFe$_{1-x}$Ru$_x$As$_{0.85}$F$_{0.15}$, the first shell contribution involves only the Fe–As/Ru–As bonds, well separated from all other distant atom contributions [11, 12, 16, 19]. To quantify the temperature dependent atomic displacements we have analysed the EXAFS due only to the nearest neighbours. The filtered first shell EXAFS oscillations are displayed as insets of figure 2. In the model fits we have varied the Fe–As/Ru–As distances and the corresponding $\sigma^2$, while other parameters including the photoelectron energy origin $E_0$ (a value obtained by modelling five different scans at low temperature), the number of near neighbours $N_i$ (an input from diffraction studies [21, 23]) and $S_i^2 (\sigma^2 = 1.0)$ were all kept fixed for the final iteration. Phase shifts and amplitude factors were calculated using the FEFF [25]. The number of independent data points for this analysis were approximately 11 ($N_{\text{data}} \sim (2\Delta k\Delta R)/\pi$, where $\Delta k = 15 \text{ Å}^{-1}$ and $\Delta R = 1.2 \text{ Å}$ the $k$ and $R$ space over which the data have been analysed) for a maximum of four parameter fits to the filtered EXAFS. The $k$-space (insets) and $R$-space model fits are also included in figure 2. The errors in the local structural parameters, determined by the EXAFS analysis, are estimated by creating correlation maps between different parameters and by the analysis of different scans that are measured in the same conditions, following the known standards [26].

Figure 3 shows near neighbour (Fe–As and Ru–As) distances as a function of temperature, obtained from the EXAFS analysis. The related $\sigma^2$ are shown in figure 4. The Fe–As distance (∼2.39 Å) is different from the Ru–As distance (∼2.42 Å) with the difference (∼0.03 Å) being smaller than that measured in isostructural compounds such as RuAs–FeAs and RuAs$_2$–FeAs$_2$ (∼0.06 Å) [27]. This suggests the active layer in SmFe$_{1-x}$Ru$_x$AsO$_{0.85}$F$_{0.15}$ is under chemical pressure from the REO spacer layer. Within experimental uncertainty the local Fe–As (and Ru–As) distance remains constant with temperature and Ru concentration, consistent with the strongly covalent nature of the Fe–As (and Ru–As) bonds known from earlier studies [13]. It is worth recalling that the reported error bars represent the maximum uncertainty (which is much higher than actual errors in most of the data points)—they are determined by considering the correlation between the fit parameters, i.e., $R_i$ and $\sigma^2$.

The temperature dependence of $\sigma^2$ permits a distinct identification of the random static disorder and the dynamic atomic displacement. The EXAFS’ $\sigma^2$ is the sum of the temperature independent ($\sigma^2_0$) and temperature dependent $\sigma^2(T)$ terms [6], i.e.,

$$\sigma^2 = \sigma^2_0 + \sigma^2(T) \quad (2)$$

The temperature dependent term can be described by the correlated Einstein model [28, 29],

$$\sigma^2(T) = \frac{h}{2\mu\omega_E} \coth \left( \frac{h\omega_E}{2k_B T} \right) \quad (3)$$

where $\mu$ is the reduced mass and $\omega_E$ is the Einstein frequency for the pair of atoms involved (i.e., Fe–As and Ru–As bonds). The related Einstein temperature $\Theta_E = h\omega_E/4k_B$. The fits to the correlated Einstein model are shown as dotted lines in figure 4. $\Theta_E$ for the Fe–As bond is found to be 324 ± 17 K, 323 ± 20 K,
321 ± 24 K and 316 ± 20 K for the x = 0.0, 0.05, 0.25 and 0.5 samples, respectively. The optical phonon modes in SmFeAsO [30, 31] are 201 cm⁻¹ (A₁g involving As atom displacements) and 208 cm⁻¹ (B₁g involving Fe atom displacements). These frequencies are quite similar to the EXAFS findings where the Einstein frequency for Fe–As is about 225 cm⁻¹ (θₑ ∼ 324 K). θₑ for the Fe–As bond is lower than that for the Ru–As bond. θₑ for the Ru–As bond is found to be 353 ± 42 K and 354 ± 26 K for the x = 0.25 and 0.5 samples, respectively. $\sigma_0^2$, representing the random static disorder, is significantly higher for the x = 0.5 sample, ~0.0026 Å², compared to ~0.0006 Å² for the x = 0.0, 0.05 and 0.25 samples. Similar static disorder and force constants (5.09, 5.06, 4.99 eV Å⁻² respectively) for the Fe–As bond in x = 0.0, 0.05 and 0.25 indicate that the atomic disorder in the FeAs layer may not have a direct effect on electronic transport. Indeed, the residual resistivity $\rho_0$ changes anomalously as a function of Ru concentration. $\rho_0$ is ~0.3 mΩ cm for the pure SmFeAsO₀.₈₅F₀.₁₅ system and increases sharply with Ru substitution, reaching a maximum value of about 2 mΩ cm for x = 0.25 while the $T_c$ decreases [21]. With further Ru substitution, $\rho_0$ decreases by half at x = 0.5 ($\rho_0$ ∼ 2 mΩ cm) and has a similar value of $\rho_0$ ∼ 0.3 mΩ cm for x = 1. Therefore, it appears that impurity scattering from substituted...
Ru is dominant in the description of the transport phenomena for $x \leq 0.25$.

On the other hand, the larger static disorder of the Fe–As bonds in the $x = 0.5$ sample ($\sigma_0^2 \sim 0.0026 \AA^2$), albeit with the force constant being similar to the other samples (4.83 eV Å$^{-2}$), suggests that some different mechanism is active in the description of electronic transport, i.e., a decreased $\rho_0$ and $T_c$ for $x \geq 0.25$. In addition, the force constant for the Ru–As distance remains the same for the $x = 0.25$ and 0.5 samples, (6.04 and 6.07 eV Å$^{-2}$, respectively). Therefore, it is likely that the title system is phase separated even at $x = 0.25$, and the reduced $\rho_0$ from $x = 0.25$ and $x = 0.5$ is merely due to the increased density of states with increasing Ru because of the more extended Ru 4d states than Fe 3d states, consistent with density functional theory calculations [21]. It should be mentioned that the active states than Fe 3d states, consistent with density functional

In summary, we have studied the temperature dependent local structure of the SmFe$_{1-x}$Ru$_x$AsO$_{0.55}$F$_{0.15}$ system at varying Ru concentrations using As K-edge EXAFS analysis. We find that the effects of Ru substitution are mainly confined to the electronically active FeAs layer, and the Ru substituted system has different Fe–As and Ru–As distances. The force constants for the Fe–As and Ru–As bonds do not show any change with Ru concentration, indicating coexisting electronic phases in isoelectronic substitution. The static disorder in the Fe–As bonds remains unchanged, as is the bond strength for $x \leq 0.25$, suggesting that the transport properties of the system should be described mainly by the impurity scattering in FeAs layers. With further Ru substitution, the extended Ru 4d states substantially affect the electronic density of states at the Fermi level, and hence the transport phenomena. On the basis of present results we can conclude that on isoelectronic substitution the title system breaks down into coexisting nanoscale electronic phases due to the frustration of interlayer atomic correlations.

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References

[1] 2011 Celebrating 100 years of superconductivity—special issue on iron based superconductors Rep. Prog. Phys. 74 124501
[2] Johnston D C 2010 Adv. Phys. 59 803
[3] Johrendt D, Hosono H, Hoffmann R-D and Pöttgen R 2011 Z. Kristallogr. 226 435
[4] Lee C-H, Iyo A, Ikyo K, Kito H, Shiraage P M and Eisaki H 2012 Solid State Commun. 152 644
[5] Zhao Z, Dong X and Sun L 2011 Solid State Commun. 152 660
[6] Lee C-H, Iyo A, Eisaki H, Kito H, Fernandez-Diaz M T, Ito T, Kihou K, Matsuhashi H, Braden M and Yamada K 2008 J. Phys. Soc. Japan 77 083704
[7] Kuroki K, Usui H, Onari S, Arita R and Aoki H 2009 Phys. Rev. B 79 224511
[8] Vildosola V, Pourovskii L, Arita R, Biermann S and Georges A 2008 Phys. Rev. B 78 064518
[9] Prins R and Koningsberger D C (ed) 1988 X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, XANES (New York: Wiley)
[10] Saini N L, Lanzara A, Oyanagi H, Yamaguchi H, Oka K, Ito T and Bianconi A 1997 Phys. Rev. B 55 12759
[11] Saini N L, Oyanagi H, Lanzara A, Di Castro D, Agrestini S, Bianconi A, Nakamura F and Fujita T 2001 Phys. Rev. B 64 132510
[12] Saini N L, Bianconi A and Oyanagi H 2001 J. Phys. Soc. Japan 70 2092
[13] Oyanagi H, Tsukada A, Naito M and Saini N L 2007 Phys. Rev. B 75 024511
[14] Bianconi A and Saini N L 2005 Struct. Bond. 114 287
[15] Zhang C J, Oyanagi H, Sun Z H, Kamihara Y and Hosono H 2008 Phys. Rev. B 78 214513
[16] Zhang C J, Oyanagi H, Sun Z H, Kamihara Y and Hosono H 2010 Phys. Rev. B 81 094516
[17] Iadecola A, Agrestini S, Filippi M, Simonelli L, Fratini M, Joseph B, Mahajan D and Saini N L 2009 Europhys. Lett. 87 26005
[18] Joseph B, Iadecola A, Fratini M, Bianconi A, Marcelli A and Saini N L 2009 J. Phys.: Condens. Matter 21 432201
[19] Xu W, Marcelli A, Joseph B, Iadecola A, Chu W S, Di Gioacchino D, Bianconi A, Wu Z Y and Saini N L 2010 J. Phys.: Condens. Matter 22 125701
[20] Xu W, Joseph B, Iadecola A, Marcelli A, Chu W S, Di Gioacchino D, Bianconi A, Wu Z Y and Saini N L 2010 Europhys. Lett. 90 57001
[21] Ricci A, Joseph B, Poccia N, Xu W, Chen D, Chu W S, Wu Z Y, Marcelli A, Saini N L and Bianconi A 2010 Supercond. Sci. Technol. 23 052003
[22] Joseph B, Iadecola A, Puri A, Simonelli L, Mizuguchi Y, Takano Y and Saini N L 2010 Phys. Rev. B 82 020502
[23] Joseph B, Iadecola A, Malavasi L and Saini N L 2011 J. Phys.: Condens. Matter 23 112202
[24] Iadecola A, Joseph B, Simonelli L, Mizuguchi Y, Takano Y and Saini N L 2010 Europhys. Lett. 90 67008
[25] Iadecola A, Joseph B, Puri A, Simonelli L, Mizuguchi Y, Testemprale D, Proux O, Hazemann J-L, Takano Y and Saini N L 2011 J. Phys.: Condens. Matter 23 425701
[18] Iadecola A, Joseph B, Simonelli L, Puri A, Mizuguchi Y, Takeya H, Takano Y and Saini N L 2012 J. Phys.: Condens. Matter 24 115701
[19] Iadecola A, Joseph B, Simonelli L, Maugeri L, Fratini M, Martinelli A, Palenzona A, Putti M and Saini N L 2012 Phys. Rev. B 85 214530
[20] Nikitenko S, Beale A M, van der Eerden A M J, Jacques S D M, Leynaud O, O’Brien M G, Detollenaere D, Kaptein R, Weckhuysen B M and Bras W 2008 J. Synchrotron Radiat. 15 632
[21] Tropeano M et al 2010 Phys. Rev. B 81 184504
[22] Sanna S, Carretta P, Bonfà P, Prando G, Allodi G, De Renzi R, Shiroka T, Lamura G, Martinelli A and Putti M 2011 Phys. Rev. Lett. 107 227003
[23] Martinelli A et al 2008 Supercond. Sci. Technol. 21 095017
[24] Ryan D H, Cadogan J M, Ritter C, Canepa F, Palenzona A and Putti M 2009 Phys. Rev. B 80 220503
[25] Mustre de Leon J, Rehr J J, Zabinsky S I and Albers R C 1991 Phys. Rev. B 44 4146
Rehr J J and Albers R C 2000 Rev. Mod. Phys. 72 621
[26] 2000 Error Reporting Recommendations International XAS Society, Standards and Criteria Committee http://ixs.csrrt.iit.edu/IXS/
[27] Heyding R D and Calvert L D 1957 Can. J. Chem. 35 449
Heyding R D and Calvert L D 1961 Can. J. Chem. 39 955
[28] Sevillano E, Meuth H and Rehr J J 1979 Phys. Rev. B 20 4908
[29] See, e.g., a review by Rehr J J and Albers R C 2000 Rev. Mod. Phys. 72 621
[30] Marini C et al 2008 Europhys. Lett. 84 67013
[31] Hadjiiev V G, Iliev M N, Sasmal K, Sun Y-Y and Chu C W 2008 Phys. Rev. B 77 220505R
[32] Laplace Y, Bobroff J, Brouet V, Collin G, Rullier-Albenque F, Colson D and Forget A 2012 Phys. Rev. B 86 020510