

# Study of the electronic and magnetic properties as a function of isoelectronic substitution in $\text{SmFe}_{1-x}\text{Ru}_x\text{AsO}_{0.85}\text{F}_{0.15}$

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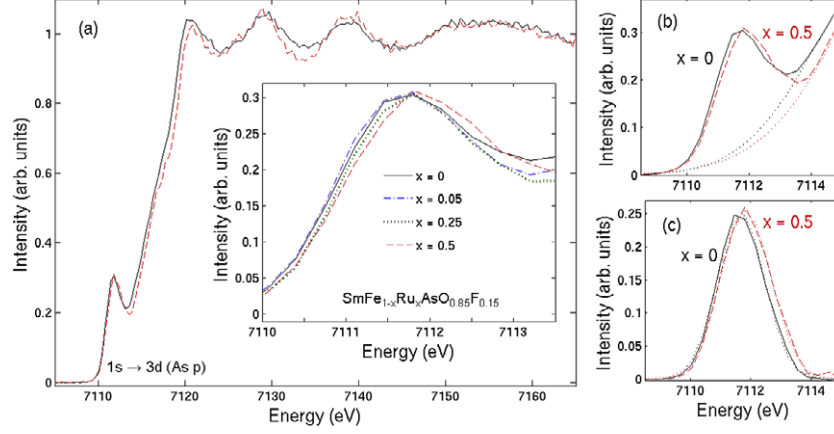
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## 1. Introduction

The recent discovery of iron-based superconductors [1] raises immediate questions about the nature of the unconventional superconducting state and the pairing mechanism. Due to the proximity of superconductivity and magnetism, spin fluctuations were proposed to be the natural candidate for the pairing mechanism [2–7]. In particular, the so-called  $S_{\pm}$  state, in which lattice effects (i.e. electron–phonon coupling) play a minor role, has been in the limelight. The effect of disorder can be a direct probe for the validity of this model, since the superconducting critical temperature ( $T_c$ ) should require to a delicate balance; even a small amount of disorder can be enough to destroy the superconductivity. In particular strong  $T_c$  suppression due to interband impurity scattering is



**Figure 1.** (a) Partial fluorescence yield (PFY) spectra at the Fe K-edge of  $\text{SmFe}_{1-x}\text{Ru}_x\text{AsO}_{0.85}\text{F}_{0.15}$  with different Ru substitution. With increasing Ru, the absorption edge shows a shift towards higher energy. The inset shows a zoom of the pre-peak. (b) Pre-peak for  $x = 0$  and  $0.5$  where the tail of a pseudo-Voigt function describes the background due to the rising edge (dotted curve). (c) Pre-peak for  $x = 0$  and  $0.5$  after the background subtraction. The dotted lines are the fits obtained with a pseudo-Voigt function.

( $x > 0.5$ ) where the system is metallic and the presence of Ru frustrates the magnetic moment on the Fe ions [11]. Instead, the EXAFS data reveal distinct Fe–As and Ru–As bond lengths (coexisting local electronic phases) and increasing local disorder due to Ru substitution confined in the FeAs layer. It has been found that the coupling between the FeAs and the SmO layers gets weaker by increasing the Ru substitution and the FeAs layers get thinner (a smaller As height from the Fe–Fe plane). Interestingly, the short-range static magnetic order recovers with the Ru substitution, revealed by muon spin resonance ( $\mu\text{SR}$ ) measurements [13].

With the aim of obtaining site-specific information on the electronic and magnetic properties, we have employed high-resolution x-ray absorption (XAS) and x-ray emission (XES) spectroscopy to study  $\text{SmFe}_{1-x}\text{Ru}_x\text{AsO}_{0.85}\text{F}_{0.15}$  as a function of Ru concentration. On the basis of XAS and XES, together with the earlier EXAFS [16, 19] results, we could identify different regimes of Ru substitution, characterized by a distinct effect of local disorder. For a small Ru content the Fe local magnetic moment,  $\mu$ , tends to decrease due to impurity scattering as a result of the wide d-band Ru atoms. For larger Ru contents the effect of phase separation prevails, degrading the superconducting ground state due to increased  $\mu$ , consistent with reentrance of static magnetic order [13]. The unusual effect of Ru substitution on the superconductivity and magnetic moment suggests that the  $\text{S}\pm$  model without proper consideration of lattice disorder may not be enough for a realistic description of the electronic and magnetic properties of iron-based materials.

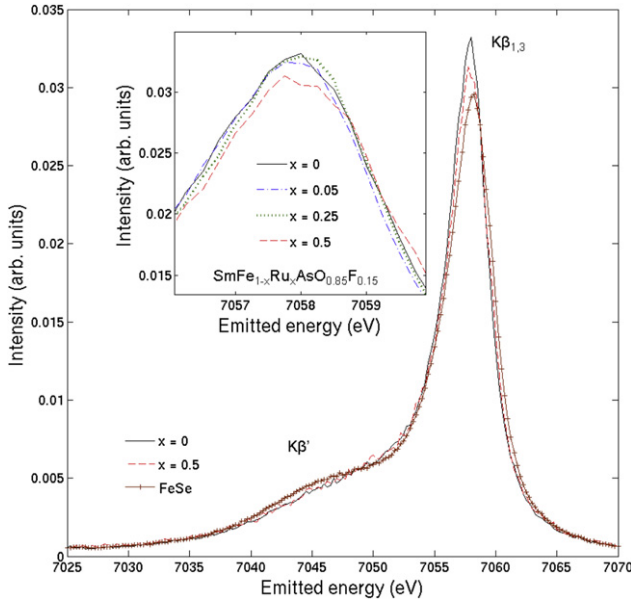
## 2. Experimental details

XES and high-resolution XAS measurements were carried out at room temperature on a series of polycrystalline  $\text{SmFe}_{1-x}\text{Ru}_x\text{AsO}_{0.85}\text{F}_{0.15}$  samples. Details of the sample synthesis and characterization of the transport and structural properties can be found elsewhere [11]. The superconducting  $T_c$  values, determined by resistivity measurements, are 51, 43,

14, 15 and 8 K, respectively, for samples with  $x = 0, 0.05, 0.25, 0.33$  and  $0.5$  [11]. The experiments were performed on the new inelastic x-ray scattering beamline ID20 at the European Synchrotron Radiation Facility. The incident x-rays were monochromatized by a Si(111) double crystal monochromator. The experimental setup consists of a spectrometer based on the use of bent analyser Ge(620) crystals (bending radius  $R = 1$  m) and an avalanche photon diode (APD) detector in Rowland circle geometry. The scattering plane was horizontal and parallel to the linear polarization vector of the incident x-ray beam. The measurements were carried out at room temperature with a total energy resolution of about 1.4 eV full width at half maximum, determined from the quasi-elastic scattering of a thin polymer sample.

## 3. Results and discussion

Figure 1(a) shows the normalized Fe K-edge partial fluorescence yield (PFY) absorption spectra of  $\text{SmFe}_{1-x}\text{Ru}_x\text{AsO}_{0.85}\text{F}_{0.15}$  for different Ru concentrations, obtained by setting the analyser energy to the maximum of the Fe  $K\beta_{1,3}$  emission line and scanning the incident energy across the absorption edge. The spectral sharpening with respect to a conventional XAS spectrum is clearly visible thanks to the reduced lifetime broadening [20, 21]. The spectra are normalized with respect to the atomic absorption estimated by a linear fit far away from the absorption edge. The K-edge absorption process is mainly governed by  $1s \rightarrow \epsilon p$  dipole transitions. The spectra also show a strong pre-peak due to  $1s \rightarrow 3d$  quadrupole transitions into unoccupied Fe 3d states hybridized with As 4p states. The pre-peak is sensitive to the electronic structure, and its energy position, splitting and intensity distribution are known to change with spin state, oxidation state and local geometry [22]. In figures 1(b) and (c) we report the pre-peaks relative to  $x = 0$ , and  $0.5$  before and after the background subtraction. The spectra are typical of  $\text{Fe}^{2+}$  complexes [23, 24] with a symmetric pre-peak at  $\approx 7111.7$  eV, suggesting an almost low spin  $\text{Fe}^{2+}$  state for all the samples studied



**Figure 2.** Fe  $K\beta$  emission spectra of polycrystalline  $\text{SmFe}_{1-x}\text{Ru}_x\text{AsO}_{0.85}\text{F}_{0.15}$  samples [11] for different Ru concentrations. The spectra are normalized to the integrated area and compared with that of FeSe. The inset shows a zoom on the main  $K\beta_{1,3}$  emission line.

[24, 25, 22]. With increasing Ru content, the absorption edge shows an apparent shift towards higher energy (figure 1(a)). This corresponds to an average contraction of near-neighbour bond lengths due to isoelectronic substitution, consistent with earlier studies [16, 19]. The pre-peak profile also shows a clear change with increased spectral weight towards higher energy. This is an indication of increased mixing between the Fe 3d and As 4p states [26, 24]. Furthermore, apparent changes in the features at higher energy are visible due to changes in the local structure induced by the Ru substitution.

Independent and complementary information can be obtained from the Fe  $K\beta$  XES. Figure 2 shows the Fe  $K\beta$  emission line of  $\text{SmFe}_{1-x}\text{Ru}_x\text{AsO}_{0.85}\text{F}_{0.15}$  for different Ru contents. The overall spectral shape is dominated by the (3p, 3d) exchange interactions [20]. In particular, the presence (absence) of a pronounced feature at lower energy ( $K\beta'$ ) is an indication of a high spin (low spin) state of Fe [20]. Also the energy position of  $K\beta_{1,3}$  provides information on the spin state reflecting the effective number of unpaired 3d electrons [20]. By increasing the Ru content, the main  $K\beta_{1,3}$  emission line shifts towards higher emitted energy indicating an increase in the local Fe magnetic moment ( $\mu$ ).

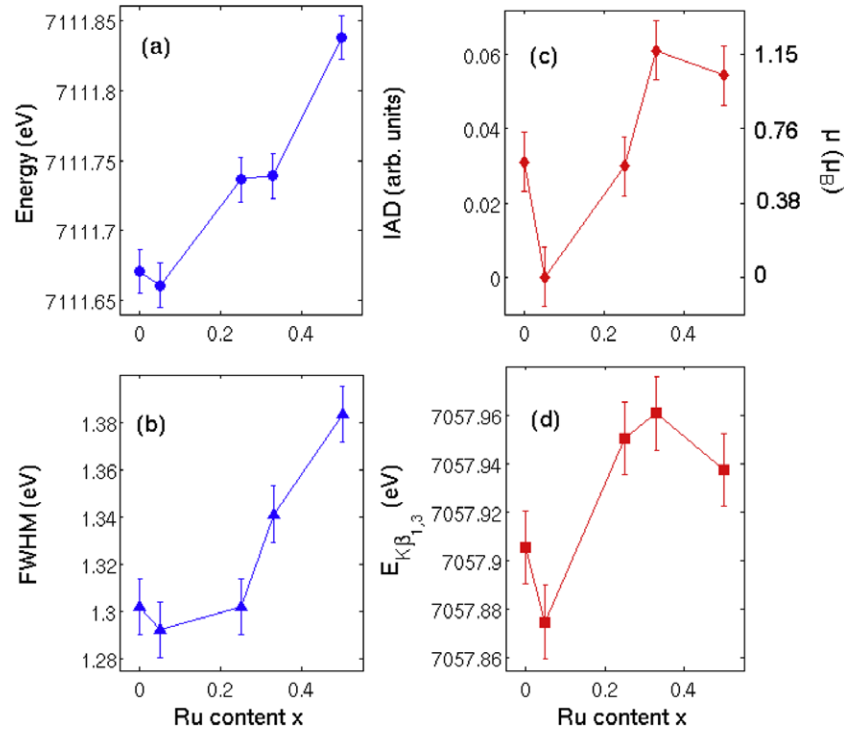
The Fe K-edge XAS and XES were analysed more in detail to quantify the change in the electronic and magnetic properties with the Ru substitution. Figure 3(a) shows the energy of the absorption pre-peak ( $E_{pp}$ ) as a function of Ru content, extracted by a pseudo-Voigt fit. For small values of Ru substitution, the  $E_{pp}$  is almost constant. With further increase of Ru,  $E_{pp}$  shows an increase, indicating an increased mixing of Fe 3d and As 4p states [26, 24]. Since the main absorption edge shifts towards higher energy (figure 1), there is a clear contraction of near-neighbour distances. At the same time, the pre-peak intensity suggests higher mixing of Fe 3d–As

4p, indicating that As atoms are getting nearer to the Fe–Fe plane. We have also shown that the full width at half maximum (FWHM) of the absorption pre-peak (figure 3(b)) remains almost constant before showing an increase for higher Ru concentrations. Again, this is consistent with changing mixing of the Fe 3d–As 4p orbitals with increasing Ru concentration. Indeed, the results are in agreement with those of local structural studies showing [16] thinning of the FeAs layer with increasing Ru substitution.

The increasing pre-peak width also suggests a change in  $\mu$  [25]. It is possible to quantify  $\mu$  from the integrated area of the absolute XES difference with respect to a low spin [27]. Since  $\text{SmFe}_{0.95}\text{Ru}_{0.05}\text{AsO}_{0.85}\text{F}_{0.15}$  seems almost non-magnetic, we have taken it as a reference to obtain the integrated absolute difference (IAD), which is approximately proportional to  $\mu$ . In order to determine quantitative values, we have used the room temperature FeSe  $\mu$  value ( $2 \mu_B$ ) as a reference considering this as a model for an intermediate spin  $\text{Fe}^{2+}$  system. Assuming that  $\text{SmFe}_{0.95}\text{Ru}_{0.05}\text{AsO}_{0.85}\text{F}_{0.15}$  is non-magnetic ( $\mu = 0 \mu_B$ ) we have obtained  $\mu = 0.59 \pm 0.15 \mu_B$  for  $x = 0$  in agreement with earlier theoretical estimates [11]. Figures 3(c) and (d) show the IAD ( $\mu$ ) and the energy position of the  $K\beta_{1,3}$  main line as a function of Ru content. The two quantities are expected to provide the same information and a qualitatively similar trend can be seen. The maximum variation in  $\mu$  turns out to be small ( $\leq 1.15 \mu_B$ ), confirming that the system remains in the low spin state for the whole Ru concentration range.

Comparing the present results with earlier studies [16, 19, 11], different substitution regimes can be identified for Ru contents up to 0.5. For small Ru substitution, the local Fe magnetic moment tends to decrease—which should be due to impurity scattering with the extended d states of Ru. This is consistent with the theoretical calculations revealing broadening of quasiparticle spectral lines due to disorder with the large spatial extent of Ru 4d orbitals having strong implications for the hopping strength [28]. Indeed, the 3D character of the Fermi surface is increased, hence the reduced magnetic moment should mainly be due to the scattering with Ru atoms with extended 4d orbitals. The results are in agreement with the density functional theory (DFT) calculations [12] describing the effect of Ru substitution on the electronic structure of  $\text{SmFe}_{1-x}\text{Ru}_x\text{AsO}_{0.85}\text{F}_{0.15}$ .

On the other hand, while the 3D nature of the band structure continues to enhance with the Ru substitution, there is a clear increase in the Fe local magnetic moment. At the same time, the system becomes phase separated at the nanoscale in coexisting phases, as shown by experiments sensitive to the local structure [16, 19]. In the phase separated system, the FeAs active layers become thinner and decoupled from the spacer layers [16], and an increased local magnetic moment is a natural consequence of this. Therefore, increased magnetic moment should be related to the nanoscale phase separation in RuAs and FeAs-like phases. This is consistent with the reentrance of a local magnetic moment that has been observed in  $\mu\text{SR}$  experiments, providing information on nanoscale phase separation and local magnetic fluctuations [13]. The results are also consistent with earlier XES measurements on the  $\text{FeSe}_{1-x}\text{Te}_x$  system in which nanoscale phase separation due to isoelectronic substitution [29–31] appears to induce an increase in the local magnetic moment [24].



**Figure 3.** (a) Absorption pre-peak energy ( $E_{pp}$ ) as a function of Ru content. (b) Absorption pre-peak full width half maximum (FWHM) as a function of Ru content. (c) Integrated absolute difference (IAD) and (d) energy position of the  $K\beta_{1,3}$  main line as a function of Ru content.

#### 4. Summary

In summary, we have studied the electronic and magnetic properties of the superconducting  $\text{SmFe}_{1-x}\text{Ru}_x\text{AsO}_{0.85}\text{F}_{0.15}$  system by high-resolution XAS and XES measurements. We have found that the local Fe magnetic moment tends to decrease at low levels of Ru substitution, probably due to impurity scattering introduced by extended Ru states. With increasing Ru, a clear increase in  $\mu$  is seen, consistent with a nanoscopic phase separation in this system. The results provide further information on the evolution of electronic and magnetic properties with isoelectronic substitution in 1111-superconductors.

The reported results on the Ru substitution are very unusual if we consider the  $S\pm$  symmetry of the superconducting order parameter, since the sign-changing order parameter survives for a large concentration of strong impurities. Indeed, the superconductivity does not show the expected effect in the  $S\pm$  model in which a small Ru impurity should be enough to break the  $S\pm$  symmetry. In addition, the unusual changes in the local magnetic moment indicate a complex interplay between the magnetism and superconductivity. Nevertheless, the lattice disorder and 4d orbitals seem to have substantial effect on the superconductivity and the magnetic moment. These observations suggest that the lattice and orbital degrees of freedom should be considered for describing properties of the Fe-pnictides. Therefore, in the present form, the  $S\pm$  may not be enough for a proper description of the superconductivity of iron-based materials, and other models taking proper consideration of orbital and lattice fluctuations need further exploration.

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