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X-ray spectra and electronic structures of the iron arsenide superconductors $R\text{FeAsO}_{1-x}\text{F}_x$ (R=La,Sm)

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The electronic structures of undoped and fluorine-doped LaFeAsO superconductors and fluorine-doped SmFeAsO superconductors are studied using soft x-ray absorption and emission spectroscopy combined with full potential linearized augmented planes waves (FP LAPW) calculations. The comparison between the numerical simulations and the experimental Fe L-emission spectra shows that the Fe states are concentrated near E_F, suggesting that the materials are not highly correlated systems. The comparison of the O K-edge and F K-edge spectra with the calculated density of states shows that the F dopants do not directly participate in the electronic structure near E_F, and so they serve the same purpose as an oxygen vacancy leading to an increase in the number of available charge carriers. Increasing the amount of fluorine doped into the structure of SmFeAsO is shown to cause a narrowing of the bandwidth of occupied O valence states.

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The discovery of high-temperature superconductivity [T_c between 25 and 55 K (Refs. 1–7)] and high upper critical magnetic fields [H_{c2} of up to 65 T (Ref. 8)] in $\text{RFeAsO}_{1-x}\text{F}_x$ (Rn=La, Ce, Pr, Nd, Sm, and Gd) has spurred great interest in layered oxypnictides (LnO) (MPn) (where $M=3d$ metals, Pn=P and As). The magnetic $3d$ elements in such a material would normally be expected to produce magnetic moments that give rise to a long-range ferromagnetic order, which would be unfavorable for superconductivity with singlet pairing, and so the mechanism behind the superconductivity is of great interest.

The layered structure of the oxypnictides is similar to that of high-T_c cuprates, with the FeAs plane in the former being analogous to the CuO-based planes in the latter. The Fe ions are arranged in a simple square lattice, and comparison with the cuprate materials leads to the supposition that the superconducting mechanism includes electron hopping in the Fe lattice and doping from an oxide charge reservoir layer. The room-temperature behavior of the two classes of materials differs, however, as the undoped RFeAsO behaves similar to a metal at room temperature, while the cuprates are correlated insulators.

To understand the electronic structure of the superconductors and the interplay between the crystal structure and the magnetic states, first-principles density-functional theory (DFT) calculations in the local-density approximation (LDA) have been performed for the undoped and fluorine-doped LaFeAsO.[9–12] Most of the LDA calculations show a high density of Fe $3d$ states at the Fermi level, whereas previously reported dynamical mean-field theory (DMFT) calculations in the paramagnetic phase, including strong correlation effects beyond LDA, show that for $U=4$ eV, a large amount of that spectral weight is shifted away from the Fermi level.[12] In the present Rapid Communication, we examine the resonant x-ray emission spectra (RXES) at the Fe L edge and nonresonant oxygen and fluorine K emission and absorption spectra of undoped and fluorine-doped LaFeAsO, as well as the oxygen and fluorine K emission and absorption spectra of $\text{SmFeAsO}_{1-x}\text{F}_x$ ($x=0.05$ and 0.15), providing an experimental verification of the distribution of Fe $3d$, O $2p$, and F $2p$ occupied and vacant electronic states.

Polycrystalline samples with nominal composition $\text{SmFeAsO}_{1-x}\text{F}_x$ ($x=0.05$ and 0.15) were synthesized by a conventional solid-state reaction using high-purity SmAs, SmF_3, Fe, and Fe_2O_3 as starting materials. SmAs was obtained by reacting Sm chips and As pieces at 600 °C for 3 h and then 900 °C for 5 h. The synthesis of the $\text{LaFeAsO}_{1-x}\text{F}_x$ ($x=0$ and 0.13) is identical except for the substitution of LaAs and LaF_3 in the starting materials. For a more complete description of the sample preparation see Ref. 4.

The soft x-ray absorption and emission measurements of the fluorine-doped LaFeAsO and SmFeAsO were performed at the soft x-ray fluorescence end station at beamline 8.0.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory.[13] We have measured the resonant and nonresonant Fe $L_{2,3}$ ($3d4s \rightarrow 2p$ transition) and nonresonant F $K\alpha$ and O $K\alpha$ ($2p \rightarrow 1s$ transition) x-ray emission spectra (XES). The instrument resolution for F $K\alpha$ and Fe $L_{2,3}$ x-ray emission spectra was 0.8 eV and for O $K\alpha$ XES, –0.5 eV. X-ray absorption spectra (XAS) were measured in the total fluorescence mode with a resolving power of $E/\Delta E=5000$. All spectra were normalized to the incident photon current using a clean gold mesh in front of the sample to correct for intensity fluctuations in the photon beam.

All band-structure calculations were performed within the full-potential augmented plane-wave method as implemented in the WIEN2K code.[14] For the exchange-correlation potential we used the gradient approximation[15] in the Perdew-Burke-Ernzerhof variant. The Brillouin-zone integrations were performed with a $12\times12\times5$ special point grid and $R_{MT}^{\min}K_{\max}$

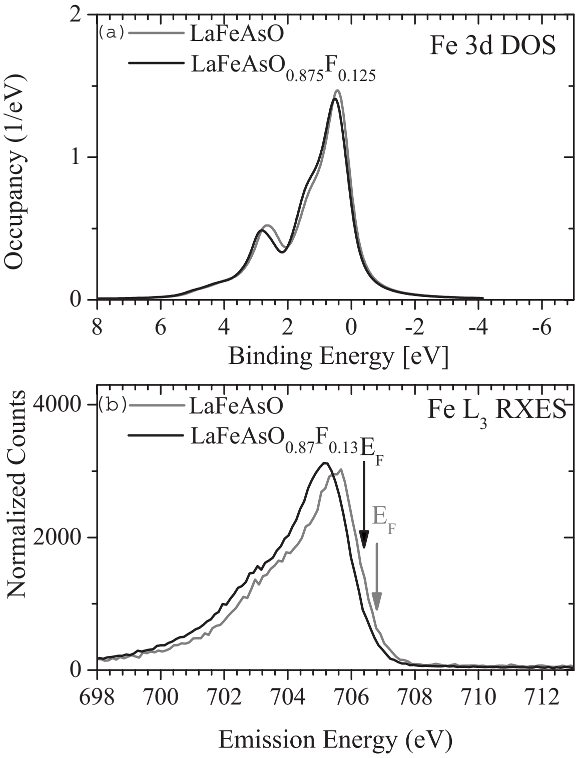

FIG. 1. (a) Fe 3*d* FP LAPW DOS of LaFeAsO and $LaFeAsO_{0.875}F_{0.125}$ and (b) Fe L_3 RXES of LaFeAsO and $LaFeAsO_{0.87}F_{0.13}$ showing relationship of Fe 3*d* states to E_F.

=7 (the product of the smallest of the atomic sphere radii R_{MT} and the plane-wave cut-off parameter $K_{\max}$) was used for the expansion of the basis set. The experimentally determined lattice parameters as well as internal positions of LaFeAsO ($a=4.03007$ Å and $c=8.7368$ Å)[3] were used. The sphere radii were chosen as $R_{\mathrm{Fe}}=2.40$, $R_{\mathrm{As}}=2.13$, $R_{\mathrm{La}}=2.35$, $R_{\mathrm{O}}=2.09$, and $R_{\mathrm{F}}=2.09$ a.u. They were chosen in such a way that the spheres are nearly touching. To calculate the band structure of $LaFeAsO_{7/8}F_{1/8}$, we constructed a $2a \times 2a \times c$ supercell [where a and c are experimentally determined lattice parameters of $LaFeAsO_{0.92}F_{0.08}$ (Ref. 16)] in which one of the oxygen atoms was replaced by a fluorine atom. The resulting unit cell has a lower symmetry than the initial unit cell of LaFeAsO, space group P-4m2 (115). Calculations of the electronic structure of $LaFeAsO_{7/8}$ were performed for the same crystal structure as for $LaFeAsO_{0.92}F_{0.08}$ but with a vacancy in place of a fluorine atom. The inclusion of this vacancy in the supercell does not change its symmetry from that of the previous supercell. For the comparison with the experimental spectra the obtained density of states (DOS) curves were broadened with the Lorentz functions of width 0.3 eV.

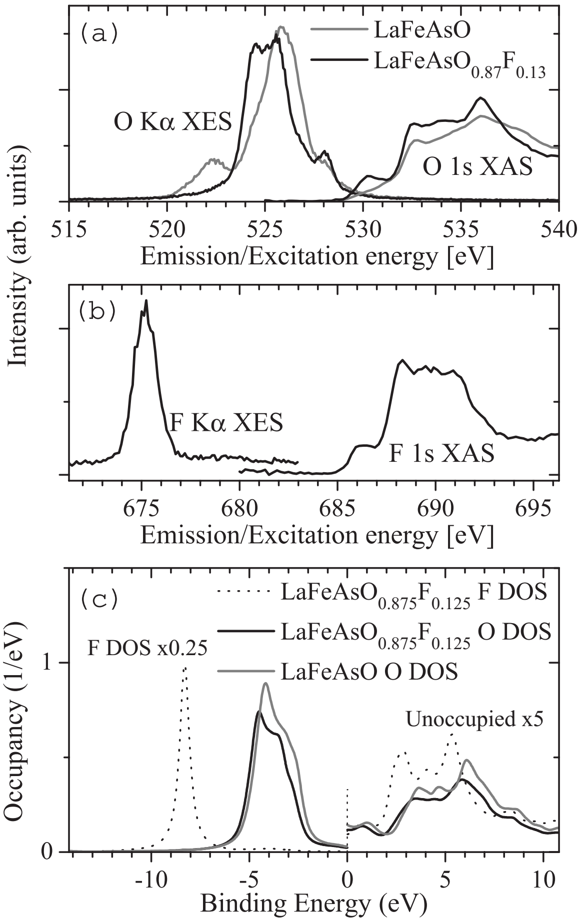

FIG. 2. (a) O-edge and (b) F *K*-edge XES and XAS of LaFeAsO and $LaFeAsO_{0.87}F_{0.13}$ compared to (c) FP LAPW DOS calculations of LaFeAsO and $LaFeAsO_{0.875}F_{0.125}$ showing relative positions of O and F bands.

As seen in Fig. 1(a), the full potential linearized augmented plane waves (FP LAPW) DOS predicts that the Fe bands are concentrated near E_F, in agreement with the LDA calculations reported by Singh *et al.*[9] and Haule *et al.*[12] The arrows marking the locations of the Fermi levels E_F in the measured Fe RXES spectra [Fig. 1(b)] were placed at the top of the Fe 3*d* valence bands; the positions of these points correspond to peaks in the second derivatives of the spectra, which, we have recently shown, can provide an effective means of determining the location of the tops of energy bands from x-ray fluorescence measurements.[17] Using this method, the E_F of LaFeAsO is found to be 706.8 eV, which is the same as the Fe $2p_{3/2}$ binding energy of LaFePO (706.8 eV)[18] determined through x-ray photoelectron spectra (XPS). Lacking XPS data for the Fe $2p_{3/2}$ binding energy of LaFeAsO were assumed that the LaFePO binding energy provided a good approximation of the value, and so this point was aligned to correspond with zero binding energy in Fig. 1(a). This method suggests that the $LaFeAsO_{0.87}F_{0.13}$ E_F occurs at 706.4 eV. Through the comparison with the measured emission spectra, it is seen that the current numerical methods provide an adequate description of the Fe 3*d* DOS and that dynamic mean-field-theory[12] calculations are not needed in describing the measured spectra, casting doubt on the classification of the materials as a highly correlated system. The low-energy shoulders in the 700–704 eV region of the Fe RXES are clearly reproduced in the 2–6 eV region of the FP LAPW DOS calculations. These features are indicative of the hybridization of the Fe sites with the O 2*p* (Fig. 2), As 4*p*, and La 6*p* states (not shown).

Oxygen and fluorine absorption and emission spectra are compared to the calculated O and F densities of states in Fig.

2. The alignment of the spectra with the densities of states is similar to what is discussed above although, unfortunately, no O 1*s* or F 1*s* XPS data are available to aid in the alignment of the spectra with the calculated DOS. We therefore proceed under the assumption that the current model provides an effective representation of the valence-band and conduction-band electronic structures. The numerical simulations show that the onsets of the O and F unoccupied states occur at the same energy, and so the energy axes of the measured spectra were aligned to reflect this. The onsets of the O and F XAS spectra were placed at 529.2 and 685.5 eV, respectively, as indicated by peaks in their second derivatives. The shapes of both XAS spectra agree extremely well with the DOS calculations, suggesting that the core-hole effect is negligible and also supports the accuracy of the current numerical model. The shapes of the O XES are not particularly well represented by the occupied DOS, particularly in the case of the undoped LaFeAsO. The origin of disparity is unclear, although the possible influence of the previously reported[1] LaOF impurity phases cannot be neglected. The low-energy feature of O $K\alpha$ XES at ~522 eV of undoped LaFeAsO may reflect the presence of an impurity carbonate phase [most probably $La_2(OH)_2CO_3$]; however, this feature is absent in O $K\alpha$ XES of $LaFeAsO_{1-x}F_x$. The peaks seen at 528.1 eV may be associated with high-energy satellites or to an underestimation of the degree of hybridization between the O 2*p* and Fe 3*d* states in the DOS calculations.

It is clear from the DOS calculations that the F *p* electrons have very little contribution to the valence states of the $LaFeAsO_{0.85}F_{0.15}$. The F substitution therefore has the same effect as an oxygen vacancy—an increase in the number of carriers in the material. This is reflected in both the numerical simulations and in the measured data. The FP LAPW simulations of the O and F DOSs of $LaFeAsO_{0.85}F_{0.15}$ and $LaFeAsO_{0.85}$ (not shown) are effectively identical, showing that the O DOS in the presence of fluorine doping differs negligibly from that in the presence of an equivalent number of O vacancies. The relationship between the O and F sites in $SmFeAsO_{1-x}F_x$ ($x=0.05$ and 0.15) in Fig. 3 is similar to what is seen in doped LaFeAsO. The spectra in Fig. 3 suggest that aside from inducing a narrowing of the bandwidth of occupied O states, an increase in the amount of F dopant in the material has only a small effect on the electronic structure. The relative positions of the O and F states remain unchanged, save for a shift of −0.3 eV in the location of the F $K\alpha$ XES.

In conclusion we have studied the electronic structure of undoped oxygen-deficient and fluorine-doped FeAs superconductors with RXES and XAS measurements and *ab initio* band-structure calculations. The resonantly excited Fe L_3 x-ray emission spectra show that the occupied Fe 3*d* DOS has a two-part structure with the main feature (approximately 1.5 eV below the Fermi level) formed by pure Fe 3*d* states and a low-energy subband, spanning the region from 2 to 6 eV below E_F formed through hybridization of the Fe 3*d* states with O 2*p*, As 4*p*, and La 6*p* states. Electronic structure calculations performed for $LaFeAsO_{0.85}$ and $LaFeAsO_{0.85}F_{0.15}$ show that oxygen deficiency and fluorine doping have the same effect on the valence-band and conduction-band electronic structures, suggesting that the F electrons do not directly participate in the electronic behavior of the samples; their role is to remove an oxygen site from the structure resulting in an increase in the number of available charge carriers, as is seen in fluorine-doped cuprate semiconductors. This was also shown to be the case in the related superconductors $SmFeAsO_{0.85}F_{0.15}$ and $SmFeAsO_{0.95}F_{0.05}$, the study of which showed that the amount of F doping has a negligible effect on the densities of states of the materials.

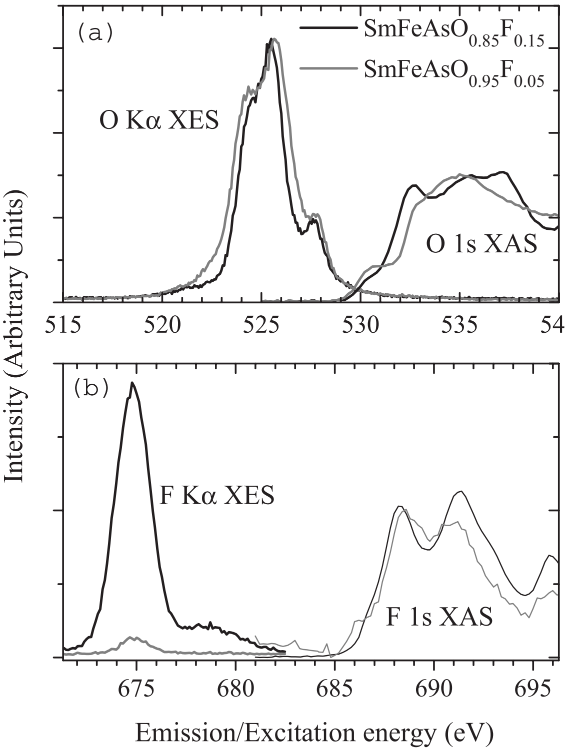

FIG. 3. (a) O and (b) F *K*-edge XES and XAS of $SmFeAsO_{0.85}F_{0.15}$ and $SmFeAsO_{0.95}F_{0.05}$ showing relative positions of O and F bands.

Note added. Recently, several additional publications related to the role of electron correlations in *R*FeAsO compounds have appeared.[19–21] As discussed above, LDA + DMFT calculations[12] suggested that the compounds are highly correlated and close to the Mott transition, while Anisimov *et al.*,[19] using the same interaction parameters present results showing weak correlations. There are similar contradictory results shown in other manuscripts.[20–22] The calculations by Craco *et al.*[20] and Laad *et al.*[21] support a model with strong correlation, while Anisimov *et al.*[22] found strong evidence that FeAs-compounds are poorly correlated materials. Anisimov *et al.*[22] have shown the importance of hybridization of Fe 3*d*-As 4*p* states; accounting for this fact leads to a spectral density of electronic states that does not manifest the typical features of strongly correlated systems: the electron spectrum has no Hubbard bands and Kondo peak at the Fermi level. These results agree quite well not only with our X-ray emission but also with ultraviolet photoemission[23] and x-ray photoelectron valence band spectra.[24] The simple line shape of the XPS Fe 2*p* core-level spectrum of LaFeAsO, without presence of any satellite structure typical for correlated systems, suggests an itinerant character of the Fe 3*d* electrons.[24] Thus, there is increasing evidence that FeAs-compounds are the systems with weak, or perhaps moderate, electronic correlations. The XPS Fe 3*d* and O 1*s* binding energies measured for LaFeAsO[24] are very similar to those which we used for determination of the Fermi level on the iron L- and oxygen K-x-ray spectra.

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