



On the Electronic Structure of Electron Doped LaFeAsO_{1-x}F_x

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We investigated the recently found superconductor LaFeAsO_{1-x}F_x by X-ray absorption spectroscopy (XAS). A shift in the chemical potential is visible in both the Fe *L*_{2,3} and O *K* edge spectra which emphasizes the importance of band effects and moderate correlations in these compounds. From experimental Fe *L*_{2,3} edge spectra and charge transfer multiplet calculations we gain further information on important physical values such as hopping parameters, the charge transfer energy Δ , and the on-site Hubbard *U*. Furthermore we find the system to be very covalent with a large amount of ligand holes.

KEYWORDS: Oxyaptnitides, Spectroscopy, Electronic Structure

Core level spectroscopic measurements such as X-ray absorption spectroscopy (XAS) are appropriate experimental methods to shed new light on the electronic structure of the recently discovered superconductor LaFeAsO_{1-x}F_x¹. In XAS, a core electron is excited into an unoccupied state near the Fermi level, i.e. one probes the empty states. In this article, we present experimental data from Fe *L*_{2,3} and O *K* absorption edges together with theoretical descriptions such as charge transfer multiplet and local density approximation (LDA) calculations. For the presented measurements we chose undoped LaOFeAs and electron doped LaFeAsO_{1-x}F_x polycrystalline samples in a doping range between $x=0.0$ and 0.15 . Polycrystalline samples were prepared as pellets as described in Ref. 2, the XAS signal has been taken by recording the fluorescence signal. Fe *L* and O *K* edge spectra have been normalized at 750 eV and 610 eV, respectively. Further experimental details are given in Ref. 3.

According to the dipole selection rules, the Fe *L*_{2,3} absorption edges correspond to excitations of Fe *2p* core level electrons into unoccupied Fe *3d* electronic states. In Fig. 1(a) the experimental Fe *L*₃ edge XAS spectra for different doping levels are shown. Two main changes appear with F doping. The energy position of the main peak around 708 eV shifts slightly with doping towards lower energies. This shift amounts to ≈ 150 meV on going from $x=0.0$ to $x=0.15$ and can be explained by the observation that the XPS Fe *2p* core level excitations do not shift relative to the chemical potential with doping within the experimental resolution⁴, while the chemical potential shifts by 200 meV with doping from $x=0.0$ to $x=0.2$ ⁵. In other words, this excitation energy as seen in Fig. 1 decreases upon doping.

Moreover, the onset of the *L*₃ edge⁶ shifts to higher photon energies by ≈ 600 meV. Note that such a shift could also cause an asymmetric peak narrowing and affect the position of the peak maxima. A shifted onset is consistent with additional electrons at the Fe sites, which diminishes the number of holes, i.e. the total intensity at the Fe *L*-edge. Therefore, the doped electrons reside (partially) at the Fe

sites, which is supported by valence band photoemission spectroscopy (PES)⁵. The observed shift of the onset of the Fe *L* edge spectra is especially remarkable since it emphasizes the importance of band effects and the absence of strong correlations as they have been observed for e.g. the cuprates. The onset of the spectra shifts monotonically to higher photon energies (see Fig. 1(b)) caused by a shift of the chemical potential as it has been observed by PES measurements⁵.

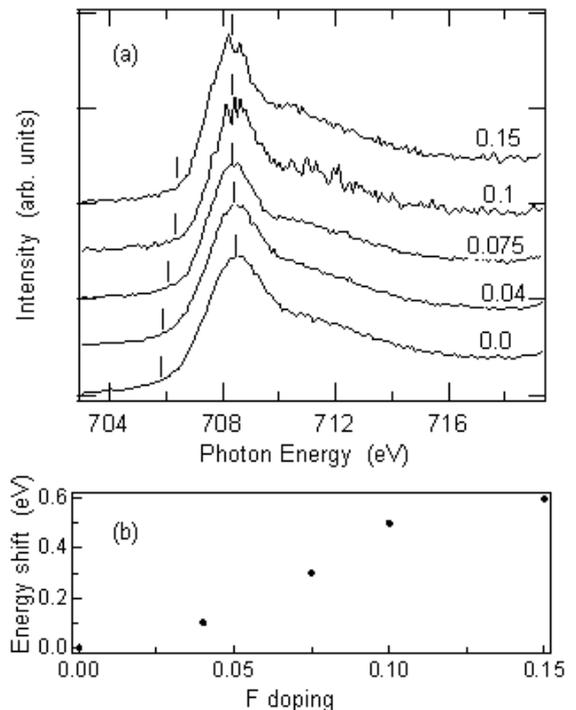


Fig. 1. LaO_{1-x}F_xFeAs: Doping dependence of the Fe *L*-edge. (a) Experimental *L*₃-edge for various doping levels. (b) Shift of the onset of the main peak in eV relative to $x = 0.0$ as a function of F doping x .

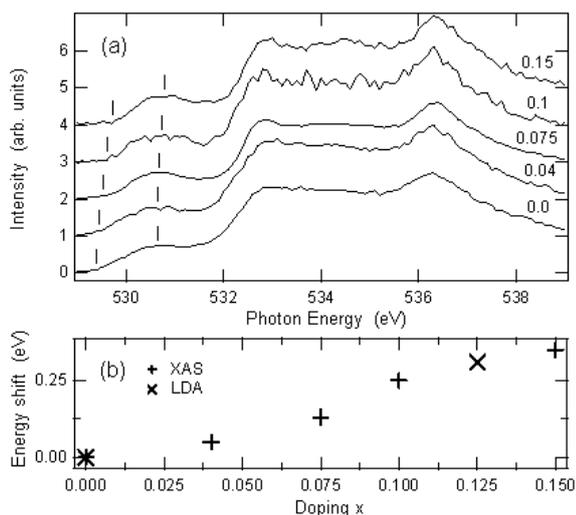


Fig. 2. $\text{LaFeAsO}_{1-x}\text{F}_x$: (a) Doping dependence of XAS O K edge spectra. (b) Energy shift of the onset of the 1st peak as compared to $x=0.0$ for experimental and theoretical results.

Simulations of the Fe $L_{2,3}$ edge require consideration of multiplet splitting, hybridization, and crystal field effects. For further insight, we performed charge transfer multiplet calculations for divalent Fe^{2+} (d^6) in tetrahedral (T_d) symmetry. Note that a band effect such as the shift of the chemical potential is beyond this local approach. The parameter set that reproduces the experimental data best (not shown here, e.g. Ref. 3) is $10Dq=0.2$ eV, $\Delta=E(d^7\bar{L})-E(d^6)=1.25$ eV (\bar{L} denotes a ligand hole), $U=1.5$ eV, and $pd\pi=0.27$ eV. The core hole potential Q is normally about 1-2 eV larger than U and has been set to $Q=U+1$ eV. The Slater-Condon parameters have been reduced to 80% of their Hartree-Fock values as it is reasonable in solids, which leads to the two Hund's couplings $J_{eg}=0.90$ eV and $J_{2g}=0.78$ eV for the ground state. Such a parameter set leads to a highly covalent system and a high spin state of $S=2$. The shoulder at ≈ 712 eV is provoked by charge transfer effects and emphasizes the hopping values above. Since the core hole potential is rather small ($Q=2.5$ eV), the excited states are not shifted far out of the Fe $3d$ band⁷⁾, and therefore band effects become visible in the experimental spectra.

A second edge that is worth to investigate is the O K edge. Note that the O ions are located within the $\text{LaO}_{1-x}\text{F}_x$ layer, and therefore do not behave like ligands at the transition metal ion contrary to cuprates or cobaltates. In Fig. 2(a), O K edge spectra for different doping levels are shown for photon energies between 529 and 539 eV. This region can be assigned to excitations from the O $1s$ core level into unoccupied O $2p$ states. In the XAS spectra, the onset of the 1st peak shifts by 350 meV towards higher photon energies with doping⁶⁾, whereas the 1st peak itself (at 531 eV) shifts only by ≈ 100 meV and the 2nd peak (at 532.7 eV) does not shift.

When comparing the experimental spectra to the partial density of states (PDOS) as gained from LDA calculations, one observes that the overall agreement is good³⁾, and LDA is able to explain all main features, and assign the 1st peak to hybridizations between O and Fe states and the 2nd peak to

hybridizations between O and La states. From X-ray photoemission spectroscopy (XPS) experiments⁵⁾ it has been observed that the La $4d$ level shifts relative to the chemical potential by about 200 meV from $x=0.0$ to $x=0.1$ while the As $3d$ level hardly shifts. This can be ascribed to a change of the Madelung potential between the As and La layers upon doping, in agreement with O K XAS. When focussing on the onset of the 1st peak, i.e. on the change in the chemical potential, a clear doping dependence is observed. This is further illustrated in Fig 2(b) where the shift of the onset of the 1st peak as compared to $x=0.0$ is shown. Such an increase is supported by the PDOS since the shift in the onset of the 1st peak between $x=0.0$ and $x=0.125$ matches well the slope found from the experimental data. This agreement between theory and experiment stresses the observation that the experimental O K edge is strongly affected by the shift of the chemical potential with doping. Furthermore, in LDA no on-site Hubbard U is taken into account. When switching it on at the Fe site, this will have an effect on the energetic position of the Fe $3d$ spectral weight. As the relative position of the O K XAS peaks matches those determined by LDA calculations within one eV, the on-site Hubbard U can be expected not to be significantly larger than the band width. Note that the strong electronic correlations in cuprates such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_2$, are clearly visible in the O K absorption edges⁸⁾.

In summary, from X-ray absorption spectroscopy measurements together with LDA and charge transfer multiplet calculations, deeper insight into the electronic structure of $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ has been proposed. The O K -edge is well described by LDA calculations. The shift in the chemical potential is clearly visible in the absorption edge. Furthermore, the band width could be assigned as an upper limit of the on-site Hubbard U .

Band effects have a significant influence also on the shape of the Fe L edge absorption spectra. A shift in the chemical potential towards higher energies is observed in agreement with the results of the O K edge, which stresses the existence of a moderate (or low) Hubbard U . Further valuable information could be extracted from Fe $L_{2,3}$ absorption edge together with charge transfer multiplet calculations in tetrahedral symmetry. The low Hubbard U fits to the upper bound as concluded from the comparison between O K -edge XAS spectra and DOS. Furthermore, due to small values of the charge transfer energy Δ and the Hubbard U the system turns out to be very covalent.

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