On the electronic structure of electron doped LaOFeAs as seen by X-ray absorption spectroscopy

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(Dated: June 19, 2008)

We investigated the recently found superconductor LaO$_{1-x}$F$_x$FeAs by X-ray absorption spectroscopy (XAS). From a comparison of the O $K$-edge with LDA calculations we find good agreement and are able to explain the structure and changes of the spectra with electron doping. An important result from this edge is a limitation of the Hubbard $U$ to values not significantly larger than 1 eV. 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 $\Delta$, and the on-site Hubbard $U$. Furthermore we find the system to be very covalent with a large amount of ligand holes. A shift in the chemical potential is visible in the O $K$- and Fe $L_{2,3}$-edge spectra which emphasizes the importance of band effects in these compounds.

Recent reports of superconductivity in LaO$_{1-x}$F$_x$FeAs [1, 2] stimulated enormous scientific efforts. In fact, a large oxypnictides family Ln(0$_{1-x}$F$_x$)FeAs (Ln=La, Ce, Pr, Nd, Sm, Gd) has been found to be superconducting with a transition temperature up to 55 K [3, 4, 5, 6, 7] and high upper critical fields [8]. These compounds are particularly interesting as the first example of possible unconventional superconducting gap like gap [18]. Electronic structure calculations within the local–density–approximation (LDA) show a high density of states near the Fermi level, whereas the density of states for all other ions is low [3, 6, 7, 8, 9].

In order to gain a better understanding of these new compounds, various experiments and theoretical calculations have been carried out. Possible unconventional multiband behavior [5, 10] and evidence for gap nodes [11, 12] have been considered from experiments and theoretical studies, while various scenarios for the superconducting mechanism have been discussed [3, 4, 13, 14]. Nuclear Magnetic Resonance (NMR) measurements find evidence for line nodes in the superconducting gap and spin–singlet pairing in the superconducting state [17] while Andreev spectroscopy finds a single nodeless BCS like gap [18]. Electronic structure calculations within the local–density–approximation (LDA) show a high density of Fe 3d states near the Fermi level, whereas the density of states for all other ions is low [3, 6, 7, 8, 9]. LDA plus dynamical–mean–field–theory (DMFT) as well as LDA calculations that include Hubbard’s $U$ conclude an intermediate strength of $U \sim 1$ eV and Hund’s exchange coupling $J_H \sim 0.3 - 0.9$ eV at the Fe site [3, 20, 21, 22, 23, 24, 25], and the undoped system has been predicted to exhibit a bad metallic behavior [21, 26].

Core level spectroscopic measurements such as X-ray absorption spectroscopy (XAS) are appropriate experimental methods to shed new light on this topic. In XAS, a core electron is excited into an unoccupied state near the Fermi level, i.e. one probes empty states. Combined with a theoretical description that takes the core hole and other contributions properly into account, it can provide valuable information on the electronic structure of the investigated system, such as the Hubbard $U$, the charge transfer energy $\Delta$, Hund’s coupling $J$, or the electronic hopping parameters. In this article, we present experimental data from O $K$- and Fe $L_{2,3}$-absorption edges. For these measurements we chose undoped LaOFeAs and electron doped LaO$_{1-x}$F$_x$FeAs polycrystalline samples in a doping range between $x = 0.0$ and 0.15. These data will be discussed and compared to LDA calculations as well as to Fe 3d charge transfer multiplet calculations.

Polycrystalline samples of LaO$_{1-x}$F$_x$FeAs were prepared as pellets as described in Ref. [27] and consist of 1 to 100 $\mu$m sized grains of LaO$_{1-x}$F$_x$FeAs. Their X-ray absorption spectroscopy studies at the O $K$- and Fe $L_{2,3}$-edge were performed at the PM3 beamline of the synchrotron radiation source Bessy II. The energy resolution was set to 180 and 300 meV at 530 and 710 eV photon energy, respectively. Data were recorded by measuring the fluorescence signal. Compared to electron yield data, the penetration depth is larger for fluorescence which is more preferable in this case. In order to obtain appropriate surfaces, the pellets were filed in-situ in a vacuum environment of $1 \times 10^{-7}$ mbar and measured at $1 \times 10^{-8}$ mbar.

In Fig. 1(a) O $K$-edge spectra are shown for photon energies between 529 and 539 eV. This region can be assigned to excitations from the O 1s core level into un-
occupied O 2p states. In the XAS spectra the onset of peak (1) shifts by 0.35 eV towards higher photon energies with doping [28], whereas peak (1) itself shifts only by ≈100 meV and peak (2) (and also peak (4)) do not shift. From X-ray photoemission spectroscopy (XPS) experiments [29] 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.

Further insight is gained from LDA calculations [10] as shown in Fig. 1(b) and (c) for different doping level. The oxygen $p$-projected density of states (PDOS) has been broadened by a Gaussian with FWHM of 0.18 eV and a Lorentzian with FWHM of 0.2 eV. From the LDA PDOS, peak (1) can be ascribed to a hybridization of O states with Fe 3d states and peak (2) to hybridization with La 4f states. The position of peak (1) essentially measures the Madelung potential at the Fe layers, while the position of peak (2) is related to the Madelung potential at the La layer. One effect of doping is a change in the Madelung potentials. According to LDA, the Madelung potential for La sites should hardly change as compared to the O site, whereas for Fe it leads to a shift of peak (1) towards higher energies, which is corroborated by the XAS data at the O K–edge. A second and more important effect with electron doping is a shift of the chemical potential due to a change in the carrier number. By this, the onset of peak (1) is further shifted to higher energies as compared to the La peak.

When comparing the experimental and theoretical results, one observes first of all that the overall agreement is good, which tells that apparently the core hole effect in the absorption process is small. Therefore a direct interpretation of XAS measurements in terms of the partial unoccupied density of states is possible, analogous to a one electron addition process [30]. Note that the energies as given in Fig. 1(a) and (b,c) correspond to different reference values. In XAS the photon energy relates to the energy difference between the core level and the unoccupied states, whereas in the DOS the energy difference between the Fermi level and the unoccupied states is given. For the sake of clarity the energy regions in Fig. 1(b) and (c) are chosen in such a way that peak (2) aligns with the experimental data. When focussing on the onset of peak (1), i.e. on the change in the chemical potential, a clear doping dependence is observed. This is illustrated in Fig. 1(d) where the shift of the onset of peak (1) as compared to $x = 0.0$ is shown. Such an increase is supported by the PDOS since the shift in the onset of peak (1) between $x = 0.0$ and $x = 0.125$ matches well to 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 1 eV. Note that the strong electronic correlations in cuprates such as La$_{2–x}$Sr$_x$CuO$_2$, are clearly visible in the O K–absorption edges [31].

In order to gain more information on the electronic structure of this system, XAS experiments at the Fe $L_{2,3}$–edge have been performed. According to the dipole selection rules, the Fe $L_{2,3}$ absorption edges correspond to excitations of Fe 2p core level electrons into unoccupied

FIG. 1: (Color online) LaO$_{1–x}$FeAs: (a) Doping dependence of XAS O K–edge spectra. The spectra have been normalized at 610 eV where they become structure less and doping independent. (b) and (c) Oxygen $p$–projected partial density of states for $x = 0.0$ and $x = 0.125$. (d) Energy shift of the onset of peak (1) as compared to the undoped sample for experimental and theoretical results.
Fe 3d electronic states. Upon variation of the energy of the incident light, different Fe 3d orbitals can be probed [32]. Contrary to what occurs at the O K-edge, core holes cannot be neglected for Fe 3d excitations. Therefore, simulations of the Fe L2,3-edge require consideration of multiplet splitting, hybridization, and crystal field effects. Fe L2,3-edge experimental data have been taken by recording the fluorescence yield and corrected for a self-absorption process in the fluorescence signal [33]. Self-absorption is stronger at the L3 edge, which cannot be fully corrected and thereby the L3-edge intensity will be somewhat underestimated as compared to the L2-edge. All data have been normalized at 750 eV where the signal corresponds to excitations into continuum states.

In Fig. 2(a) and (b) the experimental Fe L3-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 \( \approx 150 \text{ meV} \) 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 resolution [34], while the chemical potential shifts by \( \approx 200 \text{ meV} \) with doping from \( x = 0.0 \) and \( x = 0.2 \) [29]. In other words, this excitation energy as seen in Fig. 2 decreases upon doping. Moreover, the onset of the L3-edge [28] shifts to higher photon energies by \( \approx 600 \text{ meV} \), similar to the O K-edge. Such a shift could also cause an asymmetric peak narrowing and affect the position of the peak maxima. In Fig. 2(a) a blowup of the low energy side of the L3-peak is shown. Note that for the sake of clarity, the spectra only in Fig. 2(a) were shifted to the same energy of their 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) on the Fe sites. These findings are supported by valence band photoemission spectroscopy. When doping with electrons, an increase in intensity just below the Fermi energy where the Fe states are located has been observed [25]. Since the conduction band is partially filled, this shift leads to the experimentally observed effect on the Fe L2,3-edge and emphasizes the importance of band effects on the absorption edge in these compounds. Similar to what has been observed at the O K-edge, the onset of the spectra shifts monotonically to higher energies (see inset in Fig. 2(b)) and stresses the shift of the chemical potential as the origin of both effects.

Although As is formally As\(^{3-}\), its 4p shell is not completely filled due to hybridization with the Fe 3d shell. The radial function of 4p states is far ranging compared to the 2p states of O as in copper oxides. Therefore, a large overlap of the wave functions between Fe and As occurs which leads to a strong hybridization and a further delocalization of the Fe 3d electrons. With F doping delocalized additional charge is introduced into this layer. When looking at the crystal structure, the FeAs layers consist of Fe ions on a square lattice that are tetrahedrally surrounded by four As ions. These As tetrahedra are slightly tetragonally distorted which reduces the local symmetry from \( T_d \) to \( S_4 \). The crystal field splitting \( 10Dq \) has been predicted to be rather small (\( \sim 0.25 \text{ eV} \)) [9, 21, 24]. From LDA plus DMFT calculations the \( d_{x^2-y^2} \) and \( d_{3z^2-r^2} \) orbitals have been found to be still degenerate [26], and the \( E_{g}/T_d \) splitting to be dominant over the tetragonal distortion. Therefore, it is reasonable to use \( T_d \) local symmetry as a starting point for simulations of the Fe L-edge. In an X-ray absorption excited state, a 2p core hole has been created which interacts with valence electrons via Coulomb interactions. Its energy scale is in the range of a few eV and leads to an additional multiplet splitting [35]. This interaction justifies a local description also of a metallic system as long as it is strong enough to lift the excited states out of the conduction band.

![Figure 2](image_url)
In order to interpret the experimental data further, we performed charge transfer multiplet calculations for divalent Fe$^{2+}$ (3d$^6$). The calculations have been done for $T_d$ symmetry and the hopping relation $V_e = \frac{1}{2} V_L$, assuming the relation $pd\sigma = -\frac{\sqrt{3}}{2} pd\pi$. Note that a band effect such as the shift of the chemical potential is beyond this local approach. In Fig. 2(c) a comparison of the XAS fluorescence data and charge transfer multiplet calculations is shown. The agreement between experiment and theory at the $L_{2,3}$–edge is good. Note that the intensity of the $L_{2}$–edge is overestimated by the self-absorption correction. The parameter set that reproduces the experimental data best is $10Dq = 0.2\,\text{eV}$, $\Delta = d^7L - d^6 = 1.25\,\text{eV}$ ($L$ denotes a ligand hole), $U = 1.5\,\text{eV}$, and $|pd\pi| = 0.27\,\text{eV}$. The core hole potential $Q$ is normally about $1 - 2\,\text{eV}$ larger than $U$ and has been set to $Q = U + 1\,\text{eV}$. 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 $J_{eg} = 0.90\,\text{eV}$ and $J_{t2g} = 0.78\,\text{eV}$ for the ground state. The shoulder at $\approx 712\,\text{eV}$ is provoked by charge transfer effects and emphasizes the hopping values above. A square band containing 5 states and a bandwidth of 2.5 eV for the ligand hole state has been added in the charge transfer calculations. The multiplet intensities have been broadened by a Gaussian (0.3 eV) and a Lorentzian (0.6 eV at $L_3$ and 0.8 eV at $L_2$ due to different lifetime broadenings). Since the core hole potential is rather small ($\approx 2.5\,\text{eV}$), the excited states are not shifted far out of the Fe 3d band at $\approx 2\,\text{eV}$ above the Fermi energy, and therefore band effects become visible.

When writing the wave function as a sum of three configurations with different ligand holes $\psi = ad^6 + bd^7L^1 + cd^8L^2 (a^2 + b^2 + c^2 = 1)$, the hole occupation can be given. Using the parameters as written above, it follows that $a^2 = 0.558$, $b^2 = 0.393$, and $c^2 = 0.049$. For all possible parameter sets, a high spin situation $S = 2$ has been determined in agreement with LDA+DMFT. The energy difference to the intermediate spin state $S = 1$ is $\approx 0.4\,\text{eV}$ which is enough to omit the role of this latter state. This can be understood by the small values of the crystal field and hopping parameters. A low ligand field splitting involves the filling of energy levels following Hund’s rule and forces the system into a high spin configuration.

In summary, from X-ray absorption spectroscopy measurements together with charge transfer multiplet and LDA calculations, deeper insight into the electronic structure of LaO$_1-x$F$_x$FeAs has been proposed. The O $K$–edge is well described by LDA calculations. The influence of the Madelung potential on different ions coincides in both experimental and theoretical spectra. The shift in the chemical potential is clearly visible in the absorption edge. Furthermore, an upper limit of the on-site Hubbard $U$ could be assessed to $\approx 1\,\text{eV}$.

Band effects have a significant influence also on the shape of the experimental 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 low Hubbard $U \approx 1\,\text{eV}$. Further valuable information could be extracted from Fe $L_{2,3}$–edge absorption spectroscopy together with charge transfer multiplet calculations in $T_d$ symmetry. The extracted parameter set appears to be similar to what has been suggested from DFT calculations, especially the low crystal field splitting and the small hopping parameters. 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 $\Delta$ and the Hubbard $U$ the system turns out to be very covalent similar to what has been predicted from DFT calculations.

This investigation was supported by the DFG (SFB 463 and KR 3611/1-1) and DFG priority program SPP1133.
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