



Correlated Electronic Structure of $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$

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We compute the electronic structure, momentum resolved spectral function and optical conductivity of the new superconductor $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ within the combination of the density functional theory and dynamical mean field theory. We find that the compound in the normal state is a strongly correlated metal and the parent compound is a bad metal at the verge of the metal insulator transition. We argue that the superconductivity is not phonon mediated.

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In the Bardeen-Cooper-Schrieffer theory of superconductivity, electrons form Cooper pairs through an interaction mediated by vibrations of the crystal. Like lattice vibrations, antiferromagnetic fluctuations can also produce an attractive interaction creating Cooper pairs, though with spin and angular momentum properties different from those of conventional superconductors. Such interactions were implicated for class of heavy fermion materials based on Ce, U, and Pu with rather low transition temperatures, and cuprate superconductors with the highest known transition temperatures. Recently a surprising discovery of superconductivity in the iron-based compound $\text{LaO}_{1-x}\text{F}_x\text{FeP}$ [1] with $T_c \sim 7$ K sparked a new direction to explore superconductivity in a completely new class of materials. Very recently a substitution of P by As raised T_c to 26 K [2] becoming already one of the superconductors with the highest T_c among noncuprate based materials. Exploring superconductivity in similar iron-based compounds holds a lot of promise for increasing T_c .

In this Letter we explore the electronic structure and optical properties of $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ within density functional theory (DFT) and dynamical mean field theory (DMFT).

LaOFeAs has a layered tetragonal crystal structure shown in Fig. 1. Layers of La and O are sandwiched between layers of Fe and As. The Fe atoms form a square two dimensional lattice with Fe-Fe lattice spacing of 2.853 Å. To understand the material properties, it is important to identify the character of dominant bands near the Fermi level, their energy and momentum distribution. For this purpose, the first principles density functional theory is the invaluable tool. We used the full-potential augmented plane-wave method as implemented in the WIEN2K code [3]. The lattice parameters and internal atomic positions have been determined experimentally ($a = 4.035$, $c = 8.741$, $z_{\text{La}} = 0.142$, $z_{\text{As}} = 0.651$). For the exchange correlation potential we used the generalized gradient approximation [4] (GGA) in the Perdew-Burke-Ernzerhof variant, and $12 \times 12 \times 5$ k points.

This method predicts that the dominant states at the Fermi level come from Fe 3d atomic states extending roughly between -2 eV and 2 eV as shown in Fig. 2.

The important feature of LaOFeAs compound is that DFT predicts a very steep and negative slope of the density of states (DOS) at the Fermi level. In the rigid band approximation, neglecting the many body effects, the hole doping will lead to increases of the DOS at the Fermi level, while the electron doping will be accompanied by a decrease of DOS. Hence, for the conventional phonon mediated superconductor, one would expect decrease (increase) of T_c when doping electrons (holes), contrary to what is observed in experiment [2]. This gives a clear hint that the superconductivity in this compound might not be phonon mediated. Indeed an explicit calculation of the phonon coupling constants within the DFT, using the code of Ref. [5], gives a value too small to explain the observed critical temperature ($T_c < 1$ K).

While the dominant electronic character near the Fermi level is due to Fe, a strong mixing with As is apparent at -2.7 eV, where the As 4p band is strongly peaked. There

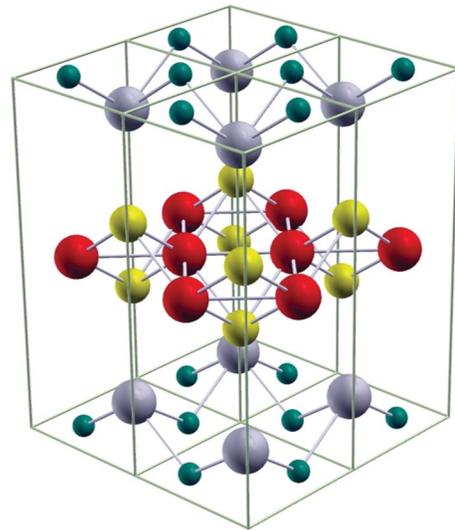


FIG. 1 (color). Crystal structure of LaOFeAs . The middle layer consists of Fe atoms (red spheres) which form a two-dimensional square lattice and As atoms (yellow). The second plane consists of O (green) and La (gray) atoms. We use the two unit cell coordinate system to describe the orbital character in Fig. 3.

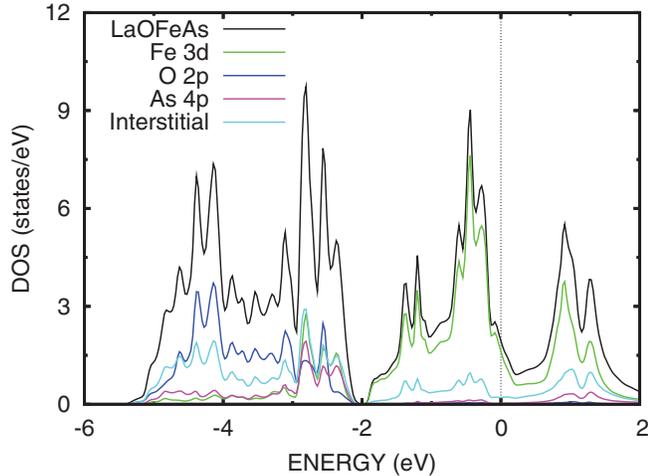


FIG. 2 (color). Density of states within the GGA approximation. The partial character of Fe, O, and As is shown separately. Because of the presence of As, a lot of electronic charge is found in the interstitial regions and cannot be assigned an atomic character.

is a noticeable similarity between the Fe-As mixing and oxygen-transition metal mixing in transition metal oxides. However, there is an important difference between the two. The As bands are much more itinerant and broader than oxygen $2p$ bands. Consequently, plenty of As electronic charge is found in the interstitial region far from any of the constituting atoms, which is shown separately in Fig. 2.

While the crystal field splitting in most transition metal oxides leads to a clear separation of transition metal d bands into the t_{2g} and e_g part, this is not the case in LaOFeAs due to the itinerant character of As. All five Fe- d bands, therefore, participate in the bonding and in the Fermi surface of the compound.

Within DFT, the parent compound is very close to a magnetic instability and at normal pressure DFT selects a ferromagnetic or an antiferromagnetic state. The ferromagnetic moment is very small (of the order of $0.15\mu_B$) and the ferromagnetic state becomes unstable for a 10% compressed solid.

The bandwidth of the iron $3d$ bands is only around 3 eV while the Coulomb repulsion in this orbital is around 4 eV [6]. For a single band system with this bandwidth and Coulomb repulsion, one would expect a Mott insulating ground state. On the other hand, the perfectly degenerate system with five degenerate d bands would still be below the Mott transition, since the critical U for the disappearance of the Fermi liquid solution within DMFT is proportional to N , where N is the band degeneracy of the system (in case of d electrons 5). The five d bands of Fe in LaOFeAs are not perfectly degenerate, but one would still expect a relatively large critical U for the Mott transition for the odd number of electrons in the d band. In the parent compound LaOFeAs, the number of d electrons is 6. The Coulomb repulsion can strongly enhance the splitting between the bands [7] and the gap can open at the Fermi

level. This interplay of crystal field splitting and correlation effects was addressed in many model Hamiltonian studies [7–9] and it was shown how a bad metal or bad semiconductor can appear on the metallic side at finite temperature. In LaOFeAs we checked that a slightly enhanced Coulomb repulsion ($U = 4.5$ eV) leads to a finite gap in the d band. For typical Coulomb repulsion of Fe ($U = 4$ eV) the system is still metallic, but a bad metal having some characteristics of a bad semiconductor. The metallic state is however still very correlated with a quasiparticle renormalization amplitude between $Z \sim 0.2$ – 0.3 .

To describe this type of system, one needs to go beyond the traditional band structure methods and concentrate on the spectral function $A(\mathbf{k}, \omega)_{LL'}$ of the system, which describes the probability to add or remove an electron with momentum \mathbf{k} , angular momentum $L = (l, m)$ and energy ω .

To compute the spectral function of LaOFeAs, we used dynamical mean field theory (DMFT) [10,11] which takes into account the strong Coulomb repulsion among the correlated set of bands and can describe the dual nature of the electrons in correlated compounds, namely, the itinerant part of spectra which forms narrow quasiparticle bands at low energy, and the localized part of spectra at higher energy, which correspond to the nearly localized atomic nature of the electron. In this method, the spectral function is obtained from the one electron Green's function $A(\mathbf{k}, \omega) = (G^\dagger(\mathbf{k}, \omega) - G(\mathbf{k}, \omega))/(2\pi i)$ where the latter takes the form

$$G(\mathbf{k}, \omega) = \frac{1}{O_{\mathbf{k}}(\omega + \mu) - H_{\mathbf{k}} - \Sigma(\omega)}. \quad (1)$$

The one electron part of the Hamiltonian $H_{\mathbf{k}}$ and overlap matrix $O_{\mathbf{k}}$ is obtained by the LDA method [12] while the self-energy is computed by solving an auxiliary quantum impurity problem embedded in a self-consistent medium, for which we used the numerically exact continuous time quantum Monte Carlo method [13]. The on-site Coulomb repulsion on Fe- $3d$ bands is estimated to be 4 eV [6] and the Hund's coupling of $J = 0.7$ eV. The temperature is fixed at 116 K.

The local spectral function $A(\omega) = \sum_{\mathbf{k}} A(\mathbf{k}, \omega)$ at temperature $T = 116$ K is shown in Fig. 3(a) together with the corresponding LDA density of states. The DMFT approach predicts a renormalized low energy band with a fraction of the original width ($Z \sim 0.2$ – 0.3) while most of the weight is transferred into a broad Hubbard band at the binding energy ~ -4 eV. The system remains metallic at finite temperatures but a very bad metal with a scattering rate at the Fermi level as high as 0.4 eV at 116 K. With decreasing temperature the Fermi surface shrinks and the semiconducting gap is likely to open at zero temperature. Indeed slightly enhanced Coulomb repulsion ($U = 4.5$ eV) opens the gap even at room temperature. The correlation enhanced splitting between different orbitals leads to separation of bands into those that act as fully filled or a fully

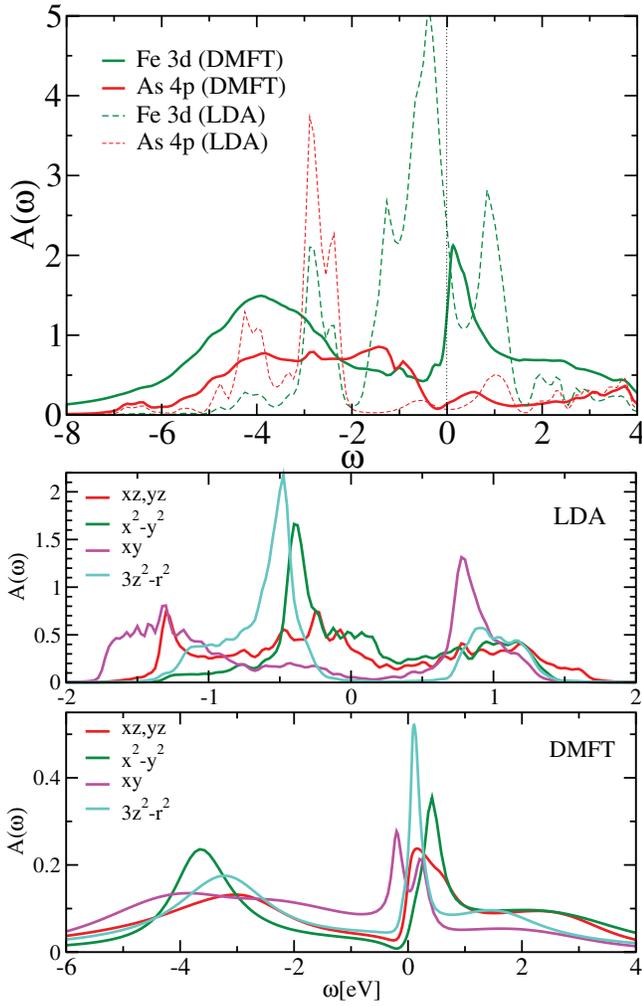


FIG. 3 (color). (a) DMFT density of states compared with LDA DOS. (b) Orbitally resolved Fe-3d density of states within LDA and DMFT.

empty bands at low energy. The high energy Hubbard bands are only weakly affected by such splitting. The Coulomb repulsion thus strongly reduces the carrier density and pushes the parent compound on the verge of the transition between a bad metal and a bad semiconductor. At the same time, the localization of electrons leads to local moment formation and enhancement of the spin susceptibility in the doped compound.

Many of the unconventional superconductors are known to have a very simple low energy band structure. For example, in the copper oxides, a single band is crossing the Fermi level. Similarly, the Fermi surface of the Na doped cobaltates [14] has primarily a a_{1g} single sheet Fermi surface. The situation is very different in LaOFeAs within LDA. As can be seen in Fig. 3(b) LDA predicts that all five Fe 3d orbitals have finite weight close to or at the Fermi level. The situation is not simplified when the Coulomb correlation is accounted for. The spectral weight splits into a high energy incoherent part and a low energy part, which is very asymmetric and considerably reduced

due to the proximity to the semiconducting state. Upon doping, the quasiparticle peaks move to the Fermi level, the scattering rate is reduced, and the system becomes a better conductor. Experimentally, doping leads to the superconducting ground state at low temperature, which is likely to be of unconventional origin. The Cooper pairs are likely to be formed out of composite singlets of spin and orbital degrees of freedom.

Figure 4(a) shows the momentum resolved spectral function $\sum_L A(\mathbf{k}, \omega)_{LL}$ in color coding together with the LDA bands in the energy range between -5 and 2.5 eV and momentum dispersion in the high symmetry directions of the first Brillouin zone. The higher energy band structure at $\omega > 2$ eV and $\omega < -5$ eV is not considerably different in the two approaches. In the intermediate frequency region between -1.5 and 1.5 eV a depletion of the spectral weight is apparent in the DMFT approach. While LDA predicts a large number of bands in this region, DMFT redistributes most of this weight further away from the Fermi level to the range between -2 and -4 eV. Consequently, a set of states with a large scattering rate and short lifetime is predicted by DMFT. Finally, the low energy part of the spectra is considerably modified when Coulomb correlation is taken into account. The hole pockets around the Γ

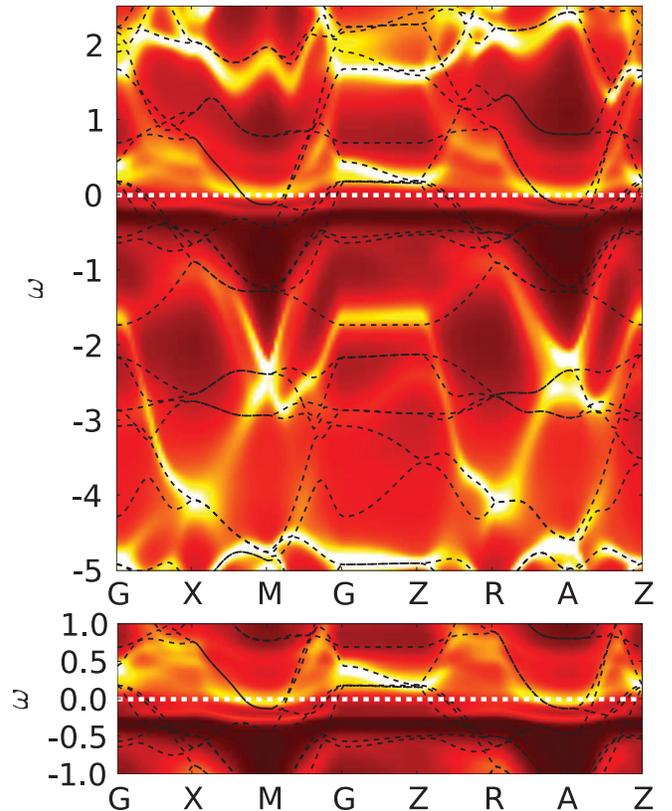


FIG. 4 (color). Momentum resolved spectral function $A_{4d}(\mathbf{k}, \omega)$ within DMFT (color coding) together with the LDA band structure (dashed lines). The upper panel corresponds to the undoped parent compound while the lower panel shows the 10% electron doped compound in the virtual crystal approximation.

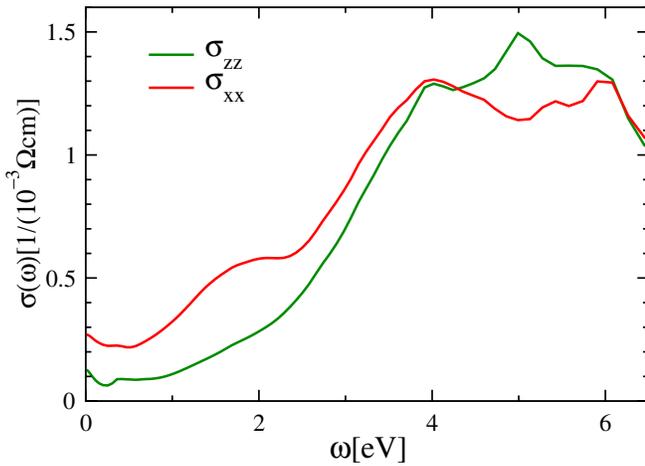


FIG. 5 (color online). Optical conductivity of LaOFeAs within DMFT: in plane and out of plane.

point are barely identifiable and the electron pockets centered at M and A almost disappear—they are only touching the Fermi level and the weight below the Fermi level is only due to a large scattering rate. Thus a semiconducting type of the gap is opening at the Fermi level. The correlations thus enhance the crystal field splittings, which ultimately lead to a state being a band-semiconductor acting as a bad metal at finite temperatures.

The situation is different in the doped compound [see Fig. 4(b)] where the electron pockets clearly cross the Fermi level. The band velocity and effective mass are considerably enhanced (3–5 times) while the scattering rate still remains large. Finally, the hole pockets around Γ remain highly scattered.

We also compute the optical conductivity of LaOFeAs within DMFT in both the xy plane and along the z direction. Considerable anisotropy can be identified in Fig. 5. The Drude peak, which is a hallmark of metallicity and Fermi liquid state, is absent because of a proximity to the semiconducting state. Our calculations predict a small number of carriers and large scattering rate, due to partial localization of carriers in this compound, and consequently low conductivity. One can identify a shoulder in optical conductivity close to 2 eV. It corresponds to transitions between Fe-3d and As 4p states. The large peak at 4 eV is mostly due to transitions within the d shell from the lower Hubbard band to the quasiparticle peak above the Fermi level.

In this work we used the single site dynamical mean field theory which approximates the full momentum dependent dynamical self-energy by its purely local component $\Sigma(\omega)$ [see Eq. (1)] which is still a 10×10 matrix in the orbital space of Fe- d orbitals. While this approximation successfully describes the physics of many f and d electron systems, it does not capture the low energy physics of cuprate superconductors where momentum space differentiation leads to a Fermi surface of arc shape. The cluster

extensions of DMFT can capture some of the reach physics of cuprates. We cannot exclude the possibility that the low energy band structure of doped LaOFeAs will also require similar nonlocal correlations, and we leave this question open for future work.

Finally, we comment on possible routes to understand the superconductivity near a bad semiconductor in this compound. Since the Coulomb correlation is below the critical U for this system to undergo a Mott transition, an itinerant approach might be adequate. This will involve a generalization of the spin-fluctuation exchange mechanism to a multiorbital situation. In addition, the pairing interaction might involve not just spin but also orbital fluctuations within the d subshell.

In conclusion, we studied the band structure of the newly discovered superconductor LaO $_{1-x}$ F $_x$ FeAs, and we predict the orbital and momentum resolved spectral function and optical conductivity of the compound. Density functional theory predicts that a set of Fe 3d bands are crossing the Fermi level with no clear splitting into the e_g and t_{2g} manifold. The Coulomb correlations among the six electrons in the set of five Fe-3d orbitals is strong enough to push the compound close to the metal insulator transition. The correlation enhances the crystal field splitting among the d orbitals, which in turn increase correlations. At temperature $T = 116$ K studied here, the parent compound LaOFeAs is still metallic, although a bad metal with a very large scattering rate and a strongly reduced number of carriers. Doping the parent compound leads to electron pockets centered at the M and A point in the momentum-resolved spectral function.

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- [1] Y. Kamihara *et al.*, J. Am. Chem. Soc. **128**, 10012 (2006).
 - [2] Y. Kamihara, T. Watanabe, H. Masahiro, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
 - [3] P. Blaha, K. Schwarz, G. K. H. Madsen, K. Kvasnicka, and J. Luitz, *WIEN2K* (Karlheinz Schwarz, Technische Universität Wien, Austria, 2001).
 - [4] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
 - [5] J. H. Shim, S. K. Kwon, and B. I. Min, Phys. Rev. B **64**, 180510 (2001).
 - [6] T. Miyake and F. Aryasetiawan, Phys. Rev. B **77**, 085122 (2008).
 - [7] P. Werner and A. J. Millis, Phys. Rev. Lett. **99**, 126405 (2007).
 - [8] N. Manini, G. E. Santoro, A. Dal Corso, and E. Tosatti, Phys. Rev. B **66**, 115107 (2002).
 - [9] A. I. Poteryaev, M. Ferrero, A. Georges, and O. Parcollet, arXiv:cond-mat/0801.4356.
 - [10] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
 - [11] G. Kotliar *et al.*, Rev. Mod. Phys. **78**, 865 (2006).
 - [12] S. Y. Savrasov, Phys. Rev. B **54**, 16470 (1996).
 - [13] K. Haule, Phys. Rev. B **75**, 155113 (2007).
 - [14] K. Takada *et al.*, Nature (London) **422**, 53 (2003).