Orbital-selective Mottness in layered iron oxychalcogenides: the case of Na$_2$Fe$_2$OSe$_2$

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Abstract
Using a combination of local density approximation and dynamical mean-field theory calculations, we explore the correlated electronic structure of a member of the layered iron oxychalcogenides group, Na$_2$Fe$_2$OSe$_2$. We find that the parent compound is a multi-orbital Mott insulator. Surprisingly, and somewhat reminiscently of the underdoped high-$T_c$ cuprate scenario, carrier localization is found to persist upon hole doping because the chemical potential lies in a gap structure with almost vanishing density of states. On the other hand, in remarkable contrast, electron doping drives an orbital-selective metallic phase with coexisting pseudogapped (Mott-localized) and itinerant carriers. These remarkably contrasting behaviors in a single system thus stem from drastic electronic reconstruction caused by large-scale transfer of dynamical spectral weight involving states with distinct orbital character at low energies, fitting the oxychalcogenides neatly into the increasingly visible pattern for Fe-based systems of having orbital-selective Mott phases. We detail the implications that follow from our analysis, and discuss the nature and symmetries of the superconductive states that may arise upon appropriately doping or pressurizing Na$_2$Fe$_2$OSe$_2$.

Keywords: Fe-arsenides and selenides, correlated electrons, unconventional superconductivity

(Some figures may appear in colour only in the online journal)

1. Introduction
Recent findings of unconventional high-$T_c$ superconductivity (HTSC) in Fe arsenides and selenides have reinvigorated the HTSC revolution. In particular, the outstanding and vigorous debates concerning the normal state giving way to HTSC in cuprates have also left their mark upon the discussion of mechanisms of HTSC in Fe-based superconductors (FeSC): does HTSC result as a pairing instability of a conventional Landau Fermi liquid (LFL) [1], or as a pairing instability of a non-LFL, like in the cuprate case [2]. Clearly, one possible way to resolve this very important issue is to investigate as many members of the Fe-based family as possible.

To date, both normal paramagnetic and antiferromagnetically ordered phases in various members have been extensively studied. It has slowly emerged that, in their normal, paramagnetic state, the FeSC (both pnictides and chalcogenides) increasingly fall into the bad metal category. Generally, in correlated systems, the generic picture is now known to be one where a high-$T$ bad metal undergoes a $T$-dependent crossover to a correlated or heavy LFL at low temperature ($T$). This is due to the development of a severely renormalized lattice coherence scale, driven by the increasing relevance of electronic correlations as $T$ reduces. We will refer to this behavior as ‘standard’ for correlated metals, and thus any fundamental deviation from this generic behavior will be termed ‘anomalous’. According to this definition, an increasing number of Fe-based compounds fall into the anomalous class, in the sense that LFL behavior is seemingly not recovered at low $T$ when superconductivity (SC) is suppressed by appropriate perturbations. In SmFeAsO$_{1-x}$F$_x$ [3], for example, destruction of SC by high magnetic fields reveals a low-$T$ insulator-like
state as in high-$T_c$ cuprates [4]. NdFeAsO$_{1−x}$F$_x$ shows similar behavior upon irradiation-induced disordering [5]. In both cases, the residual resistivity $\rho(T)$ is $\rho(T) = \propto -\log T$, suggesting an anomalous field or radiation (disorder) driven transition from bad metal to insulator at low $T$ in the normal state, and that the normal state might thus not be as normal as had been thought. SC even arises directly from an even more incoherent semiconductor-like normal state in FeSe$_{1−x}$Te$_x$ [6]. Optical and spectroscopic studies of 122-iron selenide superconductors show large-scale spectral weight transfer (SWT) as a function of temperature across the magnetic and superconducting instabilities, a fingerprint of Mottness [8]. Both $\rho(T)$ being $\propto T$ and bad metallicity above $T_c$ or the Néel temperature ($T_N$) are features shared with other non-LFL metals close to a Mott instability [9]. Thus, the non-LFL metallic state in the above cases strongly points toward a fundamental role for Mott localization [10–12].

In this context, the recent finding of an insulating, AF ground state in layered Fe oxychalcogenides [12–16] is interesting, since it confirms theoretical suggestions that Mott insulating parent compounds in the FeSC systems could be found by increasing the ratio of the interaction to the hopping ($U/W$) beyond a critical value for a Mott transition [17, 11]. Evidence for compounds with Fe layers with different intergrowth structures is very interesting: the generic effect is to reduce the one-electron bandwidths [12] ($W$) by employing two-dimensional secondary building units, making it possible to realize almost isolated two-dimensional Fe layers. The newly discovered Fe oxychalcogenides thus help to sharpen the fundamental debate [18] on the degree of electronic correlations in FeSC in general. The finding of a large local moment value on Fe, $M_{Fe} ≃ 2.23 \mu_B$ [14], along with large activation energies [13, 14, 12, 15], suggests strong electronic localization. The consequences of Mottness for physical responses of oxychalcogenides have, however, not received the attention that they deserve.

Here we adopt a Mottness view with the incorporation of sizable multi-orbital (MO) correlations in the Fe d shell. As shown below, all five d bands must be kept at a minimally realistic level in order to satisfactorily resolve the Mott insulating and bad metallic regimes obtained, respectively, in pure and doped compounds. In Mott insulators, sizable electronic correlations drive new physical effects upon (electron, hole) doping. They can induce a pseudogap regime referred to above, where the potential chemical lies in an energy region of vanishing density of states (DOS) [19], or orbital-selective (OS) incoherent states, naturally yielding coexistent insulating and bad metallic states as in cuprates or in an increasing number of pnictides [20–22]. In this work, we use the local density approximation plus dynamical mean-field theory (LDA + DMFT) [23] to study these issues. We also use these results to discuss the influence of Mottness on issues mentioned above for lightly doped Na$_2$Fe$_2$OSe$_2$ and follow this up with specific predictions which can be tested in future experiments.

Figure 1. Crystal structure of Na$_2$Fe$_2$OSe$_2$. The red, blue, yellow and purple balls represent Fe, O, Na, and Se ions, respectively.

2. Results and discussion

The crystal structure of Na$_2$Fe$_2$OSe$_2$ (space group $I4/mmm$) shown in figure 1 is built from an alternate stacking of Fe$_2$OSe$_2$ blocks and double layers of Na along the $c$-axis. In the Fe$_2$OSe$_2$ unit, the Fe$^{2+}$ ($d^6$ configuration) ion is located between oxygen atoms, forming a square-planar layer, which is an anti-configuration with respect to the CuO$_2$ layer of high-$T_c$ cuprates. Using the cell parameter values [15], we performed LDA calculations for Na$_2$Fe$_2$OSe$_2$ within the linear muffin-tin orbital (LMTO) scheme [24], in the atomic sphere approximation. Self-consistency was reached by performing calculations with 163 irreducible $k$-points. The radii of the atomic spheres were chosen as $r = 2.512$ (Fe), $r = 3.05$ (Na), $r = 3.422$ (Se) and $r = 1.99$ (O) au in order to minimize their overlap. Within the LDA, the one-electron part of the Hamiltonian reads $H_0 = \sum_{k,\alpha,\sigma} \epsilon_0(k)c_{k,\alpha,\sigma}^\dagger c_{k,\alpha,\sigma}$, where $a = (3z^2 − r^2, xz, yz, x^2 − y^2, yz)$ labels the (diagonalized in the orbital basis) five Fe 3d bands, which are the only ones that we retain, since the non-d-orbital DOS have negligible or no weight at $E_F$.

2.1. Electronic structure

In figure 2 we show the LDA one-electron band structure computed with actual experimental lattice parameters. As expected, the active electronic states involve the Fe d carriers. Many features worth mentioning stand out: a sizable reduction (O(30)%) of the average LDA bandwidth ($W_{LDA}$) relative to that of tetragonal FeSe [11], induced by hybridization with oxygen atoms and stronger band-distorting effects of the extra Na or Se layers, is obtained. A puzzling aspect of the result is that the $xz − yz$-orbital degeneracy is eradicated...
at the outset in Na$_2$Fe$_2$OSe$_2$, even while the nominal crystal structure remains tetragonal. This splitting is thus unrelated to a structural transition (as is ubiquitous in the 1111-Fe-based and 122-Fe-based systems), and it is interesting to inquire about its origin. Looking more carefully at the structure in figure 1, one sees that the local coordination of the Fe ion in this case is at variance with those of the 1111 and 122 systems, and, in particular, each Fe ion is coordinated with two Na and two Se ions. The different charge densities induced by this arrangement result in an effective D$_{2h}$ (‘orthorhombic’) environment, as opposed to the usual S$_4$ symmetry found generically. This naturally gives rise to the splitting of the $xz$, $yz$-orbital degeneracy, as observed in calculations.

To confirm this reasoning, we have performed LDA calculations for properly optimized crystal structure. The structure was relaxed without symmetry or box shape constraints using the Kohn–Sham self-consistent density functional method in the local density (LDA; Perdew–Zunger parameterization) approximations [25]. Electronic states were expanded using a double-$\xi$ basis set with polarization functions constituted of numerical orbitals, with a norm-conserving Troullier–Martins [26] pseudopotential description of the core electrons. The charge density was represented on a real-space grid with an energy cutoff of 300 Ryd. A Monkhorst–Pack $k$-point mesh of $8 \times 8 \times 4$ ensured the convergence of the electronic part. The relaxed structure was tetragonal, with cell parameters $a = 4.0475$ Å, $c = 14.0514$ Å. The final atomic coordinates were Na (0.0, 0.0, 0.3258), Fe (0.0, 0.5, 0.5), Se (0.0, 0.0, 0.1274) and O (0.0, 0.0, 0.5). In nice accord with the above qualitative expectation, results for the optimized structure show a very similar orbital-resolved LDA density of states; see figure 2. Moreover, we never found any evidence for a structural phase transition which would lower the symmetry from tetragonal to orthorhombic.

The anisotropies in the LDA band structure are manifested in figure 2. As is common to all FeSC, the $3z^2 - r^2$, $xy$ orbitals exhibit the bonding/antibonding splitting characteristic of the tetragonal unit cell. These bands, almost totally band gapped near the Fermi energy ($E_F$) in the FeSC systems, go over into highly orbitally polarized, narrow bands in Na$_2$Fe$_2$OSe$_2$. A similar feature is found for the $xz$ orbital. Moreover, the real crystal-field splitting also severely renormalizes the LDA orbital occupancies (promoting enhanced orbital polarization) of the $3z^2 - r^2$, $xz$, $xy$ states. As found above, lifting of degeneracy of the $xz$, $yz$ orbitals leaves an AF ground state at low $T$ without any tetragonal-to-orthorhombic structural phase transition. It thus follows that the novelties found in FeSC, relating to electronic nematic instabilities in the tetragonal phase near the borderline of structural and magnetic transitions, will not play an active role in oxychalcogenides. Thus, oxychalcogenides should show very different responses upon carrier doping: elucidating precisely this aspect with a well-controlled approach will be our aim in this work.

We now discuss our LDA + DMFT results obtained within the $d^6$ configuration of the Fe$^{2+}$ in Na$_2$Fe$_2$OSe$_2$. Starting with the five Fe $d$ orbitals in LDA, we use MO-DMFT [10] to derive the correlated $d$-band spectral functions. We use the MO iterated perturbation theory as an impurity solver for DMFT [27]. This perturbative, many-particle scheme has a proven record of recovering correct LFL behavior, and bad metallicity in correlated oxides. In the MO problem, $H = H_0 + H_{\text{int}}$ with

$$H_{\text{int}} = U \sum_{i,a} n_{i,a \uparrow} n_{i,a \downarrow} + \sum_{i,a \neq b} \left[ U' n_{i,a \uparrow} n_{i,b \downarrow} - J_H S_{i,a} \cdot S_{i,b} \right],$$

and $U' = U - 2J_H$ ($U'$) is the intra-orbital (inter-orbital) Coulomb repulsion and $J_H$ is the Hund’s rule coupling [23]. We choose values of $U = 4.0$ eV, $J_H = 0.7$ eV as employed in our earlier works [10, 28]. Though not determined 

\textit{ab initio}, our parameter choice is consistent with our earlier and other theoretical works and with our underlying view that Fe pnictides and chalcogenides are better regarded as sizably correlated metals [28, 29]. As shown previously, FeSe is already a bad metal close to a Mott insulator [11], and the significantly smaller $W_{\text{LDA}}$ for Na$_2$Fe$_2$OSe$_2$ then naturally implies favoring a Mott insulator in oxychalcogenides.

![Figure 2. Orbital-resolved LDA density of states (DOS) for the Fe d orbitals for the actual [15] (dotted line) and optimized (solid line) lattice parameters of Na$_2$Fe$_2$OSe$_2$. Notice the very good accord between the two results.](image-url)
2.2. The Mott insulating phase

In the case of undoped Na$_2$Fe$_2$OSe$_2$, our LDA + DMFT results, shown in figure 3, exhibit a clear Mott insulating gap in the one-particle spectral function. Several interesting features clearly stand out. (i) The Mott gap is orbital dependent, i.e., intrinsically anisotropic. (ii) Examination of the orbital-resolved spectral functions reveals a behavior hitherto known only for FeSC systems; namely, all orbitals are partially populated due to $U'$-induced dynamical inter-orbital entanglement [27], while the total orbital population is integral, as it should be for undoped ($\delta = 0$) Na$_2$Fe$_2$OSe$_2$. As seen in figure 3, strong dynamical MO correlations originating from $U$, $U'$ and $J_H$ lead to sizable spectral weight redistribution over large energy scales and the formation of a severely reconstructed (compared to LDA) correlated electronic structure. This feature is characteristic of multiband Mott systems, with concomitantly modified upper and lower Hubbard bands at high energies: these latter features are related to the strongly coupled spin–orbital local moments defining a Mott insulator without long-range orbital or magnetic order. Though our results pertain to $T \equiv 0$, they are thus formally a valid description of the high-$T$ Mott insulator state described before.

2.3. The filling-controlled electronic transition

What happens upon carrier doping? Even though we have no data, the generic appearance of novel metallic states with low-energy pseudogaps and the instabilities of such states to unconventional order, and, in particular, to HTSC, in a wide variety of other correlated matter, make this a very important question to inquire about. As alluded to in the introduction, our aim here is to build upon the strengths of correlated electronic structure modeling to predict the effect of carrier doping. In particular, on the basis of explicit calculations, we will present a set of predictions which could be tested in future experimental work.

In figure 4 we show the changes in the correlated electronic structure upon hole doping ($n \equiv 6 + \delta$, with $\delta < 0$) the Mott insulator. An intriguing observation is that the Mott localization–delocalization phase transition does not occur at small doping. However, as $|\delta|$ increases, a selective Mott state develops, in which the $xz$, $yz$, $x^2 - y^2$ spectral functions show the behavior of a Mott insulator with vanishing DOS at $E_F$, while the $3z^2 - r^2$, $xy$ orbitals now show (selective) metallic behavior, characterized by the presence of incoherent in-gap states at $E_F$. This is a clear demonstration of strong Mottness [19] and an orbital-selective Mott transition (OSMT) in Na$_2$Fe$_2$OSe$_2$. What is the origin of these features? In an MO system like the oxychalcogenides, strong (incoherent) scattering between different carriers in orbital states split relative to each other due to the specific crystal field (see the discussion of this aspect above) leads to two main effects: (i) it leads, via static Hartree contributions (from the static part of the orbital-dependent self-energies) to orbital-dependent shifts of the d bands relative to each other; and (ii) strong dynamical correlations due to sizable $U$, $U'$, $J_H$ cause appreciable SWT over large energy scales, from high to low energy, upon carrier doping. This second feature leads to a drastic modification of the spectral lineshapes. In full accord with our earlier qualitative discussion, the increase of the effective $U/W$ ratio in the present case relative to FeSe and Fe arsenides leads to increased low-energy incoherence, as the pronounced pseudogap and very broad low-energy spectral features clearly show. Microscopically, strong incoherent scattering, arising from the coexistence of Mott-localized and bad metallic states, leads to an almost complete suppression of the LFL quasiparticles and the emergence of an incoherent (pseudogapped) spectra, which is reminiscent of what is seen in cuprate oxides. Microscopically, infrared LFL behavior (narrow Kondo resonance in DMFT) in the $3z^2 - r^2$, $xy$ orbitals is almost extinguished by strong scattering between the Mott-localized $xz$, $yz$, $x^2 - y^2$ and the quasi-itinerant
Figure 4. Hole doped LDA + DMFT ($U = 4.0$ eV, $J_H = 0.7$ eV) spectral functions for the Fe d orbitals of Na$_2$Fe$_2$OSe$_2$. As in cuprates [19], strong hole localization is found in the lightly doped regime: only narrow gap states are formed in the slightly more delocalized $3z^2 - r^2$, $xy$ orbitals.

Figure 5. Effect of electron doping on the LDA + DMFT ($U = 4.0$ eV, $J_H = 0.7$ eV) spectral functions for the Fe d orbitals of Na$_2$Fe$_2$OSe$_2$. Electron delocalization and the appearance of narrow quasiparticle resonances near the Fermi energy are seen within the $3z^2 - r^2$, $xz$, $yz$ channels. Selective localization and pseudogap features are the fingerprints of electronic correlations within the $x^2 - y^2$, $xy$ orbitals.

$3z^2 - r^2$, $xy$ components of the (DMFT) matrix spectral function, due to the sizable $U'$, $J_H$, and is a clear manifestation of the OSMT in the five-band Hubbard model that we use.

Since there is no particle–hole symmetry in the system, it is interesting to inquire as to the effects of electron doping ($n = 6 + \delta$, $\delta > 0$) in Na$_2$Fe$_2$OSe$_2$. In particular, we want to study whether electron doping is qualitatively different, i.e., whether incoherent non-LFL behavior still survives in the infrared, or whether a coherent LFL response is favored. Figure 5 exhibits the answer: the $x^2 - y^2$, $xy$ spectral functions show clear pseudogap behavior, while, very interestingly and in stark contrast to the hole doped case, the $3z^2 - r^2$, $xz$, $yz$ spectral functions now show narrow LFL-like quasiparticles at $E_F$. Hence, electron doped Na$_2$Fe$_2$OSe$_2$ is predicted to lead to a more coherent (in the LFL sense in the infrared) state than its hole doped counterpart above. The situation seems to be somewhat similar to that for the 122-FeAs systems [30], where both coherent LFL-like and strongly incoherent non-LFL responses, dependent on the type and extent of doping, are seemingly observed. We point out, however, that such comparisons are inevitably fraught with danger, especially since the $xz$, $yz$-orbital degeneracy and the soft orbital fluctuations characteristic of the 122-FeAs systems do not play a role in the Fe oxychalcogenides.

The electron–hole asymmetry and selective Mott transition in Na$_2$Fe$_2$OSe$_2$ are further visible in the orbital-resolved self-energies, $\Sigma_{\sigma\sigma}(\omega)$, shown in figure 6. Noticeable features include the following. (i) The insulating state is manifested
Figure 6. Orbital-resolved imaginary parts of the self-energies for the Fe d orbitals of stoichiometric and (electron/hole) doped Na$_2$Fe$_2$OSe$_2$ with $U = 4.0$ eV, $J_H = 0.7$ eV. Notice the evolution of the sharp pole in the self-energies near $E_F$ across the doping-induced selective Mott delocalization.

by a sharp pole in $\text{Im } \Sigma_{\sigma} (\omega)$ as well by divergent $\text{Re } \Sigma_{\sigma} (\omega)$ (not shown) close to $E_F$. (ii) In the doped regime, only the higher (in energy) $xy$ orbital shows the LFL ($\text{Im } \Sigma_{\sigma} \approx -\omega^2$) form at small $\omega$. (iii) On the other hand, the imaginary part of the self-energy of the $3z^2 - r^2$ orbital at $E_F$ is finite (i.e., $\text{Im } \Sigma_{3z^2 - r^2} (\omega = 0) < 0$). As is known, such behavior is caused by strong scattering between Mott-localized and quasi-itinerant electronic states in the MO-DMFT problem, which maps onto an effective spinful Falicov–Kimball model in the local limit. These results imply that underdoped oxychalcogenides should be located in the pseudogap regime and the metallic state obtained by the filling-controlled Mott transition is unconventional [10]. The origin of this unconventional metal is the lattice orthogonality catastrophe that occurs due to orbital-selective blocking of the coherent motion of the doped hole in the DMFT due to the sizable $U'$, $J_H$ in the MO Hubbard model.

In view of the above and our previous LDA + DMFT results [10, 28], we now attempt to predict features of the physical responses for the paramagnetic state of Na$_2$Fe$_2$OSe$_2$. In figure 7, we show the total LDA + DMFT spectral functions. Clear Mott insulator features are visible for $\delta = 0$, and we propose that future photoemission and x-ray absorption spectroscopy results, which probe one-electron subtraction and addition spectra, can be directly compared with these: in particular, a broad incoherent peak below $-0.8$ eV should be seen in both pure and doped cases. Additionally, drastic modification of the LDA + DMFT spectra with $\delta \neq 0$ is clearly visible. Our results for the hole doped and electron doped spectral functions ($n = 5.8, 6.2$) reveal clear differences, as found above: for the hole doped case, we find an almost totally incoherent spectral response due to the almost total blocking of the coherent one-electron dynamics due to the lattice ‘orthogonality catastrophe’, as noted above. For electron doping, however, a small quasicoherent LFL component is visible, notwithstanding the large-scale dynamical spectral weight transfer common in both cases. These are stringent tests for our proposal, and experimental verification should place it on solid ground. More distinguishing tests would be characteristic signatures in transport: for example, incoherent bad metallicity with clear non-LFL dependence on $T$ of the resistivity, $\rho(T) \propto T^n$ with $0 < n < 1.5$, should be seen in the hole doped non-LFL cases, while much more conventional LFL-like resistivity, $\rho(T) \propto T^2$, should be seen in the electron doped cases.

One of our central results is the finding of coexisting orbital-selective incoherent and heavily dressed but coherent charge carriers. This behavior is reminiscent of what is found in the pseudogap regime in the underdoped HTSC cuprates. However, in cuprates, this differentiation of electronic states occurs in momentum space: carriers in the nodal region are more quasicoherent than ones along the antinodal direction, which remain incoherent and in Mott-localized states. It has been demonstrated, using a cluster-to-orbital mapping [31] that this nodal/antinodal differentiation in one-band Hubbard models is the momentum-space analog [32] of the orbital-selective Mott transition in models with several active orbitals. This is also borne out by our findings here, where the frequency dependences of the imaginary parts of a subset (of orbital self-energies) in figure 6 show Mott insulator features, while others show quasicoherent behavior. Viewing this in terms of the above mapping, an analogy can be drawn with the observations of cellular DMFT studies [32, 23], wherein similar features within the two-site cluster DMFT were found:
suppressed coherence of antinodal quasiparticles originated from Mott physics while the nodal states remained protected against Mott localization. Selective localization in momentum (high-$T_c$ cuprates) or in orbital (FeSC) space thus seems to be a common element that provides a common, microscopic origin for the suppression of LFL coherence and the emergence of non-LFL normal state properties of unconventional metals [4].

2.4. Mechanisms of unconventional superconductivity

Finally, motivated by a host of studies [33–35, 1] which propose the possibility and gap-function symmetry of superconducting states on the basis of the nature (LFL or non-LFL) of the normal state and the nature of the renormalized Fermi surface(s), we attempt to carry out a qualitative program in our case. Specifically, we will focus on two normal state features: (i) the LFL or non-LFL character of the normal state(s) found above and (ii) the nature of the renormalized Fermi surfaces, to explore the range of superconducting state(s) that may result.

(i) **Hole doping.** Since the LFL picture has been totally extinguished in the normal state for hole doping, it follows that the instability to any unconventional superconducting state cannot, by definition, proceed via the conventional route of BCS-like pairing of (heavily dressed or otherwise) long-lived quasiparticles: it is then much more likely, as is the case for critical metals [34], that SC pairing occurs as a result of the relevance of the inter-site, inter-orbital two-particle residual interactions in the incoherent metal. As worked out for the multiband situation characteristic of Fe-based systems, such a residual interaction should involve pair-hopping electronic processes with intrinsically coupled spin–multi-orbital character. In the hole doped case above, with metallic $xy$, $3z^2-r^2$ states crossing $E_F$, we expect pairing to primarily involve solely the $xy$ band or both $xy$, $3z^2-r^2$ states if the Fermi surface has appreciable warping along $k_z$. Once SC has stabilized in the $xy$ band, an interband proximity effect characteristic of multiband SC [36] must eventually take over to give full three-dimensional SC. Since the two-particle hopping is expected to acquire the frustrated form factor $\gamma(k) = (\cos k_x + \cos k_y) + \alpha \cos k_x \cos k_y$ (since the residual interaction scales as the second power of the one-electron hopping) [34], the SC gap function may or may not have in-plane nodes, depending on whether the renormalized $xy$-band dispersion intersects the superconducting gap function.

(ii) **Electron doping.** Since more quasicoherent normal state behavior sets in for electron doping, a more conventional analysis for superconducting pairing is mandatory. Remarkably, since LFL-like behavior in the infrared now obtains for the $xz$, $yz$, $3z^2-r^2$ bands, the situation that emerges is similar to the one [33, 1, 37] found for the 1111-FeAs systems in early itinerant-based studies, though the present result places these bands much closer to the Mottness regime, as an examination of our results above shows. Thus, it is possible that small additional perturbations might tilt it into the incoherent regime. This analogy can now be used to directly predict that the superconducting state will most probably have in-plane $s_\pm$ pair symmetry. Further, depending on the extent of the $c$-axis corrugation of the three-dimensional (3D) Fermi surface, it will (or will not) have accidental $c$-axis nodes [34, 38]. Since ferro-orbital order and associated electronic nematic fluctuations cannot possibly resemble those expected near quantum criticality in the absence of any T–O structural transition(s), if unconventional superconductivity sets in, it will most probably compete with short-ranged or long-ranged antiferromagnetism induced by selective Mottness. Since the selective Mott transition is also necessarily associated with Mott–Lifshitz instabilities involving loss of parts (or subsets of sheets) of the LDA Fermi surface, soft electronic modes associated with dualistic character of fermions near correlation driven Mott-like instabilities (namely, coexisting ‘itinerant’ and Mott-localized ones) may turn out to be an electronic ‘glue’ that may facilitate Cooper pairing in this case: this situation is famously encountered in hole doped cuprates [9] and certain f-electron-based compounds [39]. If unconventional superconductivity

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**Figure 7.** Total density of states for the Fe d orbitals of stoichiometric and (electron/hole) doped $\text{Na}_2\text{Fe}_2\text{OSe}_2$ with $U = 4.0$ eV. Notice the modification of the LDA + DMFT spectra from a Mott insulator ($n = 6$) to an almost totally incoherent electronic state ($n = 5.8$), due to large-scale transfer spectral weight. Selective microscopic coexistence of coherent–incoherent low-energy electronic states is predicted for electron doped ($n = 6.2$) $\text{Na}_2\text{Fe}_2\text{OSe}_2$. 

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can be induced by suitable means, verification of our proposal may help put our predictions on firmer ground.

It is thus quite remarkable that both the nature and the extent of the orbital selectivity in hole and electron doped cases play a critical role in selecting the detailed set of conditions which determine the nature and symmetry of the superconducting state in each case. The diversity of pairing states in Fe-based systems, by now appreciated to be a consequence of the MO nature of these systems, may thus be exposed in Fe oxychalcogenides if these can be driven superconducting by appropriate pressure, chemical and/or electrical doping. Whether this fascinating state of affairs unfolds in the future only time will tell.

3. Conclusion

To summarize, we have used LDA + DMFT for a minimally realistic five-band Hubbard model to perform a detailed study of a doped Mott insulator in the recently discovered Fe oxychalcogenides. In particular, considering Na3Fe2O5Se2 as a suitable template, we have carefully analyzed its paramagnetic Mott state, revealing the orbital-selective Mott gap as an effect of multi-orbital Hubbard correlations. Much more interesting behavior is predicted when we consider electron and hole doping of this state: upon the latter, hole localization or incoherence persists because the chemical potential lies in a gap region with vanishing density of states, or in the low-energy pseudogap, which we ascribe to the blocking of coherent motion of doped holes due to a lattice orthogonality catastrophe induced by orbital-selective Mottness. On the other hand, in remarkable contrast, electron doping this Mott insulator leads to an orbital-selective low-energy quasicoherent states coexisting with pseudogapped states, implying a low-energy strongly correlated Fermi-liquid state with a small quasiparticle weight. These predictions could be directly tested by a combination of future spectral and transport measurements. Finally, on the basis of the reconstructed Fermi surfaces implied by our results as well as upon the non-LFL or LFL nature of the metallic phases found here, we discuss the nature and symmetry of the possible unconventional superconducting states that one may find upon appropriately doping or pressurizing the system. Such studies are called for, and should confirm or refute our predictions.

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