α-FeSe as an orbital-selective incoherent metal: An LDA+DMFT study

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α-FeSe, a prototype iron-chalcogenide superconductor, shows clear signatures of a strange incoherent normal state. Motivated thereby, we use LDA+DMFT to show how strong multi-band correlations generate a low-energy pseudogap in the normal state, giving an incoherent metal in very good semi-quantitative agreement with observations. We interpret our results in terms of α-FeSe being close to Mottness. A wide range of anomalous responses in the “normal” state are consistently explained, lending strong support for this view. Implications for superconductivity arising from such an anomalous state are touched upon.

High Temperature Superconductivity (HTSC) in the recently discovered Iron pnictides (FePn) is the latest surprise among a host of others in d- and f band materials. While unconventional superconductivity (U-SC) sets in close to the border of a frustration-induced10 striped-spin-density-wave (SSDW) state with doping in the so-called 1111-FePn, no magnetic long range order (LRO) is seen in the tetragonal (α) phase of Iron Selenide (FeSe)12 and FeSe1−xTex labelled 11 systems, for small x in ambient conditions.

The 11- systems are structurally simpler than the 1111- and the 122-FePn, without As or O. A rich variety of ground states reveal themselves upon perturbations like doping, pressure and strain.11 Undoped α-FeSe exhibits superconductivity with Tc = 9 K: upon applying pressure, Tc dramatically rises to 37 K 12 U-SC is extremely sensitive to stoichiometry - minute non-stoichiometry in Fe1+ySe destroys SC.12 U-SC at Tc = 34 K is even observed in the high pressure orthorhombic structure in FeSe12 in strong contrast to the 1111-FePn, where it is only stable in the tetragonal structure. Interestingly, a two-step increase in Tc as a function of pressure (with a large dTc/dP beyond Pd ≈ 1.5 GPa), reminiscent of the f-electron U-SC, CeCu2Si215 is observed.14 In contrast, U-SC in FeSe is suppressed under tensile strain.19

In FeSe, the absence of charge reservoir layers (in contrast to the 1111 and 122 FePn) leads to a reduction in c-axis length. This has interesting consequences: in a correlated multi-band situation, changes in chemical composition are expected to sensitively affect the electronic and structural properties within Fe2Se2 layers16 changing the delicate balance between competing ordered states. This might explain the extreme sensitivity of the superconducting state to stoichiometry in FeSe. Thus, one may ask, “how different, or similar, is α-FeSe from doped Iron arsenide superconductors?”

Extant experiments for the normal state show clear strong correlation fingerprints. Photoemission (PES) experiments12,13 clearly evidence an incoherent, pseudogapped metallic state in α-FeSe, instead of a narrow Landau quasiparticle peak at EF. Extant LDA calculations14 compare poorly with PES data, as is checked by direct comparison (also see below). In addition, the ultrahigh-resolution PES spectra show a low energy kink at ≈ 8 meV (Ref. 13). As in 1111-compounds,15,16 this kink sharpens with cooling, and evolves smoothly across Tc. In contrast to the 1111-FePn, in α-Fe(Se1−xTex), the antiferromagnetic (AF) ordering wave-vector, QAF = (δσ, δσ) is very different from that predicted by LDA: this has an important consequence. If SC is mediated by AF spin fluctuations,2 this implies that LDA is fundamentally inadequate to address magnetic fluctuations in the “normal” state. Depending upon x, SC either arises from an insulator-like normal state, or from a bad metal with ρdc(T) ∝ T19. Further, NMR data19 show marked enhancement of antiferromagnetic (AF) spin fluctuations: no Korringa-like behavior is seen in 1/T1. The uniform spin susceptibility anomalously increases for T above Tc. The first two are reminiscent of those observed in high-Tc cuprates up to optimal doping19 and the third is also found in the 1111-FePn as well as in another poorly understood U-superconductor system Na4Co2O2.20 Finally, a minute amount of alloying by Cu drives α-FeSe to a Mott-Anderson insulator.21 Thus, α-FeSe is close to a metal-insulator transition, i.e, to Mottness. Needless to say, a proper microscopic understanding of the coupled charge-orbital-spin correlations manifesting in such anomalous behavior in α-FeSe is a basic prerequisite for understanding how SC emerges from such a “normal” state. Extant theoretical understanding is restricted to one-electron band structure calculations.14

LDA based approaches are unable, by construction, to describe the incoherent metal features documented above. Here, we undertake a systematic LDA+DMFT study of α-FeSe, and find that the electronic properties of this layered superconductor are partially reminiscent of slightly underdoped 1111-FePn superconductors. Sizable electronic correlations are shown to be necessary for gaining proper insight into the anomalous normal state responses in this system. Very good semi-quantitative agreement with PES (Ref. 12) strongly supports this proposal. Armed with this agreement, we analyze the non-Fermi-liquid (non-FL) metal in detail and predict specific anomalous features; these serve as a “smoking gun” for our proposal.

We start with the tetragonal (space group: P4/nmm) structure of α-FeSe with lattice parameters derived by
Hsu et al. (Ref. 22). One-electron band structure calculations based on local-density-approximation (LDA) were performed for α-FeSe using the linear muffin-tin orbitals (LMTO)-22 scheme. Our LDA results for the total density of states (DOS) is shown in Fig. 1 (dotted line). Similar total DOS were also obtained by other groups, showing that the electronic states relevant to Fe-superconductors are Fe $d$-band states. As found in previous calculations, the Fe-$d$ bands hybridize with Se-$p$ bands around 3.8 eV, giving rise to a small, separated band below 3 eV binding energy. Interestingly, the resulting “gap” at high energy is not seen in PES experiments, and must involve deeper analysis of the LHB in PES. Hence, estimation of the degree of correlation signatures cited above, the full, multi-orbital (MO) Coulomb interactions must be included. These constitute the interaction term, which reads $H_{\text{int}} = U \sum_{\alpha,\sigma} n_{\alpha \uparrow} n_{\alpha \downarrow} + U' \sum_{\alpha \neq \beta} n_{\alpha \uparrow} n_{\beta \downarrow} - J_H \sum_{\alpha,\beta} S_{\alpha \uparrow} S_{\beta \downarrow}$. To pinpoint the relevance of sizable MO electronic interactions in the system, we present LDA+DMFT results for $U = 2, 3, 4$ eV, $U' = U - 2J_H$ eV, and fixed $J_H = 0.7$ eV. To solve the MO-DMFT equations, we use the MO iterated-perturbation-theory (IPT) as an impurity solver. Though not quantitatively exact, this solver is numerically very efficient, is valid at $T = 0$, and self-energies $[\Sigma_{\alpha}(\omega)]$ can be computed very easily. Given the complexity in FeSe with five $d$ bands, these are particularly attractive features not shared by more exact solvers.

We now present our results for the normal phase of α-FeSe. Fig. 1 shows how LDA+DMFT modifies the LDA band structure. MO dynamical correlations arising from $U, U'$ and $J_H$ lead to spectral weight redistribution over large energy scales and the formation of lower- (LHB) and upper-Hubbard (UHB) bands. As seen, the UHB at 2.4 eV for $U = 2$ eV (and, $U' = 0.6$ eV) moves to higher energies with increasing $U$. The LHB is not clearly resolved below $2$ eV. Indeed, we observe a relatively sharp and quasi-coherent low-energy peak, with a prominent shoulder feature instead of the LHB at $\omega \approx -1.0$ eV. Similar features are visible in other results (Ref. 26) for similar $U$ values. Correlation effects, however, become more visible at $U \geq 3$ eV. In contrast to the $U = 2$ eV result, a LHB at 3.8 eV binding energy is clearly resolved with $U = 3$ eV. With increasing $U$, the LHB is shifted toward energies where the Se-$p$ bands occur in the LDA.

Interestingly, this superposition of the $pd$-band and LHB for $U = 4$ eV makes it impossible to cleanly resolve the LHB in PES. Hence, estimation of the degree of correlations in FeSe cannot be based solely on the “absence” of the LHB in PES, and must involve deeper analysis of PES, in conjunction with other probes, before a definitive conclusion can be drawn.

Fig. 1 shows that the DOS at $E_F$ is pinned to its LDA value for $U \leq 3$ eV. This is the expected behavior for a FL metal. With increasing $U$, however, our LDA+DMFT results show drastic modification of the spectral functions near $E_F$. Revealingly, in addition to large-scale SWT, we find that the FL-like pinning of the LDA+DMFT DOS to its LDA value, found for small $U$, is lost for $U = 4$ eV. Instead the metallic state shows a clear pseudogap at $E_F$, with no Landau FL quasiparticles (see below). A related bad metallic state has also been found in earlier LDA+DMFT work for the 1111-FePn, and, as shown there, is in very good semi-quantitative agreement with a host of experimental observations.

In Fig. 2 we compare our $U = 4$ eV (and, $U' = 2.6$ eV) results with PES for doped FeSe$_{1-x}$26. Very good semi-quantitative agreement with experiment is visible for $n = 5.8$, where $n$ is the total band filling of the $d$ shell. In particular, the broad peak at $\approx -0.17$ eV in PES is faithfully reproduced by LDA+DMFT. (Comparison with Fig. 1 also shows clear disagreement between PES and the LDA as well as $U \leq 3$ eV results.) For comparison, the computed LDA+DMFT spectra for the undoped ($n = 6.0$) and electron doped ($n = 6.1$) cases show clear disagreement with PES at low energies. In contrast to
this, the correlated spectral functions close to $E_F$ are insensitive to (small) changes in the electron (hole) concentration; we predict that combined PES/XAS on doped FeSe samples will show this in future. Interestingly, we see that, in contrast to the PES spectra, XAS lineshapes are less sensitive to 3.0 $\leq U \leq$ 4.0 eV (see Fig. 1). Recall that we obtain a correlated FL for $U = 3.0$ eV going over to an incoherent metal for $U = 4.0$ eV. We suggest, therefore, that inspection of XAS spectra alone is inadequate to address the issue of the degree of correlations in the Fe pnictides in general, and, to do so, one must consider the full one-particle spectral function via PES+XAS data taken together.

We now focus on orbital resolved spectral functions of $\alpha$-FeSe. Clear orbital-selective (OS) incoherence is visible in Fig. 3 a low-energy pseudogap is clearly visible in the $xz, yz, x^2 - y^2$ DOS, and only the $xy, 3z^2 - r^2$ DOS show very narrow FL-like resonances at $E_F$. Examination of the self-energies in Fig. 4 shows that, for $n = 5.8$, only $\text{Im} \Sigma_{x^2,y^2} (\omega) \approx -\omega^2$ for $\omega < E_F (=0)$. Using the Kramers-Krönig relation, it follows that the Landau FL quasiparticle residue, $Z$ vanishes near-identically for the $xz, yz, x^2 - y^2$ band carriers [from $\text{Re} \Sigma (E_F)$], direct numerical evaluation gives $Z_{x^2,y^2} = 0.023, Z_{x^2,y^2} = 0.04)$. Correspondingly, spectral lineshapes for these bands are nicely fit by a power-law fall-offs (not shown) in the range $-2.0 < \omega < -0.2$ eV; this local “critical” behavior is cut-off by the normal state pseudogap for $-0.2 < \omega < E_F$. Hence, at small but finite $T$, the “normal” metal will be totally incoherent, without any FL quasiparticles. Remarkably, such behavior results from strong scattering between effectively (Mott) localized and itinerant components of the full DMFT matrix propagators, and is caused by an Anderson orthogonality catastrophe (AOC) in the impurity problem of DMFT. This is intimately linked to OS Mott-like physics within DMFT.

Our identification of normal state incoherence in $\alpha$-FeSe with the AOC has many interesting consequences. Since the optical conductivity ($\sigma (\omega)$) in DMFT is a direct convolution of the full one-particle propagators, we predict that $\sigma (\omega)$ should show a pseudogapped form at small $\omega$, followed by a smooth crossover to a power-law ($\sim \omega^{-n}$) behavior at higher energy. The dc resistivity at “high” $T$ will be controlled by the renormalized scattering rate, $\tau^* (\omega)^{-1} = \omega \text{Re} \Sigma (\omega) \approx \omega^n$. Thus, $\rho_{dc} (T) \approx T$ at “high” $T$, as is ubiquitous to FeSe for $T > T_c$. Using the Shastry-Shraiman relation relating the $B_{1g}$ electronic Raman scattering (ERS) intensity to the optical conductivity, we predict that the ERS lineshape will also show a low-energy pseudogap, followed by a weakly $\omega$-dependent continuum at higher energy. These are stringent tests for our proposal, and experimental verification would place it on solid ground.

Also, the extreme sensitivity to Cu doping, which drives FeSe to a Mott insulator, is readily rationalized in our picture. In an incoherent metal with singular or near singular behavior of the one-particle propagator, disorder is a strongly relevant perturbation, and minute concentration of impurities qualitatively changes the low-$T$ behavior of the system from an incoherent metal to a
A kind of Anderson-Mott insulator. We emphasize that such sensitivity to minute impurity concentration is neither expected, nor found, in a weakly correlated FL. As it turns out, this is also additional evidence for \( \alpha \)-FeSe being close to Mottness.

Finally, our finding of an incoherent non-FL state implies that interband one-electron mixing is irrelevant in the normal state, since single electrons cannot coherently tunnel between different orbitals in such a metal. In analogy with coupled Luttinger liquids, two-particle coherence (arising from a second-order process involving interband one-particle mixing) should then take over. As \( T \) is lowered, therefore, various two-particle instabilities, either in the particle-hole (magnetism) or particle-particle (superconductivity) sector, will destabilize such a non-FL metal. Detailed consideration of these instabilities and such a mechanism for SC is out of scope of this work and is left for the future.

To conclude, based on a first-principles LDA+DMFT study, we have shown that orbital-selective incoherence characterizes the “normal” metallic phase in \( \alpha \)-FeSe. Very good semi-quantitative agreement with PES spectra and rationalization of a variety of unusual observations in a single picture lend strong support for our proposal. Sizable multi-orbital correlations are shown to be necessary to derive this orbital-selective incoherent metal. Emergence of SC at low \( T \), along with extreme sensitivity of the ground state(s) to minute perturbations in FeSe\(_{1-x}\)Te\(_x\) or Cu\(_{1-y}\)Fe\(_1-y\)Se should thus be considered as some manifestations of the myriad possible instabilities of such an incoherent non-Fermi liquid metal in close proximity to a Mott insulator.

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