Theory of Normal State Pseudogap Behavior in FeSe$_{1-x}$Te$_x$

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The normal state of the recently discovered Iron Selenide (FeSe)-based superconductors shows a range of inexplicable features. Along with bad-metallic resistivity, characteristic pseudogap features and proximity to insulating states, reminiscent of the underdoped high-$T_c$ cuprates, mark these systems as strongly correlated non-Fermi Liquid metals. Here, using the first-principles LDA+DMFT method, we show how strong multi-orbital correlation-induced orbital-selective Mott-like physics leads to an orthogonality catastrophe underpinning these inexplicable incoherent features. Excellent agreement with a range of resistivity and Seebeck data strongly support our proposal. We discuss pseudogap regime microscopically, along with implications for the nature of the instability at lower $T$, and propose that related systems could be of use in thermoelectric devices.

The Iron Selenides (FeSe), with or without Tellurium (Te) substitution, are the latest addition to a rapidly growing list of Fe-based unconventional superconductors [1]. These latter systems are structurally simpler than their 1111-oxyarsenide counterparts: they nevertheless exhibit a host of very unusual physical responses. These (by no means a complete list): (i) a linear-in-$T$ dependence of the bad metallic normal state resistivity, $\rho_{dc}(T) \approx \rho_0 + AT$ above $T_c$, and a Te- and Cu-substitution induced metal-insulator transition (MIT) in FeSe$_{1-x}$Te$_x$ [8] and Fe$_{1-x}$Cu$_x$Se [9], (ii) The NMR relaxation rate is distinctly of the non-Korringa form, and the static (uniform, $q = 0$) spin susceptibility, $\chi(T) \approx T^{1+n}$ with $0 < n < 1$, in FeSe [8]. (iii) An almost non-existent Drude peak, with dominant incoherent features in the optical conductivity [4]. (iv) Incoherent pseudogap like low-energy features in angle-integrated photoemission (PES) [5]. Also, an ARPES study for the antiferromagnetic compositions shows that the AF ordering wave-vector, $Q_{AF}$, is very different from that predicted by local-density-approximation (LDA) [6].

In particular, susceptibility and PES data show up the normal state pseudogap (PG) in FeSe$_{1-x}$Te$_x$. Several of the above features are reminiscent of the high-$T_c$ cuprates in the under- optimally doped regime, and, taken together, defy an interpretation in terms of the Landau Fermi Liquid (LFL). These PG features must manifest themselves in other probes as well. In fact, recent normal state resistivity and Seebeck data also exhibit PG features which closely correlate with each other [the PG in $\rho_{dc}(T)$, as seen in $(dp/dT)$ and $(d^2\rho/dT^2)$ near the PG scale $T^* \equiv T_{PG}$, correlates well with the related anomaly in $S(T)$ at the same $T = T^*$] [8, 10]. Further, at low $T$, the thermopower does not show the $S(T) \approx aT$ behavior; the $T$ dependence is distinctly slower than linear just above $T_c$. Along with $\rho_{dc}(T) \approx AT$, this confirms that the normal state in FeSe$_{1-x}$Te$_x$ is not a LFL metal. In addition, $S(T)$ at high-$T$ flattens out [4], being well described by a Heikes-like law; this is exactly the behavior expected from a Hubbard-like model at high $T$. Finally, $S(T,x)$ data [9] reveal an approximate isosbestic point at $T \approx 100$ K. This is strong evidence for a crossover scale, associated with effectively localized (Heikes law in $S(T)$) to incoherent metallic conduction, in FeSe$_{1-x}$Te$_x$.

Taken together, the above also imply that the FeSe$_{1-x}$Te$_x$ are strongly correlated materials proximate to a Mott insulator. The microscopic electronic correlation processes underlying the emergence of an incoherent pseudogapped metallic phase above $T_c$ ($T_N$) in FeSe$_{1-x}$Te$_x$, however, await a consistent theoretical understanding. Like the 1111-systems, Fe-selenides are multi-orbital (MO) systems with all five $d$ bands crossing the Fermi energy ($E_F$) in band (LDA) calculations. Given the global non-LFL features found experimentally, however, non-trivial extensions of the LDA to account for dynamical correlation-driven incoherence and breakdown of LFL theory are mandatory. Here, using the state-of-the-art LDA+dynamical-mean-field-theory (LDA+DMFT), already used with good success [11] for a range of correlated systems, we study this pseudogapped incoherent metallic state in FeSe$_{1-x}$Te$_x$ in detail.

In earlier work, we have shown that the incoherent metal [12] as well as the Te-doping induced metal-insulator transition (MIT) [13] can be quantitatively understood using LDA+DMFT with sizable $d$ band MO correlations. Here, we extend these to characterize the PG phase in detail. Specifically, we show how the Seebeck co-efficient (thermopower), $S(T)$ is also quantitatively described, and correlate the specific PG anomalies in both $S(T)$ and $\rho_{dc}(T)$ with doping, $x$. Very good quantitative accord with extant data reinforces the basic hypothesis about crucial role of strong correlations. To our best knowledge, this is a first attempt to uncover such features in an incoherent metal within LDA+DMFT for a real system. Finally, we show how the itinerant-localized duality (Mottness) makes for a high thermoelectric figure-of-merit ($ZT$) in such systems at low $T$, and suggest possibilities for thermoelectric applications using related systems.

Since the basic LDA+DMFT formulation has been...
used for a variety of real systems with good quantitative success [11], we do not present it here, but directly describe the electronic transport within LDA+DMFT scheme. The Seebeck coefficient, like the conductivity, is exactly computable within DMFT using the fully renormalized LDA+DMFT propagators. We generalized the DMFT result [14,15] to the five-band case relevant for FeSe$_{1-x}$Te$_x$. This involves the following steps:

We begin with the general expressions for Seebeck and thermal conductivity, which, respectively, measure the mixed electrical-thermal correlations $[S(T)]$ and the heat-current correlations $[k(T)]$ at finite $T$:

$$ S(T) = \frac{1}{T} \frac{A_1(T)}{A_0(T)}, $$

$$ k(T) = \frac{1}{T} \left( A_2(T) - \frac{A_1^2(T)}{A_0(T)} \right), $$

with $A_n(T) = \frac{2}{\pi n} \int_{-\infty}^{\infty} d\omega \phi^{\alpha\beta}(\omega)[-f'(\omega)](\omega-\mu)^n$ and

$$ \phi^{\alpha\beta}(\omega) = \frac{1}{V} \sum_{\mathbf{k}} T_{\alpha,\beta}(\mathbf{k}) \rho_{\alpha}(\mathbf{k},\omega)v_{\alpha,\beta}(\mathbf{k},\omega) \rho_{\beta}(\mathbf{k},\omega). $$

Here, $\rho_{\alpha}(\mathbf{k},\omega) = -\frac{1}{2}Im \omega \Sigma_{\alpha}(\mathbf{k},\omega)_{\text{DMFT}}$ is the LDA+DMFT spectral function, $a = (xy, xx, xz, yz, x^2-y^2, 3z^2-r^2)$ represent the five $d$ orbitals, $\mu$ is the chemical potential, $v_{\alpha,\beta}(\mathbf{k})$ is the group velocity, $f(\omega)$ is the Fermi-Dirac function and $V$ the sample volume. In DMFT, the $A_n(T)$ are convertible to integrals over the unperturbed DOS.

The only approximation made here is to ignore the $\mathbf{k}$ dependence of $v_{\alpha,\beta}(\mathbf{k})$, i.e. $v_{\alpha,\beta}(\mathbf{k}) \rightarrow v_{\alpha,\beta} = v$. In an incoherent metal, such as we have here, this is justified, since, between successive hops, a carrier in an incoherent state does not exist long enough in a given $\mathbf{k}$ eigenstate.

Another related reason is the bad-metallicity resistivity, implying $k_Ft \simeq O(1)$ and leading to the same conclusion. With this simplification, Eq. (3) for the intra-band contribution reads $\phi^{\alpha\beta}(\omega) = \frac{e^2}{V} \sum_{\mathbf{k}} \rho_{\alpha}^2(\mathbf{k},\omega)$.

We now describe our results. In Fig. 1, we show the resistivity, $\rho_{dc}(T) \equiv 1/A_0(T)$ in FeSe$_{1-x}$Te$_x$, derived earlier [13]. It clearly shows the “S-like” shape characteristic of a PG metal. At low $T$, $\rho_{dc}(T) \simeq AT$ and the LFL-like $T^2$ form is never observed. With increasing $x$, $\rho_{dc}$ becomes more bad-metallic, smoothly going over to an insulator-like form up to very low $T \simeq 2.0$ K. In reality, at much higher $T$, either antiferromagnetic (AF) or unconventional superconducting (USC) transition will cut off this extremely low crossover to a metal. For non AF/USC ordered systems, even a minute amount of non-magnetic disorder on FeSe layers (e.g. Cu [4]) will immediately destroy metallicity, leading to a metal-insulator transition, as indeed seen in Fe$_{1-x}$Cu$_x$Se for $x < 1$. Focussing on $x = 0$ to make contact with experiment [10], we show $(d\rho_{dc}/dT)$ and $(d^2\rho_{dc}/dT^2)$ in the top panels of Fig. 1. The PG scale, $T^* = AT$, the temperature at which $(d\rho_{dc}/dT)$ shows a maximum, while $(d^2\rho_{dc}/dT^2)$ crosses zero [10]. The Seebeck co-efficient, $S(T)$, should also show an anomalous feature, i.e. a minimum, around $T^*$ [9,10].

Very good quantitative agreement with extant data [9,10] is also clearly visible in $S(T,x)$, Fig. 2. Our results are obviously valid only for $T > T_c$, and, at very low $T$, correspond to what would be observed in a non-SC system in absence of disorder. A number of characteristic features, intimately correlated with those in the resistivity derivatives, are noteworthy: (i) $S(T)$ is approximately $T$-independent at $T > T_{\text{min}}(x)$, in nice accord with Heikes law. Here, it arises due to thermal transport involving Mott localized carriers in our five-orbital Hubbard model. (ii) In the relevant range of $0 \leq x \leq 0.6$, we find that $S(T)$ smoothly decreases, going through a minimum at another scale $T^*(x)$. Interestingly, the deviation from Heikes law sets in around $T_{\text{PG}} = 150$ K. Further, this scale coincides with the PG scale extracted from resistivity derivatives (see Fig. 1), pinning down the temperature below which a low energy PG opens up in transport. (iii) $S(T,x)$ crosses zero twice at $T_{\text{low}}(x), T_{\text{high}}(x)$ (labelled $T_{\text{an}}, T^*$ in Ref. [10]), again in precise accord with data. (iv) Even at low $T \simeq 10$ K, $S(T)$ does not recover the linear-in-$T$ form: an examination shows a $T^\eta$ law with $\eta \leq 1$, suggesting that collective bosonic fluctuations dominate the low-$T$ thermopower. (v) Also the approximate isosbrectic point in $S(T,x)$ as $x$ is varied is reproduced by LDA+DMFT. (vi) Interestingly, $S(T)$...
only shows two sign changes for metallic (above $T_c$) compositions. For large $x > 0.5$, appearance of insulator-like behavior above $T_c$ [13] goes hand-in-hand with only one sign change at high $T^* \simeq 150$ K in $S(T)$, also consistent with findings [8].

FIG. 2: (Color online) Seebeck coefficient (top left) and thermal conductivity (top right) for FeSe$_{1-x}$Te$_x$ within LDA+DMFT. Notice the $S(T) \equiv \text{const.}$ form at high-$T$, decreasing around $T_{\text{PG}}$ and showing a second crossing at much lower $T_{\text{an}}$, all in excellent agreement with data [8, 10]. The thermoelectric figure of merit, $ZT$, is shown in the lower panel. Notice the high value of $ZT$ for $x = 0.6$.

Remarkably, the full set of our theoretical $\rho_{\text{dc}}(T, x)$ and $S(T, x)$ results are in very good agreement with a range of extant results obtained by two groups [8, 10]. Our work is the first detailed theoretical study of electrical and thermal transport in Fe-based superconductors. These remarkable results clearly call for a deeper microscopic rationalization. Since vertex corrections to conductivities vigorously vanish in DMFT [10], these features must be intimately linked to the detailed evolution of the LDA+DMFT spectral functions with $T$ and $x$. In Fig. 3, we show the LDA+DMFT orbital-resolved DOS, $\rho_{\alpha}(\omega)$, for the doping values above. Clear signatures of normal state incoherent metal behavior, along with a low-energy PG, are visible in the DOS, providing a clear link between PG features in transport and spectral responses. In particular, we observe important changes in the LDA+DMFT DOS with $x$, and these must be correlated with features in transport. The $d_{z^2}$ DOS always has a deep PG, while the $d_{xy}$ DOS rapidly loses the small LFL coherence with $x$. The $d_{x^2-y^2}$ DOS shows a progressively deeper PG feature with $x$, while the reverse occurs for the $d_{3z^2-r^2}$ DOS. These go hand-in-hand with large changes in spectral weight transfer (SWT), a characteristic feature of Mottness [18]. Further, clear power-law fall-off of the DOS at energies above the (small) PG feature around $E_F$ instead of a LFL peak at $E_F$ is seen for the $d_{xz,yz,x^2-y^2}$ DOS. Finally, the low-energy kink feature clearly seen for $x = 0$ (solid curve) is smoothened with $x$. Based on the agreement with transport above, we predict that PES (ARPES) measurements on FeSe$_{1-x}$Te$_x$ as a function of $x$ should show all these features in the spectral function with $x$.

Also the anomalies in $S(T)$ and $(d^n \rho_{\text{dc}}/dT^n)$ with $n = 1, 2$ at the much lower $T_{\text{an}}$ [17], observed for the first time in a correlated system [10], are recovered too within our LDA+DMFT. In a band-LFL picture, this behavior would be associated with hole conduction, but such a connection is tenuous in the incoherent metal we find. In real FeSe$_{1-x}$Te$_x$, USC and/or AF actually cuts off this behavior, leading to $S(T \rightarrow 0) = 0$. Looking closer at the $T \rightarrow 0$ limit within our uniform, symmetry-unbroken, state calculation, we find that $S(T \rightarrow 0) \simeq T^\eta$ with $\eta \leq 1$. Correspondingly, $\rho_{\text{dc}}(T) \simeq AT^\eta$ up to lowest $T$. Neither $\rho_{\text{dc}}(T) \simeq T$ nor $S(T) \simeq T^\eta$ with $\eta \leq 1$ at low $T$ are interpretable in terms of transport associated with LFL quasiparticles; rather, they suggest transport in terms of incoherent, collective excitations in the non-LFL metal. If the above features are related to the mechanism of superconductivity (SC) [10], our analysis has far-reaching implications for the SC-instability. Specifically, our results now imply that SC must arise directly as an instability of a normal non-LFL metal without long-lived fermionic quasiparticles, and that the $d_{xz,yz,x^2-y^2}$ bands will play a central role in pairing, with the rest playing a secondary role, as in a proximity effect scenario. Recall that, in our earlier LDA+DMFT study
of FeSe\cite{12,13}, the non-LFL metal arises from orbital selective incoherence having its origin in the interplay between strongly orbital-dependent hopping (as in LDA) and strong dynamical inter-orbital correlations (DMFT); the non-LFL features are assigned to the generation of an Anderson orthogonality catastrophe in the local problem of DMFT\cite{12}. Once this occurs, the spectral functions will exhibit a low energy PG with power-law like tails at higher energy, precisely as we find in the DMFT. In such a metal, the transport properties are dominated by collective, multi-particle bosonic excitations\cite{19}, rather than by LFL quasiparticles. Our LDA+DMFT results are consistent with this incoherence scenario based on Mottness, and excellent agreement with data from a number of groups, as shown above, strongly supports our contention.

Therefore, we extend our analysis to propose that related materials have the potentiality to be of use as good thermoelectrics, at least at low $T$. To this end, we also need the thermal conductivity, $k(T)$, also computable exactly in DMFT in terms of the LDA+DMFT propagators. In Fig 2, we show the electronic part of the thermal conductivity $[k(T)]$, along with the thermoelectric figure of merit, \(ZT = \frac{\sigma^2 T}{k}\). We find $k(T) \simeq T^2$ at low $T$, indicating that bosonic contributions dominate the electronic contribution to $k(T)$. We suggest that measuring $k(T)$ at low $T$ will bare this contribution. At higher $T > 10$ K, additional phononic contributions will increase $k(T)$ and decrease the electrical conductivity $\sigma(T) \equiv A_0(T)$, reducing $ZT$. Thus, given the weak electron-phonon coupling in the Fe-based SC\cite{20}, we expect a small-to-moderate reduction in $ZT$ at low $T$. Nevertheless, the high value of $ZT$, albeit at low $T$, is encouraging, and ways of improving $ZT$ at higher $T$, based on appropriate engineering are an attractive possibility. In particular, consideration of more geometrically frustrated members of the family of Fe arsenides and selenides could yield an appreciable $S(T) \simeq T$ at high $T$ arising from large spin and orbital fluctuations, as in NaCo$_2$O$_4$\cite{21}, and increasing $ZT$.

Given an incoherent non-LFL metal with low energy PG as above, the low $T$ instabilities cannot involve usual particle-hole (p-h) (AF) or particle-particle (p-p) (USC) pairings in a LFL, since there are no coherent LFL quasi-particles in the non-LFL state in the first place. We believe that these instabilities will then arise by studying the dominant two-particle instabilities of such a metal. As in coupled $D = 1$ Luttinger liquids\cite{22}, in a regime where one-particle inter-orbital mixing is irrelevant, generation of effective two-particle (pair hopping) terms in both p-h and p-p sectors at two-loop level in a renormalization group treatment around the impurity (DMFT) limit lead to ordered states emerging directly from the incoherent metal\cite{23}. We leave the details of the mechanism of USC from an incoherent metal derived above to the future.

In conclusion, we have studied the detailed nature of the incoherent metal with a low energy pseudogap using the first-principles LDA+DMFT. The anomalous character of the transport properties is interpreted in terms of electrical and heat transport by collective, multi-particle excitations. These arise from an Anderson orthogonality catastrophe having its origin in the selective-Mott localization in LDA+DMFT. Excellent semiquantitative agreement with a whole host of transport ($p_{dc}(T)$ and $S(T)$) data with $x$ puts our mechanism on solid ground. Our study puts strong theoretical constraints on how the ordered states (AF/USC) arise directly from the incoherent metal, and shows the crucial importance of Mottness in this context.

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