Correlation induced spin freezing transition in FeSe: a dynamical mean field study

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The effect of local Coulomb interactions on the electronic properties of FeSe is explored within dynamical mean field theory combined with finite-temperature exact diagonalization. The low-energy scattering rate is shown to exhibit non-Fermi-liquid behavior caused by the formation of local moments. Fermi-liquid properties are restored at large electron doping. In contrast, FeAsLaO is shown to be located on the Fermi-liquid side of this spin freezing transition.

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The recent discovery of high-temperature superconductivity in iron-based pnictides$^1$ and chalcogenides$^2$ has led to an intense discussion concerning the role of Coulomb correlations in these materials. Although compounds such as FeAsLaO (1111), BaFe$_2$As$_2$ (122), LiFeAs (111), and FeSe (11) all have rather similar one-electron properties, a variety of experiments suggest significant differences. For instance, photoemission measurements show that FeAsLaO is moderately correlated, with about 50% 3d band narrowing and effective mass enhancement of about 2 to 3$^3$. In contrast, several photoemission data on FeSe$_{1−x}$Te$_{x}$ samples reveal larger effective mass enhancement and stronger band narrowing$^4$$^5$. Optical measurements exhibit incoherent spectral features indicative of a pseudogap$^9$, and several transport measurements show large deviations from Fermi-liquid behavior$^{10}$.$^{13}$. Moreover, recent theoretical work$^{14}$ suggests that Coulomb interactions in (11) compounds ought to be less well screened than in (1111) systems.

The aim of this paper is to elucidate the origin of the experimentally observed bad-metallic behavior of FeSe. Using an accurate single-particle description of the electronic structure together with appropriate interaction parameters$^{14}$, and evaluating the influence of local Coulomb interactions within dynamical mean field theory (DMFT)$^{13}$, we show that correlations are strong enough to give rise to the formation of Fe 3d local moments, implying non-Fermi-liquid behavior, where electronic states at the Fermi energy exhibit a finite lifetime. Moreover, we demonstrate that these properties are caused by a nearby doping-driven spin-freezing transition, i.e., Fermi-liquid behavior is restored towards larger electron doping, whereas hole doping reinforces bad-metallic properties. Using the same approach for FeAsLaO we show that Coulomb interactions are too weak to cause spin freezing, so that this system merely exhibits moderate effective mass enhancement$^{16}$.

Thus, FeSe appears to be a material which exhibits bad-metallicity induced by a spin freezing transition, a mechanism recently identified by Werner et al.$^{17}$ in a three-band model. For FeAsLaO, Haule et al.$^{18}$ showed that large Coulomb interactions lead to the formation of local moments and large scattering rates, while Ishida and Liebsch$^{19}$ discussed the spin freezing transition as a function of Coulomb interaction and doping. Bad-metallic behavior in FeSe was also found in DMFT studies by Craco et al.$^{20}$ and Aichhorn et al.$^{21}$. The spin-freezing origin of this behavior, however, was not investigated in these works.

To account for local Coulomb interactions among Fe 3d electrons we use exact diagonalization$^{22}$ (ED) which we have recently extended to five orbitals$^{19}$. Discretization of the lattice surrounding the local impurity is achieved by using ten bath levels, which yields excellent projections of the lattice Green’s function onto the cluster consisting of impurity plus bath. Because of the very large size of the Hilbert space of this 15 level system (the largest spin sector has dimension $\sim 40 \times 10^6$) the spacing of excited states is very small so that finite size errors are greatly reduced. Moreover, ED has the advantage of allowing for rotationally invariant Hund exchange. This is of crucial importance for the spin freezing transition since omission of spin-flip and pair-exchange interactions leads to a significant shift of the Fermi-liquid to non-Fermi-liquid phase boundary. For computational reasons we restrict ourselves to the lowest excited states, which are relevant near the $T \to 0$ limit. Only the paramagnetic phase is considered. Further calculational details can be found in Ref.$^{19}$.

The electronic properties of FeSe are formulated in terms of the effective low-energy model recently derived by Miyake et al.$^{14}$. In this scheme, standard band structure calculations within the local density approximation (LDA) were carried out, analogous to previous work in Refs.$^{23}$.$^{24}$. From these results, maximally localized Wannier functions were constructed for the Fe 3d bands, following the procedure discussed in Ref.$^{25}$. The inter-site transfer integrals are then derived from the matrix elements of the Kohn-Sham Hamiltonian $H(k)$ in the basis of these Wannier functions. Finally, the constrained random-phase-approximation (RPA) developed by Aryasetiawan et al.$^{26}$ was used to determine the effective Coulomb and exchange interaction parameters, which account for screening via Se 4p orbitals. Because
The average intra-orbital Coulomb interaction is given by the parameters $U_{mn}$ and $J_{mn}$ for FeSe, as shown in Tables VII and VIII of Ref. [14], respectively. The average one-electron transfer integrals $t_{mn}(\mathbf{R})$ and interaction matrices $U_{mn}$ and $J_{mn}$ for FeSe are given in Tables VII and VIII of Ref. [14], respectively. The average intra-orbital Coulomb interaction is $\langle U \rangle = 4.2$ eV and the average Hund exchange is $\langle J \rangle = 0.5$ eV. The $x,y$ axes point along Fe second-neighbor directions.

Fig. 1(a) shows the low-energy limit of the 3d self-energy components, $\gamma_m = -\text{Im} \Sigma_m(i\omega_n \to 0)$, as a function of Fe 3d occupancy. The one-electron transfer integrals and interaction matrix elements are kept fixed at the values for $n = 6$. Ordinary Fermi liquid behavior is found for $n > 6.5$, but increasing low-energy scattering rates are obtained at lower electron doping, except for the $d_{xy}$ orbital. Even stronger scattering occurs on the hole doping side, $n < 6$. The reason for the different behavior of $\gamma_{xy}$ is that $\rho_{xy}(\omega)$ is about 0.5 eV wider than the other density of states components [14].

To identify the origin of this change from Fermi-liquid to non-Fermi-liquid behavior we have evaluated the spin-spin correlation function $C_m(\tau) = \langle S_mz(\tau)S_mz(0) \rangle$, where $\tau$ denotes imaginary time. In the case of a Fermi-liquid, these functions decay with $\tau$, so that $C_m(\tau = \beta/2)$ is very small ($\beta = 1/T = 100$ eV$^{-1}$). The susceptibilities $\chi_m \sim \int_0^\beta d\tau \langle S_mz(\tau)S_mz(0) \rangle$ then are Pauli-like, i.e., independent of temperature. Fig. 1(b) shows that the results for $n > 6.5$ are consistent with this behavior. At smaller electron doping, the $C_{m\neq xy}(\tau)$ components reach increasingly larger constant values near $\tau = \beta/2$. The corresponding susceptibilities $\chi_m$ then become proportional to $1/T$, as expected for Curie-Weiss behavior.

A similar spin-freezing transition was recently found by Werner et al. [17] for a degenerate three-band model near $n = 2$, i.e., at one electron away from half-filling. Using continuous-time quantum Monte Carlo DMFT, the paramagnetic phase at moderate $U$ was shown to exhibit Fermi-liquid properties at small $n$. For $n > 1.5$, an incoherent metallic phase appears, where the self-energy exhibits a finite onset at $\omega = 0$ due to the formation of local moments. Because of particle-hole symmetry, the same Fermi-liquid to non-Fermi-liquid transition appears on the electron-doped side, i.e., when reducing the occupancy below $n \approx 4.5$.

Fig. 2 shows the 3d orbital occupations as a function of doping. At $n = 6$, these values differ significantly from their uncorrelated values: $n_{xz,yz,x^2-y^2,xy,z^2} = (0.54, 0.54, 0.56, 0.60, 0.76)$, indicating strong interorbital charge transfer induced by Coulomb interactions. In particular, $n_{xy}$ reaches nearly unity, while the other $n_m$ are close to half-filling. Despite this orbital polarization, the spectral distributions (not shown here) reveal considerable intensity near $E_F$, suggesting that the system is not in a Mott phase, where one of the subbands is filled and the others are split into lower and upper Hubbard bands. These kinds of partial Mott transitions, with certain subbands empty or full, are found in several three-band $t_{2g}$ materials, such as LaTiO$_3$ [27, 28], V$_2$O$_3$ [29, 30], and Ca$_2$RuO$_4$ [31, 32].

To investigate the relationship between orbital parameters and the electronic structure, we have evaluated the interaction matrices $U_{mn}$ and $J_{mn}$ for FeSe, as shown in Tables VII and VIII of Ref. [14], respectively. The average one-electron transfer integrals $t_{mn}(\mathbf{R})$ and interaction matrices $U_{mn}$ and $J_{mn}$ for FeSe are given in Tables VII and VIII of Ref. [14], respectively. The average intra-orbital Coulomb interaction is $\langle U \rangle = 4.2$ eV and the average Hund exchange is $\langle J \rangle = 0.5$ eV. The $x,y$ axes point along Fe second-neighbor directions.
five-band model with Bethe lattice density of states with spin correlations derived within ED/DMFT for a degenerate $U = 4$ eV. For $U = 4$ eV, $J = 0.75$ eV, the spin-freezing transition occurs at $n = 6.2$, with Fermi-liquid behavior at $n > 6.2$ and increasing bad-metallicity for $n < 6.2$. For $U = 4$ eV, $J = 0.5$ eV (not shown), the transition occurs at $n = 6.1$.

To understand better to what extent the results for FeSe shown in Fig. 1 depend on the details of the single-particle Hamiltonian, we have carried out analogous ED/DMFT calculations by replacing $H(\mathbf{k})$ with the tight-binding Hamiltonian derived by Graser et al. for FeAsLaO [37]. Since the 3d density of states components of this compound are qualitatively similar to those of FeSe, there ought to be also a spin-freezing transition. Indeed, if we retain the FeSe interaction parameters with an average Coulomb energy of 4.2 eV, the overall behavior of the low-energy scattering rates $\gamma_m$ and spin-spin correlations $C_m$ are qualitatively similar to those shown in Fig. 1, except for a less pronounced orbital polarization. For instance, at $n = 6$, $\eta_{xy} = 0.77$ rather than 0.95. Nevertheless, the Fermi-liquid to non-Fermi-liquid transition also occurs near $n = 6.5$, suggesting that this phenomenon is remarkably robust, i.e., insensitive to the details of the one-electron properties. These results further support the key point of the degenerate-band example presented in Fig. 3, namely, that the spin freezing transition is not driven by orbital polarization.

According to the work by Miyake et al. [14], the crucial difference between FeSe and FeAsLaO is that, because of more efficient $dp$ screening and more extended Wannier orbitals, local Coulomb interactions in the latter system are considerably smaller, with $(U) \approx 2.7$ eV and $\langle J \rangle \approx 0.4$ eV. In previous ED/DMFT calculations for FeAsLaO [10] based on orbital independent Coulomb and exchange energies we showed that spin freezing may occur at about $U = 3$ eV for Hund exchange $J = 0.75$ eV. Using the recently published orbital dependent $U_{mn}$ and $J_{mn}$ matrices derived within constrained RPA [14], we are now able to make a more accurate prediction of the spin freezing transition in FeAsLaO. The transfer integrals and interaction parameters are again held fixed at their values for $n = 6$. As shown in Fig. 4, the transition now is located almost exactly at $n = 6$. Thus, in contrast to FeSe, Fermi-liquid properties in FeAsLaO prevail and the 3$d$ bands exhibit only moderate effective mass enhancement, $m^* \approx 2 \ldots 3$ [10]. Nonetheless, hole doping $n < 6$ gives rise to local moment formation and bad-metallic behavior, with a finite lifetime at $E_F$, while electron doping stabilizes the Fermi-liquid properties. (Note the weaker orbital polarization compared to the results for FeSe in Fig. 1. Also, because of orbital dependent $U_{mn}$, $J_{mn}$, the magnitudes of $\gamma_m$ and $C_m(\beta/2)$ differ from those for orbital independent $U$, $J$ in Ref. [19].)
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basis, such as the one used in Ref. [21].

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On the basis of these results we arrive at the phase
diagram depicted in Fig. 5. FeSe is located well inside
the non-Fermi-liquid phase, whereas FeAsLaO lies on the
Fermi-liquid side of the spin-freezing transition. Both
systems exhibit ‘parent’ Mott phases in the limit \( n = 5 \).

We finally discuss the role of spin-flip and pair-
exchange interactions. In Ref. [15] it was shown that
the omission of these terms in the many-body impurity
impot leads to a significant shift of the Fermi-liquid
to non-Fermi-liquid phase boundary to \( \sim 1 \) eV smaller
\( \langle U \rangle \). Thus, for FeSe bad-metallic behavior would become
even stronger. Since FeAsLaO, however, lies very close
to the phase boundary, this approximation has severe
consequences. Instead of a Fermi-liquid characterized by
moderate effective mass enhancement, this compound is
then also bad-metallic, in conflict with experiments.

The present work is based on a consistent combination of single-particle Hamiltonian, constrained RPA interaction parameters, and DMFT many-electron calculations within a \( 5 \times 5 \) d electron basis. It would be interesting to
compare the spin-freezing transition obtained within this
scheme to analogous formulations within a \( pd \) electron basis, such as the one used in Ref. [21].

In summary, we have evaluated the effect of local cor-
relations in FeSe, using accurate single-particle properties and constrained RPA results for the orbital depend-
et Coulomb and exchange matrices, combined with
ED/DMFT. The finite scattering rates derived from the
3d components of the self-energy are shown to be linked
to the formation of local moments. Thus, FeSe is bad-
metallic, in agreement with experimental findings. Spin
freezing ceases for large electron doping, giving rise to
Fermi-liquid behavior. In contrast, hole doping enhances
bad-metallicity. Applying the same scheme to FeAsLaO
we find that, as a result of the more efficiently screened
coulomb interactions, local moment formation is con-
fined to hole doping \( n < 6 \). Thus, FeAsLaO and FeSe

seem to be located on opposite sides of the Fermi-liquid
to non-Fermi-liquid spin freezing transition.

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