Correlated electronic systems with geometric frustration have spawned intense interest recently, because of the startling diversity of physical properties they manifest. The crucial roles of electronic correlation and frustration, working in tandem, are nevertheless poorly understood from a fundamental viewpoint: strong correlations generically drive Mott transitions (accompanied by orbital/magnetic order) and manifest spectacular changes in physical responses under minute perturbations [1]. In correlated systems, geometric frustration gives rise to large, exponential degeneracy of classical ordered states, and to unconventional order via an order by disorder mechanism [2]. The variety of new, hitherto unexplored, phases of matter emerging in systems where both correlation and frustration are operative is a fascinating, more-or-less open problem.

The layered (in XY plane) ferromagnetic (FM) system GdI$_2$, studied by several authors [3, 4, 5, 9], may turn out to be an interesting example. Gd ions in the 4f$^75d^1$ state form a triangular lattice, separated by iodine layers. Itinerant electronic states in the partially filled d-bands coupled to localized f-electrons drive an FM state ($T_c \approx 300$ K). Interestingly, GdI$_2$ shows significant magnetoresistance $\rho$ (40% per Tesla) close to $T_c$ [10]. In addition, it is iso-structural to the well known dichalogenides with hexagonal layered structure [11], showing charge density wave (CDW) order at low temperatures. In fact, GdI$_2$ is a bad metal below $T_c$ and becomes insulating for $T < 80$ K. Might this be an indication that the features seen in dichalogenides also occur in GdI$_2$?

The unusually high (significantly higher than $\rho_{\text{Mott}}$) resistivity of GdI$_2$ even in the metallic state is strongly at odds with a simple FM $s(d) - f$ lattice model, where FM order implies a good metal for a translationally invariant system. In fact, experiments yield $k_F l < 1$ ($l$ is electron mean-free path) in GdI$_2$, indicating a strong inelastic scattering of carriers and resulting in an incoherent metallic state, without Fermi liquid quasi-particles. On the other hand, the FM spin fluctuations [12] are well-described by a classical picture of two-dimensional (2D) FM Heisenberg model. The saturation magnetic moment in the FM state is about $7.33 \mu_B$ per atom, considerably lower than the maximum attainable value ($5 \mu_B$), indicating the relevance of the competition between strong correlation effects and itinerancy among the 5d electrons of Gd. The above observations force one to seek additional, non-magnetic, strong correlation effects deep in the FM state to reconcile magnetism with transport in GdI$_2$. Moreover, owing to its 2D structure, the role of correlation is expected to be very important in GdI$_2$.

Strong magnetic fluctuations found experimentally [13] and a series of magnetic ground states obtained in a correlated electronic model [5], also underline the relevance of Gd-d-shell correlation.

Band structure results for GdI$_2$ [3, 4] indicate a spin splitting of the conduction band. The crystal field in GdI$_2$ is relatively small and the 5d orbitals are weakly split and partially occupied. Emergence of an insulating ground state in with three partially filled d-bands is surprising, since the band-filling is off-commensurate (less than 1/3 filling). This suggests that the $T \rightarrow 0$ insulator must be associated with an additional broken symmetry. The high-$T$ bad-metal phase implies that this must emerge from an instability of an incoherent metallic state, pointing to the strong correlation limit. This raises deeper questions: (i) what is the specific nature of the inelastic scattering processes leading to the “bad metal”? (ii) How does such an incoherent FM state evolve into a $T \rightarrow 0$ insulator? Is any additional symmetry breaking (in charge, orbital sectors) involved?

These observations should go hand-in-hand with the evolution of the correlated electronic structure of GdI$_2$ with temperature. In this letter, we address these issues in detail. Using dynamical mean-field theory (DMFT), we solve a multi-orbital Hubbard model with the LSDA band-structure of GdI$_2$ [4]. We show that strong co...
relations localize two degenerate bands with \(d_{x^2-y^2}, d_{xy}\) orbital character, leaving a renormalized band with \(d_{z^2}\) character to cross \(E_F\). The renormalized Fermi surface is strongly modified by correlations, eroding the LSDA hole pockets (see below). Further, we argue that the shape of the correlated Fermi surface naturally drives a charge-ordered (CO) ground state with \(\sqrt{3} \times \sqrt{3}\) order on the triangular lattice (breaking the underlying translational symmetry). Using LSDA+DMFT, we propose a simple effective model that allows us to suggest experimental signatures of such a ground state.

The LSDA band structures obtained [9] using LMTO method [14] shows that the most relevant bands crossing \(E_F\) are mainly derived from the 5\(d\) orbitals (occupations of \(d_{x^2-y^2}, d_{xy}, d_{z^2}\) are 0.31, 0.31, 0.30 respectively), split about 0.9 eV into majority and minority spin sub-bands by strong exchange interaction \((J_{fd})\) with the completely spin-polarized 4\(f\) shell. The corresponding hexagonal Fermi surface, exhibits six hole pockets (not shown).

LSDA+U calculations were performed treating Gd \(f\) states as completely spin-polarized quasi-core states (U applied only to Gd \(d\) states). For the double counting term the so-called “atomic limit” was used [9, 10]. We find (Fig. 1) that \(d_{x^2-y^2}, d_{xy}\) and \(d_{z^2}\) bands are pulled down by \(static, orbital\) correlations, and the \(d_{xy}\), \(d_{x^2-y^2}\) bands are localized. However, LSDA+U \(overestimates\) band-splittings, while LSDA cannot split partially occupied bands. A reliable picture requires a full incorporation of \(dynamic\) \(d\)-band correlations, using LSDA+DMFT, to which we turn below.

The correlated multi-orbital model Hamiltonian for \(GdI_2\) is described by \(H = H_0 + H_{int}\), where

\[
H_0 = \sum_{k,\alpha} \epsilon_k(k) c_{k\alpha}^\dagger c_{k\alpha} + \sum_{i,\alpha,\sigma} \Delta_i \hat{n}_{i\alpha\sigma}
\]  

is the band part with \(a, b =d_{x^2}, d_{x^2-y^2}, d_{xy}\), and

\[
H_{int} = U \sum_{i,\alpha} \hat{n}_{i\alpha\uparrow} \hat{n}_{i\alpha\downarrow} + U' \sum_{i,\alpha \neq \beta} \hat{n}_{i\alpha} \hat{n}_{i\beta} - J_{fd} \sum_{i,\alpha} S_{i\sigma} S_{i\alpha}
\]

(2)
describes the correlation part. In addition to \(U, U'\) acting in the \(d\)-manifold, we include \(J_{fd}\) for the scattering and spin polarization of the \(d\)-bands by well-localized \(Gd 4f\)-states (treated classically, i.e., neglecting spin-flip, as \(S = 7/2\)). As parameters relevant to \(GdI_2\), we choose \(U = 7.0\ eV, U' = 5.0\ eV, \) and \(J_{fd} = 1.5\ eV,\) with the LSDA bandwidths between 5 – 6 eV. In addition to scattering induced by \(U, U'\), \(J_{fd}\) acts like a \(classical\) scattering potential on the \(d\)-band states. We consider the FM phase without additional (charge, orbital) symmetry breaking and use multi-orbital iterated perturbation theory (MO-IPT) [13] to solve the multi-orbital impurity problem in the \(d\)-sector. LSDA+DMFT has been used with good quantitative success in many 3d-oxides [17, 18]. The strong scattering induced by \(J_{fd}\) is not accounted for in multi-orbital DMFT and is therefore combined with the solution of the Falicov-Kimball (FK) model in the local approximation [18].

DMFT renormalizes the LSDA results in two steps. First, the multi-orbital Hartree self-energy renormalizes the relative (LSDA) band positions depending upon their occupations and (energy) separations. More importantly, the frequency-dependent self-energy causes spectral-weight transfer across large energy scales, drastically modifying LSDA spectra. Its importance is directly seen in photoemission experiments on a host of correlated systems [17]: DMFT generally gives good quantitative agreement with photoemission. While LDA(LDA+U) generically gives correct \(ground\) states with orbital and magnetic order for weakly correlated(correlated) solids, its inability to describe both the narrowed quasiparticle bands and high-energy satellite features is well-documented [17].

Our DMFT results are drastically different: the Hartree self-energy pushes the degenerate \(d_{x^2-y^2}, d_{xy}\) bands down, and for \(U' = 6\ eV\), moves them completely below \(E_F\), leaving only the narrowed \(d_{z^2}\) band to cross \(E_F\) (Fig. 2). Smaller values of \(U'\) did not yield this selective localization. As alluded to above, large scale spectral weight transfer to the Hubbard bands drastically modifies the LSDA DOS. In contrast to multi-orbital systems showing correlated Fermi-liquid behavior at low-\(T\), no sharp quasiparticle peak (i.e., \(Im\Sigma(\omega \rightarrow 0, T \rightarrow 0) \neq 0\) is obtained in the DOS here. This implies an \(incoherent\) metallic behavior, with lifetimes so short that the quasiparticle concept loses meaning. This agrees with the high metallic resistivity in \(GdI_2\), which can be classified now as an orbital selective “bad metal”.

In fact, with Mott localization of the \(d_{x^2-y^2}, d_{xy}\) bands, the problem effectively reduces to a FK model
at low energy where the itinerant $d_{z^2}$ electrons scatter off the localized $d_{x^2−y^2}$ and $d_{xy}$ electrons. The infrared X-ray edge singularities rigorously known to exist for the FKM in $D = \infty$ give an infrared divergent local, inter-orbital excitonic susceptibility, $\chi_{ab}(\omega) = \int dt \langle [a_{\sigma}^\dagger(t)b_{\sigma}(t); b_{\alpha}^\dagger(0)a_{\alpha}(0)]e^{i\omega t} \rangle$, implying the existence of soft, inter-orbital ($a, b = d_{z^2}, (d_{x^2−y^2}, d_{xy})$) excitonic modes. Coupling itinerant $d_{z^2}$ electrons to these soft modes then destroys Fermi-liquid coherence leading to a “bad metal”. Given finite $T = 0$ entropy in this bad metal, we expect that a broken symmetry phase will preempt this unstable state at lower $T$. The quasi-nested regions of the renormalised Fermi surface (Fig. 3) indicate that this broken symmetry state is likely to be a CO state.

We can now draw the following straightforward conclusions. Since the $d_{x^2−y^2}, d_{xy}$ bands are pushed below $E_F$ by multi-orbital DMFT, the small hole pockets found in the LSDA disappear in the renormalised Fermi surface, which now corresponds to the correlation-narrowed $d_{z^2}$ band crossing $E_F$. The DMFT orbital occupations are altered to 0.35,0.35,0.22 for the $d_{x^2−y^2}$, $d_{xy}$ and $d_{z^2}$ bands. Similar features are seen in DMFT work [19] on Na$_2$CoO$_2$, in agreement with ARPES [20] showing no hole pockets. We predict that (i) an ARPES measurement performed for 80 K $< T < T_c$ would show up a single hexagonal Fermi surface sheet, and (ii) ARPES lineshapes will be anomalously broad without any Fermi-liquid peaks at low energy, reflecting the “bad metal” state.

A very interesting aspect of the renormalised Fermi surface, however, is that, similar to dichalcogenides [11], it exhibits a built-in tendency to favour emergence of low- $T$ CO state of the $\sqrt{3} \times \sqrt{3}$ type [11]. The movement of the van-Hove-like peak in the $d_{z^2}$ DOS very close to $E_F$ in the LSDA+DMFT (in stark contrast to LSDA and LSDA+U results) further corroborates this argument. Such features in Fermi surface and DOS may lead to unconventional CO states with gapless excitations [3]. Rigorous results for the existence of such CO states exist in the context of FK model (see below).

The essential results can be understood in a simpler, effective model for the FM state at low energy. With electrons in $d_{x^2−y^2}, d_{xy}$ bands unable to hop, we introduce an effective Hamiltonian, defined by

$$H_{\text{eff}} = \sum_k \epsilon_{z^2}(k) d_{z^2,k}^\dagger d_{z^2,k} + \Delta \sum_\alpha (\hat{n}_{i,z^2} - \hat{n}_{i,\alpha}) + U_1 \sum_{i,\alpha} \hat{n}_{i,\alpha} \hat{n}_{i,z^2}$$

(3)

where $\alpha = d_{x^2−y^2}, d_{xy}$. We solve $H_{\text{eff}}$ without further approximation within DMFT, with the LSDA occupations (0.31, 0.31, 0.30 for $d_{xy}$, $d_{x^2−y^2}$ and $d_{z^2}$ orbitals). The inter-orbital correlation $U_1$ reduces the DOS at $E_F$ considerably (Fig. 4) and a bad metallic phase, with $E_F$ in the low-energy pseudogap emerged. The DOS shows a gap for $U_1 = 0.70$ eV; the Fermi level, though, is never in the gap owing to the partial occupancy of the band. The local inter-orbital susceptibilities, $\chi_{z^2,xy}(\omega), \chi_{z^2,x^2−y^2}(\omega)$ exhibit power-law divergences (in the $D = \infty$ FKM [18]), yielding incoherent metallic behavior.

Reduction to an effective FKM has further, concrete consequences. Since only the $d_{z^2}$ states are itinerant, the local constraint of single occupancy on each site in $H_{\text{eff}}$ leads to the emergence of varied, band-filling dependent
CO states. This is rigorously known \cite{21} for FKM, and,
with three (orbital) components in Hamiltonian Eqn. (3),
we expect related CO patterns to unfold as a function of
band filling. Indications of this may already have been
seen in GdI$_2$ \cite{22}. We propose that such an “ordered”
state also drives GdI$_2$ insulating at low T. Moreover, the
detailed shape of our LSDA+DMFT Fermi surface sug-
gests an in-built propensity towards an unconventional
CO state with an anisotropic gap at $E_F$.

The Mott-Hubbard localization of $d_{z^2-r^2}$, $d_{xy}$ band
states found above leads to a local $U(1)$ invariance forcing \cite{23} $(d_{z^2}^\dag d_{z^2}) = 0$ identically ($a=d_{z^2-r^2}$, $d_{xy}$).
This implies rigorous absence of inter-orbital excitonic order
in the bad metal. Technically, this also precludes use of
usual Hartree-Fock RPA approach for broken symmetry
phases here. Interestingly enough, exactly this circumstance generates \cite{18} infrared singular, local, excitonic modes in the uniform phase, as shown above indicating
that the FM bad metal in GdI$_2$ is an excitonic liquid.
The LSDA+DMFT results do show, however, that the uniform phase is intrinsically unstable (given soft excitons \cite{24}) to an inter-orbital excitonic order at low temperature. We propose that the unconventional CO state
should also be viewed as an unconventional excitonic solid.
We speculate that this could turn out to be a new, specific microscopic manifestation of a seemingly more
generic feature in dichalcogenides \cite{11}. Suitable external
tuning parameters (e.g., pressure, doping) may melt this
state into an excitonic liquid. With discrete (Ising) nature
of orbitals, frustration on a triangular lattice may lead
to partially ordered solid-like, or more exotic dimer
or plaquette ordered phases before the unconventional
state melts completely.

The structural similarity of GdI$_2$ to other dichalco-
genides like 2H-TaS$_2$, 2H-TaSe$_2$, etc, suggests related
phenomena in GdI$_2$. In particular, it is possible that
the unconventional CDW or excitonic solid (or liquid)
states manifest themselves - favorable cases would be
those that are near the metal-insulator transition \cite{25}.
High pressure or chemical doping could then tune the sys-
tem into a very anomalous metallic state with strong, un-
conventional, excitonic liquid correlations. Whether such
exciton-liquid correlations also drive unconventional super-
conductivity (USC) \cite{11} is an additional, fascinating
issue in this context.

To conclude, based on LSDA+DMFT calculations, we
propose that the FM “metallic” phase of GdI$_2$ is an ex-
citonic liquid. At low T, this is argued to order into an
unconventional excitonic CDW insulator. Our approach
can also be used fruitfully for the investigation of other
dichalcogenides of great current interest.

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4}
\caption{(Color online) The density of states for the effective
band from the model Hamiltonian Eqn. (3). The red and
green curves are for $U_1 = 0.70$ and 0.30eV. The blue one is
the DOS for the tight binding fit to the LSDA band that
crosses the Fermi level. The chemical potentials are set at
zero.}
\end{figure}

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