Mott Transition and Kondo Screening in f-Electron Metals

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We study how a finite hybridization between a narrow correlated band and a wide conduction band affects the Mott transition. At zero temperature, the hybridization is found to be a relevant perturbation, so that the Mott transition is suppressed by Kondo screening. In contrast, a first-order transition remains at finite temperature, separating a local-moment phase and a Kondo-screened phase. The first-order transition line terminates in two critical end points. Implications for experiments on f-electron materials such as the cerium alloy $Ce_{0.8}La_{0.1}Th_{0.1}$ are discussed.

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The Mott transition, i.e., how electrons evolve from localized to itinerant as a function of an external parameter such as pressure, is a fundamental problem in condensed matter physics. It is a key phenomenon in d-electron materials, such as transition-metal oxides, in which a set of bands with d character is well separated and close to the Fermi level. In this case, the phase with localized electrons is insulating, and that with itinerant electrons is metallic. Dynamical mean-field (DMFT) studies [1] have deepened our understanding of this phenomenon and led to many interesting experimental predictions that have recently been verified experimentally [2].

In several f-electron materials, a transition between a phase where f electrons are more localized and another in which they are more itinerant is also observed (such as the isostructural γ-α phase transition of cerium) [3,4]. In these materials, however, there is a broad band with spd character close to the Fermi level (in addition to the f orbitals), and both phases are metallic. It was suggested early on by Johansson [5] that the concept of a Mott transition within the f-electron subspace may still be relevant in this context. A different view is the Kondo volume-collapse (KVC) model [6,7], in which the transition is driven by the change in the hybridization between the two phases with different unit-cell volumes. In this picture, the broad band of conduction electrons plays a key role, while it is merely a spectator in the Mott picture. The interplay of these two mechanims in cerium have recently received a great deal of attention [8–11].

In this Letter, we study the localization-delocalization transition within a simple model, which nevertheless retains the key ingredients present in f-electron materials. The model interpolates between a Hubbard model for the f orbital and the periodic Anderson model (PAM) in which this orbital is hybridized to a broad band. Our goal is to understand whether, in a purely electronic model, the Mott transition present when the f band is isolated remains a robust feature in the presence of a finite hybridization to a broad band. Our key finding is that the answer to this question *depends on temperature* in a crucial manner. At zero temperature, the Kondo effect always sets in and screens the local moment. As a result, in a purely electronic setting, the Mott transition is *suppressed by an arbitrarily small hybridization.* In contrast, *a first-order transition remains at finite temperature.*

The similarities between the phase diagram of the PAM and that of the Hubbard model at finite temperature have been pointed out previously [12]. However, the distinction between a first-order transition with coexisting electronic phases and a mere crossover was not addressed. More importantly, the $T = 0$ case was investigated in the case where the hybridization vanishes at the Fermi level [13,14]: this is a nongeneric case in which the transition survives down to $T = 0$. In the generic case of a finite hybridization, the connection between the smooth behavior at $T = 0$ and the finite-temperature transition has not been addressed before. Our model study also has direct implications for the volume-collapse transition of materials such as $Ce_{0.8}La_{0.1}Th_{0.1}$ [15] and its dependence on magnetic field [16].

We study a generalization of the PAM defined by the Hamiltonian:

$$H = -t\Sigma_{\langle ij\rangle\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + V\Sigma_{i\sigma} c^{\dagger}_{i\sigma} f_{i\sigma} - \alpha t\Sigma_{\langle ij\rangle\sigma} f^{\dagger}_{i\sigma} f_{j\sigma} + U\Sigma_i (n^f_{i\uparrow} - \tfrac{1}{2})(n^f_{i\downarrow} - \tfrac{1}{2}). \quad (1)$$

In addition to the usual hybridization and interaction terms, it contains a direct hopping between the f orbitals: $t_{ff} = \alpha t$. The model reduces to the PAM when $\alpha = 0$. When $V = 0$, it describes two independent fluids: free conduction electrons and a narrow band of f electrons described by the Hubbard model. For simplicity, our study is restricted to the particle-hole symmetric case ($\langle n_f \rangle = \langle n_c \rangle = 1$). In this case, one has a (renormalized) hybridization-gap insulator when the direct f-f hopping is small, as studied in [17] (for $\alpha = 0$ and large U this is the Kondo insulator). For α large enough, however, the gap closes and the model describes a metal. As shown below, the criterion for a metallic ground state is essentially independent of U and reads $\alpha > (V/D_c)^2$ (with D_c the conduction electron bandwidth).

In this Letter, we study this metallic regime within DMFT (which becomes exact in the limit of infinite coordination), focusing on the paramagnetic phase. When $V = 0$, the situation is well documented [1,2]: the f electrons are described by a Hubbard model which undergoes a Mott transition. The transition is first order at finite temperature, with a transition line $U_c(T)$ ending at a critical end point (U_c, T_c). For $U < U_c(T)$, the f electrons are itinerant, while for $U > U_c(T)$ they behave as local moments. These two behaviors correspond to two locally stable mean-field solutions, which coexist in the domain $U_{c1}(T) < U < U_{c2}(T)$ delimited by two spinodal lines. The transition persists down to $T = 0$: there, the quasiparticle weight of the correlated itinerant solution vanishes continuously at $U_{c2}(T = 0)$. The main issue we want to address is whether a regime with unscreened local moments survives in the presence of a finite hybridization ($V \neq 0$) to the broad conduction electron band, and what happens to the phase transition.

DMFT associates with this lattice model a single-impurity Anderson model for the f orbital, subject to an effective self-consistently determined hybridization function $\Delta_{\text{eff}}(i\omega_n)$. For the case of semicircular densities of states for both the c and f electrons, the cavity construction [1] yields the self-consistency condition:

$$\Delta_{\text{eff}}(i\omega_n) = \alpha^2 t^2 G_{ff}(i\omega_n) + \frac{[V - \alpha t^2 G_{cf}(i\omega_n)]^2}{i\omega_n - t^2 G_{cc}(i\omega_n)}. \quad (2)$$

In this expression, G_{ff}, G_{cf}, and G_{cc} are the different components of the on-site interacting Green's function, which must be computed self-consistently from the effective impurity model. This expression has a transparent interpretation: the screening of the f moment on a given site in the local picture of the lattice model has two origins reflected in each term of this equation. The first term describes the screening due to the motion of the f electrons onto other sites: it is effective only when the f electrons are itinerant, and its vanishing at low energy is associated with the Mott phenomenon. The second term describes the local screening due to the conduction electrons. This screening is affected by the f-electron motion, resulting in a reduced frequency-dependent effective hybridization $V_{\text{eff}}(i\omega_n) = V - \alpha t^2 G_{cf}(i\omega_n)$.

Let us consider first the case $T = 0$. Physical intuition suggests that an arbitrarily small hybridization V is enough to screen the local moment through the formation of a Kondo singlet with the conduction electrons. The energy scale associated with screening will be very small, but finite, at small V. Hence, at $T = 0$, the hybridization is a singular perturbation when starting from the paramagnetic Mott phase, suggesting that *the $T = 0$ Mott transition is unstable* against the introduction of hybridization. This intuition is supported by a low-frequency analysis of Eq. (2). In a Mott phase with unquenched f moments, the Green's function and self-energy behave as $\Sigma_f(i\omega) \sim 1/i\omega$, $G_{ff}(i\omega) \sim i\omega$ at small ω. Inserting this into (2), one sees that $\Delta_{\text{eff}}(i\omega) \sim i\omega$ as $\omega \to 0$ if $V = 0$, which is consistent with the original assumption of a local moment as it implies a gap in the hybridization density of states $\text{Im}\Delta_{\text{eff}}(\omega + i0^+)$. However, as soon as $V \neq 0$, $\Delta_{\text{eff}}(i\omega)$ tends to a finite (imaginary) value as $\omega \to 0$ because of the second term in (2). This implies a finite value of $\text{Im}\Delta_{\text{eff}}(\omega + i0^+)$ at low frequency, inconsistent with a free local moment. Hence, at $T = 0$ and when $V \neq 0$, the self-energy has a local Fermi-liquid form $\Sigma_f(i\omega) \sim i\omega(1 - 1/Z) + \cdots$ for all values of U, with Z the f-quasiparticle weight. At large U, Z is very small and sets the scale for screening. This yields two quasiparticle bands, which read (neglecting lifetime effects) $2\omega_{\mathbf{k}}^{\pm} = (1 + \alpha Z)\epsilon_{\mathbf{k}} \pm [(1 + \alpha Z)^2 \epsilon_{\mathbf{k}}^2 + 4ZV^2]^{1/2}$. This corresponds to the noninteracting band structure, with renormalized parameters: $\alpha_{\text{eff}} = Z\alpha$, $V_{\text{eff}} = \sqrt{Z}V$. A hybridization gap is present only if $V_{\text{eff}} > \sqrt{\alpha_{\text{eff}}} D_c$. The quasiparticle weight Z drops out from this criterion: hence, the two quasiparticle bands overlap and one has a metal when $V < \sqrt{\alpha} D_c$, independently of U as announced above. Accordingly, it follows from this low-frequency analysis that, at $T = 0$, the f-spectral function is pinned at $\omega = 0$ to its noninteracting value: $A_{ff}(0) = \alpha^{-1}\rho_0(V/\sqrt{\alpha})$, for all U, as long as $0 < V \leq \sqrt{\alpha} D_c$ (with ρ_0 the noninteracting density of states of the conduction band). In this Fermi-liquid state, the "large" Fermi surface encounters $n_c + n_f = 2$ electrons per site. This analysis can be illustrated by a simple calculation using the Gutzwiller approximation (GA). In this approach, one optimizes a variational energy depending on the probability of double occupancy d, and the quasiparticle residue is obtained [18] as $Z = 16d(1/2 - d)$. The results of this approximation for our model are displayed in Fig. 1. This figure shows that the Brinkman-Rice transition (analogous to the U_{c2} found in DMFT), at which Z vanishes in the Hubbard model ($V = 0$), is no longer present at finite V. This can also be proven by generalizing to $t_{ff} \neq 0$ the method of Ref. [13], which maps the PAM onto a Hubbard model with Lorentzian density of states (for which $U_{c2} = \infty$). Within the GA, we showed analytically that, because V introduces a logarithmic singularity ($\propto Z \ln Z$) in the variational energy at small Z, the minimum is always found at a finite value of Z. This also allows us to estimate the behavior of Z at large $U \gg U_{c2}$, which has the expected exponential suppression characteristic of the Kondo effect: $Z \sim c_{\alpha,V} e^{-\pi U D_c/32V^2}$ (the prefactor $c_{\alpha,V}$ depends only weakly on α and V).

In order to confirm and extend this analysis, we performed a full quantitative solution of the DMFT equations at $T = 0$, using an exact diagonalization (ED) scheme based on the Lanczos algorithm and an adaptative discretization of the effective bath degrees of freedom [1]. In what follows all energies are expressed in units of the half-bandwidth D_f of the narrow band, and $\alpha = D_f/D_c = 0.1$. The Green's function and self-energy obtained from ED

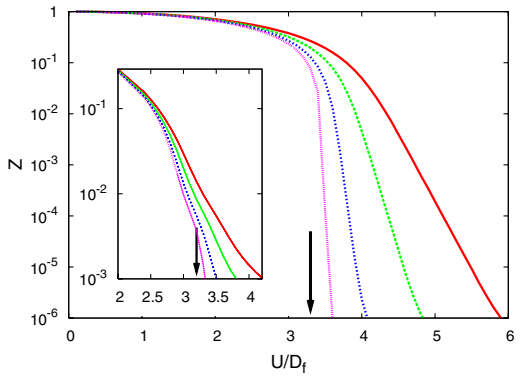

FIG. 1 (color online). Comparison of Z vs U for different values of V (from the left: $V/D_f = 0.1, 0.2, 0.3, 0.4$) obtained using the GA and $T = 0$ ED (inset). Both methods clearly show that Z never vanishes as soon as $V \neq 0$, in contrast to the $V = 0$ (Hubbard model) case, which displays a transition at the critical value of U indicated by the arrows. Note that the GA overestimates Z.

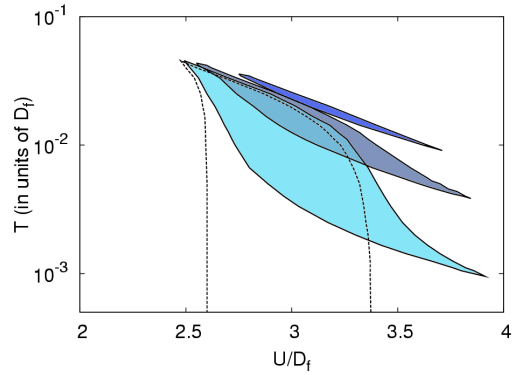

FIG. 2 (color online). Phase diagram within the IPT approximation. Regions where localized and itinerant solutions coexist are displayed for (from bottom to top) $V/D_f = 0.1, 0.2, 0.3$. Only finite-temperature transitions exist when $V \neq 0$, resulting in two critical end points. In contrast, the spinodals of the $V = 0$ case (dashed lines) reach $T = 0$ at finite critical values of U.

(not shown) do obey $G(i\omega) \sim -i\pi\alpha^{-1}\rho_0(V/\sqrt{\alpha})$, $\Sigma(i\omega) \sim i\omega(1 - 1/Z)$ at low-frequency for all $V \neq 0$, from which we obtained the quasiparticle weight displayed in Fig. 1. We also performed ED calculations for increasing and decreasing sweeps in U in order to check that *no other solution* of the DMFT equation is present at $T = 0$ when $V \neq 0$, besides the Fermi-liquid one with screened f moments and a large Fermi surface. This is in contrast to the Hubbard model ($V = 0$), which has a coexistence region $[U_{c1}, U_{c2}]$ between a Mott-localized and an itinerant solution extending down to $T = 0$.

While Kondo screening always sets in at $T = 0$ and suppresses the Mott transition, at $T > 0$ the effect of a perturbation (even if singular for the ground state) is, on general grounds, expected to be smooth. As a result, the first-order transition and the coexistence region *should be robust features* of the present model as long as V is not too large. Since small energy scales are involved ($T_c \sim D_c/40$ for the pure Hubbard model, and the Kondo screening scale is tiny at large U), an exact numerical study is difficult and we approached the problem using two approximate impurity solvers. The first is the iterated perturbation theory (IPT) approximation [19], which has proven to be semiquantitatively very successful in the study of the Mott transition. IPT is known to overestimate low-energy scales, and will not be accurate in the Kondo regime. The second method is the (dynamical) "slave-rotor" (DSR) integral equations [20], which is able to resolve low-energy scales and reproduces the correct exponential Kondo scale at large U. The phase diagram found within IPT is displayed in Fig. 2.

As anticipated, the coexistence (hysteretic) region is still present for the smaller values of V. As V increases, its extension is drastically reduced, and T_c decreases, as also found with the more accurate DSR solver (Fig. 3 compares the estimates of T_c in the two methods). The spectral functions of two coexisting solutions are displayed in Fig. 3: one has a well-formed Kondo peak corresponding to good screening of the local moment, while the other one has very small (but finite) spectral weight at low energy. In contrast to the $V = 0$ case, we find that the two spinodals no longer extend down to $T = 0$ and that, within IPT, *another critical end point* is found at low temperature at which the actual first-order transition line terminates. Note that, in view of the above analysis at $T = 0$, the two spinodal lines must, indeed, either end at a lower critical point or run away towards infinite coupling. Unfortunately, because of the low-energy scale involved, we have not been able to push the DSR method to low enough tempera-

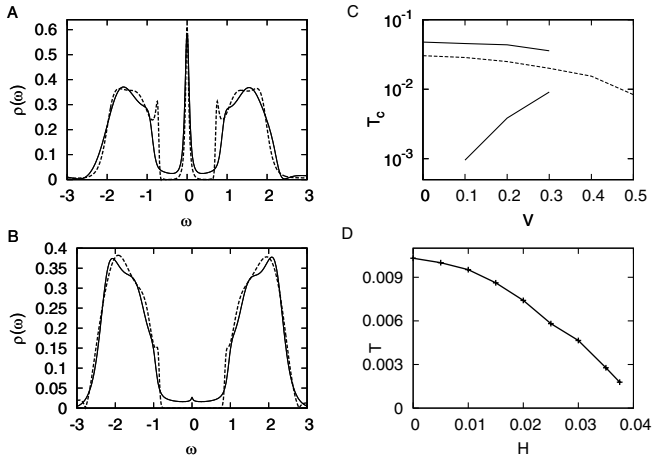

FIG. 3. Left panel: comparison between spectral densities for $V \neq 0$ (full lines) and $V = 0$ (Hubbard model, dashed lines), in the screened phase (a) and in the unscreened one (b), in DSR. (c) Upper and lower T_c of the critical end points as functions of V within IPT (full lines). Upper T_c with DSR (dashed line). (d) Transition temperature as a function of an applied magnetic field H for $U/D_f = 2.7$, calculated at $T = 0$ within ED. All energies are in units of D_f.

tures and firmly establish the existence of a lower critical end point within this technique.

We have also studied the effect of a magnetic field on the transition between the screened (low-T, itinerant) and unscreened (high-T, local-moment) regimes. This is motivated by recent experiments on the γ-α transition of the $Ce_{0.8}La_{0.1}Th_{0.1}$ alloy, showing that the transition temperature is decreased by an applied magnetic field [16]. Dzero *et al.* [21] pointed out that this can be rationalized by approximating the high-T γ phase as a collection of almost free localized magnetic moments, while assuming that the free energy of the low-T α phase does not change appreciably with magnetic field. In Fig. 3(d), we display our findings for the temperature associated with the local-moment spinodal line (lower boundary of the coexistence region), as a function of applied field. This demonstrates, within the simple microscopic model studied here, that indeed the transition is suppressed by a magnetic field as observed experimentally.

To summarize, we have studied a model that retains the key aspects of f-electron metals, i.e., a narrow correlated band hybridized with a wide uncorrelated conduction band. We found a first-order transition at finite temperature between a screened phase and a local-moment phase, ending in two critical end points. At zero temperature, the hybridization is a relevant perturbation, so that the Mott transition is suppressed by Kondo screening. This is qualitatively consistent with the KVC picture. These findings can be put in the broader context of the orbital-selective Mott transition (OSMT), which attracted a lot of attention recently [22–24]. In a general two-band case, the self-energy $\hat{\Sigma}$ takes a matrix form and the Mott transition is signaled, when approached from the metallic side, by a low-frequency singularity in $\omega.\hat{I} - \hat{\Sigma}(\omega) = \hat{Z}^{-1}\omega + \cdots$. An OSMT is characterized by $\hat{Z}$ having one zero eigenvalue, while the other one remains finite. We emphasize that this is a *basis-independent* notion. In our model, $\hat{Z}$ is diagonal, with $Z_{cc} = 1$, and hence an OSMT phase corresponds simply to the vanishing of Z_{ff}. At $T = 0$, this does occur for zero hybridization, but Kondo screening sets in as soon as a finite hybridization is turned on, preventing Z_{ff} from vanishing.

Finally, we comment on the qualitative relevance of our results for f-electron materials. There, the contribution (F_e) to the free energy from the electronic degrees of freedom that are active close to the transition have to be added to the contributions from all other bands and ions, which can be approximated by an elastic contribution (see, e.g., [7]). As a result, the volume-collapse transition does not correspond to a true divergence of the response function $\chi_e = -d^2F_e/dv^2$ of the active electronic degrees of freedom (with v the unit-cell volume). Rather, it will take place [25] when $\chi_e = B_0/v_0$, with B_0 and v_0 a typical bulk modulus and unit-cell volume. Hence the critical temperatures of the upper and lower end points are shifted upwards and downwards, respectively, by elastic terms. We therefore conclude that there are two generic situations that are consistent with our results: either the material displays a first-order transition down to $T = 0$ (for softer materials, with smaller values of B_0) or it will display two critical end points (for harder materials) (see also [6]). Experimental studies [15] suggest that the latter case may be realized in $Ce_{0.8}La_{0.1}Th_{0.1}$, in which alloying acts as a "negative pressure," thus allowing for an investigation of the localization-delocalization transition at lower temperatures than in pure cerium. Our results also imply that a $T = 0$ quantum-critical valence transition is a nongeneric case that requires the tuning of an extra parameter.

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