Electronic Coherence in δ-Pu: A Dynamical Mean-Field Theory Study

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A combination of density functional theory and the dynamical mean-field theory (DMFT) is used to calculate the magnetic susceptibility, heat capacity, and the temperature dependence of the valence band photoemission spectra for δ-Pu. We predict that δ-Pu has a Pauli-like magnetic susceptibility near ambient temperature, as in experiment, indicating that electronic coherence causes the absence of local moments. Additionally, we show that volume expansion causes a crossover from incoherent to coherent electronic behavior at increasingly lower temperatures.

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Pu embodies a forefront of both technology and theoretical condensed-matter physics. Elemental Pu displays exotic physical behavior that continues to defy explanation. For example, it exhibits six allotropic phases at ambient pressure, the low-density fcc δ phase has a negative coefficient of thermal expansion, and the volume expands by more than 25% when the system is heated from the high-density monoclinic α phase to the δ phase. Regarding the pure δ phase, a complicating factor is that it is only stable in the temperature range $580\ \mathrm{K} < T < 700\ \mathrm{K}$. However, the δ phase can be stabilized at low temperatures by a variety of alloying elements such as Ga and Am. This allows for the experimental exploration of the δ phase at low temperatures, with the caveat that it is not clear what changes the alloying element may be inducing.

Lashley *et al.* [1] have measured the magnetic susceptibility to be Pauli-like in both the α and δ phases, and hence detect no presence of localized magnetic moments. Similarly, Heffner *et al.* [2–4] have used μSR and showed that there are no ordered magnetic moments in α Pu nor in δ-stabilized Pu (i.e., 4.3% Ga) for temperatures down to 4 K. Nuclear magnetic resonance (NMR) measurements by Curro and Morales [5] also show an absence of magnetic moments.

The linear coefficient of the specific heat for δ-stabilized Pu has been measured by various groups and the resulting values are $42\ \frac{mJ}{\mathrm{mol\ K^2}}$ for alloying with 2% of Ga [1], $64\ \frac{mJ}{\mathrm{mol\ K^2}}$ for 5% of Al [6], and 35–$55\ \frac{mJ}{\mathrm{mol\ K^2}}$ for 8%–20% of Am [7]. The large variation among these measurements may be due to the fact that the δ phase has been stabilized by a different alloying element in each study.

Several previous studies have applied a combination of density functional theory and the dynamical mean-field theory (DFT + DMFT) [8] to δ Pu. DMFT requires a solution of an auxiliary quantum impurity problem, and for the corresponding impurity model of Pu, no exact method was available in the past. Savrasov *et al.* [9] used an interpolative solver to calculate the energy and the photoemission spectra of Pu. The approach yielded a significant improvement for the volume of the δ phase of Pu compared to DFT. Shick *et al.* [10] computed the photoemission spectra using the Hubbard I impurity solver and were successful in predicting the three-peak structure in the photoemission spectra. Pourovskii *et al.* [11] computed the photoemission spectra and the heat capacity using the Fluctuation Exchange Approximation (FLEX) as an impurity solver. The applicability of FLEX to Pu is questionable given the strongly correlated nature of δ-Pu. Zhu *et al.* [12] computed the photoemission spectra using the the Hirsch-Fye quantum Monte-Carlo impurity solver and show that the occupation of the f orbital is close to $n_f \sim 5$. However, the limitation of this method to treat the realistic atomic multiplet structure (Hund's rule coupling) [8] precludes a precise description of the problem. Shim *et al.* [13] predicted the photoemission spectra, the x-ray absorption spectroscopy branching ratio, and the mixed-valence nature of Pu. Although the mixed-valence state was identified in Ref. [13], the temperature and pressure dependence of the electronic state was not addressed.

In this Letter, we demonstrate the absence of magnetic moments in δ-Pu by computing the magnetic susceptibility as a function of temperature. We show that expanding the Pu lattice results in an incoherent metallic state with Curie-Weiss susceptibility at increasingly lower temperatures. Additionally, we elucidate the nature of the mixed-valence state by predicting the temperature dependence of the photoemission spectra.

DMFT maps the interacting lattice problem onto an impurity problem where the noninteracting bath function is determined self-consistently [14]. The effective impurity problem is then solved using the continuous-time quantum Monte-Carlo (CTQMC) method [15,16]. More specifically, the recently developed hybridization expansion CTQMC method is used to exactly sum the diagrams resulting from expansion in powers of the hybridization strength between the Pu atom and the DMFT fermionic bath [15]. This method allows one to include the full rotationally invariant exchange interaction without approxima-

tion, in contrast to Hirsch-Fye QMC [8]. Although our implementation of CTQMC is extremely efficient, massive parallel computer resources are required to solve the 14 orbital DMFT impurity problem for Pu. The Atlas supercomputer at Lawrence Livermore National Lab was used to perform the calculations, and time was awarded under the Atlas grand challenge program.

DFT + DMFT calculations were performed using an orthogonalized LMTO basis which provides f orbitals that have a maximal f character [17]. In accordance with previous studies, the on-site Coulomb repulsion was chosen to be $U = 4$ eV and, the Slater integrals (F_2, F_4, and F_6) were computed using an atomic physics code [18] and rescaled by 80% to account for screening in the solid. Summations over the first Brillioun zone were performed with $15 \times 15 \times 15$ meshes, with the exception of the heat capacity calculations where up to $40 \times 40 \times 40$ meshes were used to ensure convergence. Pu valencies of $N_f =$ 4–7 were retained in the QMC simulation, and retaining higher/lower valencies had no appreciable influence on the results. The total occupation of the Pu-5f orbitals in this study is approximately $n_f = 5.2$, consistent with previous calculations [13] and electron energy loss experiments of the N edge [19] and the O edge [20].

We proceed by first exploring the qualitative effect of electronic correlations on the local spectra. The real-frequency spectral function is obtained by using the maximum entropy method to analytically continue the imaginary time Green's function measured in the CTQMC simulation. The LDA spectrum displays a strong spin-orbit splitting among the $S = \frac{5}{2}$ and $S = \frac{7}{2}$ states [see Fig. 1(a)]. The DFT + DMFT spectrum without exchange indicates that spectral weight from low energies (i.e., near the Fermi energy) has transferred to higher energies [see Fig. 1(b)]. Including the full exchange interaction reduces the spectral weight in the $S = \frac{5}{2}$ quasiparticle peak and hence the electronic coherence scale. Additionally, the $S = \frac{7}{2}$ peak above the Fermi energy is broadened due to a multiplet splitting. The spectrum with full exchange interaction is similar to the three-peaked spectrum obtained by Shim *et al.* [13]. The $S = \frac{5}{2}$ has a central peak just below the Fermi energy and a peak near -1 eV, while the $S = \frac{7}{2}$ states have a peak near -0.6 eV. These features are much broader than those obtained by Shim *et al.* [13], but this is expected due to the limitations of the maximum entropy method in obtaining the real-frequency data.

The self-energy $\Sigma(i\omega)$ offers further insight into the nature of the electronic correlations in δ-Pu. The quasiparticle weight is determined by the slope of the imaginary part of the self-energy (i.e., $Z = 1/(1 - \frac{\partial \Sigma(i\omega)}{\partial i\omega})$), and within DMFT the mass enhancement of the electrons due to electronic correlations is the inverse of the quasiparticle weight (i.e., $\frac{m^*}{m} = \frac{1}{Z}$). In the absence of exchange, the $S = \frac{7}{2}$ states are very weakly correlated, having an average $Z \approx 0.7$ while the $S = \frac{5}{2}$ states have an average $Z \approx 0.41$ for the equilibrium volume of δ Pu [see Fig. 2(a)]. Weak correlations for the $S = 7/2$ states is expected given that in the absence of Hund's coupling the j-j coupling scheme is adequate, and hence the $S = \frac{7}{2}$ states are nearly empty. Alternatively, the $S = \frac{5}{2}$ states are much closer to a nonzero integer filling and are moderately correlated. When the exchange is included, the quasiparticle weight is substantially decreased, resulting in $Z_{5/2} = 0.26$, $Z_{7/2} = 0.32$ for the equilibrium volume. The exchange interaction pushes Pu towards intermediate coupling, where the $S = 7/2$ states are more mixed into the ground state and hence

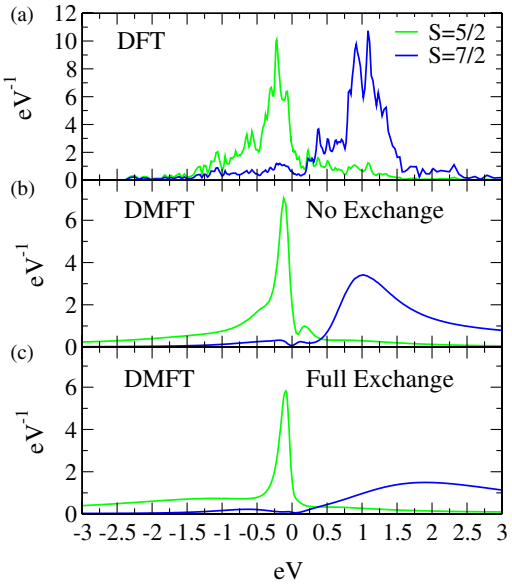

FIG. 1 (color online). The spectral functions for the Pu f-electrons within DFT (top), DFT + DMFT without exchange (middle), and DMFT + DFT with the full rotationally invariant exchange (bottom).

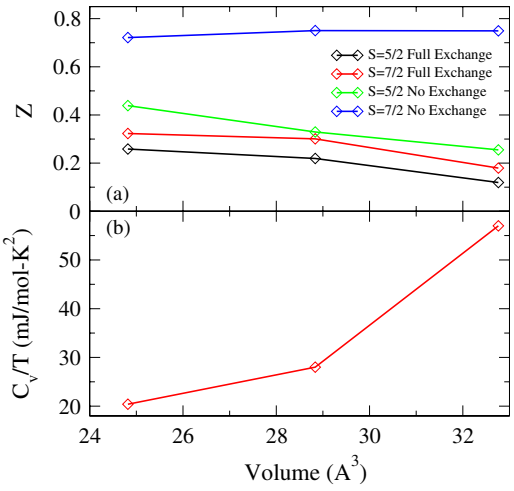

FIG. 2 (color online). The quasiparticle weight Z (top), and linear coefficient of the heat capacity (bottom) as a function of volume. The heat capacity was calculated with the full exchange interaction.

they becomes heavier. With increasing volume, the kinetic energy decreases and hence correlations increase resulting in a smaller Z. The only exception is the $7/2$ orbital in the absence of exchange, where the occupation slightly decreases with increasing volume.

We proceed to explore the heat capacity and the magnetic susceptibility. Within Fermi liquid theory, the linear coefficient of the heat capacity is given by $\gamma = \frac{2\pi k_B^2}{2}\sum_\alpha \frac{\rho\alpha(0)}{Z\alpha}$, where α runs over all orbitals, ρ_α is the local density of states, and Z_α is the corresponding quasiparticle weight. The heat capacity as a function of volume is shown in Fig. 2. As the volume is increased, the heat capacity increases due to the fact that the quasiparticle renormalization amplitude Z decreases and the spectral density at the Fermi energy increases. The predicted heat capacity for the equilibrium volume of δ-Pu is $20.4\,\frac{mJ}{\text{mol K}^2}$. The difference between the predicted value of the heat capacity and the experimentally measured values of 35–$55\,\frac{mJ}{\text{mol-K}^2}$ may be due to several factors. Given that the f-electron spectral function is extremely steep in the vicinity of the Fermi level (see Fig. 1), it is clear that the value of γ is sensitive to small changes in the Fermi energy. Therefore, approximations in the DFT calculation may have a non-negligible influence. The second potential cause of this difference might be that the electron-phonon coupling may further renormalize the hoppings and this is not included in our calculation. Given that our prediction is smaller than experiment, inclusion of electron-phonon coupling would improve agreement with current experiments. It should be noted that the largest volume point is not yet in the Fermi liquid regime, as demonstrated below, and hence the Fermi liquid formula for the heat capacity should only be considered as an estimate for the largest volume.

The local magnetic susceptibility is calculated as a function of temperature for different volumes using the following expression [15]:

$$\chi_{\text{local}} = \int_0^\beta d\tau \langle M(\tau)M(0)\rangle,$$

where $M = L + 2S$, L is the total orbital angular momentum, and S is the total spin angular momentum. For the equilibrium volume of Pu, the susceptibility is relatively flat (i.e., Pauli-like) below 600 K and diminishes at higher temperatures (see Fig. 3). This behavior is consistent with experimental measurements. Our calculations predict that the reason that magnetic moments are not seen in δ Pu is because the system is coherent and the moments are therefore screened. Physically, this means that the electrons from the *spd* bands and from neighboring f orbitals align themselves antiparallel to the moment of a particular Pu-atom, effectively cancelling the net moment. This predicted behavior is in agreement with experimental observations [1–5]. As the volume is increased by 16%, the low-temperature Pauli-like contribution has been renormalized to higher values and transitions to a Curie-like behavior around 400 K (see Fig. 3). The increase in the Pauli contribution is consistent with the decrease in Z as the volume is increased, and this illustrates an enhancement of the electronic correlations.

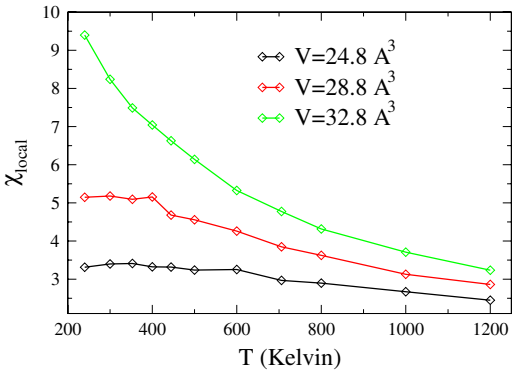

FIG. 3 (color online). Local magnetic susceptibility as a function of temperature for different volumes.

As the volume is further increased by an additional 16%, the susceptibility is Curie-like to the lowest temperatures reached in this study (see Fig. 3). These results clearly indicate a decoherence of the electrons. As the volume is increased, the coherence energy of the electrons decreases and therefore a transition from coherent to incoherent behavior (i.e., Pauli-like to Curie-like) occurs at increasingly smaller temperatures. This signifies that a local magnetic moment has emerged at progressively lower temperatures as the volume is increased.

The general behavior observed in these magnetic susceptibility calculations is consistent with experiments. First, doping Pu with Americium causes the Pu lattice to expand, effectively increasing the volume. The Pauli contribution of the Pu atom is shown to increase as the Americium content is increased and the effective volume is increased [21]. This is consistent with the enhancement of the Pauli term that we observed. Second, when hydrogen is doped into the system, the fcc Pu lattice expands by more than 50% and Curie-like behavior is measured for the magnetic susceptibility down to temperatures of 50 K [22]. This is qualitatively consistent with the largest volume expansion in our calculations.

When the electronic behavior departs from the Fermi liquid theory and enters the incoherent regime, there is a clear signature in the spectra. In Fig. 4, we show the temperature dependence of the local spectral function at ambient pressure. At high temperatures, the spectrum is diffuse. As the temperature is decreased, a quasiparticle peak continually builds and eventually saturates at $T = 500$ K. The coherence temperature may be defined as the temperature at which the quasiparticle peak nears saturation, and we define 75% saturation to be the onset of coherence. Hence our estimation for the coherence temperature is approximately 800 K, consistent with Ref. [13].

The inset of Fig. 4 shows the temperature dependence of the height of the quasiparticle peak. Notice that this be-

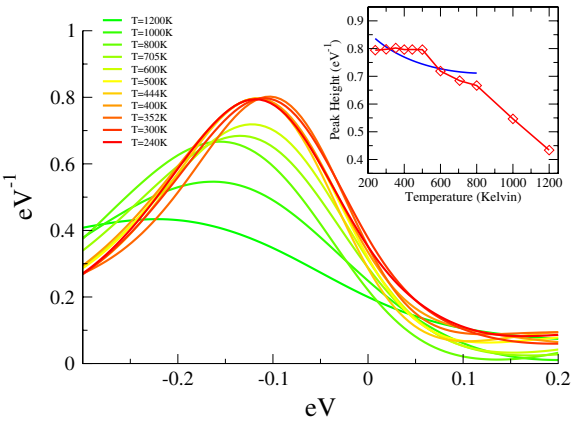

FIG. 4 (color online). The temperature dependence of the $S = \frac{5}{2}$ f-electron spectral function using the rotationally invariant exchange interaction. The inset displays the peak height as a function of temperature. The red points correspond to our data, while the blue curve is the parametrization from Ref. [24] assuming an onset temperature of 800 K.

havior is very different from the temperature dependence in heavy-Fermion compounds [23] recently parametrized in Ref. [24]. For comparison, we plot the best fit of the parametrization of Ref. [24] to our data. The inability of this parametrization to describe our data is due to the mixed-valence nature of plutonium.

In conclusion, we have performed approximation-free DMFT calculations including the rotationally-invariant exchange interaction for δ-Pu. The efficient CTQMC algorithm has allowed us to reach both high temperatures and temperatures below ambient. The quasiparticle weight for the $S = \frac{5}{2}$ states of δ-Pu is found to be $Z = 0.25$, indicating the presence of appreciable electronic correlations. Calculation of the magnetic susceptibility indicates Pauli-like behavior for the equilibrium volume of δ-Pu, in support of experimental measurements. This indicates that in δ-Pu the moments are screened. Expanding the volume causes the electrons to crossover from coherent to incoherent behavior at increasingly lower temperatures. This crossover is illustrated in the temperature dependence of the spectra. The prediction of incoherent electronic behavior, manifested as Curie-like behavior in the magnetic susceptibility, is consistent with experimental measurements in PuH_2. The importance of the inclusion of the rotationally invariant exchange is illustrated in the spectrum and in the reduction of the quasiparticle renormalization amplitude from $Z = 0.41$ to $Z = 0.25$.

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