Letter

Pseudogap in elemental plutonium

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Electronic correlations associated with incipient magnetism have long been recognized as an important factor in stabilizing the largest atomic volume δ phase of plutonium, yet their strength compared to those in the rare earths and neighboring actinides in the periodic table has largely remained a mystery. We show here using calorimetry measurements, together with prior detailed measurements of the phonon dispersion, that the $5f$ electrons of the δ phase reside in a pseudogapped state, accompanied by reductions in various physical properties below a characteristic temperature $T^* \approx 100$ K. The small characteristic energy scale of the pseudogapped state implies that the $5f$ electrons in plutonium are much closer to the threshold for localization and magnetic order than has been suggested by state-of-the-art electronic structure theory, revealing plutonium to be arguably the most strongly correlated of the elements.

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Plutonium (Pu) is located at an anomalously large discontinuity in volume between lighter and heavier elements in the actinide series of the periodic table, and itself undergoes significant discontinuous changes in volume with temperature T [1]. Coulomb interactions have been shown to be an important factor in stabilizing the largest volume δ phase of Pu relative to its other crystalline phases and those of neighboring elements [2–14], yet these same interactions are expected to produce localized $5f$ electrons and consequent magnetism, as is often observed in rare-earth elements. While abundant evidence exists for fluctuating magnetic moments at $T \approx 1000$ K [15–17], at low T it is as if Pu's magnetic moments are absent [18,19]. There is neither evidence for magnetic ordering, a phase transition, nor for free or screened magnetic moments producing large residual magnetic [17] or thermal [20] Grüneisen parameters [21].

Contemporary proposals for the absence of magnetic moments in Pu include one, based on density functional theory (DFT) [14], in which the magnetic moments are disordered and exhibit a high degree of spin and orbital compensation, and another, based on dynamical mean field theory (DMFT) [6,11,12], in which the moments are strongly hybridized with conduction electrons. It may be argued that either scenario can account for the fluctuating magnetic moments at an energy equivalent to $\approx$1000 K reported in inelastic neutron-scattering experiments [15,16,22,23]. However, both models significantly underestimate the unusually large Sommerfeld coefficient of $45 \lesssim \gamma_{\rm el} \lesssim 60$ mJ mol^{-1} K^{-2} of δ-Pu [24–26] (much larger than that of any other element) derived from calorimetry data. DFT and DMFT models of the electronic structure predict only modest values, $\gamma_{\rm el} \approx 7$ mJ mol^{-1} K^{-2}, for the Sommerfeld coefficient [11,12,14]. Hence, there is a need to (i) identify the fate of the missing magnetism in Pu, and (ii) explain why the relevant interactions have escaped being captured by the most advanced electronic structure theories.

Here, we use low-noise calorimetry data combined with the results of prior high-precision measurements of the phonon spectrum [27,28] to show that the magnetic moments in δ-Pu, rather than being absent, are concealed below $T = T^* \approx 100$ K by their participation in a narrow pseudogapped state. The energy gap $\varepsilon_{\rm g} \approx 12$ meV separating peaks in the electronic density of states is found to be at least an order of magnitude lower than those predicted by DFT and DMFT [6,11,12,14]. The hybridization between the $5f$ electrons of Pu and the conduction electrons is therefore much weaker than has generally been assumed; hence, the $5f$ electrons are close to the threshold for localization and Pu is arguably the *most strongly correlated of the elements*. The experimental signatures of the pseudogapped state are reminiscent of those in transition-metal oxides [29–33], and include a peak in the electronic heat capacity below T^*, accompanied by a thermally activated Hall coefficient [34] and a downturn below T^* in physical quantities that are sensitive to the thermally averaged electronic density of states such as the electrical resistivity, Knight shift, and magnetic susceptibility [35–40].

The δ phase of pure Pu normally exists at $T \gtrsim 600$ K, but can be stabilized down to low T by the substitution of small percentages of Am or group III elements such as Ga [41]; see Supplemental Material [42] for further details. Figure 1 shows an analysis of some of our heat-capacity ($C_{\rm meas}$) data for δ-Pu$_{1-x}$Ga$_x$. At the lowest T, the data are fitted to [50] $(C_{\rm meas}/T) = \gamma_{\rm el} + \alpha T^2$, where αT^3 is the leading order Debye phonon contribution to the heat capacity, to obtain $\gamma_{\rm el}$ values in the range discussed above. However, the phonon contribution $C_{\rm ph}$ rapidly deviates from the Debye form as T increases due to a combination of exceptionally soft acoustic-phonon branches and a high-energy Einstein-like phonon mode in δ-Pu [27]. Hence, $C_{\rm ph}$ is calculated from the phonon density of states previously determined from precision inelastic x-ray and neutron-scattering experiments [27,28,42]. The red curve in Fig. 1 shows $C = C_{\rm ph} + C_{\rm el}$ calculated in this way,

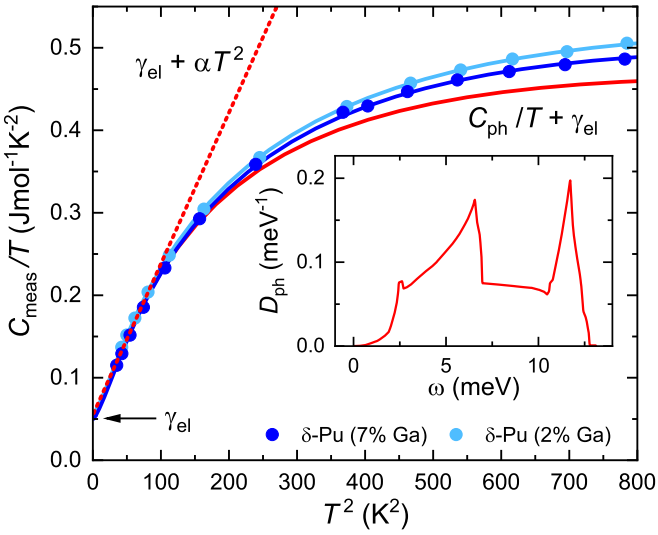

FIG. 1. Measured heat capacity C_{meas}/T vs T^2 for $x = 2\%$ and $x = 7\%$ (data from this work; light and dark blue circles). The red dashed line is a fit of $(C_{meas}/T) = (\gamma_{el} + \alpha T^2)$ to the low-T data. The red solid curve is $(C_{el} + C_{ph})/T$, where the phonon contribution to the heat capacity C_{ph} is calculated from the phonon density of states shown in the inset [27,28] (ω is the phonon energy [42]) and the electronic part C_{el} is given by the conventional Sommerfeld contribution [50] $\gamma_{el}T$. Note that the curve undershoots the experimental data, indicating that $\gamma_{el}T$ is an underestimate of C_{el} at higher T.

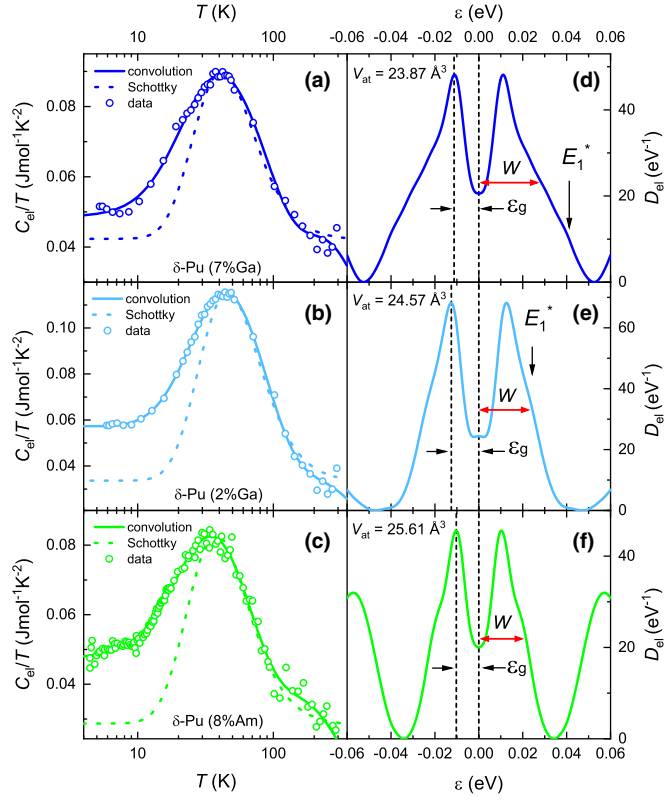

FIG. 2. (a)–(c) Electronic heat capacity divided by T, C_{el}/T (circles), vs T for $x = 7\%$ Ga, 2% Ga, and 8% Am [26]. Dotted lines are fits to the sum of a conventional Sommerfeld term and a Schottky term [Eq. (6) of Supplemental Material [42]]; the reasonable fit at intermediate to high T supports the existence of a gapped electronic density of states $D_{el}(\varepsilon)$. Solid curves are fits of Eq. (1) using an iterative numerical procedure [42] to obtain $D_{el}(\varepsilon)$. (d)–(f) Plots of the $D_{el}(\varepsilon)$ obtained vs energy ε for $x = 7\%$ Ga, 2% Ga, and 8% Am, respectively, with the pseudogap energy ε_g and W, half the electronic subband width at half maximum, indicated. V_{at} refers to the approximate atomic volume at low T for each composition. The increase in $D_{el}(\varepsilon)$ at $|\varepsilon| \gtrsim 2W$ likely originates from additional contributions to C/T above $T \approx 150$ K, such as that from anharmonic phonons and the higher-energy Schottky anomaly associated with the Invar effect [20]. Also shown in (d) and (e) is the activation energy E_1^* from magnetostriction [17].

assuming that the electronic contribution continues to behave as in conventional metals [50], i.e., $C_{el} = \gamma_{el}T$. It is notable that the red curve *undershoots* the data, suggesting that C_{el} grows significantly larger than $\gamma_{el}T$.

In order to examine this atypically large electronic contribution, C_{ph} deduced from inelastic x-ray and neutron-scattering experiments [27,28,42] is subtracted from C_{meas}; the results of this procedure are shown in Figs. 2(a)–2(c). As T increases, C_{el}/T reaches a peak—the thermodynamic hallmark of quasiparticles being thermally excited across a gap in the density of states [51].

Studies of d-electron systems [30–33] have shown that when a pseudogap forms in a narrow-band system, a significant fraction of the electronic states that would normally reside at the Fermi energy pile up on either side of the gap, leading to peaks in the electronic density of states. Thermal excitations across a gap [51] or pseudogap [30–33] always lead to a peak in C_{el}/T at $T = T_{peak}$, whose corresponding energy $k_B T_{peak}$ is a small fraction ($\approx 0.3\varepsilon_g$) of the gap energy ε_g. Therefore, the very similar behavior of C_{el}/T in Pu may well be because of the presence of a pseudogapped state. Under this assumption, the chemical potential is pinned to the middle of the gap such that [42]

$$\frac{C_{el}}{T} = \frac{R}{T}\int_{-\infty}^{\infty} D_{el}(\varepsilon)\frac{\varepsilon^2}{k_B^2 T^2}\frac{e^{\varepsilon/k_B T}}{(e^{\varepsilon/k_B T}+1)^2}d\varepsilon. \qquad (1)$$

Here, ε is the quasiparticle energy, R is the molar gas constant, and $D_{el}(\varepsilon)$ is the quasiparticle density of states per Pu atom. The fact that Eq. (1) assumes such a simple form—it is in effect a convolution of the heat capacity of a Schottky anomaly [51] with $D_{el}(\varepsilon)$—allows an iterative numerical routine to be used to extract $D_{el}(\varepsilon)$ by fitting the experimental values of C_{el}/T [42]. The resulting densities of states are shown in Figs. 2(d)–2(f).

We have confidence in this fitting procedure because of the qualitative similarity of the peaks in C_{el}/T to the heat capacity of a Schottky anomaly [51] [see dotted curves in Figs. 2(a)–2(c) and Supplemental Material [42]). This implies that the widths W of the peaks in $D_{el}(\varepsilon)$ [Figs. 2(d)–2(f)] are sufficiently narrow so as not to obscure the gap, and further suggests that the gap remains robust over $4 \lesssim T \lesssim 300$ K.

Several attributes of the derived electronic density of states of δ-Pu in Figs. 2(d)–2(f) suggest the participation of $5f$ electrons. First, the peaks in $D(\varepsilon)$ of each band are narrow, with the subbands in Figs. 2(d) and 2(e) having $W \approx 20$ meV. Such values are orders of magnitude lower than the 1–2 eV normally associated with ordinary electronic bands, but are

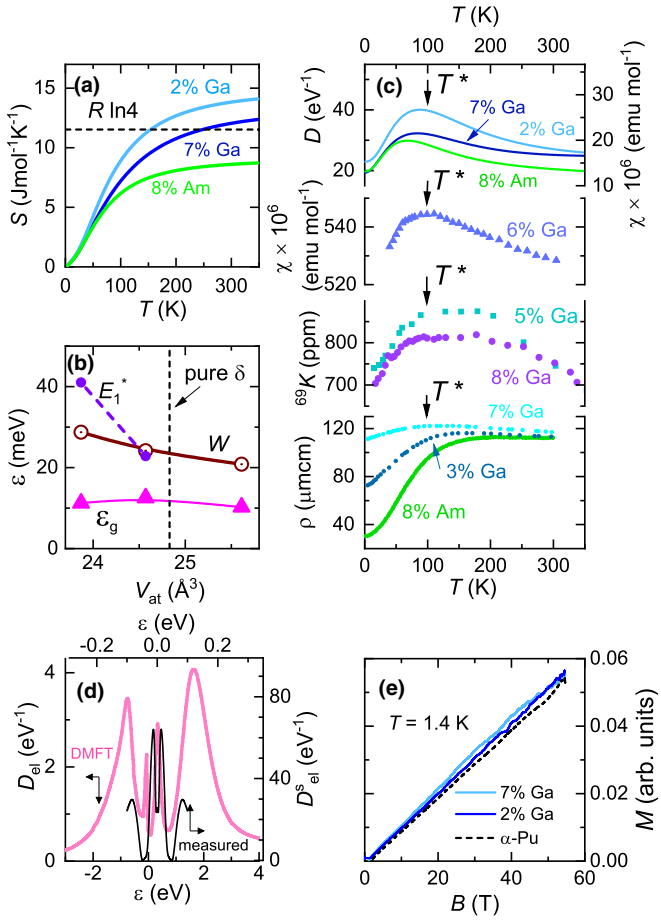

FIG. 3. (a) Calculated band entropy S vs T for each composition. (b) Electronic bandwidth W, pseudogap ε_g, and previously determined [17] excitation energy E_1^* for each composition. (c) Calculated thermally accessible electronic density of states $D(T)$ [Eq. (2)] for each composition (with the estimated spin susceptibility also shown, using $g = \frac{2}{7}$ and $J = \frac{1}{2}$, on the right-hand axis; see Methods), published susceptibility vs T [38], published NMR Knight shifts vs T [39,40], and published electrical resistivity [35,36] (divided by 3 for 8% Am). (d) Comparison of the $D_{el}(\varepsilon)$ derived in this work (black line and top and right-hand axes) for 2% Ga against that calculated by way of dynamical mean field theory (DMFT) using quantum Monte Carlo (gray line and bottom and left-hand axes) [12]. Arrows indicate the relevant axes. (e) Raw magnetization data for two Ga-stabilized δ-Pu samples and a pure α-Pu sample in pulsed magnetic fields at $T = 1.4$ K. For ease of comparison, all samples were cut to have almost identical volumes [42]. The similarity of the signals provides further evidence for a dominant Van Vleck contribution [42,53,54].

well within the range of values found in d- and f-electron systems [52]. Second, the total electronic entropy for each gapped band [Eq. (7) in Supplemental Material [42]] is found to saturate at a value close to $R \ln 4$ [see Fig. 3(a)]. Such a large value occurs for a single electron per formula unit *only* when there are an equal number of thermally accessible filled and empty electronic states [51]; this also supports our assumption that the chemical potential does not vary much with T [42]. Finally, the electronic bandwidths become progressively narrower when considered against the increasing atomic volume obtained by reducing the concentration of Ga and replacing it with Am [Fig. 3(b)]. Such behavior is the expected result of a reduction in the transfer integrals of the $5f$ electrons hopping between adjacent atomic sites as the separation of the Pu atoms increases. The absence of a proportionality of W to the Ga concentration suggests that the presence of Ga and any resulting disorder play a secondary role [42]. [We will return to this point in the discussion of Fig. 3(e) below].

Pseudogap signatures are not confined to the heat capacity [31]; in d-electron systems, below a characteristic $T = T^*$, the pseudogap causes downturns in other physical properties, including the magnetic susceptibility χ, nuclear-magnetic-resonance Knight shift, and electrical resistivity ρ [30,31]. Figure 3(c) shows that this seems equally true for the same three properties in δ-Pu. Each is determined, at least in part, by the number of accessible quasiparticle states at a particular T,

$$D(T) = \int_{-\infty}^{\infty} \frac{\partial f_D(\varepsilon, T)}{\partial \varepsilon} D_{el}(\varepsilon) d\varepsilon, \tag{2}$$

where $f_D(\varepsilon, T)$ is the Fermi-Dirac distribution function and $D_{el}(\varepsilon)$ is the density of states already derived from the fits to the heat capacity. The predictions of Eq. (2) are shown in Fig. 3(c); $D(T)$ consists of a broad maximum around $T^* \approx 100$ K and a steep downturn for $T < T^*$. A close examination of χ [38], Knight shift (reflecting the local magnetic susceptibility at substituted ^{69}Ga nuclei) [39,40], and ρ [35–37] data for δ-Pu [in Fig. 3(c)] reveals that these too exhibit similar broad maxima around T^* and steep downturns for $T < T^*$. Therefore *all* are consistent with the expected signatures of a pseudogap.

In the case of χ, the similarity in shape to $D(T)$ can be attributed to the proportionality of the contribution to χ from itinerant carriers to $D(T)$ [50]; the large temperature-independent background, meanwhile, is consistent with significant ionic and band Van Vleck contributions [42,53,54]. Qualitatively similar behavior occurs in the Knight shift [Fig. 3(c)]. Here, consistency of the relaxation rate with free moment behavior $(T_1T)^{-1} \propto (T + T_\theta)^{1.5}$ at $T > T^*$ [40] supports our proposal that the magnetic moments become incorporated into a pseudogap state for $T < T^*$. In the case of ρ, the similarity of its line shape to $D(T)$ suggests the possibility of there either being an approximate proportionality of the quasiparticle scattering rate to $D(T)$ (i.e., Fermi's golden rule [55]) or a collapse in the Drude weight in response to a reduction [30] in $D(T)$ with decreasing T. Further evidence for a pseudogap in electrical transport may be provided by the thermally activated Hall effect, which indicates a 25-fold increase in the Hall coefficient [34] at $T \lesssim T^*$ [42].

Having determined the form of the electronic density of states of δ-Pu [Figs. 2(d)–2(f)] and verified that it is consistent with the T dependence of several physical properties [Fig. 3(c)], it is useful to compare it with band-structure measurements and calculations. Our finding of sharp spectral features at the Fermi energy is consistent with T-dependent photoemission experiments [56]. However, the limited resolution ($35 \lesssim \Delta\varepsilon \lesssim 75$ meV) of photoemission measurements on δ-Pu has thus far prohibited the observation of a pseudogap as small as ≈12 meV, and is likely to have been a factor in the broader electronic bandwidth $2W \approx 200$ meV reported [56].

When only photoemission experimental results are considered, they strongly favor band-structure calculations that assume the $5f$ electrons *a priori* to have an almost localized character [4,8,11,12] over those that consider the $5f$ electrons to reside in broad electronic bands [2,3,5,7,14]. In Fig. 3(d), we find that while the approximate forms of the pseudogap electronic densities of states in Figs. 2(d)–2(f) resemble the results of DMFT calculations in which a strong hybridization between nearly localized $5f$ electrons and conduction electrons [12] produces a compensated Kondo semimetallic state [57], our experimentally determined bandwidths are roughly an order of magnitude narrower, and our densities of states are more than an order of magnitude higher. Indications are, therefore, that the degree of hybridization between the $5f$ electrons and the conduction electron states in δ-Pu is considerably weaker than is generally considered in band-structure calculations. Duality treatments in which $5f$ electrons are assumed to be partitioned between localized and itinerant states have shown that a weaker hybridization has the potential to produce sharper spectral features consistent with photoemission experiments [4,8].

A more localized $5f$ electron character implies that the magnetic properties are likely to be dependent on the lowest crystal electric field states [42,58], and that interactions between magnetic moments on neighboring sites (as well as direct f-f hopping) are more likely to be relevant in determining the pseudogap ground state in addition to the Kondo coupling between the magnetic moments and conduction electrons. Since geometric frustration is known to suppress antiferromagnetic long-range ordering in the fcc lattice [59], unconventional forms of a magnetically correlated state may be present. The fcc lattice has, for example, been proposed to provide the ideal host for a three-dimensional variant of a resonant-valence-bond spin-liquid ground state [60], thereby raising the possibility of a ground state with similarities to those considered in d-electron systems [31]. The existence of a quantum-entangled state could potentially explain why extensive levels of frozen-in radiation damage are required to liberate free spins exhibiting Curie-Weiss behavior [19], or why the pseudopgap remains robust under a magnetic field [Fig. 3(e)]. Observations consistent with a robust pseudogap state in a field include the nonmagnetic ground state found in recent magnetostriction measurements extending to 15 T [17], the small change of $C_{\rm el}/T$ (and the corresponding $D_{\rm el}$ obtained by deconvolution [42]) in a magnetic field of 14 T [18], and the absence of any significant departures of the magnetization from linearity in fields of up to 55 T [Fig. 3(e) [61,62].

The presence of strong electronic correlations only at temperatures $T < T^*$ implies that the entropy [see Fig. 3(a)] saturates quickly with increasing T, giving rise to a large T-dependent contribution to the free energy $-TR\ln 4$. This is likely to enhance the stability of the δ phase relative to lower-volume phases at high T. Our findings further suggest that the previously identified T scale of $\sim$1000 K in various experiments [15,17,20] is unrelated to the low-T correlated electronic state. Rather, it relates to an electronic configuration that is accessed exclusively at high T [17].

In summary, heat-capacity data with a high signal-to-noise ratio are used in conjunction with an accurate determination of the phonon density of states [27,28] to provide strong evidence for a pseudogap state in δ-Pu. This may be similar to those found in d-electron systems such as the cuprates and iridates [30–33]; however, nothing analogous to this has been found previously in an element. Hence, the $5f$ electrons are much closer to the threshold of localization than has been suggested by electronic-structure models [2–14], but this near localization is *not* associated with any form of conventional magnetic order. Since the pseudogap is the only source of electronic entropy at low temperatures, it is solely responsible for the missing magnetic moments in δ-Pu [18]. Of wider interest is whether the pseudogap in δ-Pu is unique or whether similar phenomena occur in Pu compounds that exhibit anomalously high superconducting transition temperatures [63]. Our findings warrant further studies by way of infrared optical spectroscopy or tunneling spectroscopy [54].

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