

Many-Body Electronic Structure of Americium Metal

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We report computer based simulations of energetics, spectroscopy, and electron-phonon interaction of americium using a novel spectral density functional method. This approach gives rise to a new concept of a many-body electronic structure and reveals the unexpected mixed valence regime of Am $5f^6$ electrons which under pressure acquire the $5f^7$ valence state. This explains the unique properties of Am and addresses the fundamental issue of how the localization delocalization edge is approached from the localized side in a closed shell system.

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Artificially produced from plutonium-239 in 1944, and widely used in smoke detectors, Americium is the first transuranic actinide where $5f^6$ electrons become localized and form a closed relativistic subshell. Its recent high-pressure studies [1] have drawn a lot of attention because understanding the volume behavior in actinides systems has important consequences on their storage and disposal. They have revealed that Am undergoes a series of structural phase transitions (denoted hereafter as I, II, III, and IV) and reproduces at least two of the structures of another mysterious element, plutonium, which links the physical behavior of all actinides materials to our fundamental understanding of bonding between their $5f$ electrons. At ambient pressure, Am I behaves as an ordinary metal with slightly enhanced electrical resistivity $\rho(T = 300 \text{ K}) = 68 \mu\Omega \text{ cm}$ and no sign of ordered or disordered magnetism. This is commonly understood as a manifestation of the 7F_0 ground state singlet of a $5f^6$ atomic configuration. However, the resistivity of Am raises almost an order of magnitude and reaches its value of $500 \mu\Omega \text{ cm}$ at the orthorhombic structure of Am IV which is realized at pressures P above 16 GPa. The most prominent feature of the pressure P vs volume V behavior is the existence of two distinct phases: the “soft” one, which occurs in Am I–III, as well as another “hard” phase, realized in Am IV. On top of that, a superconductivity in Am was first predicted [2] and then discovered [3] with T_c raising from 0.5 K in Am I to 2.2 K in Am II, falling slightly in Am III, and then exhibiting a sharp maximum in phase IV [4].

Understanding this unique behavior is a fundamental challenge in searching for a unified theory of actinides as the pressure driven delocalization of electrons is approached here from the localized side which is very different from Pu where originally delocalized electrons become localized with increasing volume. Thus, simple model Hamiltonians which contain qualitative features to produce complex energy landscapes with multiple solutions in open shell systems cannot be employed for studies of closed shell materials: without incorporating realistic structures in

the calculation, there is no hint of bistability in the model Hamiltonian approach.

To address these issues, in this work we introduce a novel many-body electronic structure method which allows us to uncover the physics of Am. It is based on dynamical mean field theory (DMFT), a modern many-body technique for treating strongly correlated electronic systems in a nonperturbative manner [5] and at the same time has computational efficiency comparable with ordinary electronic structure calculations thus allowing us to deal with complicated crystal structures of real solids by self-consistent many-body calculations. Our new method considers the local Green function $G_{\text{loc}}(\omega)$ as a variable in the total-energy functional and can be viewed as spectral density functional theory [6–8]. The advantage of such formulation as compared to original density functional theory [9] is a simultaneous access to energetics and local excitation spectra of materials with arbitrary strength of the local Coulomb interaction U .

The DMFT-based spectral density functional approach requires self-consistent solutions of the Dyson equations $[\omega - H_0(\mathbf{k}) - \Sigma(\omega)]G(\mathbf{k}, \omega) = 1$ for the one-electron Green function $G(\mathbf{k}, \omega)$. The poles of its momentum integrated $G_{\text{loc}}(\omega)$ contain information of the true local spectra of excitations. Here $H_0(\mathbf{k})$ is the effective one-electron Hamiltonian, while $\Sigma(\omega)$ is a local self-energy operator whose energy dependence makes the solution computationally very expensive. This so far has restricted applications of this promising many-body approach to either non-self-consistent determinations of spectra [10] or materials with simple crystal structures [7,11,12].

Our new approach greatly improves the speed of the calculation by recognizing that a signature of strong correlation effect results in the appearance of several distinct features or satellites in the excitation spectrum. The exact self-energy of an interacting system can always be represented by a pole expansion of the form

$$\Sigma(\omega) = \Sigma(\infty) + \sum_i V_i^+ (\omega - P_i)^{-1} V_i, \quad (1)$$

where weights V_i^+ and V_i and poles P_i are matrices. Remarkably, that such form of the self-energy allows us to replace the nonlinear (over energy) Dyson equation by a linear Schrödinger-like equation in extended subset of “pole states.” This is clear due to a mathematical identity

$$\begin{pmatrix} \omega - H_0(\mathbf{k}) - \Sigma(\infty) & V^+ \\ V & \omega - P \end{pmatrix}^{-1} = \begin{pmatrix} [\omega - H_0(\mathbf{k}) - \Sigma(\infty) - V^+(\omega - P)^{-1}V]^{-1} & \cdots \\ \vdots & \ddots \end{pmatrix}, \quad (2)$$

which relates our original matrix inversion required to find $G(\mathbf{k}, \omega)$ (first element in the matrix from the right) to the matrix inversion in the extended “pole space.”

The key insight is that the above form of the self-energy with a few poles captures [8,13] all the central features of a correlated system. This has an important implication for the calculation of the electronic structure of the strongly correlated material: once pole expansion of the self-energy is established, the spectral density functional theory reduces to solving a “Kohn-Sham-like” system of equations in an augmented space. The eigenstates here describe major atomic multiplet transitions as well as delocalized parts of the electronic states by separate auxiliary wave functions. Each wave function is not normalized to unity since it describes only part of the spectral weight for the electron living in the vicinity of a given energy; however, the integral spectral weight over all energies is correctly normalized to one. While a self-energy with a small number of poles may not capture the subtle physics of damping important for incoherent excitations, the method gives us directly the dispersions of these spectral features, which are measurable in angle resolved photoemission. Thus, the concept of the electronic structure is generalized to a strongly correlated situation. It ideally suits the description of such subtle regime as the proximity to the Mott transition where atomic multiplet structure appears simultaneously with strongly renormalized quasiparticle bands, a regime where traditional electronic structure methods fail.

Here, we study the properties of Am under pressure using this newly implemented matrix expansion algorithm for spectral density functional calculations within a full potential version of the linear muffin-tin orbital (LMTO) method [14]. In this approach, the s, p, d electrons are assumed to be weakly correlated and well described within such popular approximations to the density functional theory as the local density approximation (LDA) or generalized gradient approximation (GGA). The correlated f electrons require dynamical treatment using DMFT. Both the spin-orbit as well as the Hund’s couplings are competing in Americium and need to be taken into account. The former is a one-body term and enters through the LDA Hamiltonian, while the second is contained in the local Coulomb repulsion, which is conveniently expressed via Slater constants $F^{(i)}$. The value of the most important term $F^{(0)} = U$ is around 4.5 eV, which is suggested from various atomic spectroscopy data and our previous studies of plutonium. For the remaining constants, we take the atomic values $F^{(2)} = 7.2$ eV, $F^{(4)} = 4.8$ eV, and $F^{(6)} = 3.6$ eV [15].

For the purpose of the total-energy calculation, the f -electron self-energy is approximated by its atomic value, which is obtained by the exact diagonalization technique. This is known as the Hubbard I approximation [16], and the probabilities to find the f shell in its given many-body state are directly accessed within this method, giving us the insight into valence of the material. Within the atomic picture, excitations from the f^6 configuration contain many multiplet transitions, but clustered around three energies and we can further approximate the self-energy by the two-pole approximation. Thus, we can utilize the algorithm described by Eqs. (1) and (2). In practice, the positions of the self-energy poles P_i and their weights V^+, V become functionals of the positions of the f levels which are obtained by our LDA + DMFT calculations and adjusted during iterations towards self-consistency.

Our calculation reproduces the well-known fact that the f electrons in Am at zero pressure exists in a f^6 7F_0 configuration. This is illustrated in Fig. 1 by plotting the density of states (DOS) and energy bands reflecting the atomic multiplet transitions which demonstrate our novel matrix expansion algorithm. Our calculated density of states shown on the right consists of several distinct features related to $(f^6 \rightarrow f^5)/(f^6 \rightarrow f^7)$ electron removal/addition processes. One can see that the occupied part of the spectrum is well compared with the available photo-

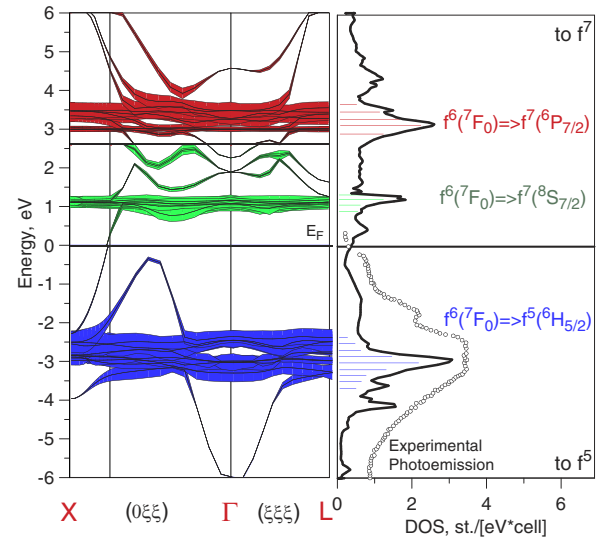


FIG. 1 (color online). Calculated many-body set of energy bands (left) which models the one-electron density of states (right) of Americium metal. Experimental photoemission spectrum [17] is also shown by open circles.

emission experiments [17], thus advancing previous bulk-surface interpretation [18] as well as density functional based calculations [19]. The idea of our new method is to model three major satellites related to ${}^7F_0 \rightarrow {}^6H_{5/2}$, ${}^7F_0 \rightarrow {}^8S_{7/2}$, and ${}^7F_0 \rightarrow {}^6P_{7/2}$ transitions with the two-pole self-energy and resolve them as many-body energy bands. (We deduce the character of these transitions by comparing with corresponding atomic Green's function calculations.) This is illustrated in the left part of Fig. 1 where the method is seen to capture the spectral weight related to electron removal and addition processes by a set of eigenstates located near -3 eV binding energy and by two sets of eigenstates located at $+1$ and $+3$ eV. Because of hybridization, the poles in spectral function get smeared out and we get broad Hubbard bands, which, in particular, results in slight mixing in their characters—a genuine band structure effect in the many-body spectrum. A simplified fcc structure with equilibrium atomic volume of Am I was used to generate the data in Fig. 1.

The computational speed gained by this algorithm allows us to study complicated crystal structures of Am. In particular, the existence of soft and hard phases in its equation of state can be predicted via our self-consistent total-energy calculations. This is illustrated in Fig. 2 where $P(V)$ behavior reconstructed from the total-energy data of phases I through IV is plotted and compared with the recent experiment. For Am I we predict the equilibrium volume equal to $27.4 \text{ \AA}^3/\text{atom}$, which is only 7% less than the experiment together with the bulk modulus equal to 450 kBar close to the experimentally deduced values lying within 400–450 kBar. The pressure ranges of all other structures are correctly reproduced. Compressibility of the highly pressurized Am IV structure is found to behave

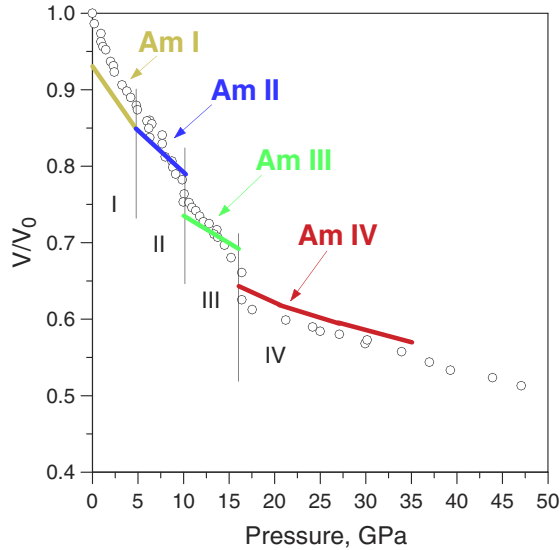


FIG. 2 (color online). Calculated equation of state for various crystal structures of Am metal. Experimental data [1] are shown by solid circles.

similarly to an experimentally observed hard phase, which indicates that f electrons start participating in bonding. Some discrepancy between the calculated and the measured compressibility of Am III can be observed in Fig. 2. This is likely to be due to simplified Hubbard I impurity solver or due to the uncertainties in the estimates of the U .

To gain further theoretical insight we now discuss the behavior of the electronic structure under pressure. To see how the increase of hybridization among f electrons affects the physical properties of Am, we carry out subsequent refined calculations, by replacing the Hubbard I approximation by a more precise one-crossing approximation [12,20]. Because of numerical complexity of the approach, we calculate only spectral functions using the fcc structure of Am and omit self-consistent determination of the energy. We, however, include all multiplet transitions within this method without exploring an approximation (1).

Figure 3 shows the density of states for Am at three different volumes, $V = V_0$, $V = 0.76 V_0$, and $V = 0.63 V_0$, which cover the lattice spacing of the entire phase diagram discussed above. Upon compression, the remarkable effect is observed as a peak near the Fermi level gets pushed down while a resonance (small shoulder) starts forming at E_f and becomes more pronounced with increasing pressure. The f^6 ground state of the atom starts admixing an f^7 configuration with a very large total momentum of $J = 7/2$. Because of hybridization with the spd bands, this large spin gets screened, thus lowering the energy of the system. This is the famous Kondo mechanism, and the energy gain increases as the hybridization increases by applying pressure.

The admixture of the f^7 configuration is counterintuitive. Naively, one expects that the application of pressure results in lowering the Fermi level in the spd band (which contains only 3 electrons), which then moves towards the f level. This reduces the occupancy of the f , admixing an f^5

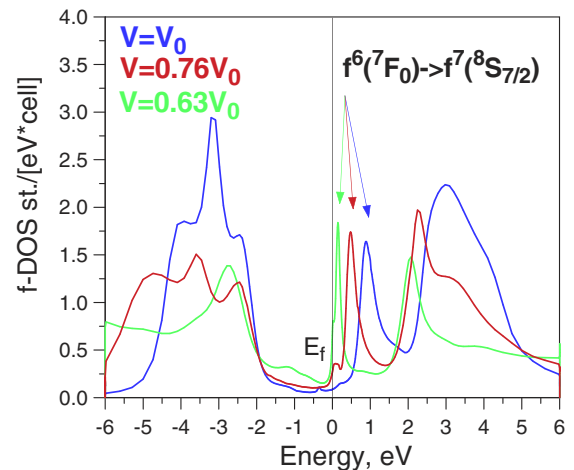


FIG. 3 (color online). Pressure dependence of Am density of states calculated using the one-crossing approximation method.

configuration, an effect that is known to induce mixed valence in Sm compounds [21]. Our first principles calculations reveal that while the position of the bare f level in Am indeed moves upwards relative to the Fermi level, application of pressure also reduces the energy of the f^7 by the gain in hybridization, and this is sufficient to compensate the increase in the distance between the bare f and the Fermi levels. This confirms the attribution of the rise in resistivity to mixed valence.

It is interesting to compare our predictions with density functional calculations. The nonmagnetic GGA calculation falls catastrophically in reproducing the equilibrium volume of the soft phase by about 50%. When spin polarization is allowed, the GGA eventually recovers most of this error but converges to the wrong magnetic state with its total (spin plus orbital) moment of about 6 Bohr magneton [19]. This prediction is at odds with the experimentally established f^6 ground state 7F_0 . Similar findings have been reported when applying a disordered local moment method [22]. This error is the result of neglecting a correlation effect. The Kohn-Sham spectrum of Am describes an f level with a small spin-orbit splitting between $f^{5/2}$ and $f^{7/2}$ (of the order of 1 eV), which leads to two energy bands located just near E_f and which are unstable against magnetism. The Coulomb interaction increases this splitting by the value of U (of the order of 4 eV) and leads to the atomiclike 7F_0 many-body state.

We finally estimate the superconducting critical temperature by computing from first principles [23] the electron-phonon coupling of the electrons in the presence of correlations. For this purpose we have extended a newly developed dynamical mean field based linear response method, which has previously proven to provide accurate phonon spectra in correlated systems [24]. We estimate the coupling constant, which comes out to be sufficiently high (~ 0.5) to predict superconductivity of the order of 1 K. The occurrence of the first maximum in experimental T_c vs pressure dependence can then be understood as the result of the variation of the spd density of states which first increases as a result of a band structure effect but then eventually decreases as the hybridization with the f electron grows with the increase of mixed valence. As we believe the location of the Mott transition is near the Am III to Am IV boundary, the raise of T_c in Am IV can then be attributed to the departure from the Mott transition point which is then decreased as the kinetic energy gets larger.

To summarize, here we provided a first many-body description of electronic properties of Am metal, but the necessity of its further extensions to evaluate the electron-phonon and the Coulomb interactions among quasiparticles in a full fledged mixed valence state together with the Kondo resonance is apparent and will be carried out in the future work.

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