Artificially produced from Plutonium-239 in 1944, and widely used in smoke detectors Americium is the first transuranic actinide where 5f electrons become localized and form a closed relativistic subshell. Its recent high-pressure studies have drawn much attention as understanding 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 \( \rho = 68 \, \mu \Omega \times cm \) and no sign of ordered or disordered magnetism. This is standardly understood as a manifestation of a ground state singlet of 5f-atomic configuration. However, the resistivity of Am raises almost an order of magnitude and reaches its value of 500 \( \mu \Omega \times cm \) 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 through III as well as another “hard” phase realized in Am IV. On top of that a superconductivity in Am was first predicted and then discovered with \( T_c \) raising from 0.5K in Am I to 2.2K in Am II, falling slightly in Am III and then exhibiting a sharp maximum in phase IV.

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 non-perturbative manner 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 \( G_{loc}(\omega) \) as a variable in the total energy functional and can be viewed as spectral density functional theory. The advantage of such formulation as compared to original density functional theory is a simultaneous access to energetics and local excitation spectra of materials with arbitrary strength of the local Coulomb interaction.

DMFT based spectral density functional approach requires self-consistent solutions of the Dyson equations

\[
[\omega - H_0(k) - \Sigma(\omega)]G(k, \omega) = 1
\]

for the one-electron Green function \( G(k, \omega) \). The poles of its momentum integrated \( G_{loc}(\omega) \) contain information of the true local spectra of excitations. Here \( H_0(k) \) 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 either to non-self-consistent determinations of spectra or to materials with simple crystal structures.

Our new approach greatly improves the speed of the calculation by recognizing that a signature of strong correlation effect results in 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

\[ \Sigma(\omega) = \Sigma(\infty) + \sum_i \frac{W_i}{\omega - P_i} \]  

(2)

Remarkably, that such form of the self-energy allows us to find \( G(k, \omega) \) (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 all the central features of a correlated system and is an excellent approximation to the Greens function of the system for the purposes of obtaining the total energy. 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 leaving 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 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 method. 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) including gradient corrections (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 \( F^{(l)} \). 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 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. The probabilities to find the f-shell in its given many body state are directly accessed within this method and give us the insight into valence of the material.

Our calculation reproduces the well known fact that the f electrons in Am at zero pressure exists in a \( t^6 \) \( \gamma F^0 \) configuration. This is illustrated in Fig. 1 by plotting density of states and energy bands reflecting the atomic multiplet transitions which demonstrate our novel matrix expansion algorithm. Our calculated one-electron density of states shown on the right consists of several distinct features related to \( t^6 \rightarrow f^5 \) electron removal and \( t^6 \rightarrow f^7 \) electron addition processes. One can see that occupied part of the spectrum is well compared with the available photoemission experiments, thus advancing previous bulk-surface interpretation as well as density functional based calculations. The idea of our new method is to model three major satellites related to \( \gamma F^0 \rightarrow \alpha H^{5/2} \), \( \gamma F^0 \rightarrow \alpha S^{7/2} \) and \( \gamma F^0 \rightarrow \alpha P^{7/2} \) transitions with two pole self-energy and resolve them as many-body energy bands. This is illustrated on 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 (blue) and by two sets of eigenstates located...
at +1 (green) and +3 eV (red). 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 Å³/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.

A compressibility of highly pressurized Am IV structure is found to behave similarly to 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 impurity solver or due to the uncertainties in the estimates of the Hubbard U.

To gain theoretical insight and understand the origin of localization-delocalization transition 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 (OCA) method to solve the Anderson impurity problem. Due to numerical complexity of the approach, we calculate only spectral functions using the fcc structure of Am and omit self-consistent determination of the energy.

Fig. 3 shows the density of states for Am at three different volumes V=V₀, V=0.76V₀ and V=0.63V₀ which covers the lattice spacing of the entire phase diagram discussed above. Upon compression, the remarkable effect is observed as peak near the Fermi level gets pushed down while a resonance (small shoulder) starts forming at Eₘ and becomes more pronounced with increasing pressure. The f⁶ ground state of the atom starts admixing an f⁷ configuration with a very large total spin of J=7/2. Due to 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 f⁷ configuration is counterintuitive. Naively one expects that 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 f⁵ configuration, an effect that is known to induce mixed valence in Sm compounds. Our first principles calculations reveal that while the position of the bare f level in Am indeed moves upwards relative to the Fermi level, the energy to absorb an electron to reach f⁷ configuration is much smaller than the energy to remove an f electron and transfer it to the Fermi level hence reaching the f⁵ configuration. Application of pressure reduces the energy of the f⁷ configuration in the bath of spd electrons by the gain in hybridization, and the resulting energy
gain is sufficient to compensate the increase in the distance between the bare f level and the Fermi level. In this way, the valence is also changed from 3 to approximately 2.8 under extreme pressure. This confirms the attribution of the rise in resistivity to mixed valence and provides the microscopic mechanism of this phenomenon. At normal pressure, the f shell is essentially closed and unable to scatter the conducting bands. This results in small resistivity. Under pressure, the reaction $f^6 + \text{spd} \rightarrow f^7$ becomes more energetically allowed resulting in the growth of resistivity.

It is interesting to compare the DMFT predictions for Am with the predictions of the density functional theory. The non-magnetic GGA calculation falls catastrophically in reproducing the theoretical equilibrium volume of the soft phase and underestimates it 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 0.5 Bohr magneton $\mu_B$. This prediction is at odds with the experimentally established $f^6$ ground state singlet $\gamma F^0$. Similar findings have been reported when applying a disordered local moment method [21]. This error is the result of neglecting an important 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. In Am the Coulomb interaction increases this splitting by the value of $U$ (of the order of 4 eV) and leads to the atomic-like $\gamma F^0$ many-body state. This stabilization of the closed shell due to the Hubbard interaction $U$ is absent in the band calculation.

We finally estimate the superconducting critical temperature by computing from first principles [24] 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 [25, 26]. 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.

To summarize, here we provided a first order picture of electronic properties of Am metal but the necessity of its further studies is apparent. These require extensions of our methods to evaluate the electron–phonon and the Coulomb interactions among quasiparticles in a full fledged mixed valence state and will be carried out in the future work.

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