Ground State Theory of δ-Pu

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Correlation effects are important for making predictions in the δ phase of Pu. Using a realistic treatment of the intra-atomic Coulomb correlations we address the long-standing problem of computing ground state properties. The equilibrium volume is obtained in good agreement with experiment when taking into account Hubbard U of the order 4 eV. For this U, the calculation predicts a $5f^5$ atomiclike configuration with $L = 5$, $S = 5/2$, and $J = 5/2$ and shows a nearly complete compensation between spin and orbital magnetic moments.

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Metallic plutonium is a key material in the energy industry and understanding its physical properties is of fundamental and technological interest [1]. Despite intensive investigations [2], its extremely rich phase diagram with six crystal structures as well as its unique magnetic properties is not well understood. It is therefore of great interest to study the ground state of Pu by modern theoretical methods using first principles electronic structure calculations, which take into account the possible strong correlation among the f electrons.

Density functional theory [3] in its local density or generalized gradient approximations (LDA or GGA) is a well-established tool for dealing with such problems. This theory does an excellent job of predicting ground state properties of an enormous class of materials. However, when applied to Pu [4,5], it runs into serious problems. Calculations of the high-temperature fcc δ phase have given an equilibrium atomic volume up to 35% lower than experiment [4]. This is the largest discrepancy ever known in density functional based calculations and points to a fundamental failure of existing approximations to the exchange-correlation energy functional.

Many physical properties of this phase are puzzling: large values of the linear term in the specific heat coefficient and of the electrical resistivity are reminiscent of the physical properties of strongly correlated heavy-fermion systems. On the other hand, the magnetic susceptibility is small and weakly temperature dependent [6]. Moreover, early LDA calculations [5] predicted δ-Pu to be magnetic with a total moment of 2.1 Bohr magnetons in disagreement with experiments.

The reason for these difficulties has been understood for a long time: Pu is located on the border between light actinides with itinerant $5f$ electrons and the heavy actinides with localized $5f$ electrons [7]. Near this localization-delocalization boundary, the large intra-atomic Coulomb interaction as well as the itineracy of the f electrons has to be considered on the same footing, and it is expected that correlations must be responsible for the anomalous properties. The parameter governing the importance of correlations in electronic structure calculations is the ratio between effective Hubbard interaction U and the bandwidth W. When the distance between atoms is small, the correlation effects may be not important, since the hybridization, and consequently the bandwidth becomes large. The low-temperature α phase of Pu has an atomic volume which is 25% smaller than the volume of the δ phase. To the extent that the complicated monoclinic structure of the α phase can be modeled by the simplified fcc lattice, it becomes clear that the LDA or GGA calculations which ignore the large effective U converge to the low-volume α phase (for which $U/W < 1$). When volume is increased, this ratio is turned around, and LDA loses its predictive power. This results in the long-standing problem of accurate prediction of the volume of δ-Pu.

In the present Letter it will be shown that a proper treatment of Coulomb correlations allows us to compute the equilibrium atomic volume of δ-Pu in good agreement with experiment. Moreover, our calculations suggest that there is a nearly complete compensation between the spin and the orbital contributions to the total magnetic moment which is consistent with experiment. Thus the strong correlation effects in δ-Pu are not manifested in the static magnetic properties.

To incorporate the effects of correlations we use the LDA + U approach of Anisimov and co-workers [8]. This approach recognizes that the failure of LDA is related to the fact that it omits the Hubbard-like interaction among electrons in the same shell, irrespectively of their spin orientation. A new orbital-dependent correction to the LDA functional was introduced to describe this effect. In its most recent, rotationally invariant representation, the correction to the LDA functional has the following form [9]:

$$\Delta E[n] = \frac{1}{2}\sum_{\{\gamma\}}(U_{\gamma_1\gamma_2\gamma_3\gamma_4} - U_{\gamma_1\gamma_2\gamma_4\gamma_3})n^c_{\gamma_1\gamma_2}n^c_{\gamma_3\gamma_4} - E_{dc}\,, \tag{1}$$

where $n^c_{\gamma_1\gamma_2}$ is the occupancy matrix for the correlated

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orbital (d or f), and γ stands for the combined spin, (s), and azimuthal quantum number, (m), indexes. The electron-electron correlation matrix $U_{\gamma_1\gamma_2\gamma_3\gamma_4} = \langle m_1 m_3|v_C|m_2 m_4\rangle \delta_{s_1 s_2}\delta_{s_3 s_4}$ can be expressed via Slater integrals $F^{(i)}$, $i = 0, 2, 4, 6$ in the standard manner [9]. The term E_{dc} accounts for the double counting effects. This scheme, known as the "LDA + U method," gives substantial improvements over the LDA in many cases [10]. The value of the U matrix is an input which can be obtained from a constrained LDA calculation [11] or just be taken from the experiment. The philosophy of this approach is that the delocalized s, p, and d electrons are well described by the LDA while the energetics of the more localized f electrons require the explicit introduction of the Hubbard U. In the spirit of this method, in this work we will treat the s, p, and d electrons by the generalized gradient approximation [12] which is believed to be more accurate than the LDA.

Our implementation of the GGA + U functional is based on the localized-orbital representation provided by the linear-muffin-tin-orbital method for electronic structure calculations [13]. It is important to include spin-orbit coupling effects which are not negligible for $5f$ electrons of Pu. Our calculations include nonspherical terms of the charge density and potential both within the atomic spheres and in the interstitial region [14]. All low-lying semicore states are treated together with the valence states in a common Hamiltonian matrix in order to avoid unnecessary uncertainties. These calculations are spin polarized and assume the existence of long-range magnetic order. For simplicity, the magnetic order is taken to be ferromagnetic [15].

We now report our results on the calculated equilibrium volume. To analyze the importance of the correlation effects, our calculations have been performed for several different values of U varying from 0 to 4 eV. For $U = 4$ eV we use the standard choice of Slater integrals: $F^{(2)} = 10$ eV, $F^{(4)} = 7$ eV, and $F^{(6)} = 5$ eV [1]. For other U's we have scaled these values proportionally. For each set of F's a full self-consistent cycle minimizing the LDA/GGA + U functionals has been performed for a number of atomic volumes. We calculated the total energy E as a function of both V and U. For fixed U, the theoretical equilibrium, V_{calc}, is given by the minimum of $E(V)$. Figure 1 shows the dependence of the calculated-to-experimental equilibrium volume ratio $V_{\mathrm{calc}}/V_{\mathrm{exp}}$ as a function of the input U. It is clearly seen that the $U = 0$ result (LDA) predicts an equilibrium volume which is 38% off the experimental result and the use of GGA gives only a slightly improved result ($V_{\mathrm{calc}}/V_{\mathrm{exp}} = 0.66$). On the other hand, switching on a very large repulsion between $5f$ electrons obviously leads to an overestimate of the interatomic distances. An optimal U deduced from this analysis is found to be close to 4 eV when using the GGA expressions for the exchange and correlation.

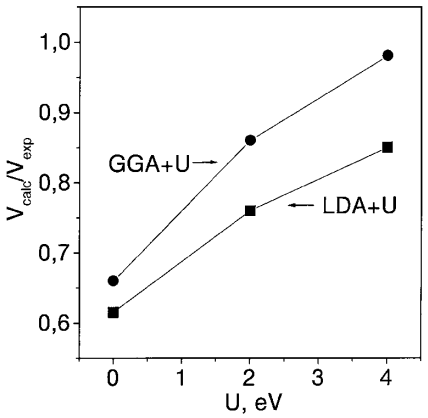

FIG. 1. Calculated theoretical volume (normalized to the experiment) of δ-Pu as a function of the Hubbard U within the LDA + U and GGA + U approaches.

This estimate of the intra-atomic correlation energy is in excellent agreement with the published conventional data [16]: The value of U deduced from the total energy differences was found to be 4.5 eV. Atomic spectral data give a similar value close to 4 eV. Thus, it is demonstrated how significant it is to properly treat Coulomb correlations in predicting the equilibrium properties of this actinide.

We now discuss the calculated GGA + U electronic structure of δ-Pu for the optimal value of $U = 4$ eV. Figure 2 shows the energy bands in the vicinity of the Fermi level. They originate from the extremely wide $6s$ band strongly mixed with the $5d$ orbitals which are strongly hybridized among themselves. The resulting band complex has a bandwidth of the order of 20 eV. On top of this structure there exists a weakly hybridized set of levels originating from the $5f$ orbitals.

In order to understand the physics behind the formation of spin and orbital moment in the f shell, it is instructive to visualize the orbital characters as "fat bands" [17]. The one-electron wave function has an expansion $\psi_{\mathbf{k}j}(\mathbf{r}) = \sum A_{lms}^{\mathbf{k}j}\phi_{lms}(\mathbf{r})$, where $\phi_{lms}(\mathbf{r})$ are the solutions of the radial Schrödinger equation normalized to unity within atomic sphere. The information about the partial lms character of the state with given $\mathbf{k}j$ is contained in the coefficients $|A_{lms}^{\mathbf{k}j}|^2$. A sum over all lms in the latter quantity gives unity (neglecting a small contribution from the interstitial region) since one band carries one electron per cell. At the same time, a sum over all j in $|A_{lms}^{\mathbf{k}j}|^2$ is also equal to one since each lms describes one state. Fixing a particular lms, we can visualize this partial character on top of the band structure by widening each band $E_{\mathbf{k}j}$ proportionally to $|A_{lms}^{\mathbf{k}j}|^2$. A maximum width Δ which corresponds to $\sum_j |A_{lms}^{\mathbf{k}j}|^2 = 1$ should be appropriately chosen. Now, at the absence of hybridization, each band originates from a particular lms state, and therefore there exists only one fat band for any given lms which has the maximum width Δ. When hybridization is switched on, there can be many bands which have the particular lms character;

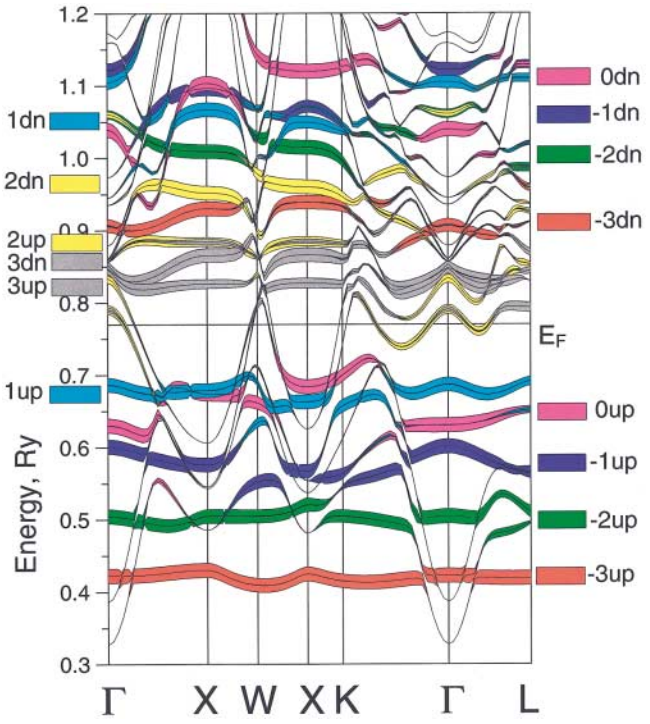

FIG. 2 (color). Calculated energy bands of δ-Pu using the GGA + U method with $U = 4$ eV. Spin and orbital characters of the f bands are shown with the color: ($m = -3 \equiv$ red, $-2 \equiv$ green, $-1 \equiv$ blue, $0 \equiv$ magenta, $+1 \equiv$ cyan, $+2 \equiv$ yellow, $+3 \equiv$ gray). Boxes from the left and from the right show approximate positions of the f levels.

they will all be widened as $\Delta|A^{\mathbf{k}j}_{lms}|^2$, while the sum of individual widths for all bands is now equal to Δ. The width of the band is then proportional to its lms character. This technique [17] gives us important information on the distribution of atomic levels as well as their hybridization in a solid. For f electrons of Pu, it is convenient to work in the spherical harmonics representation in which the f-f block of the Hamiltonian is found to be nearly diagonal.

The result of such fat bands analysis for $5f$ orbitals is shown in Fig. 2. In order to distinguish the states with different m's and spins we have used different colors ($-3 \equiv$ red, $-2 \equiv$ green, $-1 \equiv$ blue, $0 \equiv$ magenta, $+1 \equiv$ cyan, $+2 \equiv$ yellow, $+3 \equiv$ gray). Two consequences are seen from this colored spaghetti: First, spin-up and spin-down bands are all split by the values governed by the effective U and the occupancies of the levels. These are just the well known lower and upper Hubbard subbands. Second, only spin-up states with $m = -3, -2, -1, 0$, and $+1$ are occupied while all other states are empty. This simply implies $5f^5$-like atomic configuration for δ-Pu which is filled according to the Hund rule. Note that spin-orbit coupling is crucial for the existence of such an occupation scheme. In the absence of spin-orbit coupling the occupancies of the levels with $\pm m$ are the same which automatically produces zero orbital moment.

Besides providing the experimentally observed volume of the δ-Pu, our calculation suggests a simple picture of the electronic structure of this material and sheds new light on its puzzling physical properties discussed in the introduction.

The fat bands shown in Fig. 2 suggest a physical picture in which the f electrons are in atomic states forming a multiplet of the $5f^5$ configuration with $L = 5$, $S = 5/2$ spin orbit coupled to $J = 5/2$. Crystal fields can split this multiplet into a doubly degenerate state transforming according to Γ_7 representation of the cubic group and a quartet transforming according to Γ_8 representation [2], but cannot remove the orbital degeneracy completely. In a dynamic picture, the f electrons will fluctuate between the degenerate configurations, until this degeneracy is removed by the Kondo effect with the delocalized electrons in the s-p-d band. Therefore the experimentally observed characteristic heavy-fermion behavior in this system, namely, the large high-temperature resistivity and the large linear T coefficient of the specific heat, arises naturally in this picture [2].

This heavy-fermion behavior, however, should not appear in the magnetic susceptibility. The GGA + U calculation suggests that the magnetic moment of the low-lying configurations of the f electrons is much smaller than the $5\mu_B$ that one would obtain if we ignore the orbital angular momentum and assumed that the spin is fully polarized. The combination of strong Coulomb interactions and spin-orbit coupling reduces the crystal-field effects and gives rise to a large orbital moment which nearly cancels the spin moment. In an atomic picture, the $5f^5$ configuration with $L = 5$, $S = 5/2$, and $J = 5/2$ has a total moment given by $M_{\text{tot}} = \mu_B g J = 0.7\mu_B$, with Lande's g factor of 0.28. This simple relation breaks down in the presence of crystal fields, but in both the Γ_7 or the Γ_8 representation the g factor is further reduced from the atomic estimate.

The GGA + U calculation gives a spin moment M_S of 5.1 Bohr magnetons which is slightly increased relative to the 5 Bohr magnetons expected in a pure f^5 atomic configuration due to the polarization of the band electrons outside the muffin-tin shell. Evaluation of the orbital and total moments is in general a more difficult problem [18]. We have estimated the average of $\langle \mathbf{k}j|l_z|\mathbf{k}j\rangle$ summed over all occupied states $|\mathbf{k}j\rangle$. This leads to a value $M_L = -3.9\mu_B$ for the orbital moment. The total calculated moment $M_{\text{tot}} = M_S + M_L$ is thus reduced to $1.2\mu_B$. It is worth noting that an atomic analog of this estimate, $M_{\text{tot}} = \mu_B|L - 2S|$, gives exactly zero for our $5f^5$ ground state [19]. A remarkable outcome of the calculation is clearly seen: *A nearly complete compensation of spin and orbital contributions occurs* for metallic δ-Pu.

In this picture the weakly temperature dependent susceptibility which is observed in δ-Pu [2,6] is the result of a very large Van Vleck contribution and of a very small

magnetic moment resulting from the near cancellation of two large orbital and spin moments.

In a recent paper [20] Eriksson and co-workers introduced a different approach to the anomalous properties of δ plutonium. In their calculation a fraction of the f electrons is treated as core electrons while the rest are treated as delocalized. Using a combination of the constrained LDA calculation with the atomic multiplets data they obtain the correct equilibrium volume when four f electrons are part of the core, while one f electron is itinerant. The basic difference between the methods is the different treatment of the f electrons. In this paper all the f electrons are on equal footing, and their itineracy is reduced by the Hubbard U relative to the predictions of LDA or GGA calculations. Since our approach and that of Eriksson *et al.* lead to different ground state configurations of the localized f electrons (f^5 vs f^4), further experimental spectroscopic studies of δ-Pu would be of interest.

In conclusion, using a realistic value of the Hubbard $U = 4$ eV incorporated into the density functional GGA calculation, we have been able to describe ground state properties of δ-Pu in good agreement with experimental data. This theory correctly predicts the equilibrium volume of the δ phase and suggests that nearly complete cancellation occurs between spin and orbital moments. The main shortcoming of the present calculation is the assumed long-range spin and orbital order. This is the essential limitation of the LDA + U approach (or of any *static* mean field theory): in order to capture the effects of correlations it has to impose some form of long-range order. Static mean field theories are unable to capture subtle many-body effects such as the formation of local moments and their subsequent quenching via the Kondo effect. These deficiencies will be removed by *ab initio dynamical* mean field [21] calculations for which codes are currently being developed. We believe, however, that our main conclusions, i.e., that correlations lead to the correct lattice constant and a reduction of the moment, relative to the LDA results, are robust consequences of the strong correlations presented in this material and will be reproduced by more accurate treatments of the electron correlations.

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