Density-Functional Calculations of α, β, γ, δ, δ', and ϵ Plutonium

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Total energies for the six known polymorphs of plutonium metal have been calculated within spin and orbital polarized density-functional theory as a function of lattice constant. Theoretical equilibrium volumes and bulk moduli correspond well with experimental data and the calculated total energies are consistent with the known phase diagram of Pu. It is shown that a preference for the formation of magnetic moments, increasing through the $\alpha \rightarrow \beta \rightarrow \gamma$ phases, explains their position in the ambient pressure phase diagram and their anomalous variation of atomic density. A simple model is presented that establishes a relationship between atomic density, crystal symmetry, and magnetic moments which is universally valid for all Pu phases.

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Since its discovery more than half a century ago, plutonium has been a puzzling material with many anomalous properties not well understood. No doubt, this is the most complex metal in the periodic table with as many as six established phases [1,2] stabilized by moderate heating under room pressure conditions; see Fig. 1. The α and β phases are highly complex structures (monoclinic and orthorhombic), γ (orthorhombic) is intermediate, whereas δ (fcc), δ' (bct), and ϵ (bcc) are simple one atom/cell structures. Furthermore, there are significant volume expansions associated with these phase transitions. It seems plausible that this anomalous behavior is connected to the $5f$ electrons which have been shown to play a dominant role for the crystal structures and atomic densities in the light actinides [3]. It is unclear, however, what detailed mechanism is governed by the electronic structure. Quantifying this mechanism is central to the understanding of Pu and perhaps the whole actinide series of metals, because Pu plays a key role being on the border between delocalized (Th-Np) and localized (Am and on) $5f$-electron behavior. Furthermore, if the process responsible for the structural phase transitions in Pu can be clarified, other anomalous properties of Pu, such as resistivity, superconductivity, thermal expansion, and magnetic susceptibility may be better understood.

The ground-state α phase has been shown to be rather well described by first-principles calculations that properly handle the complexity of this structure [4]. Narrow $5f$ bands in Pu, positioned in the vicinity of the Fermi level, favor low symmetry structures over those with higher symmetry due to a Peierls-like symmetry breaking mechanism ("Peierls distortion") [4,5]. This investigation [4] and many others were not able to explain the occurrence of a high symmetry (fcc) δ phase of plutonium, however. Consequently, several theoretical models suitable for δ-Pu have been developed [6–11], but only one seems to be able to treat both α-Pu and δ-Pu on the same footing [10]. This latter approach, which allows for spin and orbital polarization, is therefore natural to apply for the remaining Pu phases.

In the present investigation we calculate the electronic structure and total energy of the six known ambient pressure phases of Pu using an all electron full-potential linear muffin-tin orbitals (FPLMTO) method [12] that include spin-orbit coupling and orbital polarization effects. The parameters for these calculations were similar to those given earlier [10,11], but the more important details are repeated here. The method is an implementation of density-functional theory (DFT) as applied for a bulk material [12]. The approximations in this approach are limited to the standard ones of the exchange-correlation energy functional, cutoffs in the expansion

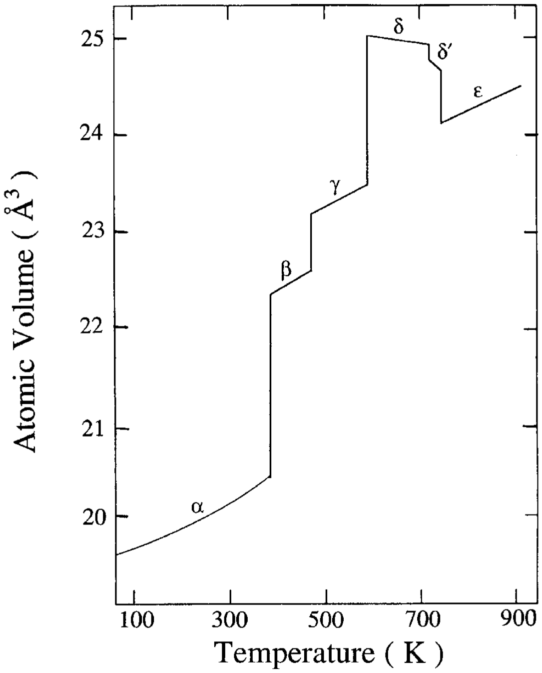

FIG. 1. The experimental[2] phase diagram of plutonium.

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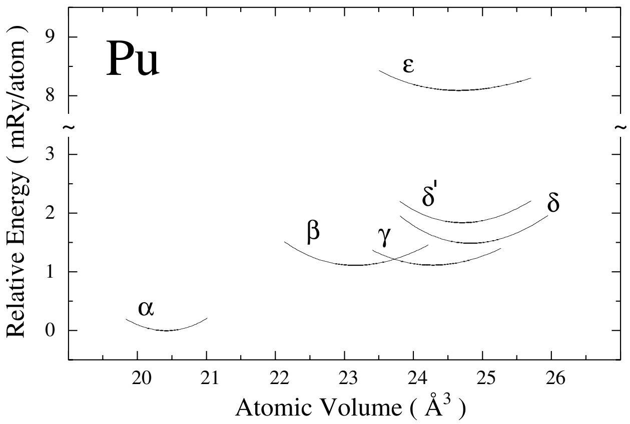

FIG. 2. Calculated total energies for the six known polymorfs of plutonium as a function of atomic volume. Note that the y axis is broken to better display the ϵ-Pu energies.

of basis functions, of k-point sampling in integrations over the Brillouin zone, and of the Born-Oppenheimer assumption. For the exchange-correlation approximation we used the generalized gradient approximation [13]. Spin-orbit coupling and spin/orbital polarization were accounted for, in the same way as have been described earlier [10].

The use of full nonsphericity of the charge density and one-electron potential is essential for accurate total energies. This is accomplished in our method by expanding charge density and potential in cubic harmonics inside nonoverlapping muffin-tin spheres and in a Fourier series in the interstitial region. The calculations included so-called semicore $6s$ and $6p$ states in addition to the valence states ($7s$, $7p$, $6d$, and $5f$).

The geometry of the structures was kept fixed to the experimental geometry [1]. This is a good approximation because relaxation effects are very small in Pu [14]. Sampling of the irreducible Brillouin zone was done using the special k-point method [15], and the number of k points used were 64 for the eight atom/cell calculations (γ, δ, δ', ϵ), 4 for β-Pu (17 atoms/cell), and 16 for α-Pu (16 atoms/cell). α-Pu, β-Pu, and γ-Pu were all calculated for antiferromagnetic (AF) optimized configurations (see below), whereas for the other three structures a disordered magnetic configuration was assumed. The latter is motivated by the belief that δ-Pu and higher temperature phases are stabilized by disorder [11,16]. The magnetic disorder was accomplished using an eight atom special quasirandom structure [17] as described previously [11].

Our main results are shown in Fig. 2, where total energies for all phases are plotted as a function of atomic volume. Notice first that they are, except for ϵ-Pu, very close and with the true ground-state α phase being the most stable, followed by β-Pu, γ-Pu, δ-Pu, δ'-Pu, and finally ϵ-Pu. The total energies for β and γ plutonium are, however, within numerical accuracy and indistinguishable (Table I). Our theory is thus fully compatible with the known phase diagram of Pu shown in Fig. 1. Furthermore, the calculated atomic volume for each phase is in very good agreement with the experimental value, see Table I, and again the numerical order is correct with α-Pu being the most and δ-Pu being the least dense phase. This is remarkable because the densities vary greatly, α-Pu is 25% denser than δ-Pu and the four remaining phases lie between. With an 11% larger atomic volume than α-Pu, β-Pu becomes stable at 390 K [1]. This expansion is very well reproduced in our calculations as is the next expansion of about 5% that occurs for γ-Pu. Even the subtle differences in atomic volume between δ-Pu, δ'-Pu, and ϵ-Pu are reproduced by our theory.

TABLE I. Experimental data from the Pu handbook [1] unless otherwise stated. Volumes (V) in Å^3, bulk moduli (B) in GPa, and energies (E) in mRy/atom. All total energies are relative to the total-energy minimum of α-Pu.

	FPLMTO			Experiment	
Phase	V	B	E	V	B
α	20.3	50	0	20.2	40–66
β	23.1	59	1.1	22.7	···
γ	24.3	33	1.1	23.5	···
δ	24.9	41	1.5	25.2	30–35[a]
δ'	24.7	44	1.8	25.1	···
ϵ	24.6	23	8.1	24.4	···

[a] Moment [19].

The bonding properties of Pu clearly change strongly with temperature heralding the great volume expansions that accompany the phase transitions. From our calculations we can infer that these expansions are related to the spontaneous formation of magnetic moments that correlate with the crystal geometry and atomic density (see below). For α-Pu the spin moments have relatively small magnitudes, see Fig. 3, and calculations ignoring spin

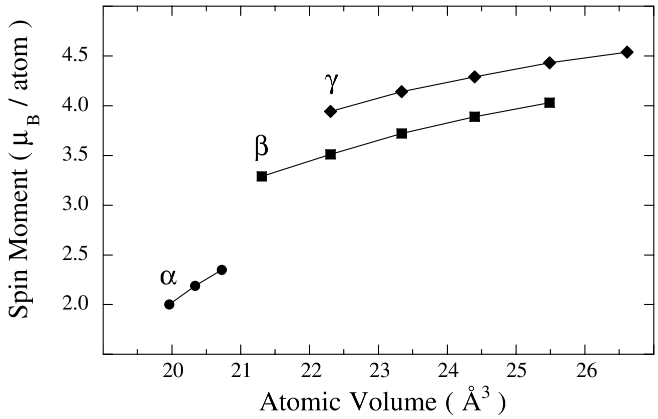

FIG. 3. Calculated average magnitude of spin moments per atom for α-Pu, β-Pu, and γ-Pu.

polarization are therefore adequate to describe this phase rather well [4,14,18]. With only a small magnetic polarization, α-Pu condenses in a low symmetry state and at a very high density. The situation for β-Pu is already significantly different, with substantial spin moments predicted by our calculations; see Fig. 3. There is a discontinuity in the average spin (and orbital, not shown) moment between α and β plutonium, which is likely related to the abrupt change in both their atomic volumes and crystal structure. Also, for the next ($\beta \rightarrow \gamma$) transition, the same behavior is predicted by our calculations, although the increase in magnetic moment is less, as is the volume expansion accompanying this phase transition.

Although elaborate and time consuming electronic-structure calculations can give us accurate total energies of plutonium phases, it is desirable to find an interpretation which offers to provide a fundamental understanding. Our calculations reveal that the spin moments and their configurations vary strongly between the different Pu phases. In addition, the total energy of a particular phase is very sensitive to the actual spin configuration. Also, larger magnetic moments seem to induce expanded equilibrium volumes. Clearly, it emerges a connection between the atomic density, crystal symmetry, and the behavior of the magnetic moments in Pu, which so far has not been recognized.

To bring this connection to light, we have conducted a comprehensive study of the local geometries of the Pu structures studied above by decomposing their unit cells into Voronoi cells. We can rigorously define the average bond length for atom i at $\mathbf{R}_i$ as

$$b(\mathbf{R}_i) = \frac{1}{2}\sum_{j \neq i} w(\mathbf{R}_i, \mathbf{R}_j)|\mathbf{R}_i - \mathbf{R}_j|, \tag{1}$$

where the sum runs over all the neighboring atoms j that contribute a surface patch to the Voronoi cell of this atom i. The weight factors, $w(\mathbf{R}_i, \mathbf{R}_j)$, are determined by the relative contribution of atom j to the total Voronoi-cell surface around atom i, and it can be expressed as

$$w(\mathbf{R}_i, \mathbf{R}_j) = \frac{\Lambda(\mathbf{R}_i, \mathbf{R}_j)}{\sum_k \Lambda(\mathbf{R}_i, \mathbf{R}_k)}. \tag{2}$$

Here $\Lambda(\mathbf{R}_i, \mathbf{R}_j)$ is the area of the Voronoi-cell face between atoms i and j. We can further study the shape of the Voronoi cells by computing the variance, s, of the nearest neighbor bond lengths:

$$s(\mathbf{R}_i) = \sqrt{\frac{1}{4}\sum_j w(\mathbf{R}_i, \mathbf{R}_j)(\mathbf{R}_i - \mathbf{R}_j)^2 - [b(\mathbf{R}_i)]^2}. \tag{3}$$

We have now defined two parameters for the local geometry: (i) b quantifies the *volume* associated with atom i, and (ii) s represents the amount of local *symmetry* around each atom. A highly symmetric structure, such as fcc, has zero variance ($s = 0$) in the distribution of its nearest neighbor bond lengths, while nonisotropic distortions increase this quantity ($s > 0$).

Next, we attempt to establish a link between the atomic density (b), crystal symmetry (s), and magnetic moments that may emerge as universally valid for all the phases of plutonium. In general, ordered magnetism in a metal is expected when the exchange energy dominates over the band energy. This is often the case when there is a high density of states at the Fermi level (E_F) that reduce the band energy required to align the spins. In Pu there are very narrow $5f$ states which provide this situation, and a spontaneous breaking of the crystal and/or spin symmetries is expected. It then appears likely that the competition between these two effects, Peierls distortion and spin polarization, can give rise to conditions in Pu which favors one effect over the other. As one extreme, one expects a nonmagnetic high-density phase with very low crystal symmetry, and as another, a magnetic low-density phase with high crystal symmetry. The magnetic phase should crystallize at a lower density because magnetically polarized and nearly filled $5f$ subbands provide little attractive bonding. To better quantify these ideas for Pu, we construct a local geometry parameter $\mathcal{G}$ that depends on b and s and has the units of b:

$$\mathcal{G} = b\left[1 - 2\left(\frac{s}{b}\right)^2\right]. \tag{4}$$

$\mathcal{G}$ can be computed straightforwardly for any Pu atom from its local geometry. In Fig. 4, we plot first-principles atom-projected spin moments, normalized with their respective total charge, for α, β, γ, and δ Pu atoms versus their corresponding geometry parameter $\mathcal{G}$. Notice that the spin moments for all the atoms, independent of their phase origin, fall on the same universal curve. Hence, we have discovered that the calculated spin moment (and orbital moment, not shown) varies *continuously* as a function of the local geometry in Pu. This is a most

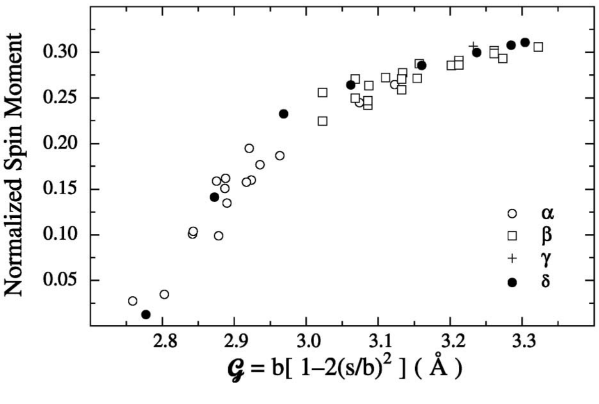

FIG. 4. Calculated normalized spin moment for atoms in α, β, γ, and δ plutonium, as a function of the geometry parameter $\mathcal{G}$ (see main text).

important insight as it shows that no fundamental changes or discontinuities of the electronic structure need to be invoked to produce the many phases of Pu, once the presence of magnetic moments is acknowledged and incorporated into the theory.

In our first-principles treatment of Pu, the magnitudes of the magnetic moments are self-consistently calculated, whereas the actual spin configuration is an input to the calculation. Therefore, it is most desirable to have some guidance as to what spin configuration is the ground state. It has been found [11,14] that an AF ordering often seems favored in Pu. Unfortunately, there are many possibilities to order the spins in antiparallel ways, especially for the more complex structures. Following our past experience [11,14], we know that it is energetically favorable to order the moments such that the AF coupling between each atom and all its nearest neighbors is maximized. The strength of this local AF interaction can be defined as

$$\mathcal{A}(\mathbf{R}_i) = -\mathbf{M}(\mathbf{R}_i) \cdot \sum_j w(\mathbf{R}_i, \mathbf{R}_j)\mathbf{M}(\mathbf{R}_j), \quad (5)$$

where $\mathbf{M}(\mathbf{R}_i)$ is the magnetic moment on atom i and $w(\mathbf{R}_i, \mathbf{R}_j)$ the weight factors defined in Eq. (2). We now propose that the maximum of the average local AF coupling,

$$\langle \mathcal{A} \rangle = \frac{\sum_{i=1}^{N_{\mathrm{atoms}}} \mathcal{A}(\mathbf{R}_i)}{\sum_{i=1}^{N_{\mathrm{atoms}}} \mathbf{M}(\mathbf{R}_i) \cdot \mathbf{M}(\mathbf{R}_i)}, \quad (6)$$

characterizes the ground states in Pu. For instance, $\langle \mathcal{A} \rangle$ is maximum in bcc for the standard AF ordering, and in fcc when aligning the moments within (001) planes opposite to the spins of the adjacent layers (the so-called $L1_0$ structure). On the other hand, for α-Pu the particular AF configuration [14,18] has little effect upon the total energy, since the magnetic contribution is small and mainly driven by a magnetic moment on site 8 [14]. For β-Pu, however, there are many sites with similar magnitudes of the magnetic moments, and therefore, many plausible magnetic configurations. In this case, analyzing $\langle \mathcal{A} \rangle$ is helpful when searching for the ground-state configuration, and from our *ab initio* calculations of several magnetic configurations we found that the largest $\langle \mathcal{A} \rangle$ does indeed correspond to the lowest total energy.

Obviously, DFT is capable of producing realistic energetics and cohesion for the many, and very different, phases of plutonium when magnetic interactions are accounted for. This fact strongly suggests that magnetism plays a role in Pu although screening or other effects may obscure its existence experimentally. We show that by defining two parameters of the crystal structure, b (density) and s (symmetry), the magnetic moments correlate in a *universal* relationship with all six phases of Pu. Hence, the Pu phases (with the exception of ϵ-Pu) are equally well described within a single framework established by DFT, and that the strength of the magnetic interactions distinguishes the various phases. From a practical point of view, we have demonstrated that reliable total energies of Pu can be calculated and now be utilized for computing equation-of-state, phase stability, mechanical properties, and developing efficient interatomic potentials for plutonium.

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