New Pseudophase Structure for α-Pu

J. Bouchet,[1] R. C. Albers,[1] M. D. Jones,[2] and G. Jomard[3]
[1]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[2]*Department of Physics and Center for Computational Research, The State University of New York, Buffalo, New York 14260, USA*
[3]*Centre d'etudes de Bruyeres le Chatel, France*
(Received 7 May 2003; published 3 March 2004)

We propose a new pseudophase crystal structure, based on an orthorhombic distortion of the diamond structure, for the ground-state α phase of plutonium. Electronic-structure calculations in the generalized-gradient approximation give approximately the same total energy for the two structures. Interestingly, our new pseudophase structure is the same as the γ-Pu structure except with very different b/a and c/a ratios. We show how the contraction relative to the γ phase, principally in the z direction, leads to an α-like structure in the $[0, 1, 1]$ plane and reproduces the short range bonds of the α phase. This is an important link between two complex structures of Pu and opens new possibilities for exploring the very rich phase diagram of Pu through theoretical calculations.

DOI: 10.1103/PhysRevLett.92.095503 PACS numbers: 61.50.Ks, 64.30.+t, 64.70.Kb

Pure plutonium is an exotic metal that is poorly understood. It appears to be going through a Mott-insulator transition in its $5f$ electronic orbitals as it transforms into different crystal structures as a function of temperature. Actinide elements lighter than Pu have itinerant $5f$ electrons; elements heavier than Pu form a second rare-earth series with localized $5f$ electrons. The α-Pu phase (zero-temperature ground state) is believed to have mainly itinerant $5f$ electrons. However, δ-phase (fcc) Pu is believed to be in neither limit (neither completely itinerant nor localized), but is instead in some kind of exotic electronic state that we may describe as partially localized, for want of any better terminology to apply to this system [1].

The understanding of this phase transformation, with its associated large volume per atom expansion, has been an exciting topic of discussion within band-structure theory and related correlated-electron extensions to it for several decades now. But almost all of the more sophisticated recent calculations have been done for the fcc δ phase [2–5]. This crystal structure has one atom per unit cell and is amenable to better, more computationally intensive techniques for handling the correlated-electron physics, which is believed to be the fundamental issue controlling the f-shell Mott-insulator transformation. Because the physics is so difficult, we believe that studying the strongly correlated δ phase in isolation is less useful than also including the more weakly correlated α phase in the study. A correct theory should get both limits right and is a strong constraint on the theoretical approaches that are used. The chief problem with including the α structure is its complicated crystal structure, which is a low symmetry monoclinic structure with space group $P21/m$ and involves 16 atoms per unit cell [6,7]. Because of this complexity, for example, a fully relaxed structure (volume and internal parameters) has not yet been obtained with density functional theory (DFT).

We believe that we have now found a solution to this problem. In this Letter, we propose a new pseudostructure for α Pu that involves only two atoms per unit cell and is a relatively symmetrical orthorhombic crystal structure. We show that the real α crystal structure involves only small distortions of various atoms around this pseudostructure and that the electronic-structure energy of both systems (at least at the band-structure level) is nearly identical.

By a pseudostructure we mean a simpler crystal structure where the atoms are quite close to the positions of the more complex real structure. Pseudostructures are interesting for two reasons: (1) They provide insight into the geometrical structure of the atoms in the original structure and possible phase-transformation pathways, and (2) they provide an alternative, less expensive crystal structure for complicated electronic and microstructural calculations. From a physics point of view, one can view the pseudostructure as an approximation to the real structure that captures the dominant total energy of the electronic structure (heat of formation) and local bonding effects; the real structure can then be viewed as just a minor distortion of the pseudostructure, with only a small energy difference between the two structures.

In the case of Pu, insight into the crystal structure is extremely important. Unlike, for example, the cubic diamond structure of Si where it is easy to understand the tetrahedral nearest-neighbor structure as a consequence of directional s-p bonds, or the close packed fcc crystal structures favored by Madelung energies in metals, it is extremely difficult to understand why the lowest temperature Pu phases are so extremely anisotropic and complex. In α Pu the nearest-neighbor structure involves a complicated arrangement of short and long bonds [8]. How can we understand this, and why do the crystal structures become more isotropic and metalliclike at high temperatures? Good pseudostructures give us the opportunity to

0031-9007/04/92(9)/095503(4)$22.50

look at these crystal structures in new ways that may eventually stimulate insights that will resolve some of the questions.

Understanding the complex phase diagram of Pu is likely to involve consideration of strong directional bonding and high density of states effects of the f electrons and how that bonding weakens under strong electron-electron correlations. Sophisticated electronic-structure calculations are necessary to make progress in this area. Unfortunately, the α and β phases (respectively, 16 and 34 atoms/unit cell) are just too computationally expensive for such calculations to be practical. To have a simple pseudophase crystal structure that can mimic the actual bonding arrangement of the extremely complicated crystal structure of the real phase makes it possible to do these very sophisticated electronic-structure calculations with little loss of accuracy or insight. If accurate pseudophases exist, they also make possible complicated microstructural models of the phase transformations that capture the dominant components of free energy differences without requiring huge numbers of parameters. For example, Ginzburg-Landau models become much more accessible through the use of pseudophases, as the α to δ phase transformation of Pu [9].

What is even more interesting is that our proposed pseudostructure is identical with the γ phase of Pu, except that the unit cell dimensions are greatly changed. This crystal structure is an orthorhombic distortion of the cubic diamond lattice. It has two atoms in the smallest unit cell, one at the origin and the second 1/4 of the way along the a, b, and c axes (which are now all different in the orthorhombic unit cell). Because both atoms have a face-centered configuration, there are eight atoms in the primitive orthorhombic unit cell (just like cubic diamond). As we will show, our pseudostructure is far better than the only other previously proposed pseudostructure for α Pu, the Crocker pseudostructure [10]. This structure was based on the insight that the α structure can be viewed as two repeating planes of a distorted hexagonal structure. Although this structure also has two atoms in its unit cell (each of the distorted hexagons are replaced by symmetric hexagons), it is also monoclinic and has not proved useful for electronic-structure calculations. We will also show that its near-neighbor shells are a poor approximation to the real α phase.

What makes Pu fascinating from an electronic-structure point of view is the instability in the $5f$ shell, which has itinerant electrons for α Pu and localizes into the core for Am and higher-Z actinides [11,12]. This Mott-like transition for the $5f$ electrons involves very strong electron-electron correlations and requires a much more complicated theory for the electrons than the usual local density approximation (LDA) for DFTs, which are like a mean-field treatment of the correlations [13]. If the parabolic decrease of the volume of the light actinides as a function of atomic number can be explained with a simple Friedel model, Pu deviates from this theoretical estimation, since Pu has a larger volume than Np. Until now there has been no definitive explanation of this upturn. In addition, it is well known that DFT in LDA or generalized-gradient approximation (GGA), due to the presence of strong correlation effects, has been unable to describe the δ phase of Pu, underestimating its atomic volume by about 20%, for example. But recently, several attempts to go beyond LDA have given some understanding of the α-δ transition. The LDA + U method [2,4] and the LDA + DMFT (dynamical mean-field theory) [3], by taking into account the localization of the f states, have shown the role of spin and orbital polarization in describing the δ phase.

Söderlind *et al.* [14–16] have performed *ab initio* relativistic total-energy calculations and offered an explanation for the crystal structure of α Pu in terms of a Peierls-Jahn-Teller-like distortion. By comparing the total energy of the α phase with total energies of symmetric (fcc, bcc, hcp) structures and other actinidelike structures (such as α-U and α-Np), they showed that the α-Pu structure minimizes the total energy for Pu, but they could not explain the upturn in equilibrium volume for Pu. More recently, Jones *et al.* [17] have performed calculations with two different methods, full-potential linearized augmented plane wave and linear combinations of Gaussian-type orbitals-fitting function for all the light actinides. Although their theoretical volumes agree well (within about 2%) with the experimental volumes for Th to Np, they show a larger discrepancy (7%) for α Pu and no upturn between Np and Pu. No attempt was made to relax the structural parameters of the α phase. They also speculated that some localization effects could already be present in α Pu, accounting for the discrepancy between the computed and measured atomic volume and causing the upturn. To our knowledge, no fully relaxed electronic-structure calculations have been performed on the α, β, and γ phases and a complete and comprehensible picture of the Pu phase diagram still does not exist.

In our calculations, we have used the projector augmented-wave method, which combines ideas from pseudopotentials and the linearized augmented-plane-wave method [18]. Forces and the full stress tensor can be easily calculated and used to relax atoms into their instantaneous ground state. This is implemented in the plane-wave basis VASP code [19] with spin-polarized DFT and the GGA of Perdew and Wang [20]. Ultrasoft Vanderbilt pseudopotentials were used to represent the core electrons. This allowed us to perform for the first time a fully relaxed calculation of the α phase. Results are presented in Table I. As in previous calculations [15,17], the atomic volume is slightly lower compared to the experimental value. This discrepancy is partially due to the absence of spin-orbit coupling in our calculations [17,21]. The relaxed structure is very close to the experimental one (the energy difference is about 4 mRy), and the positions of the atoms relaxed by only 2% or 3%,

TABLE I. Structural and internal parameters (Å) for the experimental and theoretical α (Th.), Crocker, pseudo-α, and γ structures of Pu. For α (Th.), the volume and all the internal parameters have been relaxed. The energies (mRy) are relative to the α structure, which is the ground state for all the calculations, with or without spin-orbit coupling.

	Pu-α		Crocker	γ	Pseudo-α
	Expt.	Th.			
a	6.19	5.96	2.94	2.85	3.50
b/a	0.78	0.76	1.56	1.83	1.61
c/a	1.77	1.83	1.93	3.22	2.09
β	101.8	101.8	116.3		
Volume	20.0	18.0	17.3	17.0	18.0
Energy (GGA)		0	20	36	3
Energy (GGA + SO)		0	18		3

TABLE II. Nearest neighbor distances (Å) for the Crocker structure, the γ Pu, the pseudo-α, and the α Pu at the theoretical equilibrium volume.

	Distances (number)				
	Crocker	γ Pu	Pseudo	α	
1 n.n.	2.44(2)	2.73(4)	2.47(4)	2.46–2.55(4)	Short bonds
2 n.n.	2.79(2)	2.85(2)	3.31(4)		
3 n.n.	2.79(2)	2.97(4)	3.50(2)	3.21–3.59(10)	Long bonds
4 n.n.	3.02(2)	3.39(4)	3.49(4)		

showing that DFT-GGA reproduces the ground state of Pu with good precision.

We have compared the total energies of the α, Crocker's, and the γ structure. As expected, the α phase has the lowest energy, while Crocker's structure is about 20 mRy larger, and the γ phase 36 mRy larger. The theoretical volume of the γ phase is very far from the experimental volume (23.14 Å^3), but very close to the experimental volume of the α phase; see Table I. If we minimize the total energy of this structure as a function of b/a and c/a, we obtain a large contraction in the z direction and a smaller one in the y direction to obtain a structure very different from γ (we will call this new structure "pseudo-α" in the rest of this Letter). The volume increases slightly and is roughly equal to the theoretical volume for the α structure. Surprisingly, the total energy is also very close to the total energy obtained for the α structure, about 3 mRy higher, almost within the accuracy of calculations. Using a full-potential LAPW method we have checked the influence of the spin-orbit coupling on our results. The total energy of the pseudostructure is still very close to the α one and the spin-orbit coupling does not help to differentiate the two structures.

It is interesting to speculate on why we find nearly the same total energy for two structures that appear to be so completely different. To understand this, it is useful to compare the interatomic distances in the γ, the pseudo-α, and the α structures, which are shown in Table II. Although the atomic environment around each atom in the α structure is very complex, we can divide it into roughly two categories: short and long bonds, well separated. Each atom has 4 nearest neighbors and 10 second-nearest neighbors, except atom I which has 3 and 13 and atom VIII which has 5 and 7. During the transformation from γ to pseudo-α the first shell of neighbors contracts around the atom while the second and the third shells expand to be very close to the fourth shell. This gives a local environment of 4 nearest neighbors and 10 second-nearest neighbors for the pseudo-α, exactly what is found in average in the α structure. In addition, the interatomic distances are very close. So the relaxation of the γ phase gives us a new structure, with nearly exactly the same distribution of interatomic distances as in the α phase. Crocker's structure, however, is quite different with only two nearest neighbors and an intermediate shell with four atoms. So, the local atomic environment is more important than the monoclinic symmetry in determining the energy of the α structure. In the α structure, the short bonds simulate a large bandwidth metal, and in the high temperature structures the longer bonds provide less $f - f$ overlap and hence push Pu into a more localized limit and a magnetic solution. In fact, adding correlations in the calculations shows that for a certain value of the Coulomb interaction the pseudo-α expands suddenly towards the γ structure [22].

In Fig. 1, we show the density of states (DOS) obtained for the three structures at their theoretical volumes. They are very similar, with the Fermi level in a pseudogap and two broad features, one above and one below the Fermi level. The DOS of the γ Pu with the experimental parameters has been compared to the pseudo-α structure and we can see the presence of a peak at the Fermi energy,

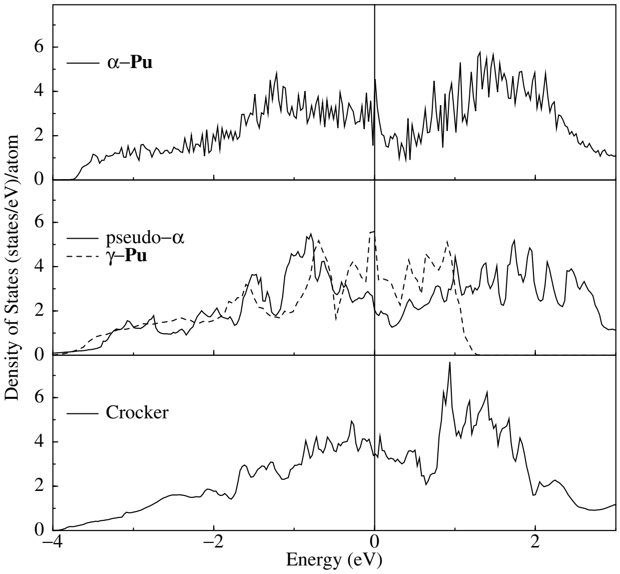

FIG. 1. DOS for α Pu, pseudo-α, and γ Pu, and Crocker's structure, calculated at the theoretical equilibrium volume.

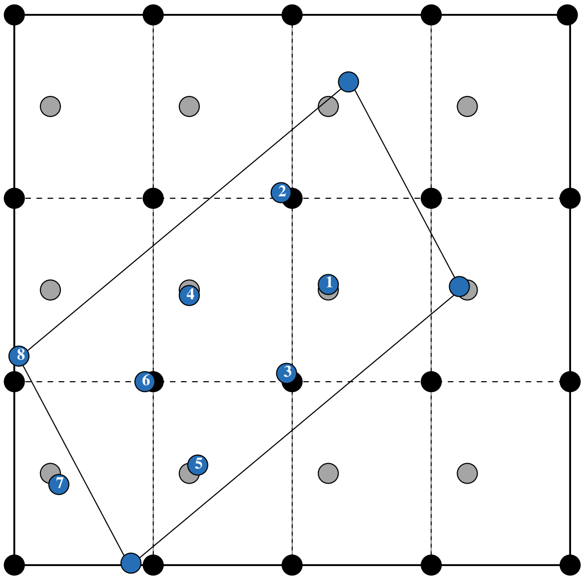

FIG. 2 (color). Distorted diamond structure (pseudo-α) in the (011) direction. The blue atoms are the eight positions in the α structure.

so during the contraction of the cell along the b and c axes there is the opening of a large pseudogap with the reduction of the density of states at the Fermi level.

Looking at the [011] plane of the pseudo-α structure (see Fig. 2), one can almost visualize the α phase. The atoms in dark and grey are the two distinct atoms in the pseudo-α structure, and we have superimposed in blue the α-structure atoms. They are very similar despite the complexity of the α pattern and the relative simplicity of the distorted diamond structure. We have calculated the distance between related atoms in the two different crystal structures, which has an average of about 0.25 Å. These distortions are responsible for the small total-energy difference between the two structures. In addition, the [011] planes have the same interlayer distance as in the α phase (2.31 and 2.26 Å for pseudo-α and α, respectively). As we indicated earlier, the new structure respects the average surrounding of an atom in the α phase, with four nearest neighbors, but exactly as in the α phase, there are two in the same plane, one in the plane above and one in the plane below. The angle between one atom and its nearest neighbors from the two other planes is also very similar (around 137° and 130° for pseudo-α and α, respectively; in diamond, it is 109°). In addition, the connection of our pseudophase with the γ phase suggests a deep structural relationship between the low-temperature phases of Pu that needs further examination. It is interesting to observe that the b/a and c/a ratios of the real γ phase of Pu have a tendency to move toward the values for our new pseudophase as the temperature is lowered. Zachariasen and Ellinger measured the lattice constants in function of temperature. The lengths of b and c both decrease with temperature, while the length of a increases [8]. If the β phase did not interrupt this trend, it is likely that γ Pu would slowly continue in this way until it reached the phase transformation into the α phase that would then require just a tiny distortion.

In conclusion, we have discovered a very simple pseudostructure reproducing the main features of the complex ground state of Pu. Our results show that the local atomic environment in the α structure with 4 nearest neighbors and 10 second-nearest neighbors is its crucial characteristic. We have found a very simple path (following the experimental variation of the lattice constants of γ Pu with temperature) between γ and α Pu. These results show the predictive power of DFT calculations, and our new pseudostructure of the α phase opens new possibilities for exploring the behavior of Pu. It will allow approximate calculations of α Pu with far more sophisticated techniques than have been previously possible.

---

[1] R. C. Albers, Nature (London) **410**, 759 (2001).
[2] S. Y. Savrasov and G. Kotliar, Phys. Rev. Lett. **84**, 3670 (2000).
[3] S. Y. Savrasov, G. Kotliar, and E. Abrahams, Nature (London) **410**, 793 (2001).
[4] J. Bouchet, B. Siberchicot, F. Jollet, and A. Pasturel, J. Phys. Condens. Matter **12**, 1723 (2000).
[5] P. Söderlind, A. Landa, and B. Sadigh, Phys. Rev. B **66**, 205109 (2002).
[6] W. Zachariasen, Acta Crystallogr. **16**, 777 (1963).
[7] F. J. Espinosa *et al.*, Phys. Rev. B **63**, 174111 (2001).
[8] J. Donohue, *The Structures of the Elements* (Wiley, New York, 1974).
[9] A. Saxena (private communication).
[10] A. Crocker, J. Nucl. Mater. **41**, 167 (1971).
[11] B. Johansson, Philos. Mag. **30**, 469 (1974).
[12] H. Skriver, O. Andersen, and B. Johansson, Phys. Rev. Lett. **41**, 42 (1978).
[13] S. Lundqvist and N. H. March, *Theory of Inhomogeneous Electron Gas* (Plenum Press, New York, 1983).
[14] P. Söderlind, O. Eriksson, B. Johansson, J. Wills, and A. Boring, Nature (London) **374**, 524 (1995).
[15] P. Söderlind, J. Wills, B. Johansson, and O. Eriksson, Phys. Rev. B **55**, 1997 (1997).
[16] P. Söderlind, J. Wills, and O. Eriksson, Phys. Rev. B **57**, 1320 (1998).
[17] M. D. Jones, J. C. Boettger, R. C. Albers, and D. J. Singh, Phys. Rev. B **61**, 4644 (2000).
[18] P. Blaha, K. Schwarz, and J. Luitz, *WIEN97, A Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties* (Technische Universitat, Wien, Austria, 1999).
[19] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11 169 (1996).
[20] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[21] J. Kollar, L. Vitos, and H. Skriver, Phys. Rev. B **55**, 15 353 (1997).
[22] J. Bouchet and R. Albers (to be published).