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GGA and LDA + *U* calculations of Pu phases

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Abstract

The effect of correlations in Pu are studied using GGA and LDA + *U*. We have used the simplicity of an approximate α phase structure, which we call a pseudo structure, to understand the main differences between low and high temperatures phases of Pu. Our results show the importance of the local atomic environment.

Keywords: Plutonium; Correlations; LDA + *U*; Pseudophase

1. Introduction

It is well known that the unique position of Pu in the periodic table is responsible for its unusual physical properties. Before its melting point Pu passes through six different phases, where the low temperatures distorted structures, α or β (monoclinic with 16 and 34 atoms/cell respectively) contrast with the high-temperature simple structures δ (fcc) or ϵ (bcc). This crystallographic sequence is surprisingly very close to the crystallographic sequence of the actinide series with open structures for the light actinides (Ac-Np) and close-packed structures for the heavy actinides. This transition, directly related to the delocalized (light actinides) and the localized (heavy actinides) behavior of the f electrons, places Pu in the middle of a discontinuity and indicates that the delicate balance between itinerant and localized states must be responsible for its anomalous properties and for its structural diversity.

Söderlind [1] used density functional theory (DFT) and the generalized gradient approximation (GGA) to study the α phase. They found a good agreement with experiment, confirming α as the most favorable structure for Pu, and explained the presence of this structure by a narrow 5f bands with approximatively 5 electrons. On the other hand, in despite of the simplicity of the δ phase, DFT with GGA completely failed to describe this structure. Recently a new understanding has emerged, with the assumption of δ-Pu as a strongly correlated system, that requires going beyond GGA in order to take into account the Coulomb interaction between the f electrons. The LDA + *U* approach [2,3] reproduces the experimental equilibrium volume and the stability of the fcc structure for plutonium. Söderlind [6] included an energy shift of the 5f orbital via the Racah parameter to reproduce the volume of the six phases of Pu. But the problem of all these approaches is that they predict a long-range magnetic order for δ-Pu, not observed experimentally, despite a compensation between the orbital and the spin magnetic moments. Recently Savrasov [5] combined dynamical mean field theory (DMFT) with density functional methods to obtain the total energy of a correlated system. They showed the possibility of a double well for the total energy of δ-Pu as a function of volume, with one minimum assigned to the α phase and the other one, at high volume, assigned to the δ phase. But a major problem with DMFT is the complexity of the calculation and the computational time, which makes it very difficult to treat structures with more than one atom per primitive cell, such as the α, β and γ phases of Pu.

2. Results and discussion

We have recently proposed a pseudo-structure to model α plutonium [4], which is an orthorhombic structure with two atoms per unit cell. We show in Table 1 the experimental and theoretical volumes, and the total energy differences for plutonium phases relative to α-Pu. The structures have been fully relaxed. As expected, the α phase has the lowest energy. The theoretical volume of the γ phase is very far from the experimental volume (23.14 Å^3), but very close to the

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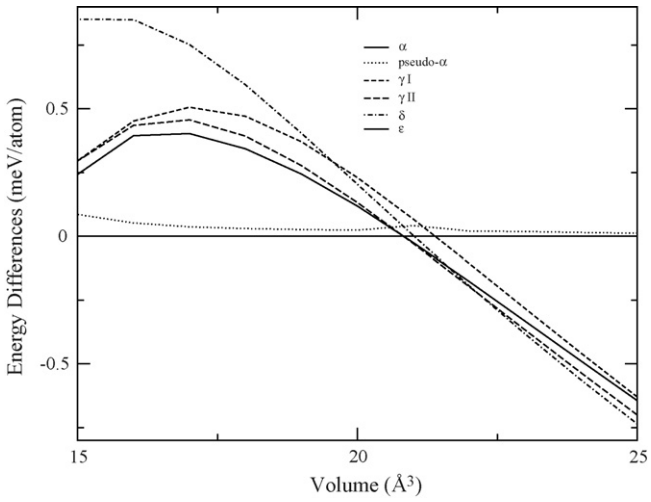

Fig. 1. Total energy differences for plutonium phases relative to α-Pu, using GGA.

Table 1
Theoretical and experimental equilibrium volume and total energy differences for all the structures of Pu, using GGA. The reference for the energies is the fully relaxed α structure

	Volume(Å^3)		$E_{Tot} - E^{\alpha}_{Tot}$(mRy)
	Th	Exp	
α-Pu (relaxed)	18.0	19.8	0
α-Pu (non relaxed)	17.8	19.8	5
β-Pu	18	22.5	21
γ-Pu (relaxed)	18.0	23.14	3
γ-Pu (non relaxed)	17.0	23.14	36
δ-Pu	17.9	25	68
δ'-Pu	18.0	24.8	64
ϵ-Pu	16.6	24	36

experimental volume of the α phase, see Table Table 1. 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. The total energy of this new structure (the pseudo-α) is also very close to the total energy obtained for the α structure, about 3 mRy higher. This is explained by the fact that the pseudo-α has nearly exactly the same distribution of nearest-neighbor distances than in the α phase [4].

Here we have used this pseudo-structure to study the complete phase diagram of Pu using the GGA, and LDA + U approximations. We use the simplicity of the pseudo phase to understand the main differences between low and high temperature (or volume) phases of Pu. We have compared the total energies of the α, pseudo-α, γ, δ, ϵ phases, using different functionals and magnetic order. To test the validity of our pseudo structure we have compared the total energies of the Pu phases, using GGA and an antiferromagnetic ordering as proposed by Söderlind [6]. See also the discussion concerning the pseudo-α phase and magnetic ordering in Refs. [7,8]. The total energies of pseudo-α and α phases are very similar for a long range of volumes and are much lower than for the other phases, see Fig. 1. This gives us confidence to use the pseudo structure instead of the real α in more computationally intensive techniques. To see the effects of the correlations, we have performed calculations with LDA + U, allowing U to vary between 0 and 4 eV. As U increases, correlation effects increase, and the γ, δ, ϵ phases rapidly develop a magnetic and high-volume solution, whereas the pseudo-α stays non-magnetic and at low volume, see Fig. 2. The volume of the δ phase increases almost linearly with U. The γ and ϵ volumes which need a critical value of U to show an effect. The equilibrium volume of the pseudo-α phase shows a different behavior. We need a larger value of U to obtain a large volume solution. Let us mention also that γ, δ and ϵ ground state have a spin magnetic moment for all U values. pseudo-α stays non magnetic at low volumes. These two kinds of behavior can be interpreted in terms of the interatomic distances of the different phases, the short bonds in the pseudo phase suppress correlations effects.

Moreover, since the pseudo-α and the γ structures are orthorhombic but with different b/a and c/a ratios, we can easily simulate a continuous transition path between these two low and high volume structures and follow the effects of the

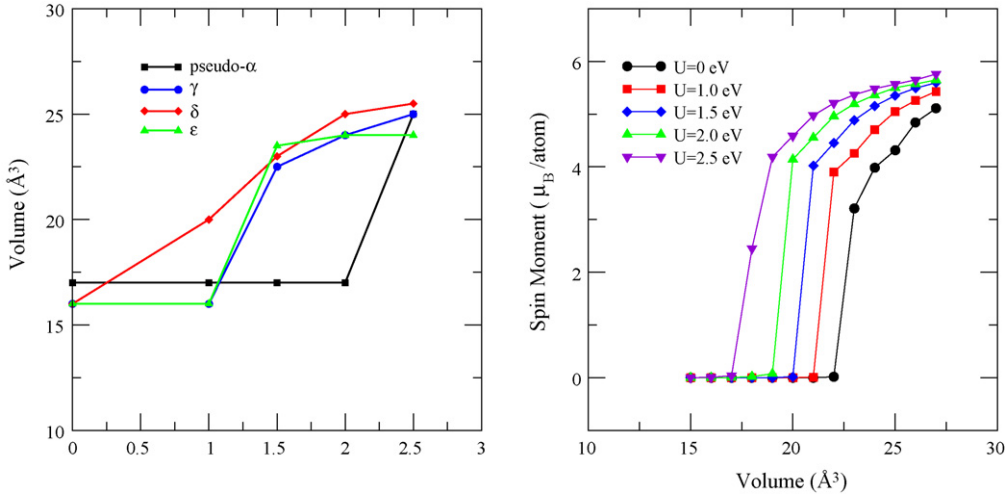

Fig. 2. Left : evolution of equilibrium volumes of pseudo-α, γ, δ and ϵ phases of Pu for different values of the Coulomb interaction U. Right : evolution of the spin moment of the pseudo-α as a function of volume and for different values of U.

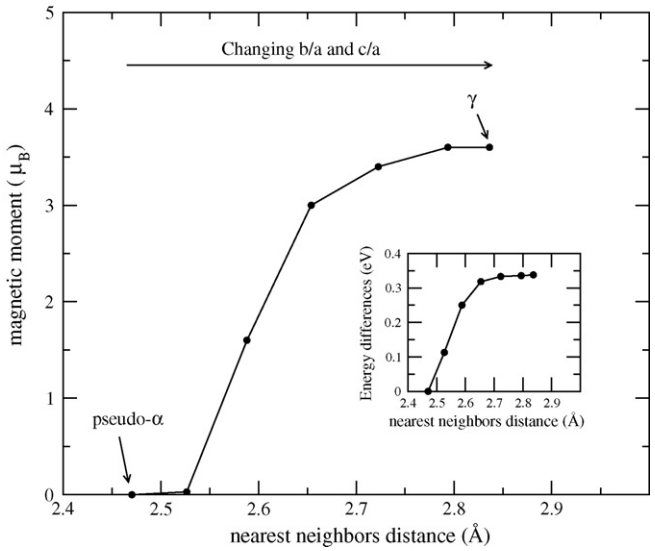

Fig. 3. Magnetic moment versus interatomic distances for the path between the pseudo-α and γ phases of Pu at the equilibrium volumes of pseudo-α Pu (18 Å^3). The inset shows the evolution of the total energy.

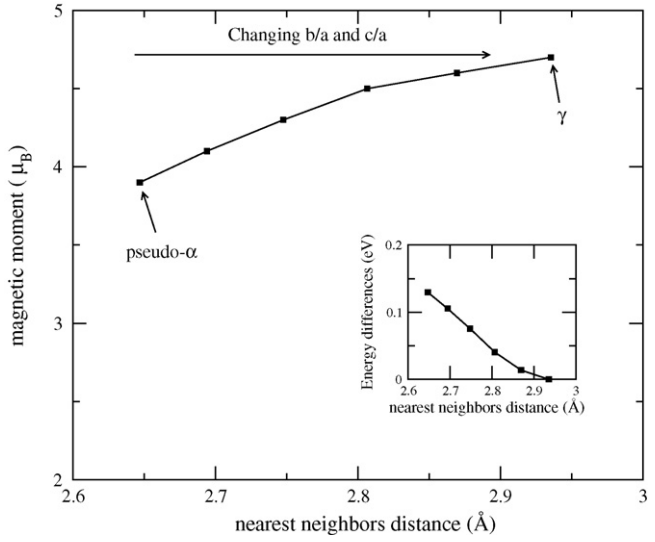

Fig. 4. Magnetic moment versus interatomic distances for the path between the pseudo-α and γ phases of Pu at the equilibrium volumes of γ Pu (23 Å^3). The inset shows the evolution of the total energy.

correlations as a function of volume. This would be, of course, impossible without the pseudo phase. In Figs. 3 and 4 we show the evolution of the magnetic moment and the total energy as a fonction of the interatomic distances for two value of the equilibrium volume. The calculations have been done with GGA and antiferromagnetic ordering, as in Ref. [6]. We changed the value of b/a and c/a to simulate the transition between the two structures. The lowest value of the nearest-neighbor distance corresponds to the pseudo structure, the largest value to the γ one. At low volume pseudo-α structure has a lower total energy than the γ one. It is the opposite at high volume. At low volume (18 Å^3) we show a threshold in the nearest-neighbor distance which controls the occurrence of magnetism, see Fig. 3. This threshold is absent at high volume where the nearest-neighbor distances are of course larger, see Fig. 4. The evolution of the magnetic moment is flat during the transition between pseudo and γ Pu. These results show that 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.

3. Conclusion

Using a pseudo phase to simulate the complex structure of the ground state of Pu, we have studied the effect of the correlations in the phase diagram of this element. Our results shows the importance of the local environment and that short bonds in α-Pu suppress correlations effects and magnetic moments.

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