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**LETTER TO THE EDITOR**

# Monte Carlo simulations of the stability of $\delta$-Pu

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**Abstract**

The transition temperature ($T_c$) for $\delta$-Pu has been calculated for the first time. A Monte Carlo method is employed for this purpose and the effective cluster interactions are obtained from first-principles calculations incorporated with the Connolly–Williams and generalized perturbation methods. It is found that at $T_c \sim 548$ K, $\delta$-Pu undergoes transformation from a disordered magnetic state to a structure with an antiferromagnetic spin alignment that is mechanically unstable with respect to tetragonal distortion. The calculated transition temperature is in good agreement with the temperature measured at the $\gamma \rightarrow \delta$ transition (593 K).

At atmospheric pressure plutonium metal exhibits six crystal structures upon heating from room temperature to its melting point of 913 K [1]. Among these phases $\delta$-Pu, which is stable in the temperature range 593–736 K, has received a significant amount of interest in the metallurgical community because of its high ductility that makes it easy to machine and form. Although technologically more important then $\alpha$-Pu, $\delta$-Pu is not well understood theoretically. This is not surprising, because Pu is located on the border between light actinides (Th–Np) with delocalized 5f electrons and the heavy actinides (Am–Cf) where they are localized [2]. The electronic structure calculations based on the density-functional theory (DFT), within the local density approximation (LDA), predict ground-state properties of the light actinides in good agreement with experiment [3–13]. Even $\alpha$-Pu is relatively well understood with cohesive and structural properties governed by narrow 5f bands containing about five electrons with high density of states (DOS) in the vicinity of the Fermi level [7, 14]. This situation gives rise to a Jahn–Teller or Peierls distortion [6], which lowers the symmetry of the crystal and help to stabilize Pu in its open and complex monoclinic structure.

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Even though the light actinides have been well described within (nonmagnetic) DFT–LDA, it fails completely to describe $\delta$-Pu [5, 10]. To remedy this, several *ad hoc* techniques [14–20] have been applied for $\delta$-Pu attempting to reproduce experimental data. One of these approaches [14, 17] assumes localization of four of the five 5f electrons in $\delta$-Pu (so-called 'constrained LDA' calculations). This idea of a 'partial' 5f localization in $\delta$-Pu was also considered in the work by Penicaud [15] where the $5f_{7/2}$ band was kept unhybridized with the other bands. Later, Penicaud [16] used an adjustable parameter to reduce the hybridization between the $5f_{5/2}$ and $5f_{7/2}$ states to fit even better to the experimental lattice constant. With this technique a good electronic specific heat coefficient ($\gamma$) was also obtained. Another semi-phenomenological approach (LDA + $U$) [18–20] requires the adjusting of a Coulomb–Hubbard repulsion energy ($U$) in order to fit to the experimental volume of $\delta$-Pu. However, the LDA + $U$ methods fail to reproduce the photoemission (PE) spectra of $\delta$-Pu. Recent PE measurements [21] indicate the appearance of a quasiparticle peak near the Fermi level that disappears in the nonmagnetic LDA and LDA + $U$ calculations [19, 20, 22, 24]. Savrasov and Kotliar [22–24] applied dynamical mean-field theory (DMFT), an electronic structure method which is able to interpolate between band-like and atomic-like behaviour of electrons in strongly correlated systems, to study the phase diagram of Pu. These authors believe that both the $\alpha$- and $\delta$-phases of plutonium are strongly correlated phases that straddle the localization–delocalization boundary, with the $\delta$-phase being on the localized side and the $\alpha$-phase slightly on the delocalized side. They further claim that only this approach gives rise to a Kondo-like peak near the Fermi level and also correctly predicts the density of $\alpha$-, $\delta$-, and even $\epsilon$-phases of Pu without a need for magnetic long-range order.

Another technique that is based on conventional DFT allowing for magnetic interactions was proposed recently. Söderlind [25], Wang and Sun [26], and Postnikov and Antropov [27] found independently that the antiferromagnetic (AF) (CuAuI) structure has a lower energy than the ferromagnetic one and therefore could be the zero-temperature ground-state magnetic configuration for $\delta$-Pu. Söderlind *et al* [28] proposed that $\delta$-Pu is a disordered magnet that upon cooling undergoes transformation to this AF structure with a mechanical destabilization and phase transition to a lower-symmetry phase as a result. Considering that the ground-state AF structure is closely followed by a disordered magnetic state, about 2–5 mRyd higher in energy, these authors came to the conclusion that the spin entropy could favour the disordered moment state at higher temperatures. The full-potential muffin-tin orbitals (FPLMTO) calculations [28] also predict that a large antiparallel orbital moment nearly cancels the spin moment, resulting in a small total moment of $\sim 1\ \mu_B$. Finally the DOS, calculated within this latter approach [28] for AF Pu, agrees very well with PE measurements [21], better than DMFT results [22–24], and as well as results obtained from the constrained DFT calculations [14, 17]. PE currently provides the best way to probe the electronic structure of Pu below the Fermi level ($E_F$), although specific heat measurements can be used to estimate the DOS at $E_F$ ($D_F$). As was pointed out [16], $\gamma$ is proportional to $D_F$, but there is a many-body enhancement factor involved that is difficult to calculate from first principles. Assuming that this factor is constant throughout the Pu phase diagram, one could relate $D_F$ for the $\alpha$- and $\delta$-phases of Pu to their corresponding experimental electronic specific heat. The experimental $\gamma^\delta/\gamma^\alpha$ ratio is about 2.41 and the calculated [25] $D_F^\delta/D_F^\alpha$ ratio is very close and about 2.1.

In this letter we apply these new ideas [28] to directly calculate the transition temperature ($T_c$) of $\delta$-Pu, something that has never been done before. In order to do so we use a simple model based on the assumption that the destabilization of the $\delta$-Pu is caused by the AF ordering or, in other words, by ordering Pu atoms with the opposite spins, $Pu^u$ (spin up) and $Pu^d$ (spin down), on the underlying fcc lattice. Because the ferromagnetic state is much higher in energy, this system may be investigated by using a simple Ising-type model in the canonical ensemble.

**Table 1.** The effective pair interactions in mRyd/atom for $Pu^u_{50}Pu^d_{50}$ at the lattice constant 4.651 Å.

| Method | $V_1^{(2)}$ | $V_2^{(2)}$ | $V_3^{(2)}$ | $V_4^{(2)}$ | $V_5^{(2)}$ | $V_6^{(2)}$ | $V_7^{(2)}$ |
|---|---|---|---|---|---|---|---|
| SIM | 7.02 | −0.09 | 0.98 | 0.46 | −0.94 | −0.56 | −0.28 |
| GPM | 6.33 | 0.16 | 0.98 | 0.46 | −0.41 | −0.16 | −0.21 |

That is, we assume that there are equal numbers of $Pu^u$ and $Pu^d$ atoms on a fixed fcc lattice, whose magnetic moments have the same magnitude and are aligned antiparallel. In fact, large super-cell calculations for different magnetic configurations show only weak dependence of the magnetic moment on the local magnetic configuration. The configurational energy of such a binary $Pu^u_{50}Pu^d_{50}$ alloy can then be presented as

$$E_{conf} = \sum_{n,s} V_s^{(n)} \xi_s^{(n)}, \tag{1}$$

where $V_s^{(n)}$ is the effective cluster interaction (ECI) that corresponds to the cluster of order $n$ and type $s$. For instance, $V_1^{(2)}$, $V_2^{(2)}$, and $V_3^{(2)}$ are the effective pair interactions in the first, second, and third coordination shells, respectively;

$$\xi_s^{(n)} = \frac{1}{n} \sum_{p \in s} \sigma_{1_p} \sigma_{2_p} \cdots \sigma_{n_p} \tag{2}$$

are the multisite correlation functions defined on the $n$th-order cluster determined by the $i_p$ lattice points. $\sigma_{i\alpha}$ is the spin-like variable that is equal to +1 (−1), depending on whether site $\alpha$ of the $i$-sublattice is occupied by a $Pu^u$ (or $Pu^d$) atom. The sum runs over all $n$th-order clusters of a given type in the lattice.

To obtain the ECI we have used two different techniques: the so-called generalized perturbation method (GPM) [29] and the structure inverse (Connolly–Williams-type) method (SIM) [30, 31]. All the corresponding electronic structure calculations have been performed by the scalar-relativistic (SR) (spin–orbit coupling (SO) was neglected) spin-polarized Green function technique in the multipole-corrected atomic-sphere approximation (KKR-ASA + $M$) [32–35]. The local Airy gas (LAG) approximation [36] has been used for the exchange–correlation energy. The paramagnetic (PM) state of $\delta$-Pu was represented within the so-called disordered local moment (DLM) model [37] incorporated within the coherent potential approximation (CPA) [38]. In order to calculate the DLM state, ones uses a random mixture of $Pu^u$ and $Pu^d$ components in the system. The technical details of the present calculations are very similar to those published in [28].

The calculations of the ECI have been carried out for the theoretical equilibrium lattice parameter of 4.651 Å which is in very close agreement with the measured [39] lattice constant of 4.648 Å at the $\gamma \rightarrow \delta$ transition temperature (593 K). First we used the GPM method that allowed us to establish the type and range of the most important ECI. It turned out that the multisite interactions were small and the most important effective pair interactions were restricted to the first seven coordination shells. Consequently, only these interactions were included in the expansion for the configurational energy (equation 1). Since the GPM interactions are obtained in the framework of the CPA, which slightly underestimated the DLM–AF energy difference [28], we have also determined the ECI by the SIM on the basis of the total energies of ten ordered structures[4] for a fixed $Pu^u_{50}Pu^d_{50}$ composition. In table 1 we present the first seven ECI obtained by both methods: they are apparently very close to each other, but we have used the SIM–ECI, as they most accurately reproduce the DLM–AF energy difference.

[4] Among them there were $L1_0$, $L1_1$, Z2, 'CH' and some others generated specifically for this alloy composition.

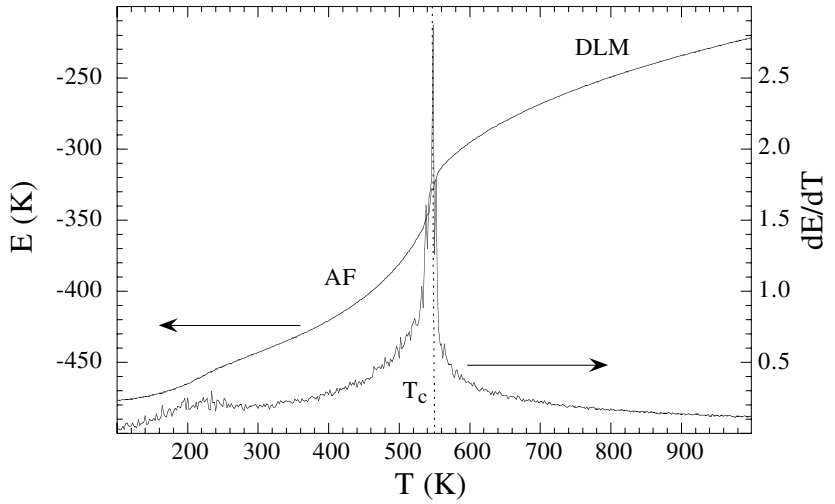


**Figure 1.** The total energy $E$ (in K/atom) and its temperature derivative ($\mathrm{d}E/\mathrm{d}T$) as a function of temperature in the MC simulation. The lattice parameter is 4.651 Å.

**Table 2.** Energies (mRyd/atom) relative to the $L1_0$ structure for $\delta$-Pu at the lattice constant 4.60 Å.

| Structure | KKR (SR) | FPLMTO (SR) | FPLMTO (SO) |
|---|---|---|---|
| $L1_1$ | 4.73 | 4.90 | 4.61 |
| CH | 0.83 | 0.83 | 0.14 |
| Z2 | 6.14 | 5.91 | 6.01 |

The Monte Carlo (MC) simulations were performed using the Metropolis algorithm [40] for a 13 824-site box ($24 \times 24$) with periodic boundary conditions. The simulation box was initially filled with randomly distributed $Pu^u$ and $Pu^d$ atoms. The temperature was subsequently lowered by 2 K after 5000 MC steps per atom (MCS/A) and the first 1000 MCS/A were discarded before the calculation of the thermodynamic averages. Figure 1 shows the total energy per atom and its temperature derivative in the MC simulations. The phase transition to the AF ordered state occurs at $T_c \sim 548$ K. However, we should point out that the zero-temperature ground-state structure obtained with both GPM and SIM interactions is not the AF structure predicted by our electronic structure calculations. In fact, the ordering in MC simulations continues down to almost zero temperature, and the final configuration is not perfectly ordered: it is made from two (001) layers occupied by $Pu^u$ and $Pu^d$ atoms, respectively, separated by two $2 \times 1$ (001) $Pu^uPu^d$ layers. It is entirely possible that some frustrated ordering of the spin moments does occur in the vicinity of the phase transition in $\delta$-Pu, as our MC simulations suggest. If this is the case, it may explain the Invar-type behaviour in $\delta$-Pu.

Although SO is not essential for the quantitative behaviour of $\delta$-Pu [28], we have applied the FPLMTO method, which includes SO, to calculate the energy of some key magnetic configurations (see footnote 4) that were used for obtaining the ECI within the SIM. In table 2 we show energy differences for these magnetic configurations calculated within the KKR technique as well as the FPLMTO technique used in [28]. Within the KKR method the calculations are SR whereas in the FPLMTO approach SR or SO treatment can be chosen. Notice first in table 2 that for the SR treatment, KKR and FPLMTO compare rather well for the calculated interactions. We conclude that for the magnetic configurations studied, the

additional complexities of the full potential in the FPLMTO method have little importance. It is also clear from table 2 that the effect of SO is limited as well: the estimated temperature of the phase transition to the AF ordered state is $T_c \sim 500$–$520$ K.

To conclude, the $\delta$-Pu transition temperature has been calculated from the first-principles theory and is in good agreement with the experimental phase diagram. The basic idea is that entropy contribution, calculated within our described MC scheme, favours a PM state at about 550 K, whereas below this temperature magnetic ordering (AF) is predicted that destabilizes the $\delta$-phase mechanically, explaining the phase transition to the $\gamma$-phase. The natural extension to this work is to use the present technique to study the effect of alloying on the stability of $\delta$-Pu. First results of this study were recently published [41].

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