

# SCIENTIFIC REPORTS



OPEN

## Physical mechanism of $\delta$ - $\delta'$ - $\varepsilon$ phase stability in plutonium

Chun-Mei Li<sup>1,2</sup>, Börje Johansson<sup>3,4,5</sup> & Levente Vitos<sup>3,4,6</sup>

Based on first-principle calculations, we have systematically explored the nature of the elastic stability and the  $\delta$ - $\delta'$ - $\varepsilon$  phase transitions in pure Pu at high temperature. It is found that, both the electron-phonon coupling and the spin fluctuation effects tend to decrease the tetragonal elastic constant ( $C'$ ) of  $\delta$ -Pu, accounting for its anomalous softening at high temperature. The lattice thermal expansion together with the electron-phonon coupling can stiffen  $C'$  of  $\varepsilon$ -Pu, promoting its mechanical stability at high temperature. The  $\delta$ - $\varepsilon$  transition is calculated to take place around 750–800 K, and is dominated by the phonon vibration. The  $\delta'$  intermediate phase is realized around 750 K mainly because of the thermal spin fluctuation.

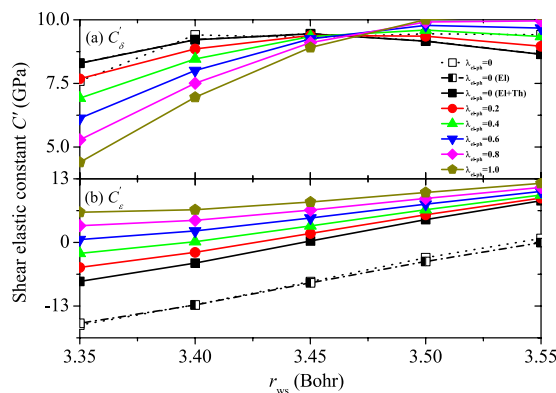
Plutonium is one of the most exotic elemental metals because of its condensed matter properties, metallurgy, and six allotropic phases<sup>1–4</sup>. Stable between 592 K and 724 K, the face-centered cubic ( $\delta$ ) phase has the lowest density and good ductility, and turns out to be technologically the most important phase, attracting a lot of research. It was reported to possess a negative thermal expansion coefficient ( $\alpha$ ), elastic anisotropy ( $2C_{44}/(C_{11} - C_{12})$ ) of about 7<sup>1</sup>, and an “abnormal” softening of the elastic modulus with temperature<sup>5,6</sup>, which is coupled to the  $\delta$ - $\delta'$ - $\varepsilon$  transitions around 750 K. All these extraordinary thermodynamic properties make  $\delta$ -Pu highly interesting, but the mechanisms behind its phase transitions are still not understood.

The anomalous thermophysical properties of  $\delta$ -Pu are expected to be related to the itinerant-to-localized crossover of  $5f$  electronic states<sup>2,7–12</sup>. Within the generalized gradient approximation (GGA), the electronic total energy calculations have successfully reproduced the equilibrium volume ( $V$ ) of  $\delta$ -Pu<sup>13</sup>. Its large elastic anisotropy was evaluated to be about 8.3 by the GGA<sup>13</sup> and 6.3 by the local density approximation (LDA) +  $U$ <sup>14</sup> calculations. Nevertheless, these 0 K calculations generally gave inaccurate values for the elastic constants themselves and especially for  $C' = (C_{11} - C_{12})/2$ <sup>13–15</sup>, for which the estimated data (7.9 GPa<sup>13</sup>) is more than 60% larger than the experimental one (4.9 GPa<sup>16</sup>). A better description of  $\delta$ -Pu requires that the electronic structure theories go beyond the ground state, by including the effects of temperature and electron-phonon coupling in the  $5f$  band picture<sup>17,18</sup>.

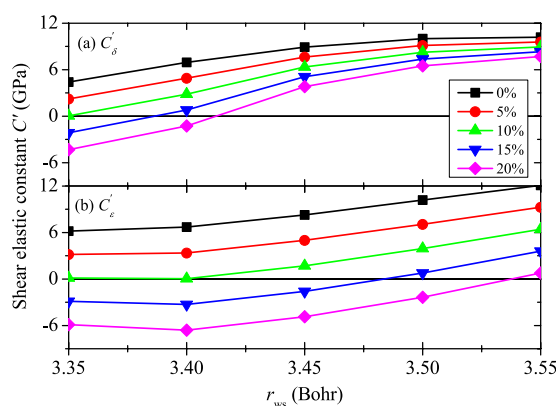
Similar to other metals and metallic alloys, the temperature-dependent lattice thermal expansion, magnetism, and phonon vibration may be considered as important factors<sup>19,20</sup>. The thermal expansion effect on the bulk modulus ( $B$ ) of  $\delta$ -Pu has been theoretically examined<sup>21</sup>, whereas its influence on  $C'$  of the  $\delta$  and  $\varepsilon$  (body-centered cubic) phases were seldom investigated. Supported by the recent studies from both neutron-scattering experiments and phonon dispersions calculations<sup>22–24</sup>,  $\delta$ -Pu is theoretically approximated with the paramagnetic (PM) state<sup>25–27</sup>, often described with the fully disordered local magnetic (DLM) model<sup>28</sup>. The dynamical fluctuations of the magnetization density (spin fluctuations) with temperature were supposed to induce strong magnetovolume and magnetoelastic couplings<sup>29</sup>, which subsequently influence the stability of the two phases and also the transition between them.

In this letter, we explore the elastic properties of the  $\delta$  and  $\varepsilon$  phases and the  $\delta$ - $\delta'$ - $\varepsilon$  transitions of the PM state of Pu, taking all the temperature-dependent electronic and magnetic entropy, electron-phonon coupling, lattice thermal expansion, phonon vibration, and spin fluctuation effects into account, and try to uncover their physical mechanisms.

<sup>1</sup>College of Physical Science and Technology, Shenyang Normal University, 110034, Shenyang, China. <sup>2</sup>Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, 110016, Shenyang, China. <sup>3</sup>Department of Materials Science and Engineering, KTH - Royal Institute of Technology, 10044, Stockholm, Sweden. <sup>4</sup>Department of Physics and Astronomy, Division of Materials Theory, Uppsala University, Box 516, 75120, Uppsala, Sweden. <sup>5</sup>School of Physics and Optoelectronic Technology & College of Advanced Science and Technology Dalian University of Technology, 116024, Dalian, China. <sup>6</sup>Research Institute for Solid State Physics and Optics, Wigner Research Center for Physics, P.O. Box 49, HU-1525, Budapest, Hungary. Correspondence and requests for materials should be addressed to C.-M.L. (email: [cmli@synu.edu.cn](mailto:cmli@synu.edu.cn))



**Figure 1.** Static (0 K) tetragonal shear elastic constants  $C'$  of  $\delta$ - and  $\epsilon$ -Pu as a function of Wigner-Seitz radius (denoted as “ $\lambda_{\text{el-ph}}=0$ ”). Shown are also results corresponding to 750 K including only the electronic entropy term (denoted as “ $\lambda_{\text{el-ph}}=0$  (El)”), both the electronic entropy and lattice thermal expansion terms (denoted as “ $\lambda_{\text{el-ph}}=0$  (El + Th)”), and the electronic entropy, lattice thermal expansion, and electron-phonon coupling three effects (denoted as “ $\lambda_{\text{el-ph}}=0.2, 0.4, \dots, 1.0$ ”).



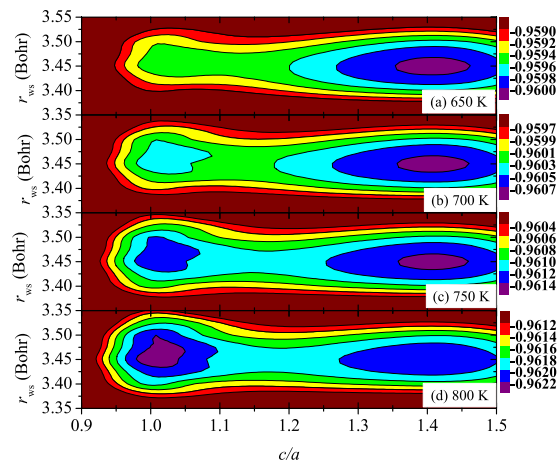
**Figure 2.** Tetragonal shear elastic constants  $C'$  of  $\delta$ - and  $\epsilon$ -Pu as a function of Wigner-Seitz radius. Results correspond to 750 K, including the electronic entropy, lattice thermal expansion, electron-phonon coupling ( $\lambda_{\text{el-ph}}=1.0$ ), and spin fluctuation effects modelled by reducing  $\mu_{\text{Pu}}$  by 0%, 5%, ..., 20% relative to the static value.

## Results and Discussion

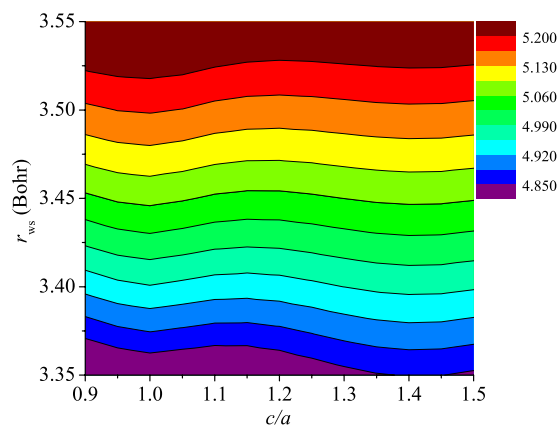
Figure 1 describes the calculated electronic entropy, lattice thermal expansion, and electron-phonon coupling effects on the  $C'$  of  $\delta$ - ( $C'_\delta$ ) and  $\epsilon$ -Pu ( $C'_\epsilon$ ). Here  $T$  is fixed to 750 K, i.e., close to the critical temperature where the  $\delta$ - $\delta'$ - $\epsilon$  transitions occur<sup>1</sup>. We vary the Wigner-Seitz radius ( $r_{\text{ws}}$ ) from 3.35 Bohr to 3.55 Bohr and the electron-phonon coupling coefficient ( $\lambda_{\text{el-ph}}$ ) from 0 to 1, with an interval of 0.05 Bohr and 0.2, respectively. At 750 K, the electronic entropy has practically no influence on  $C'_\delta$  and  $C'_\epsilon$ . The 0 K  $C'_\delta$  changes non-monotonically with increasing  $r_{\text{ws}}$  (Fig. 1a), and in the studied  $r_{\text{ws}}$  range it changes only very little. This means that the lattice thermal expansion can change  $C'_\delta$  by less than 2 GPa at 750 K. For the  $\epsilon$  phase, the thermal expansion is positive. Shown in Fig. 1b,  $C'_\epsilon$  increases linearly with increasing  $r_{\text{ws}}$  at 0 K, thus the thermal expansion increases  $C'_\epsilon$ . Actually, the lattice thermal expansion promotes the mechanical stability of the  $\epsilon$  phase at high temperature.

Including the electron-phonon coupling at 750 K,  $C'_\delta$  (Fig. 1a) increases above (decreases below)  $r_{\text{ws}} = 3.47$  Bohr with increasing  $\lambda_{\text{el-ph}}$ . For  $\lambda_{\text{el-ph}} = 1.0$ , the electron-phonon coupling changes the trend of  $C'_\delta \sim r_{\text{ws}}$  into a monotonically increasing  $C'_\delta$  with  $r_{\text{ws}}$  at 750 K. At the experimental volume of the  $\delta$  phase (around 3.43 Bohr<sup>1</sup>), the  $C'_\delta$  value corresponding to  $\lambda_{\text{el-ph}} = 1.0$  is much closer to the experimental data<sup>16, 30</sup> than its static value. The  $C'_\epsilon$  (Fig. 1b) increases at each volume with  $\lambda_{\text{el-ph}}$ . Like the lattice thermal expansion, the electron-phonon coupling tends to increase  $C'_\epsilon$ , helping to realize the mechanical stability of this phase at high temperature.

Including all the above three effects evaluated with  $\lambda_{\text{el-ph}} = 1.0$ , we now investigate the impact of spin fluctuation on  $C'_\delta$  and  $C'_\epsilon$  at 750 K, by performing calculations with the local magnetic moments of Pu ( $\mu_{\text{Pu}}$ ) reduced by 0% to 20% relative to their equilibrium values. The physical picture behind this reduction is given by the longitudinal thermal spin fluctuations<sup>31</sup>, which is due to the particular energy versus magnetic moment curve of Pu stabilizing lower local magnetic moments at high temperature, as compared to the static DLM moment. As shown in Fig. 2, both  $C'_\delta$  and  $C'_\epsilon$  become smaller with decreasing  $\mu_{\text{Pu}}$ . Therefore the spin fluctuation should present a



**Figure 3.** Free energy ( $F = E_{el} - TS_{el} + F_{vib} - TS_{mag}$ , in unit of Ry) change with respect to the Wigner-Seitz radius ( $r_{ws}$ ) and  $c/a$  of Pu using the equilibrium  $\mu_{Pu}$ . Results are shown for 650 K (a), 700 K (b), 750 K (c), and 800 K (d), respectively. The two minima at  $c/a = 1.414$  and  $c/a = 1$  correspond to the  $\delta$  and  $\varepsilon$  phases.



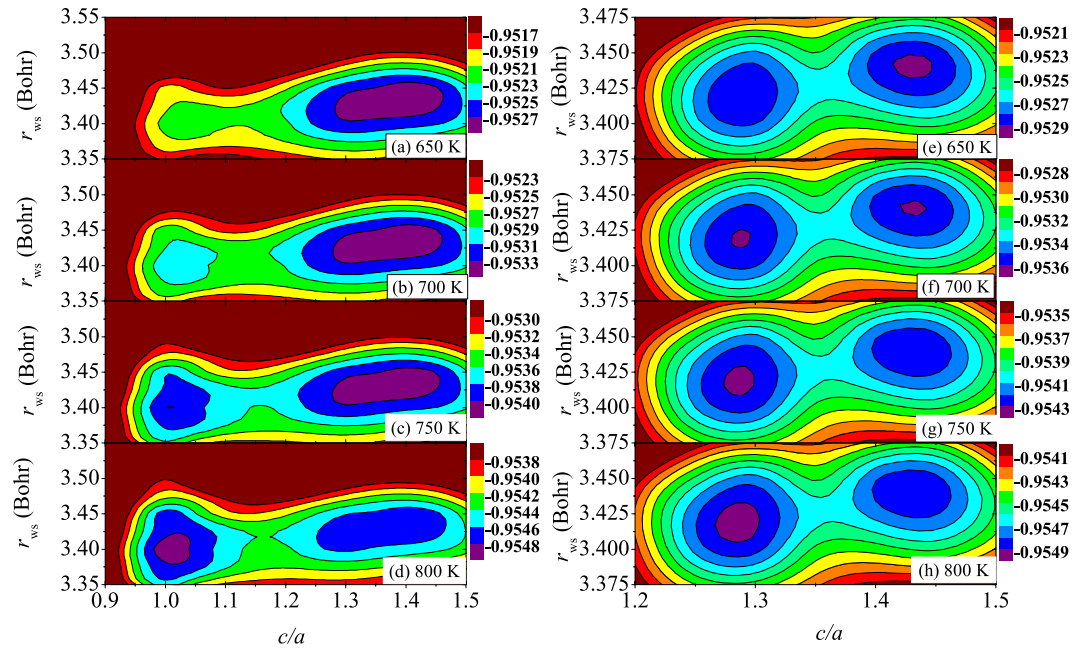
**Figure 4.** Equilibrium local magnetic moment of Pu ( $\mu_{Pu}$ , in unit of  $\mu_B$ ) plotted as a function of the Wigner-Seitz radius ( $r_{ws}$ ) and  $c/a$ .

significant contribution to the softening of the elastic moduli of  $\delta$ - and  $\varepsilon$ -Pu with increasing  $T$ <sup>5,6</sup>. With  $\mu_{Pu}$  reduced no more than 10%,  $C'_\delta$  and  $C'_\varepsilon$  remain positive within the considered volume range. With more than 10% reduction of  $\mu_{Pu}$ , they become negative, demonstrating the mechanical instability of the  $\delta$  and  $\varepsilon$  phases at 750 K. Hence, around this temperature,  $\mu_{Pu}$  may be no less than 90% of its static value for the two phases. The experimental  $C'_\delta$  is available. According to Fig. 2a, with 10% reduced  $\mu_{Pu}$ , the evaluated  $C'_\delta$  (4.9 GPa) at 750 K corresponding to the experimental volume (3.43 Bohr<sup>3</sup>) is in perfect agreement with the measured values (4.9 GPa<sup>16</sup> and 4.8 GPa<sup>30</sup>). We notice that the  $\sim 0.5 \mu_B$  reduction of the local magnetic moments obtained in the above semi-empirical estimation is surprisingly close to the predicted one based on ab initio spin fluctuation study<sup>31</sup>.

In what follows, we explore the  $\delta$ - $\delta'$ - $\varepsilon$  transitions by calculating the free energy ( $F$ ) change with respect to  $r_{ws}$  and  $c/a$  of the body-centered-tetragonal Pu. Here,  $c/a = 1$  represents the  $\varepsilon$  phase whereas  $c/a = 1.414$  corresponds to the  $\delta$  phase. The other values of  $c/a$  may correspond to the  $\delta'$  phase. First, the static electronic total energy ( $E_{el}$ ) term is found to prefer the  $\delta$  phase with  $c/a = 1.414$ . The static electronic entropy ( $TS_{el}$ ) and magnetic entropy ( $TS_{mag}$ ) terms lower the free energy but, their effects are almost the same for the two structures. As a result, the  $\delta$  phase is always stabilized whereas the  $\delta'$  and  $\varepsilon$  phases could not be obtained by considering only the above three terms into account.

Adding the phonon vibrational free energy ( $F_{vib}$ ) in Fig. 3, it is still only the  $\delta$  phase which is stable below 650 K. When  $T$  goes up to 700 K, a metastable phase appears around  $c/a = 1$ , which corresponds to the  $\varepsilon$  phase and with the relative free energy to the  $\delta$  phase ( $\Delta F_{\varepsilon-\delta} = F_\varepsilon - F_\delta$ , with  $F_\delta$  and  $F_\varepsilon$  being  $F$  for the  $\delta$  and  $\varepsilon$  phases, respectively) is about 0.35 mRy. With further increase of  $T$ ,  $\Delta F_{\varepsilon-\delta}$  is gradually lowered to about 0.15 mRy at 750 K, and then to  $-0.12$  mRy around 800 K. It indicates that with increasing  $T$ , the  $\varepsilon$  phase becomes more and more stable with respect to the  $\delta$  phase. Around 800 K, the  $\varepsilon$  phase becomes lower in energy than the  $\delta$  phase, and thus the  $\delta$ - $\varepsilon$  transition occurs. The  $\delta'$  intermediate phase, however, is not yet present.

Shown in Fig. 4, the equilibrium (static)  $\mu_{Pu}$  value depends on both  $r_{ws}$  and  $c/a$ . As it is generally expected,  $\mu_{Pu}$  increases with  $r_{ws}$  at fixed  $c/a$ . On the other hand, corresponding to each  $r_{ws}$ ,  $\mu_{Pu}$  non-monotonically changes with



**Figure 5.** Free energy ( $F = E_{\text{el}} - TS_{\text{el}} + F_{\text{vib}} + E_{\text{mag}} - TS_{\text{mag}}$ , in unit of Ry) change with respect to the Wigner-Seitz radius ( $r_{\text{ws}}$ ) and  $c/a$  of Pu using 10% reduced  $\mu_{\text{Pu}}$ . Results are shown for 650 K (a,e), 700 K (b,f), 750 K (c,g), and 800 K (d,h), respectively. The three minima correspond to the  $\delta$ ,  $\delta'$ , and  $\epsilon$  phases in the left panel, whereas in the right panel, the two minima indicate the  $\delta$  and  $\delta'$  phases.

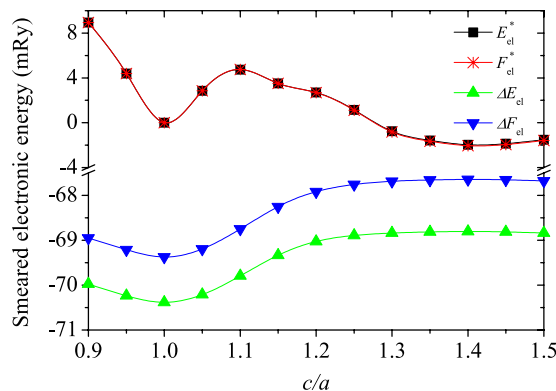
$c/a$ , and the values for the  $\delta$  ( $c/a = 1.414$ ) and  $\epsilon$  ( $c/a = 1$ ) phases are larger than those of other (low symmetry) structures. Therefore, it is expected that the decrease of  $\mu_{\text{Pu}}$  with temperature should have an influence on the structural stability of Pu.

Next, we take the spin fluctuation into account by calculating  $F$  with 10% reduction of the equilibrium  $\mu_{\text{Pu}}$ , and draw  $F$  as a function of  $r_{\text{ws}}$  and  $c/a$ . The results are shown in Fig. 5. In the left panel of the figure, with increasing temperature, the calculated  $\Delta F_{\epsilon-\delta}$  goes down from 0.46 mRy at 650 K to 0.28 mRy at 700 K, to 0.02 mRy at 750 K, and then to  $-0.18$  mRy at 800 K. Therefore, similar to Fig. 3, the  $\delta$ - $\epsilon$  transition is again obtained around 750–800 K. Hence, by reducing  $\mu_{\text{Pu}}$  by 10%, the relative stability between the two cubic phases does not change significantly.

Very interestingly, with reduced local magnetic moment, another phase appears around  $c/a = 1.28$ . We propose that this metastable phase corresponds to the  $\delta'$  phase. In order to highlight the stability of the  $\delta'$  phase relative to the  $\delta$  one, the energy map corresponding to these two structures is plotted in details in the right panel of Fig. 5. The two minima located around  $c/a = 1.414$  and  $c/a = 1.28$  correspond to the  $\delta$  and  $\delta'$  phases. With the increase of  $T$ , the free energy of the  $\delta'$  phase relative to that of the  $\delta$  one ( $\Delta F_{\delta'-\delta} = F_{\delta'} - F_{\delta}$ , with  $F_{\delta'}$  being  $F$  for the  $\delta'$  phase) decreases from 0.11 mRy at 650 K to 0 mRy at 700 K, to  $-0.04$  mRy at 750 K, and then to  $-0.08$  mRy at 800 K. This means that the  $\delta'$  phase is stabilized above 650 K. With increasing  $T$  above 750 K, the  $\delta'$  phase becomes more stable than the  $\delta$  phase, indicating the  $\delta$ - $\delta'$  transition. In comparison the left and right panel of Fig. 5, the  $\delta'$  phase is stabilized only in a short temperature range around 750 K, since at 800 K, the  $\epsilon$  phase is stabilized instead with about  $-0.10$  mRy lower energy than that of the  $\delta'$  phase.

The volumes of the  $\delta$ ,  $\delta'$ , and  $\epsilon$  phases evaluated with 10% reduced  $\mu_{\text{Pu}}$  are about  $25.2 \text{ \AA}^3$ ,  $24.8 \text{ \AA}^3$ , and  $24.4 \text{ \AA}^3$ , respectively, all in good agreement with the experimental data ( $25.2 \text{ \AA}^3$ ,  $25.1 \text{ \AA}^3$ , and  $24.4 \text{ \AA}^3$ , respectively<sup>1</sup>). The obtained  $c/a$  value (1.28) of the  $\delta'$  phase in Fig. 5 is also in line with the experimental data (1.34<sup>1</sup>). We should point out that in Fig. 3, where the  $F$  is calculated with the equilibrium  $\mu_{\text{Pu}}$ , the volumes of the  $\delta$  and  $\epsilon$  phases are about  $25.5 \text{ \AA}^3$  and  $25.8 \text{ \AA}^3$ , respectively, which are larger than the experimental ones<sup>1,16,30</sup>. Hence, the spin fluctuation tends to favor the stability of the  $\delta'$  phase relative to the  $\delta$  phase, and also contributes to the reduction of  $V$  during the  $\delta$ - $\delta'$ - $\epsilon$  transitions of Pu.

Using the equilibrium volume of the  $\delta$  phase, we calculate the 0 K density of states (DOS) change with respect to  $c/a$ , and then evaluate the smeared DOS and the corresponding energies ( $E_{\text{el}}^* = E_{\text{el}}^* - TS_{\text{el}}^*$ , with  $E_{\text{el}}^*$ ,  $F_{\text{el}}^*$ , and  $TS_{\text{el}}^*$  being the smeared electronic total energy, smeared free energy, and smeared electronic entropy, respectively) with  $\lambda_{\text{el-ph}} = 1.0$  at 750 K. In Fig. 6, the obtained  $c/a$ -dependence of  $E_{\text{el}}^*$ ,  $F_{\text{el}}^*$ , and their differences relative to the static values ( $\Delta E_{\text{el}} = E_{\text{el}}^* - E_{\text{el}}$  and  $\Delta F_{\text{el}} = F_{\text{el}}^* - F_{\text{el}}$ , with  $F_{\text{el}} = E_{\text{el}} - TS_{\text{el}}$  being the static electronic free energy) are compared. Here, the  $\epsilon$  phase ( $c/a = 1$ ) is used as reference for both the  $E_{\text{el}}^*$  and  $F_{\text{el}}^*$  evaluations. At each  $c/a$  value,  $E_{\text{el}}^*$  and  $F_{\text{el}}^*$  have almost the same values whereas  $\Delta F_{\text{el}}$  is larger than  $\Delta E_{\text{el}}$ , indicating that the electron-phonon coupling tends to evenly increase the  $-TS_{\text{el}}$  of each structure, and therefore still does not really influence the relative stability of the three phases. Increasing  $c/a$  from 0.9 to 1.5, both  $E_{\text{el}}^*$  and  $F_{\text{el}}^*$  show two minima. One corresponds to the  $\delta$  phase ( $c/a = 1.414$ ) whereas the other one means the  $\epsilon$  phase. Therefore,



**Figure 6.** Smeared electronic energies ( $E_{el}^*$  and  $F_{el}^* = E_{el}^* - TS_{el}^*$ ) and their differences relative to the static values ( $\Delta E_{el} = E_{el}^* - E_{el}$  and  $\Delta F_{el} = F_{el}^* - F_{el}$ ) with respect to  $c/a$  of Pu. The  $\varepsilon$  phase ( $c/a = 1$ ) is used as reference for both the  $E_{el}^*$  and  $F_{el}^*$  curves.

considering the electron-phonon coupling, both the  $\varepsilon$  and  $\delta$  phases are stable, but the latter is lower in energy than the former one (at 750 K). The  $\delta'$  phase, nevertheless, still can not be realized by this term at 750 K. As seen from the curve of  $\Delta E_{el} \sim c/a$ ,  $\Delta E_{el}$  has its maximum value (about  $-68.82$  mRy) for  $c/a \sim 1.30$ – $1.45$ , whereas its minimum is around  $c/a = 1$  (about  $-70.38$  mRy). This confirms that at high temperature, the phonon smearing indeed lowers  $E_{el}$  of the  $\varepsilon$  phase relative to that of the  $\delta$  or  $\delta'$  ( $c/a \approx 1.30$ ) phase, promoting the stabilization of the  $\varepsilon$  phase relative to the other two phases. Adding this effect to  $F$ , the critical temperature of  $\delta$ - $\varepsilon$  or  $\delta'$ - $\varepsilon$  transition derived above could be a little bit further lowered, and then they would be close to the experimental data (about  $753$  K<sup>1</sup>). Therefore, the phonon vibration, spin fluctuation, and electron-phonon coupling effects all contribute to the  $\delta$ - $\delta'$ - $\varepsilon$  transitions of Pu at high temperature.

## Conclusion

In summary, using first-principles theory in combination with physically sound approximations, we have systematically explored the nature of the elastic stability of  $\delta$ - and  $\varepsilon$ -Pu and the phase transitions of  $\delta$ - $\delta'$ - $\varepsilon$  at high temperature. It is found that, the temperature effects show great influence on both  $C'_\delta$  and  $C'_\varepsilon$ . The electron-phonon coupling and the reduction of  $\mu_{Pu}$  with temperature tend to reduce  $C'_\delta$ , accounting for its anomalous softening at high temperature. The lattice thermal expansion and the electron-phonon coupling stiffen  $C'_\varepsilon$ , together giving rise to the mechanical stability of the phase at high temperature. The transitions of  $\delta$ - $\delta'$ - $\varepsilon$  are controlled mainly by the phonon vibration, spin fluctuation, and electron-phonon coupling. The transition of  $\delta$ - $\varepsilon$  is observed around 750 K–800 K, and is dominated by the phonon vibration. The  $\delta'$  intermediate phase could be realized around 750 K because of the thermal spin fluctuation. The electron-phonon coupling further improves the stability of the  $\varepsilon$  phase relative to the other two phases. The present insight provides a good understanding of the nature of the elastic stability and the  $\delta$ - $\delta'$ - $\varepsilon$  phase transitions of Pu at high temperature, and gives a solid ground for further advanced theoretical investigations of the subject matter.

## Methods

The employed first-principle solver is the exact muffin-tin orbitals (EMTO) method in combination with the coherent potential approximation (CPA)<sup>32–37</sup>. The EMTO-CPA is one of the few possible approaches to deal with magnetic disorder at first-principle level. In the present self-consistent calculations, the exchange correlation is chosen to be GGA as described by Perdew, Burke, and Ernzerhof (PBE)<sup>38</sup>. The EMTO basis set includes  $s$ ,  $p$ ,  $d$ , and  $f$  components, and the scalar-relativistic and soft-core approximations are adopted. The Green's function is calculated for 32 complex energy points on a semicircular contour. For the slope matrix, two-center Taylor expansion is used, and the number of orbitals for charge density is truncated at 8. The Brillouin zone is sampled by a  $13 \times 13 \times 13$  uniform  $k$ -point mesh.

The equation of state at 0 K is determined by fitting the calculated total energies versus volume to a Morse function<sup>39</sup>. The 0 K elastic constants  $C'$  of the  $\delta$  and  $\varepsilon$  phases, characterizing the softness of the cubic lattices against tetragonal deformation, are evaluated with the methods presented previously<sup>40</sup>, and their temperature dependence including electronic entropy, lattice thermal expansion, electron-phonon coupling, and magnetism are considered. The self-consistent calculations performed at each volume for different temperatures in the Fermi-Dirac distribution give the electronic entropy effect on  $C'$ . The variation of  $C'$  due to the thermal expansion is calculated as  $\left. \frac{dC'}{dr_{ws}} \right|_{T=0} r_0 \alpha T$ , where  $r_0$  is the equilibrium Wigner-Seitz radius at 0 K. For the thermal expansion coefficient  $\alpha$ , we choose the experimental values of the  $\delta$ ,  $\delta'$ , and  $\varepsilon$  phases<sup>1</sup>,  $-9.0 \times 10^{-6} \text{ K}^{-1}$ ,  $-66.0 \times 10^{-6} \text{ K}^{-1}$ , and  $36.5 \times 10^{-6} \text{ K}^{-1}$ , respectively. The phonon-smearing effect on  $C'$  is obtained as the difference between the second-order strain derivatives of the electronic free energies  $F_{el}$ , calculated using the smeared density of states and the bare density of states, respectively, using equation (2) in our previous paper<sup>19</sup>. In real metals at elevated temperatures, the electrons experience a smeared density of state ( $N^*(E)$ ) as a result of phonon-limited lifetime. This effect can be formulated as Lorentz-type smearing of the electronic density of state<sup>41</sup>

$$N^*(E) = \int_{-\infty}^{\infty} N(\varepsilon) \frac{(\Gamma/\pi)}{(E - \varepsilon)^2 + \Gamma^2} d\varepsilon, \quad (1)$$

where  $\Gamma = \pi \lambda_{\text{el-ph}} k_B T$  is inverse proportional with the electron lifetime, with  $k_B$  being the Boltzmann constant. For most of the metals electron-phonon parameter  $\lambda_{\text{el-ph}}$  is of order of unity<sup>41</sup>. In the present study,  $\lambda_{\text{el-ph}}$  is set as 0, 0.2, ..., and 1, respectively, to explore the phonon-smearing effect on  $C'$ , whereas to investigate this effect on the free energy,  $\lambda_{\text{el-ph}} = 1$  is adopted.

The thermal spin fluctuations influence the mean local magnetic moments and thus the free energy and ultimately also the elastic constants of Pu. In a recent density functional theory study<sup>31</sup>, the thermal spin fluctuation effect for  $\delta$ -Pu was found to decrease the value of the mean magnetic moment by  $\sim 0.5 \mu_B$  as the temperature increases from 0 K to 700 K. The reduction of the local magnetic moment was found to be critical to explain the observed softening of the bulk modulus with increasing temperature. Based on these reported data, the spin fluctuation effect is here considered by calculating  $C'$  with  $\mu_{\text{Pu}}$  reduced by 0%, 5%, ..., 20% relative to the equilibrium (static) value. To further investigate the spin fluctuation effect on the free energy, 10% reduce of the equilibrium  $\mu_{\text{Pu}}$  value is used, which is similar to the ab initio reduction predicted in the above study<sup>31</sup>.

The Helmholtz free energy ( $F$ ) is decomposed as

$$F = E_{\text{el}} - TS_{\text{el}} + F_{\text{vib}} + E_{\text{mag}} - TS_{\text{mag}}. \quad (2)$$

Here, the  $E_{\text{el}}$  and  $S_{\text{el}}$  are calculated directly with the EMTO method. Since the  $\delta$ - $\delta'$ - $\varepsilon$  transitions of Pu occur above 650 K, the phonon vibrational free energy,  $F_{\text{vib}}$ , is approximated by its high temperature expansion,  $F_{\text{vib}} \approx 3k_B T \frac{\Theta - \Theta_0}{\Theta}$ <sup>41</sup>, with  $\Theta$  and  $\Theta_0$  being the Debye temperatures corresponding to a volume of a tetragonal structure (specified in terms of Wigner-Seitz radius  $r_{\text{ws}}$  and  $c/a$ ) and to the equilibrium one of the  $\delta$  phase, respectively. According to the simplest approximation which has been applied to several metals<sup>42</sup>, the Debye temperature is proportional to  $\sqrt{r_{\text{ws}} B}$ . Its temperature dependence is then easily evaluated by including the lattice thermal expansion and magnetic effects on the bulk modulus  $B$ , which are calculated with the same methods adopted above for  $C'$ . The magnetic energy,  $E_{\text{mag}}$ , is calculated as  $E_{\text{mag}} = E_{\text{el}}^{\text{fix}} - E_{\text{el}}$ , where  $E_{\text{el}}^{\text{fix}}$  and  $E_{\text{el}}$  are the static electronic total energies corresponding to the fixed and equilibrium  $\mu_{\text{Pu}}$  values, respectively. The magnetic entropy,  $S_{\text{mag}}$ , is evaluated at each  $\mu_{\text{Pu}}$  using the mean-field expression  $S_{\text{mag}} = k_B \ln(\mu_{\text{Pu}} + 1)$ <sup>43</sup>.

## References

- Wick, O. J. *Plutonium Handbook: A Guide to the Technology* (Gordon and Breach, New York, 1967).
- Albers, R. C. Condensed-matter physics: an expanding view of plutonium. *Nature* **410**, 759–761 (2001).
- Hecker, S. S., Harbur, D. R. & Zocco, T. G. Phase stability and phase transformations in Pu–Ga alloys. *Prog. Mater. Sci.* **49**, 429–485 (2004).
- Albers, R. C. & Zhu, J. C. Solid-state physics: Vacillating valence. *Nature* **446**, 504–505 (2007).
- Suzuki, Y. *et al.* Temperature dependence of elastic moduli of polycrystalline  $\beta$  plutonium. *Phys. Rev. B* **84**, 064105 (2011).
- Nadal, M. H. & Bourgeois, L. Elastic moduli of Pu and Ga stabilized  $\delta$ -Pu: experimental data and phenomenological behavior at high temperature. *J. Appl. Phys.* **108**, 073532 (2010).
- Johansson, B. Nature of the 5f electrons in the actinide series. *Phys. Rev. B* **11**, 2740–2743 (1975).
- Skriver, H. L., Andersen, O. K. & Johansson, B. Calculated bulk properties of the actinide metals. *Phys. Rev. Lett.* **41**, 42–45 (1978).
- Johansson, B. & Li, S. Itinerant  $f$ -electron elements. *Philos. Mag.* **89**, 1793–1799 (2010).
- Arko, A. J. *et al.* Electronic structure of  $\alpha$ - and  $\delta$ -Pu from photoelectron spectroscopy. *Phys. Rev. B* **62**, 1773–1779 (2000).
- Shim, J. H., Haule, K. & Kotliar, G. Fluctuating valence in a correlated solid and the anomalous properties of  $d$ -plutonium. *Nature* **446**, 513–516 (2007).
- Cooper, N. G. Challenges in plutonium science. *Los Alamos Science* **26** (Los Alamos National Laboratory, Los Alamos, 2000).
- Söderlind, P., Landa, A., Klepeis, J. E., Suzuki, Y. & Migliori, A. Elastic properties of Pu metal and Pu–Ga alloys. *Phys. Rev. B* **81**, 224110 (2010).
- Bouchet, J., Siberchicot, B., Jollet, F. & Pasturel, A. Equilibrium properties of delta-Pu: LDA + U calculations (LDA equiv local density approximation). *J. Phys.: Condens. Matter* **12**, 1723–1733 (2000).
- Söderlind, P., Landa, A., Sadigh, B., Vitos, L. & Ruban, A. First-principles elastic constants and phonons of  $\delta$  Pu. *Phys. Rev. B* **70**, 144103 (2004).
- Wong, J. *et al.* Phonon dispersions of fcc-plutonium-gallium by inelastic X-ray scattering. *Science* **301**, 1078–1080 (2003).
- Dai, X. *et al.* Calculated phonon spectra of plutonium at high temperatures. *Science* **300**, 953–955 (2003).
- Graf, M. J., Lookman, T., Wills, J. M., Wallace, D. C. & Lashley, J. C. Strong electron-phonon coupling in  $\delta$ -phase stabilized Pu. *Phys. Rev. B* **72**, 045135 (2005).
- Li, C. M. *et al.* Temperature dependence of elastic properties of  $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$  and  $\text{Ni}_2\text{Mn}(\text{Ga}_{1-x}\text{Al}_x)$  from first principles. *Phys. Rev. B* **84**, 174117 (2011).
- Li, C. M., Hu, Q. M., Yang, R., Johansson, B. & Vitos, L. Understanding the martensitic phase transition of  $\text{Ni}_2(\text{Mn}_{1-x}\text{Fe}_x)\text{Ga}$  magnetic shape-memory alloys from theoretical calculations. *Phys. Rev. B* **91**, 174112 (2015).
- Yin, Z. P., Deng, X. Y., Basu, K., Yin, Q. & Kotliar, G. Temperature-dependent electronic structures, atomistic modelling and the negative thermal expansion of  $\delta$  Pu. *Philos. Mag. Lett.* **94**, 620–628 (2014).
- Janoschek, M. *et al.* The valence-fluctuating ground state of plutonium. *Sci. Adv.* **1**, 1500188 (2015).
- Söderlind, P., Zhou, F., Landa, A. & Klepeis, J. E. Phonon and magnetic structure in  $\delta$ -plutonium from density functional theory. *Sci. Rep.* **5**, 15958 (2015).
- Li, C. M., Yang, R., Johansson, B. & Vitos, L. Anomalous thermodynamic properties and phase stability of  $\delta$ - $\text{Pu}_{1-x}\text{M}_x$  ( $M = \text{Ga}$  and  $\text{Al}$ ) alloys from first-principles calculations. *Phys. Rev. B* **94**, 214108 (2016).
- Söderlind, P., Landa, A. & Sadigh, B. Density-functional investigation of magnetism in  $\delta$ -Pu. *Phys. Rev. B* **66**, 205109 (2002).
- Landa, A., Söderlind, P. & Ruban, A. Monte carlo simulations of the stability of  $\delta$ -pu. *J. Phys. Condens. Matter* **15**, L371–L376 (2003).
- Söderlind, P. & Sadigh, B. Density-functional calculations of  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\delta'$ , and  $\varepsilon$  plutonium. *Phys. Rev. Lett.* **92**, 185702 (2004).
- Staunton, J., Gyoffy, B. L., Pindor, A. J., Stocks, G. M. & Winter, H. The “disordered local moment” picture of itinerant magnetism at finite temperatures. *J. Magn. Magn. Mater.* **45**, 15–22 (1984).
- Solontsov, A. & Antropov, V. P. Effects of spin fluctuations and anomalous thermal expansion of  $\delta$ -Pu. *Phys. Rev. B* **81**, 214402 (2010).
- Ledbetter, H. M. & Moment, R. L. Elastic properties of face-centered-cubic plutonium. *Acta Metall.* **24**, 891–899 (1976).

31. Migliori, A. *et al.* Origin of the multiple configurations that drive the response of  $\delta$ -plutonium's elastic moduli to temperature. *PNAS* **113**, 11158–11161 (2016).
32. Vitos, L. Total-energy method based on the exact muffin tin orbitals theory. *Phys. Rev. B* **64**, 014107 (2001).
33. Andersen, O. K., Jepsen, O. & Krier, G. *Lectures on Methods of Electronic Structure Calculations* 63–124 (edited by Kumar, V., Andersen, O. K. & Mookerjee, A., World Scientific, Singapore, 1994).
34. Vitos, L. *Computational Quantum Mechanics for Materials Engineers* (Springer-Verlag, London, 2007).
35. Vitos, L., Abrikosov, I. A. & Johansson, B. Anisotropic lattice distortions in random alloys from first-principles theory. *Phys. Rev. Lett.* **87**, 156401 (2001).
36. Györfy, B. L. Coherent-potential approximation for a nonoverlapping-muffin-tin-potential model of random substitutional alloys. *Phys. Rev. B* **5**, 2382–2384 (1972).
37. Soven, P. Coherent-potential model of substitutional disordered alloys. *Phys. Rev.* **156**, 809–813 (1967).
38. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
39. Moruzzi, V. L., Janak, J. F. & Schwarz, K. Calculated thermal properties of metals. *Phys. Rev. B* **37**, 790–799 (1988).
40. Li, C. M., Hu, Q. M., Yang, R., Johansson, B. & Vitos, L. First-principles study of the elastic properties of In-Tl random alloys. *Phys. Rev. B* **82**, 094201 (2010).
41. Grimvall, G. *Thermophysical Properties of Materials* (North-Holland, Amsterdam, 1999).
42. Söderlind, P. & Johansson, B. Calculated thermal expansion of *d* and *f* transition metals. *Thermochimica Acta* **218**, 145–153 (1993).
43. Grimvall, G. Spin disorder in paramagnetic fcc iron. *Phys. Rev. B* **39**, 12300–12301 (1989).

## Acknowledgements

The authors acknowledge the financial support from the National Natural Science Foundation of China under grant Nos 11674233 and 51301176, the China Postdoctoral Science Foundation under grant Nos 2014T70264 and 2013M530133, and Liaoning Province Science Foundation under grant No. 201602672. Börje Johansson and Levente Vitos acknowledge the Swedish Research Council, the Swedish Foundation for strategic Research, the Swedish Foundation for International Cooperation in Research and Higher Education and the Hungarian Scientific Research Fund (OTKA 109570) for financial support.

## Author Contributions

All authors conceived the study and reviewed the paper. C.M.L. performed calculations and wrote the article. B.J. and L.V. contributed to the discussion and the final statement of the article.

## Additional Information

**Competing Interests:** The authors declare that they have no competing interests.

**Publisher's note:** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2017