LETTER TO THE EDITOR

First-principles thermodynamic calculations for δ-Pu and ε-Pu

Yi Wang†‡ and Yunfeng Sun†

† Department of Physics, National Mesoscopic Physics Laboratory, Peking University,
Beijing 100871, People's Republic of China
‡ Institute of Applied Physics and Computational Mathematics, PO Box 8009, Beijing 100088,
People's Republic of China

Abstract.   With the aim of investigating several long-standing issues, e.g. the equilibrium atomic volumes of the high-temperature δ-phase (fcc) and ε-phase (bcc) of plutonium metal, a first-principles thermodynamic calculation has been carried out on the basis of (i) accurate calculations of 0 K total energies with the full-potential linearized augmented-plane-wave method within the generalized gradient approximation to the exchange–correlational functional and (ii) the newly developed classical mean-field statistics where both the cold and thermal parts of the Helmholtz free energy are derived entirely from the 0 K total energy. The calculated results show that at 0 K the antiferromagnetic states are energy preferable, both for the fcc and for the bcc phases. For the first time, an *ab initio* thermodynamic calculation gives calculated atomic volumes for δ-Pu and ε-Pu: these are, respectively, 24.97 Å^3 and 23.82 Å^3, which are very comparable with the corresponding experimental values of 24.89 Å^3 and 24.29 Å^3.

According to the behaviours of the 5f electrons, the actinide metals can be partitioned into two main groups where, in the light actinides Th to Np, and in the low-temperature α-phase of plutonium (Pu), the 5f electrons are delocalized, whereas in the five higher-temperature phases (β, γ, δ, δ', and ε) of Pu, and in the heavy actinides from Am on, the 5f electrons are localized to varying degrees [1]. The magnetism of the actinide metals also exhibits a similar behaviour, where the light actinides have no magnetic moments and possess temperature-independent paramagnetic susceptibilities, while the heavy actinides have localized moments and exhibit Curie–Weiss antiferromagnetic behaviour [2].

Therefore, for understanding the localization and delocalization of 5f electrons, Pu is the crucial element, where the character of the 5f electrons apparently varies from nearly purely delocalized in α-Pu, to varying degrees of localization in the elevated-temperature phases. This complex and intriguing scenario has provided a great challenge for theory as regards accurately treating the electronic structure of Pu in the last two decades [2–8]. It is often argued that the correlation effects are important for making predictions regarding Pu and that the conventional density functional theory (CDFT) is not suitable, and the recent work going beyond the CDFT by Savrasov and Kotliar [5] does indeed show that the highly anomalous atomic volume of δ-Pu can be correctly described taking into account a Hubbard U of the order of 4 eV. However, the recent work by Söderlind and co-workers (see reference [4] and references therein) demonstrated that the low-temperature phase of α-Pu could be correctly described using an accurate density functional calculation with the help of thermal expansion.

For the high-temperature phases of Pu, questions seem still to remain in the framework of the CDFT. With the very simple crystal structures of fcc for δ-Pu (with atomic volume

$\sim$24.9 Å^3) and bcc for ε-Pu (with atomic volume $\sim$24.3 Å^3), it seems that none of the CDFT calculations can give atomic volumes that could even be greater than 20 Å^3. The present work reports thermodynamic calculations for δ-Pu and ε-Pu made with a combination of our newly developed classical mean-field potential (MFP) approach [9] and the full-potential linearized augmented-plane-wave (LAPW) method [10] within the generalized gradient approximation (GGA) [11] which is an implementation of the CDFT. We demonstrate that the CDFT can correctly describe δ-Pu and ε-Pu too if the correct magnetic (antiferromagnetic) state is considered. For the first time, an *ab initio* thermal calculation within the framework of the CDFT gives calculated atomic volumes for δ-Pu and ε-Pu: these are, respectively, 24.97 Å^3 and 23.82 Å^3, which are very comparable with the corresponding experimental values of 24.89 Å^3 and 24.29 Å^3.

Since we are treating high-temperature issues relating to δ-Pu and ε-Pu, in addition to an accurate 0 K calculation, a reliable thermodynamic model is needed. In a series of works, we have developed a parameter-free classical mean-field (CMF) model [9] which, being fairly simplistic, only utilizes the 0 K isotherm calculated *ab initio*. By using this model in conjunction with accurate calculations of the one-particle thermal excitation of the electrons with one-dimensional numerical integration and simple treatment of the disordered magnetic entropy, the well-known experimental γ–α isostructural transition, the Hugoniot state (shock-wave-compressed state), and the 300 K static equation of state (EOS) of metal Ce have been well described. The CMF model had also been successfully used for calculations of Hugoniot states and 293 K isotherms for reference metals Al, Cu, Ta, Mo, and W [12].

We first briefly summarize the CMF approach. For a substance, if we can calculate the Helmholtz free energy as an explicit function of volume and temperature, all other thermodynamic parameters can be derived. Let us consider a system with a given averaged atomic volume V and temperature T. The Helmholtz free energy $F(V, T)$ per ion can be written as [13]

$$F(V, T) = E_c(V) + F_{ion}(V, T) + F_{el}(V, T) + F_{mag}(V, T) \tag{1}$$

where E_c represents the 0 K total energy, F_{ion} the vibrational free energy of the lattice ion, and F_{el} the free energy due to the thermal excitation of electrons. By constructing the mean-field potential (MFP) $g(r, V)$ in terms of the 0 K total energy $E_c(R)$ as [9]

$$g(r, V) = \frac{1}{2}(E_c(R + r) + E_c(R - r) - 2E_c(R)) \tag{2}$$

where r represents the distance that the lattice ion deviates from its equilibrium position, and R is the lattice constant with $V = R^3/4$ for fcc crystal and $V = R^3/2$ for bcc crystal, F_{ion} can be formulated as

$$F_{ion}(V, T) = -k_B T \left(\frac{3}{2} \ln \frac{mk_B T}{2\pi\hbar^2} + \ln v_f(V, T) \right) \tag{3}$$

where

$$v_f(V, T) = 4\pi \int \exp\left(-\frac{g(r, V)}{k_B T} \right) r^2 \, dr. \tag{4}$$

It should be mentioned that under the second-order approximation, the well-known Dugdale and MacDonald expression [14] for the Grüneisen parameter can be explicitly deduced using equation (2).

When the electron–phonon interactions are neglected, the electronic contribution to the free energy is $F_{el} = E_{el} - T S_{el}$, where the bare electronic entropy S_{el} takes the form [15]

$$S_{el}(V, T) = -k_B \int n(\varepsilon, V)[f \ln f + (1 - f) \ln(1 - f)] \, d\varepsilon \tag{5}$$

where $n(\varepsilon, V)$ is the electronic density of states (DOS) and f is the Fermi distribution. Using equation (5), the energy E_{el} due to the electron excitations can be expressed as

$$E_{el}(V, T) = \int n(\varepsilon, V) f \varepsilon \, \mathrm{d}\varepsilon - \int^{\varepsilon_F} n(\varepsilon, V) \varepsilon \, \mathrm{d}\varepsilon \tag{6}$$

where ε_F is the Fermi energy.

We now consider the term F_{mag} in equation (1). To the best of our knowledge, no accurate expression exists for the magnetic free energy F_{mag}. In the previous work [9], by just considering the magnetic multiplicity, we introduced F_{mag} as

$$F_{mag}(V, T) = -k_B T \ln(M_S(2L - M_S) + 1) \tag{7}$$

where $\ln(M_S(2L - M_S) + 1)$ is the magnetic entropy, M_S is the total spin magnetic moment, and L is the 4f orbital moment ($L = 3$). Since Hund's rule can be expressed in terms of the total angular moment as $J = M_S(2L - M_S)/2$ with integer M_S, it is obvious that equation (7) can be regarded as a generalization of Hund's rule to the case of a non-integer magnetic state.

To calculate the 0 K total energy $E_c(V)$, the full-potential LAPW method within the GGA is employed. Three calculation cases, namely non-magnetic, ferromagnetic, and anti-ferromagnetic, are considered. To treat the antiferromagnetic fcc case, the method of Zhou *et al* [16] has been followed, i.e. a tetragonal lattice unit cell which includes two atoms at $(0, 0, 0)$ and $(1/2, 1/2, 1/2)$ is used. To treat the antiferromagnetic bcc case, a simple cubic unit cell with two atoms is used. Constant muffin-tin radii (R_{mt}) of 2.50 au are used for all lattice constants. The plane-wave cut-off K_{cut} is determined by $R_{mt} K_{cut} = 10.0$. 8000 k-points in the full zone are used for reciprocal-space integrations. The basis sets include the semicore 6s and 6p partial waves, and the valence 7s, 7p, 6d, and 5f partial waves. All of these orbitals are defined within one energy panel. The remaining electrons were considered as belonging to the core, but their wave functions were relaxed, i.e., recalculated in each iteration.

Our 0 K results show that the antiferromagnetic state is energy preferable to the ferromagnetic state, while the ferromagnetic state is energy preferable to the non-magnetic state. For the non-magnetic fcc Pu, our results are exactly the same as those given by Jones *et al* [8]. In figure 1 and figure 2 we show for fcc Pu and bcc Pu respectively the calculated 0 K total energies as functions of lattice constant for the non-magnetic, the antiferromagnetic, and the ferromagnetic states. Note that the ferromagnetic results are very unusual, as in the case of fcc Pu the smoothness of the curve is very poor while in the case of bcc Pu there are even double minima in the curve. Our results are fundamentally different from those of van Ek *et al* [6], who stated that the antiferromagnetically ordered forms of δ-Pu were found to be higher in energy than ferromagnetic δ-Pu. Regarding the magnetism of δ-Pu, there is some debate, as only Solovyev *et al* [2] mentioned a surprisingly small experimental moment of about 1 μ_B, whereas all others have said that δ-Pu is non-magnetic. In the following calculations, we only consider antiferromagnetic states.

Utilizing the 0 K antiferromagnetic total energies while considering antiferromagnetic disorder due to the high temperature, we have calculated the equilibrium atomic volumes (V_a), the adiabatic bulk moduli (B_S), and the volume thermal expansion coefficients (β) for fcc Pu (computing at 650 K) and bcc Pu (computing at 850 K) with the above-mentioned thermodynamic calculation scheme. These results are listed in table 1 together with the experimental data summarized by Wallace [1]. Inspecting table 1, one notes that the calculated atomic volumes are surprisingly good as compared with the experimental values.

For the bulk moduli, although they give significantly improved results over the previous calculations the present calculations still give results that are too large relative to those from the experiment by a factor of 1.8. For the thermal expansion coefficients, our calculations do
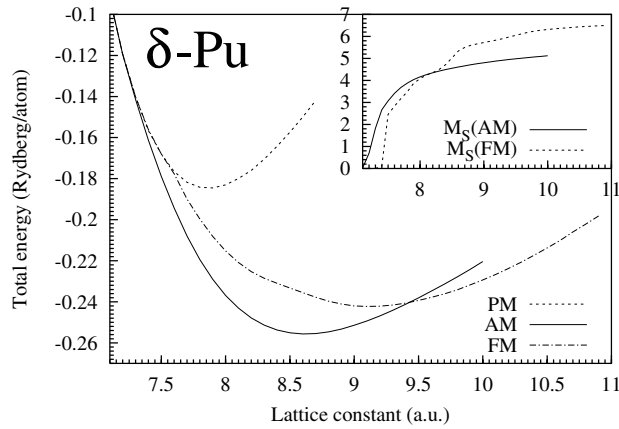
Figure 1. The 0 K total energy for fcc Pu, calculated for the non-magnetic (dashed line), anti-ferromagnetic (solid line), and ferromagnetic (dot–dashed line) cases, as a function of the lattice constant. The inset shows the net spin magnetic moments of the magnetic cases.
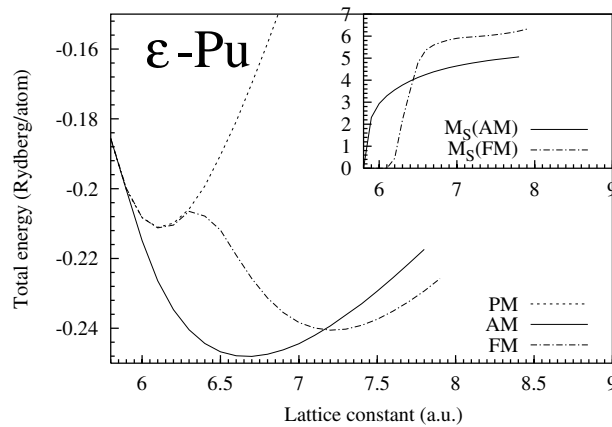

Figure 2. The 0 K total energy for bcc Pu, calculated in the non-magnetic (dashed line), anti-ferromagnetic (solid line), and ferromagnetic (dot–dashed line) cases, as a function of the lattice constant. The inset shows the net spin magnetic moments of the magnetic cases.

Table 1. The calculated (employing the antiferromagnetic 0 K isotherm) and experimental [1] equilibrium atomic volume V_a (in Å^3), adiabatic bulk modulus B_S (in GPa), and volume thermal expansion coefficient β (in units of 10^{-6} K^{-1}) for elevated-temperature phases of plutonium, δ-Pu, and ε-Pu.

Method	δ-Pu ($T = 650$ K)			ε-Pu ($T = 850$ K)		
	V_a	B_S	β	V_a	B_S	β
Theory	24.97	43.0	93.9	23.82	36.2	111.9
Experiment	24.89	23.7	−26	24.29	23.0	110

not reproduce the negative value for δ-Pu. These discrepancies may in part be ascribable to the phase coexistence of δ-Pu and ε-Pu.

To give further support for the present calculation, the 300 K equations of state, calculated

by utilizing the antiferromagnetic total energies, for fcc Pu and bcc Pu are compared with the experimental results in figure 3. Note that bcc Pu is indeed appropriate as a model for the higher-pressure phase of Pu, as pointed out by Söderlind [4].
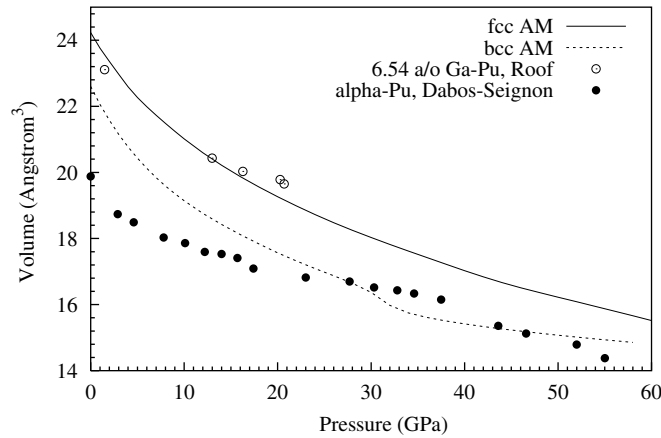

Figure 3. The 300 K equation of state of Pu. The solid and dashed lines represent results calculated using the antiferromagnetic fcc configuration and the antiferromagnetic bcc config-uration respectively. The open circles represents the experimental values for δ-Pu given by Roof [17] and the filled circles represent the recent experimental values for α-Pu given by Dabos-Seignon *et al* [18].

In summary, we have calculated the equilibrium atomic volumes, the adiabatic bulk moduli, and the volume thermal expansion coefficients of δ-Pu (computing at 650 K) and ε-Pu (computing at 850 K), utilizing the 0 K antiferromagnetic total energies calculated with full-potential LAPW methods in conjunction with the newly developed classical mean-field statistics. The antiferromagnetic states are found to be energy preferable for both the fcc and the bcc phases. For the first time, an *ab initio* thermal calculation within the framework of the conventional density functional theory has given calculated atomic volumes for δ-Pu and ε-Pu: these are, respectively, 24.97 Å^3 and 23.82 Å^3, which are very comparable with the corresponding experimental values of 24.89 Å^3 and 24.29 Å^3. Therefore, the absence of ferromagnetism in experiments can be explained readily in terms of the antiferromagnetic orderings.

References

[1] Wallace D C 1998 *Phys. Rev.* B **58** 15 433
[2] Solovyev I V, Liechtenstein A I, Gubanov V A, Antropov V P and Andersen O K 1991 *Phys. Rev.* B **43** 14 414
[3] Skriver H L, Andersen O K and Johansson B 1978 *Phys. Rev. Lett.* **41** 42
[4] Söderlind P 1998 *Adv. Phys.* **47** 959
[5] Savrasov S Y and Kotliar G 2000 *Phys. Rev. Lett.* **84** 3670
[6] van Ek J, Sterne P A and Gonis A 1993 *Phys. Rev.* B **48** 16 280
[7] Vitos L, Kollár J and Skriver H L 1997 *Phys. Rev.* B **55** 4947
[8] Jones M D, Boettger J C, Albers R C and Singh D J 2000 *Phys. Rev.* B **61** 4644
[9] Wang Y 2000 *Phys. Rev.* B **61** R11863

[10] Blaha P, Schwarz K and Luitz J 1997 *WIEN97* Vienna University of Technology
      This is an improved and updated Unix version of the original copyrighted WIEN code, which was published by
      Blaha P, Schwarz K, Sorantin P and Trickey S B 1990 *Comput. Phys. Commun.* **59** 399
[11] Perdew J P, Burke S and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[12] Wang Y, Chen D and Zhang X 2000 *Phys. Rev. Lett.* **84** 3220
[13] Boettger J C and Wallace D C 1997 *Phys. Rev.* B **55** 2840
[14] Dugdale J S and MacDonald D K C 1953 *Phys. Rev.* **89** 832
[15] Jarlborg T, Moroni E G and Grimvall G 1997 *Phys. Rev.* B **55** 1288
[16] Zhou Y, Zhang W, Zhong L, Nie X and Wang D 1997 *J. Magn. Magn. Mater.* **167** 136
[17] Roof R B 1981 *Adv. X-ray Anal.* **24** 221
[18] Dabos-Seignon S, Dancausse J P, Gering E, Heathman S and Benedict U 1993 *J. Alloys Compounds* **190** 237