



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# First-principles elastic properties of (alpha)-Pu

P. Soderlind, J. E. Klepeis

November 12, 2008

Physical Review B

## **Disclaimer**

---

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

# First-principles elastic properties of $\alpha$ -Pu

Per Söderlind and John E. Klepeis  
*Lawrence Livermore National Laboratory,*  
*P.O. Box 808, Livermore, CA 94550*

(Dated: November 6, 2008)

## Abstract

Density-functional electronic structure calculations have been used to investigate the ambient pressure and low temperature elastic properties of the ground-state  $\alpha$  phase of plutonium metal. The electronic structure and correlation effects are modeled within a fully relativistic anti-ferromagnetic treatment with a generalized gradient approximation for the electron exchange and correlation functionals. The 13 independent elastic constants, for the monoclinic  $\alpha$ -Pu system, are calculated for the observed geometry. A comparison of the results with measured data from resonant ultrasound spectroscopy for a cast sample is made.

PACS numbers: 62.20.de, 71.15.Mb, 71.20.Eh, 71.27.+a, 75.10.Lp

## I. INTRODUCTION

Plutonium remains one of the more controversial metals because its complex physics and chemistry are not well understood on a fundamental level. The electronic structure is responsible for many interesting properties of Pu. For instance an intriguing and unusual phase diagram<sup>1</sup> in which atomic arrangements of sharply contrasting symmetry and density compete closely with each other (Fig. 1). Although it is generally accepted that this scenario arises from chemical bonding that is flexible enough to accomplish this, the controversy focuses on the description and understanding of the underlying electronic structure. On one hand, dynamical mean-field theory (DMFT)<sup>2</sup> may provide a means to describe the electron-correlation effects, while on the other, total energies obtained from density-functional theory (DFT) appear consistent with many ground-state properties of plutonium as well as the aforementioned phase diagram.<sup>3,4</sup>

The only possibility to distinguish these and other models is of course to compare with results of experimental investigations. Fortunately, there have been several recent electronic structure measurements for Pu<sup>5</sup> and a new experiment has been proposed<sup>6</sup> that may help in this regard. Certainly, progress on the theoretical side, DFT, DMFT, or otherwise, provides further motivation for an ongoing experimental effort on plutonium.

Here we are applying DFT to calculate the 13 independent elastic constants of the monoclinic ( $P2_1/m$ ) ground-state  $\alpha$  phase of Pu. The results of these computations are important for several reasons. First, the elastic moduli reflect a detailed picture of the chemical bonding and are therefore relevant when discerning the quality of the DFT electronic structure. Second, single crystal elastic stiffness components for Pu have been measured<sup>7</sup> for  $\delta$ -Pu, for which theoretical data also exist,<sup>8</sup> but never for the  $\alpha$  phase. The present elastic constants therefore serve as predictions and could be used for comparison with other models or to constrain semi-empirical descriptions<sup>9,10</sup> of  $\alpha$ -Pu.

In Sect. II we describe technical details of the computational method including our theoretical model for  $\alpha$ -Pu. This is followed by Sect. III in which we report calculated elastic constants for  $\alpha$ -Pu and make comparisons to data on cast  $\alpha$ -Pu. We provide some concluding remarks in Sect. IV and a detailed description of strains applied to the lattice and the corresponding elastic constants in the Appendix, Sect. A.

## II. COMPUTATIONAL DETAILS

The electronic structure and total energy for  $\alpha$ -Pu are obtained from density-functional calculations which require the atomic geometry and the atomic number (94 for Pu). The monoclinic crystal structure has been determined by x-ray diffraction<sup>11</sup> and is rather complex with 16 atoms/cell. Theoretically it is in principle possible to allow all parameters of this structure to relax, but the associated computational burden makes it prohibitive with the present technique. However, our previous study of the  $\alpha$ -Pu structure<sup>12</sup> leads us to believe that relaxation effects are rather small.

For the experimental geometry<sup>11</sup> very small strains ( $\leq 1\%$ ) are applied so that the elastic constants can be extracted using relevant equations which are, for completeness, included in the Appendix, Sect. A. About 4-8 magnitudes of strains are used for every elastic constant and a fourth degree polynomial is fitted to the corresponding energies so that the harmonic coefficient, relevant for the elastic constants (Eq. A2), can be obtained. In all cases, fitting to a second order polynomial gives a result not different by more than about 10%. The use of higher orders of polynomials do not change the results significantly. No structural relaxation is allowed during the strain because of computational limitations. This simplification, however, was shown to be justified for the elastic-constant calculation of  $\alpha$ -U<sup>13</sup> and we believe this is the case also for  $\alpha$ -Pu. Nonetheless, it is plausible that allowing such relaxations could lower the elastic energies a small amount.

For the present calculations we use a full-potential version of the linear muffin-tin orbital method (FP-LMTO) implemented by Wills and coworkers.<sup>14</sup> Electron correlations are more pronounced in Pu than most other metals. Here, these effects are modeled by the generalized gradient approximation<sup>15</sup>, spin polarization, and spin-orbit coupling. This approach is the same as has been used for Pu in the past<sup>3,12</sup> with the exception of the orbital polarization (OP) present in the previous calculations. Although ideally preferred, inclusion of OP severely impacts the efficiency of the computations and for the demanding task of calculating the elastic constants for  $\alpha$ -Pu this complication is neglected. The effect of OP is known to be substantial for  $\delta$ -Pu<sup>16,17</sup> but electron-correlation effects are significantly weaker in  $\alpha$ -Pu. In Table I we compare data obtained from calculations for  $\alpha$ -Pu with and without OP, together with recent measurements for cast  $\alpha$ -Pu. We notice that OP expands the equilibrium volume, resulting in a very close agreement with room-temperature data.<sup>18</sup> The

theoretical bulk moduli compare favorably with measured data. The elastic constants are computed for a fixed atomic volume, and because the OP volume is closer to the experimental one, we chose to fix the volume to its value ( $20.3 \text{ \AA}^3$ ).

The use of full non-sphericity of the charge density and one-electron potential is essential for accurate total energies and in particular when elastic constants are calculated. This is accomplished in our method by expanding the charge density and potential in cubic harmonics inside non-overlapping muffin-tin spheres and in a Fourier series in the interstitial region. In all calculations we use two energy tails associated with each basis orbital and for  $6s$ ,  $6p$ , and the valence states ( $7s$ ,  $7p$ ,  $6d$ , and  $5f$ ) these pairs are different. With this “double basis” approach we include six energy tail parameters and 12 basis functions per atom. Spherical harmonic expansions are carried out through  $l_{max} = 6$  for the bases, potential, and charge density. The sampling of the irreducible Brillouin zone is done using the special k-point method<sup>19</sup> and 54 k points are utilized for this purpose. Test calculations increasing this number to 128 resulted in no significant change of the elastic constants (less than 3%). To each energy eigenvalue a Gaussian was associated with 20 mRy width to speed up convergence.

Total energies are converged to the  $\mu\text{Ry}/\text{atom}$  level which typically requires about 100 self-consistent-field cycles.

The spin-orbit coupling is implemented in a first-order variational procedure<sup>20</sup> for the valence  $d$  and  $f$  states, as was done previously,<sup>3</sup> and for the core states the fully relativistic Dirac equation is solved.

### III. ELASTIC CONSTANTS

Only in the last few years have calculations of elastic constants for more complex geometries been attempted from first principles, such as our own study on PtSi which is an 8 atom/cell orthorhombic system.<sup>21</sup> More recently the elastic constants of coesite, a monoclinic high-pressure polymorph of silica, were calculated<sup>22</sup> and these compared favorably with experimental data. Another low-symmetry system,  $\alpha\text{-U}$  (a closer neighbor to Pu), has been investigated within DFT and the obtained elastic properties compare well between various computations<sup>13,23,24</sup> and measured data.

Here, we present the first calculated elastic constants for  $\alpha\text{-Pu}$ , a material with a high

degree of complexity both as regards the crystal and electronic structure. The monoclinic lattice has 13 independent moduli which can be determined by calculating the total-energy response to small distortions. A general elastic constant,  $c_{ij}$ , is obtained at a fixed atomic volume ( $V_0$ ) through Eq. A1 given in the Appendix. The 13 applied strains, all summarized in the Appendix, depend on a distortion parameter  $\delta$ .

In Fig. 2 we show the total energies as functions of  $\delta$  for the strains defined in Eqs. A3-A5 which relate to  $c_{11}$ ,  $c_{22}$ , and  $c_{33}$ , respectively. These elastic constants are associated with elongations along the  $x$ ,  $y$ , and  $z$  directions. Because these strains are not conserving the atomic volume (the determinants of the corresponding strain matrices are not unity) the undistorted total energy is only lowest if the calculation is performed at the equilibrium volume. Here the total energies are computed at a volume of  $20.3 \text{ \AA}^3$ , which is somewhat larger than the calculated equilibrium volume ( $19.0 \text{ \AA}^3$ ), see Table I, as discussed in the previous section. This then immediately explains why a negative  $\delta$ , that compresses the lattice, lowers the total energy in Fig. 2. Notice also in this figure that these axial strains (Eqs. A3-A5) show parallel dependence on  $\delta$ . The similarity of these curves suggests that relaxation effects with respect to the axial ratios ( $b/a$  and  $c/a$ ) are small, as pointed out in our earlier investigation<sup>12</sup> of  $\alpha$ -Pu.

In Fig. 3 we show the total energies for the strains defined by Eqs. A6-A8. These strains correspond to the elastic constants  $c_{44}$ ,  $c_{55}$ , and  $c_{66}$ , which are associated with the angle between the respective axis. One of these lowers the total energy a very small amount for a 0.25 % strain, suggesting that the experimental structure is not the lowest-energy structure in the calculations but close. Overall, however, the total-energy dependencies on these strains, combined with the remaining ones (Eqs. A9-A15, not shown), suggest that the theoretical treatment reproduces the details of the monoclinic structure quite well.

In Table II we present the calculated elastic quantity associated with each strain, defined in the Appendix. The first six strains (Eqs. A3-A8) immediately define the elastic constants  $c_{ii}$ , whereas the other strains (Eqs. A9-A15) give linear combinations of  $c_{ij}$ . The number of independent equations equals the number of unknown elastic moduli resulting in a well defined system of linear equations that can be solved straightforwardly. Notice in Table II that all distortions give rise to elastic quantities that are positive, which implies that  $\alpha$ -Pu is mechanically stable with respect to all 13 strains.

Next, by solving the linear equations for the  $c_{ij}$ , we collect the entries in Table III.

Some of the elastic constants, such as  $c_{12}$  for example, are negative but this should not be interpreted as an instability because the actual applied distortions did not cause any instability, as mentioned above. It is also evident that  $c_{11} \approx c_{22}$  while  $c_{33}$  is smaller. This likely means that the  $c/a$  axial ratio is more sensitive to external influences, such as pressure and temperature, than the  $b/a$  axial ratio.

The bulk modulus ( $B$ ) is a special elastic constant that is related to a uniform change of the atomic density or volume. On one hand, it can be directly obtained from calculations of the total energy as a function of the atomic volume (equation-of-state). In practice, the total energy is often fitted to an analytical form from which  $B$  is defined. In our case we use the Murnaghan form<sup>25</sup> for this purpose, and the results are presented in Table I. On the other hand,  $B$  can also be evaluated from the elastic compliance constants  $s_{ij}$  (tabularized in Table IV), which are components of the inverse to the elastic-constant matrix:<sup>22</sup>

$$B^{-1} = s_{11} + s_{22} + s_{33} + 2(s_{12} + s_{13} + s_{23}). \quad (1)$$

Computing  $B$  from the equation-of-state yields a value of 25 GPa (Table I), whereas using Eq. 1 (after first numerically inverting the elastic-constant matrix) gives 21 GPa. The fact that the bulk modulus obtained from these independent methods agree reasonably well indicates a consistency of the calculations but also reveals some numerical uncertainties because they are not identical.

As mentioned in the introduction, there are no experimental single crystal elastic constants to compare our theoretical counterparts with. Instead we attempt to compare our results with polycrystal data. Recently Migliori *et al.*<sup>18</sup> determined quantities they labeled as “ $c_{11}$ ” and “ $c_{44}$ ” from their resonant ultrasound spectroscopy measurements of longitudinal and shear sound speeds of arc-cast  $\alpha$ -Pu. The latter refers to an isotropic average of the polycrystal shear modulus,  $G$ , while the former we will call  $\tilde{c}_{11}$  to distinguish it from the single crystal  $c_{11}$ . For an isotropic material they are related to the bulk modulus through the equation

$$B = \tilde{c}_{11} - \frac{4G}{3}. \quad (2)$$

Thus, we can compare the measured<sup>18</sup>  $B$ ,  $\tilde{c}_{11}$ , and  $G$  with our calculated single crystal elastic constants using Eq. 1, Eq. 2, and an average value for the shear modulus:

$$G_V = \frac{1}{15}[c_{11} + c_{22} + c_{33} + 3(c_{44} + c_{55} + c_{66}) - (c_{12} + c_{13} + c_{23})]. \quad (3)$$

This is the Voigt upper bound<sup>26</sup> on the effective shear modulus for a macroscopically isotropic polycrystal and it gives us  $B = 21$ ,  $G = G_V = 49.9$ , and  $\tilde{c}_{11} = 87.5$  GPa, compared to<sup>18</sup> 54.4, 43.7, and 112.8 GPa. Since we are using the Voigt upper bound for the shear modulus, but the exact expression (Eq. 1) for the bulk modulus, it is interesting to also use the Voigt upper bound for the bulk modulus to be consistent with the shear modulus:

$$B_V = \frac{1}{9}[c_{11} + c_{22} + c_{33} + 2(c_{12} + c_{13} + c_{23})]. \quad (4)$$

This then gives us slightly different values which are summarized and compared with those of Migliori *et al.* in Table V.

Clearly, the theoretical bulk modulus compares least favorably with that of experimental data, while both  $G$  and  $\tilde{c}_{11}$  are in better agreement. In addition,  $G_V$  is larger than the experimental value which is expected because it represents an upper bound.

#### IV. CONCLUSION

We have reported the first theoretical elastic constants for  $\alpha$ -Pu. The electron-correlation effects are modeled by an anti-ferromagnetic spin configuration<sup>3</sup> in connection with spin-orbit coupling. The elastic-constant calculations show that the experimentally observed monoclinic structure<sup>11</sup> is stable and very close to what is predicted by the theory. Also, the  $b/a$  and  $c/a$  axial ratios are predicted to be rather similar in their dependence on external influences such as pressure or temperature, with the  $c/a$  likely being somewhat more dependent.

The computed elastic constants serve as predictions and can be used for comparison with other theories or for development of inter-atomic potentials and semi-empirical models for  $\alpha$ -Pu. Although an indirect comparison, present single crystal elastic constants do not appear to be inconsistent with recently reported data from polycrystal  $\alpha$ -Pu obtained from resonant ultrasound spectroscopy, see Table V. The largest relative difference with experiment is for the bulk modulus. It is small when evaluated at  $20.3 \text{ \AA}^3$ , but much better when calculated at the equilibrium volume (Table I) and this is due to our neglect of orbital polarization. To

improve on the bulk modulus one needs to take the OP electron-correlation correction into account.

Another reason for the discrepancy between calculations and measurements is the effect of temperature on the elastic constants. Our calculations do not address lattice vibrations whereas the measurements are performed at room temperature.

The measured elastic constants show very pronounced softening (decrease) with temperature<sup>18</sup> and it was suggested that this behavior is linked to  $5f$ -electron localization. Our own investigations<sup>27,28</sup> (not shown) of  $\alpha$ -Pu, employing Debye-Grüneisen methodology and other quasi-harmonic treatments, suggest that the thermal softening of moduli can largely be accounted for by quasi-harmonic phonon contributions with no temperature dependence of the electronic structure. If this is true,  $5f$ -electron localization is probably not the primary driver for the thermal softening of the moduli.

### Acknowledgments

J. Pask is acknowledged for help with matrix manipulations. R. Rudd is thanked for helpful discussions. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

### APPENDIX A

In this Appendix, we present the strains of the monoclinic ( $\alpha$ -Pu) structure applied to calculate the 13 independent elastic constants of this phase. The internal energy of a crystal under strain,  $\delta$ , can be Taylor expanded in powers of the strain tensor with respect to that of the unstrained crystal in the following way:

$$E(V, \delta) = E(V_0, 0) + V_0 \left( \sum_i \tau_i \xi_i \delta_i + \frac{1}{2} \sum_{i,j} c_{ij} \delta_i \xi_i \delta_j \xi_j \right) + O(\delta^3). \quad (\text{A1})$$

The volume of the unstrained system is denoted  $V_0$  and  $E(V_0, 0)$  is this system's internal energy, which corresponds to the total energy obtained from the electronic structure. The Voigt notation has been used in the equation above, i.e.,  $xx$ ,  $yy$ ,  $zz$ ,  $yz$ ,  $xz$ , and  $xy$  are replaced with 1 through 6. Of course,  $yz$ ,  $xz$ , and  $xy$  are equal to  $zy$ ,  $zx$ , and  $yx$  and for that reason  $\xi_i$  is equal to 1 for  $i = 1, 2, 3$  and 2 for  $i = 4, 5, 6$ .  $\tau_i$  above is a component of

the stress tensor. In practice this equation is here used for all 13 strains and the equation can be written as

$$E(V, \delta) = E(V_0, 0) + V_0(\tau\delta + \frac{1}{2}C\delta^2) \quad (\text{A2})$$

where we have introduced  $\tau$  representing a linear combination of stress components and  $C$ , a linear combination of elastic constants.  $C$  will be specified below as we introduce the various strains, while we are not concerned here about the stress terms. Next, we present the strains and their corresponding elastic constant(s)  $C$ .

$$\begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, C = c_{11}. \quad (\text{A3})$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 + \delta & 0 \\ 0 & 0 & 1 \end{pmatrix}, C = c_{22}. \quad (\text{A4})$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 + \delta \end{pmatrix}, C = c_{33}. \quad (\text{A5})$$

$$\frac{1}{(1 - \delta^2)} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \delta \\ 0 & \delta & 1 \end{pmatrix}, C = 4c_{44}. \quad (\text{A6})$$

$$\frac{1}{(1 - \delta^2)} \begin{pmatrix} 1 & 0 & \delta \\ 0 & 1 & 0 \\ \delta & 0 & 1 \end{pmatrix}, C = 4c_{55}. \quad (\text{A7})$$

$$\frac{1}{(1 - \delta^2)} \begin{pmatrix} 1 & \delta & 0 \\ \delta & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, C = 4c_{66}. \quad (\text{A8})$$

$$\frac{1}{(1 - \delta^2)} \begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 - \delta & 0 \\ 0 & 0 & 1 \end{pmatrix}, C = c_{11} + c_{22} - 2c_{12}. \quad (\text{A9})$$

$$\frac{1}{(1-\delta^2)} \begin{pmatrix} 1+\delta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1-\delta \end{pmatrix}, C = c_{11} + c_{33} - 2c_{13}. \quad (\text{A10})$$

$$\frac{1}{(1-\delta^2)} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1+\delta & 0 \\ 0 & 0 & 1-\delta \end{pmatrix}, C = c_{22} + c_{33} - 2c_{23}. \quad (\text{A11})$$

$$\frac{1}{(1-\delta^2)} \begin{pmatrix} 1+\delta & 0 & \delta \\ 0 & 1-\delta & 0 \\ 0 & 0 & 1 \end{pmatrix}, C = c_{11} + c_{22} + c_{55} - 2(c_{12} - c_{15} + c_{25}). \quad (\text{A12})$$

$$\frac{1}{(1-\delta^2)} \begin{pmatrix} 1+\delta & 0 & \delta \\ 0 & 1 & 0 \\ 0 & 0 & 1-\delta \end{pmatrix}, C = c_{11} + c_{33} + c_{55} - 2(c_{13} - c_{15} + c_{35}). \quad (\text{A13})$$

$$\begin{pmatrix} 1 & \delta & 0 \\ 0 & 1 & \delta \\ 0 & 0 & 1 \end{pmatrix}, C = c_{44} + c_{66} + 2c_{46}. \quad (\text{A14})$$

$$\frac{1}{(1+\delta)} \begin{pmatrix} 1+\delta & 0 & \delta \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, C = c_{11} + c_{55} + 2c_{15}. \quad (\text{A15})$$

- <sup>1</sup> D.A. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991).
- <sup>2</sup> A. Georges, G. Kotliar, W. Krauth, and W. Rozenberg, *Rev. Mod. Phys.* **68**, 13 (1996); G. Kotliar *et al.*, *Rev. Mod. Phys.* **78**, 865 (2006); A.B. Shick and V.A. Gubanov, *Europhys. Lett.* **69**, 588 (2005); L.V. Pourovskii, M.I. Katsnelson, A.I. Lichtenstein, L. Havela, T. Gouder, F. Wastin, A.B. Shick, V. Drchal, and G.H. Lander, *Europhys. Lett.* **74**, 479 (2006).
- <sup>3</sup> P. Söderlind, *Europhys. Lett.* **55**, 525 (2001); P. Söderlind and B. Sadigh, *Phys. Rev. Lett.* **92**, 185702 (2004).
- <sup>4</sup> G. Roberts, A. Pasturel, and B. Siberchiot, *J. Phys.: Condens. Matter* **15**, 8377 (2003); *ibid.*, *Europhys. Lett.* **71**, 4112 (2005);

- <sup>5</sup> G. van der Laan, K.T. Moore, J.G. Tobin, B.W. Chung, M.A. Wall, and A.J. Schwartz, Phys. Rev. Lett. **93**, 097401 (2004); J.G. Tobin, K.T. Moore, B.W. Chung, M.A. Wall, A.J. Schwartz, G. van der Laan, and A.L. Kutepov, Phys. Rev. B **72**, 085109 (2005); K.T. Moore, G. van der Laan, R.G. Haire, M.A. Wall, and A.J. Schwartz, Phys. Rev. B **73**, 033109 (2006); K.T. Moore, G. van der Laan, M.A. Wall, A.J. Schwartz, and R.G. Haire, Phys. Rev. B **76**, 073105 (2007); J.G. Tobin *et al.*, J. Phys.: Condens. Matter **20**, 125204 (2008).
- <sup>6</sup> S.W. Yu, J.G. Tobin, and P. Söderlind, J. Phys.: Condens. Matter **20**, 422202 (2008).
- <sup>7</sup> J. Wong *et al.*, Science **301**, 1078 (2003).
- <sup>8</sup> O. Eriksson, J.D. Becker, A.V. Balatsky, and J.M. Wills, J. Alloys Compd. **287**, 1 (1999); X. Dai *et al.*, Science **300**, 953 (2003); P. Söderlind *et al.*, Phys. Rev. B **70**, 144103 (2004).
- <sup>9</sup> M.I. Baskes, Phys. Rev. B **62**, 15532 (2000).
- <sup>10</sup> J.A. Moriarty *et al.*, J. Phys.: Condens. Matter **14**, 2825 (2002).
- <sup>11</sup> W.H. Zachariasen, Acta Crystallogr. **5**, 660 (1952); **5**, 64 (1952).
- <sup>12</sup> B. Sadigh, P. Söderlind, and W.G. Wolfer, Phys. Rev. B **68**, 241101 (2003).
- <sup>13</sup> P. Söderlind, Phys. Rev. B **66**, 085113 (2002).
- <sup>14</sup> J.M. Wills, O. Eriksson, M. Alouani, and D.L. Price, in *Electronic Structure and Physical Properties of Solids*, edited by H. Dreysse (Springer-Verlag, Berlin, 1998), p. 148.
- <sup>15</sup> J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, and D.J. Singh, Phys. Rev. B **46**, 6671 (1992).
- <sup>16</sup> P. Söderlind, Phys. Rev. B **77**, 085101 (2008).
- <sup>17</sup> F. Cricchio, F. Bultmark, and L. Nordström, Phys. Rev. B **78**, 100404 (2008).
- <sup>18</sup> A. Migliori *et al.*, J. Alloys Compd. **444-445**, 133 (2007).
- <sup>19</sup> D.J. Chadi and M.L. Cohen, Phys. Rev. B **8**, 5747 (1973); S. Froyen, *ibid.*, 3168 (1989).
- <sup>20</sup> O.K. Andersen, Phys. Rev. B **12**, 3060 (1975).
- <sup>21</sup> O. Beckstein, J.E. Klepeis, G.L.W. Hart, and O. Pankratov, Phys. Rev. B **63**, 134112 (2001).
- <sup>22</sup> H. Kimizuka, S. Ogata, and J. Li, J. Appl. Phys. **103**, 053506 (2008).
- <sup>23</sup> C.D. Taylor, Phys. Rev. B **77**, 094119 (2008).
- <sup>24</sup> J. Bouchet, Phys. Rev. B **77**, 024113 (2008).
- <sup>25</sup> F.D. Murnaghan, Proc. Nat. Acad. Sci. U.S.A., **30**, 244 (1944).
- <sup>26</sup> J.P. Watt, J. Appl. Phys. **51**, 1520 (1980).
- <sup>27</sup> P. Söderlind, (unpublished).

<sup>28</sup> L. Benedict, (unpublished).

## FIGURES

FIG. 1: (Color online) The experimental<sup>1</sup> phase diagram of Pu.

FIG. 2: (Color online) Total energy as a function of strain parameter ( $\delta$ ). The symbols denoted Eq. A3, Eq. A4, and Eq. A5, correspond to the strains defined by Eqs. A3-A5 in the Appendix.

FIG. 3: (Color online) Total energy as a function of strain parameter ( $\delta$ ). The symbols denoted Eq. A6, Eq. A7, and Eq. A8, correspond to the strains defined by Eqs. A6-A8 in the Appendix.

## TABLES

TABLE I: Present calculations without orbital polarization and published with orbital polarization<sup>3</sup> (OP). Atomic volumes,  $V$ , in  $\text{\AA}^3$  and bulk moduli,  $B$ , in GPa. Experimental data<sup>18</sup> for cast  $\alpha$ -Pu at 297 K.  $B_{fix}$  is the bulk modulus evaluated at  $20.3 \text{ \AA}^3$ .

Method	$V$	$B$	$B_{fix}$
Present theory	19.0	59	25
With OP	20.3	50	50
Experiment	20.4	54.4	–

TABLE II: Elastic constants (GPa) associated with the strains defined by Eqs. A3-A15 in the Appendix.

A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	A14	A15
120.0	108.8	86.2	43.4	50.6	43.7	247.4	204.0	217.9	301.8	255.0	87.6	126.4

TABLE III: Elastic constants (GPa) obtained from the calculated moduli given in Table II combined with Eqs. A3-A15 in the Appendix.

$c_{11}$	$c_{22}$	$c_{33}$	$c_{44}$	$c_{55}$	$c_{66}$	$c_{12}$	$c_{13}$	$c_{23}$	$c_{15}$	$c_{25}$	$c_{35}$	$c_{46}$
120.0	108.8	86.2	43.4	50.6	43.7	-9.30	1.10	-11.5	2.21	2.02	2.19	-0.25

TABLE IV: Elastic compliance constants ( $10^{-3}$  GPa $^{-1}$ ) obtained from inverting the elastic-constant matrix (Table III).

$s_{11}$	$s_{22}$	$s_{33}$	$s_{44}$	$s_{55}$	$s_{66}$	$s_{12}$	$s_{13}$	$s_{23}$	$s_{15}$	$s_{25}$	$s_{35}$	$s_{46}$
9.52	10.9	14.0	23.0	28.3	22.9	2.03	1.58	3.10	-5.65	-6.58	-8.00	0.13

TABLE V: Presently calculated Voigt averages of  $B$ ,  $G$ , and  $\tilde{c}_{11}$  together with experimental data<sup>18</sup> for cast  $\alpha$ -Pu at 297 K. The unit is GPa.

Method	$B$	$G$	$\tilde{c}_{11}$
Present theory	30.6	49.9	97.1
Experiment	54.4	43.7	112.8





