PHYSICAL REVIEW B **108**, 104112 (2023)

Lattice dynamics and thermodynamics for δ-plutonium from density functional theory

Per Söderlind,[1] A. Landa,[1] L. H. Yang,[1] B. Sadigh,[1] and Sven P. Rudin[2]
[1]*Lawrence Livermore National Laboratory, Livermore, California 94550, USA*
[2]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

(Received 21 July 2023; accepted 15 September 2023; published 27 September 2023)

We present results from density functional theory (DFT) calculations of the lattice dynamics (phonons) and thermodynamics for δ-phase plutonium. The fully relativistic electronic structure is calculated assuming a three-dimensional noncollinear magnetic structure in conjunction with DFT and the general gradient approximation for the electron exchange and correlation interactions. The electronic-structure model is further enhanced by addressing strong orbital-orbital coupling via the conventional orbital-polarization (OP) scheme as has been successfully done for plutonium. The temperature dependence of the phonons is calculated within the self-consistent *ab initio* lattice dynamics approach. The obtained phonons compare very well with measurements although a modest overestimation of the transverse L-point $[\xi\xi\xi]$ phonon is acknowledged. Calculated thermal vibration amplitudes and the associated Debye-Waller temperatures are close to experiments. Lattice, electronic, and magnetic contributions to the heat capacity are predicted and consistent to a few percent with that deduced from experimental data. Good agreement is only achieved when a magnetic contribution to the specific heat is recognized. The parameter-free DFT+OP electronic model is thus capable of predicting phonon properties and thermodynamic behavior of δ-phase plutonium rather accurately.

DOI: 10.1103/PhysRevB.108.104112

I. INTRODUCTION

Plutonium metal remains a puzzle with an extraordinary phase diagram and other fascinating properties driven by its electronic structure for which there is currently no consensus [1]. The nature of the $5f$ electrons has been described in theoretical models ranging from localized [2,3], to partially localized [4–7], delocalized-fluctuating [8], delocalized but perturbed by significant relativistic and magnetic effects [9], or nonmagnetic with delocalized $5f$-band states [10]. Ironically, underscoring the confusion, two extremes of these $5f$-electron theories, the strongly localized [3] and the nonmagnetic delocalized [10], have been suggested to govern the $5f$-electron bonding and formation of the monoclinic ground-state α phase of plutonium. Regardless, if one seeks a theory that can bridge the α-δ transition, only models that describe the $5f$ electrons as delocalized (itinerant) or bonding survive [8,9]. Nonetheless, models specific for either the face-centered-cubic (fcc) δ phase [4–7] or the monoclinic α phase [3,10] may provide some limited insight into plutonium.

Naively, one expects experiments to identify the appropriate theory quickly, but plutonium does not make it easy. For example, focusing on the δ phase, photoemission data agree well with three very different models [2,5,9], as discussed in Ref. [11], and phonons are also well described by starkly contrasting theories [2,12,13]. After years of controversy regarding their existence, neutron-scattering experiments discovered magnetic moments [14]. Still, the measured magnetic form factor is equally well interpreted in a localized [14] or a delocalized [9] $5f$-electron model. Although magnetism is interesting in its obscurity, our opinion is that the nature of the $5f$ electrons in terms of their bonding character is more central to understanding plutonium than the details of the magnetism. For example, a dynamic moment [14] can for practical purposes be appropriately modeled by a static magnetic configuration, either in a paramagnetic disordered magnetic model [15] or, as has been suggested more recently, a noncollinear magnetic structure [13]. The reason is straightforward; if the moments fluctuate, the corresponding energy states must be close. Therefore, an appropriately chosen nonfluctuating (static) magnetic state must also be close in energy.

In this paper we return to the issue of lattice dynamics of δ-plutonium. We mentioned that phonons have rather successfully been calculated before (see a close comparison between various $5f$-electron models in Ref. [13]). In all these theories, however, two features in the phonon dispersions disagree with experiments [16], namely, (i) the slope of the lower-energy transverse (T_1) $X-\Gamma$ phonon approaching the Γ point, and (ii) the L-point transverse $[\xi\xi\xi]$ phonon (L_T). For (i), the slope is too stiff in the modeling, and for (ii), the L_T phonon is predicted to have significantly too high energy (frequency). We shall discuss the possible causes of these two inconsistencies. In addition, we calculate and present the thermal dependence of the δ-plutonium phonon dispersions. From these phonon results we deduce elastic-thermal behavior and thermodynamic properties such as thermal atomic mean-square displacements (vibration amplitudes) and their thermal dependence in terms of the Debye-Waller temperature. Considering phonon, electronic, and magnetic contributions, we calculate and compare the heat capacity with experiments.

Section II deals with computational details and methodology, and in Secs. III and IV we present our results and conclusions.

II. COMPUTATIONAL DETAILS AND METHODOLOGY

We model plutonium from first principles as a material with delocalized $5f$-band electrons that correlate through spin polarization, spin-orbit coupling, and orbital polarization [9] within density functional theory (DFT). The fundamental and necessary assumption in DFT relates to electron exchange and correlation, and the generalized gradient approximation is generally preferred for actinides including plutonium. The Perdew-Burke-Ernzerhof (PBE) form is adopted here [17]. We are foregoing the most accurate all-electron methods for the more efficient VASP pseudopotential method [18,19], where we have implemented variational orbital polarization (OP) as previously described in detail [20,21]. The Racah parameter of 65 meV, necessary in the DFT+OP formulation, has been calculated self-consistently with a separate all-electron full-potential linear muffin-tin orbital method [20]. In addition, we apply a simple fix for the p states that otherwise cause issues due to the spin-orbit interaction; see discussions and references in Ref. [20]. The procedure is to ignore the spin-orbit coupling for the p states.

The magnetic configuration is treated as a constraint to the calculations, and we have chosen to adopt the three-dimensional noncollinear 3Q arrangement proposed recently by Rudin [13]. The 3Q label (sometimes referred to as 3k) is due to the spin structure that combines three (equivalent) wave vectors Q in each of the three dimensions for the corresponding spin component. This configuration results in a structure where all equivalent bonds have the same bonding character, a feature also shared by the disordered moment model [15]. For these two magnetic states, the fcc structure is dynamically stable while for an antiferromagnetic configuration, such as $L10$, this is not the case [12,13,22]. Hence, the present electronic-structure model is as Rudin's [13], including orbital polarization and the modification of the spin-orbit coupling for the p states [20]. The physical effect of orbital polarization in plutonium is a stabilization (lowering of the energy) of the δ phase relative to the α phase (and other phases) for a more accurate representation of the phase diagram, while at the same time producing better atomic volumes for all six plutonium polymorphs [23]. We refer to our review paper for more details on DFT+OP and plutonium [9].

In VASP, the electronic states are treated with the projector augmented-wave method [24], with Fermi-Dirac broadening (0.2 eV), and a cutoff energy for the plane waves of 500 eV. Calculations with much smaller Fermi-Dirac broadening around 0.05 eV introduced insignificant changes to the phonon spectra, suggesting an insensitivity to the broadening scheme.

In Fig. 1, we compare the small-displacement-method [25] phonon calculations utilizing our 3Q DFT+OP approach together with Rudin's 3Q DFT results [13]. Here, the lattice constant is kept close to the experimental ($T = 600$ K), $a = 4.64$ Å, for both calculations. This value is reasonably close to our DFT+OP (zero-temperature) equilibrium value (4.613 Å), but rather expanded relative to Rudin's equilibrium DFT lattice constant [13] (4.52 Å). For the lattice dynamics calculations, we utilize a 64-atom supercell with one atomic displacement of $\delta\mathbf{a}$=(0.004, −0.004, 0.004) relative to the supercell Bravais lattice vectors and the phonons are obtained in the harmonic approximation at zero temperature [25]. The two calculations produce similar phonons that agree well with experiments, except in two places. Notice in Fig. 1 that the slope corresponding to the elastic constant C' is too large and the L_T zone-boundary phonon is too stiff. The calculated C' is overestimated by about 20%, and the L_T phonon is about 67% too large. It is worth noting that the calculations are performed for pristine and perfect plutonium while the sample in the experiments is a Pu-Ga alloy with various imperfections due to the nature of radiation damage in plutonium. We will return and discuss the discrepancies for C' and the zone-boundary phonon in the Results section.

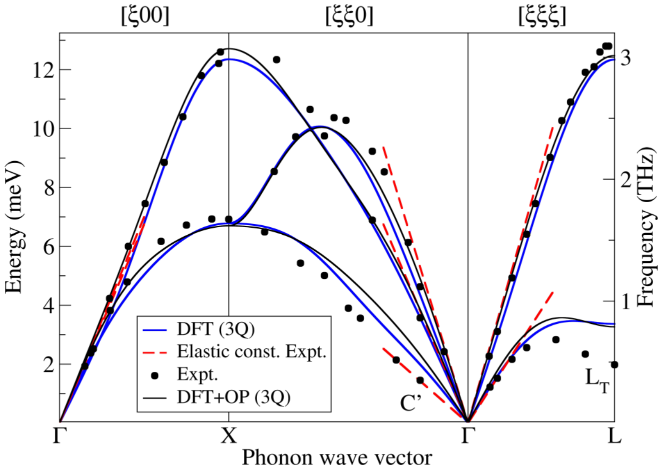

FIG. 1. Zero-temperature harmonic phonons obtained from the small-displacement method and x-ray thermal diffuse scattering at 300 K for 2 at. % Ga [16]. DFT refers to Rudin's results [13] and DFT+OP denotes present results. The red-dashed lines correspond to measured elastic constants [16]. The lattice constant in the calculations is 4.64 Å while it is 4.625 Å for the 2 at. % Ga alloy.

First-principles temperature effects on δ-plutonium′s phonon dispersions are addressed here by the relatively efficient self-consistent *ab initio* lattice dynamics (SCAILD) method [26]. Analogous to the small-displacement phonon calculation at zero temperature, we describe the fcc structure with a 64-atom supercell and consider five temperatures, 100, 300, 400, 500, and 600 K, while maintaining a fixed lattice constant at 4.64 Å. SCAILD, however, goes beyond the harmonic approximation and includes phonon-phonon interactions, thus taking anharmonic effects into account. For normal metals, one must consider thermal expansion but in the case of δ-plutonium, and particularly the 2 at. % Ga alloy, it is essentially zero due to the invar effect [27]. The invar effect has not been fully explained, but spin fluctuations [9,28] and anomalous phonon behavior [13] likely play important roles. SCAILD is an iterative method, and one must carefully confirm convergence before presenting a conclusive result. In the Results section we show explicitly the convergence of the free energies for the various temperatures.

The heat capacity C_v is calculated at a constant volume (lattice constant 4.64 Å). Because thermal expansion is near zero for δ-plutonium and the Ga-stabilized alloys [27], this is a reasonable approximation of the measured specific heat at constant pressure C_p. We divide the heat capacity into three terms,

$$C_v(T) = C_v^{\mathrm{lat}}(T) + C_v^{\mathrm{el}}(T) + C_v^{\mathrm{mag}}(T), \quad (1)$$

and we ignore any explicit contribution associated with electron-phonon coupling. There are phenomenological expressions for this contribution, but no straightforward way to compute from first principles. In Eq. (1), the first lattice term is determined from the SCAILD phonon density of states, while the second electronic term is modeled by the electronic density of states at the highest occupied energy level (Fermi level), $D(E_F)$, as

$$C_v^{\mathrm{el}}(T) = \frac{\pi^2}{3} D(E_F) k_B^2 T = \gamma_{\mathrm{el}} T. \tag{2}$$

The k_B parameter is the usual Boltzmann constant and γ_{el} the Sommerfeld electronic coefficient.

The last term in Eq. (1) is typically a small contribution from magnetism, and for δ-plutonium we have previously introduced a spin-fluctuation model where longitudinal spin fluctuations thermally populate excited energy states, $E_{\mathrm{LSF}}(T)$, that have been calculated [9,28]. These excitation energies deviate only slightly from linear with temperature and can be very accurately represented with a cubic polynomial for easy differentiation. From these excitation energies we establish the magnetic contribution to the specific heat as the partial derivative,

$$C_v^{\mathrm{LSF}}(T) = \left(\frac{\partial E_{\mathrm{LSF}}}{\partial T} \right)_V. \tag{3}$$

In principle, there should also be a magnetic contribution from transverse modes in a spin-fluctuation system, but we still need to develop the formalism to calculate this contribution. However, as we alluded to in the Introduction, transverse (rotating in space) spin fluctuations in δ-plutonium, based on our noncollinear calculations, are not expected to absorb much heat. Energies associated with such excitations are small and therefore the associated heat-capacity contribution is anticipated to be limited.

Strictly, the calculated heat-capacity contributions are all obtained at a constant volume, but as outlined above, the thermal expansion is negligible in the δ-plutonium system, so C_v is a good approximation of C_p derived from experimental data at ambient conditions.

III. RESULTS

In this section, we will introduce our temperature-dependent results. The SCAILD method is employed for this purpose and because it is a self-consistent approach, one must carefully ensure that the results are converged. For δ-plutonium, the process converges very effectively as shown in Fig. 2 which displays the lattice free energy as a function of SCAILD iterations for the various temperatures. The energies are shifted as noted in the plot for clarity. The phonon frequencies and phonon density of states also converge to a degree where no changes between iterations could be detected in a graphical representation.

Several calculations [2,12,13] of the phonon dispersions of the δ phase, all unalloyed at zero temperature, are in rather good agreement with the room-temperature measurement of the 2 at. % Ga alloy [16]. However, we show in Fig. 1 that the phonon dispersions associated with the elastic constant C' and the zone-boundary transverse L-point phonon are overestimated by about 20% and 67%, respectively. These are substantial discrepancies also present in other modelings [2,12,13]. Possible reasons for these inaccuracies could be that the calculations ignore the Ga content in the measured alloy or that temperature plays a role. Here, we address these possibilities and first note that calculations for C' as a function of Ga content in the δ phase show very strong Ga-induced softening of the order of 10% for the 2 at. % Ga alloy [29]. Hence, to a large degree, this explains the stiffer corresponding phonons for the unalloyed phase considered in the modeling. We have also performed so-called frozen phonon calculations for the zone-boundary phonon in question. This was done along the lines of what we published previously [30], but here for the 2 and 4 at. % Ga alloy within a sophisticated alloy treatment, namely, the coherent-potential approximation (EMTO-CPA-DLM; see Ref. [30] for details). These results are shown in Fig. 3. Notice that the L_T phonon depends close to linearly on Ga content (at a fixed lattice constant, 4.64 Å) with a negative

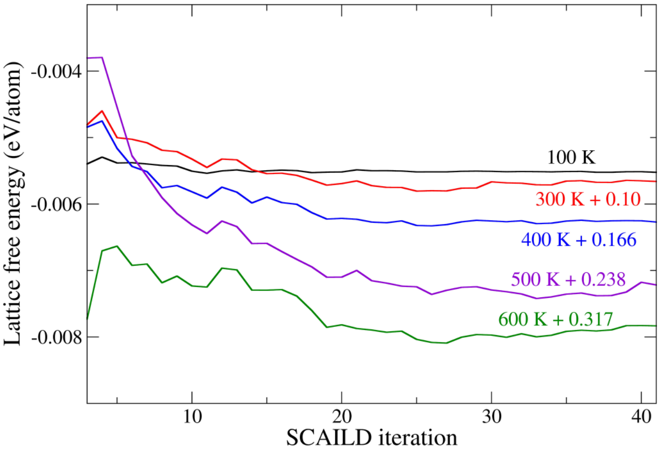

FIG. 2. Lattice free energies obtained from SCAILD at various temperatures as functions of the number of SCAILD iterations. The lattice constant is 4.64 Å.

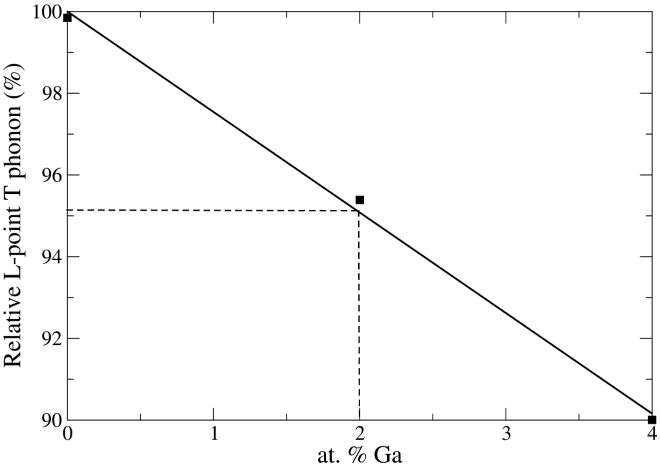

FIG. 3. Relative zone-boundary phonons obtained from frozen-phonon calculations with EMTO-CPA-DLM for the alloy treatment, at lattice constant 4.64 Å. The line represents a linear fit to the data. The dashed lines indicate the L_T phonon for the 2 at. % Ga alloy.

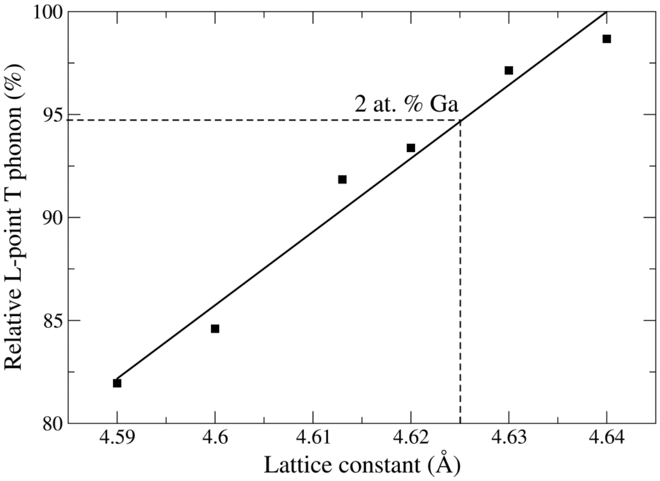

FIG. 4. Relative L_T phonon as a function of lattice constant calculated from the small-displacement phonon method at zero temperature. The solid line is a linear fit and the dashed lines indicate the lattice constant for the 2 at. % Ga alloy and the corresponding L_T phonon.

slope. At 2 at. % Ga, the calculations suggest a modest softening of about 5%. There is also a volume effect because the 2 at. % Ga has a smaller lattice constant (4.625 Å) than our phonon calculations assume (4.64 Å).

Next, we investigate the effect of the volume change on the L_T phonon driven by Ga. Rudin [13] already showed that the L_T phonon softens considerably with decreasing lattice constants. Here, we utilize the DFT+OP electronic structure and the small-displacement method at zero temperature and calculate full phonon spectra as functions of lattice constants. The results look like Rudin's [13], so they are not shown again, so instead we focus on the magnitude of the L_T phonon. In Fig. 4 we plot the relative L_T phonon magnitude for several lattice constants and aside from some numerical noise they fall on a line that suggests a 5% decrease of the L_T phonon for the change in volume due to the 2 at. % Ga. Hence, the total Ga effect on this zone-boundary phonon is about 10% when the alloy volume is considered. Next, we investigate the temperature dependence of the phonons to see if that is a cause of the predicted error for L_T.

In Fig. 5 we show our SCAILD phonons at $a = 4.64$ Å for $T = 100$, 300, 400, 500, and 600 K. These calculations indicate an overall softening of the phonons with temperature. That is an anomalous behavior because in conventional metals, temperature induces a thermal pressure that leads to a stiffening of the phonons. But δ-plutonium behaves oppositely, and its unique phonon characteristics combined with magnetic effects are likely the reasons for its peculiar thermal volume expansion and thermal softening of the bulk modulus [28,29]. Returning to the L_T phonon (see Fig. 5), it is insensitive to the temperature in agreement with x-ray thermal diffuse scattering [16]. The magnitude is somewhat smaller (0.70 THz) than predicted by the small-displacement method (0.81 THz) shown in Fig. 1, but the results in Fig. 5 are more accurate because SCAILD goes beyond the harmonic approximation and includes anharmonic contributions from phonon-phonon coupling.

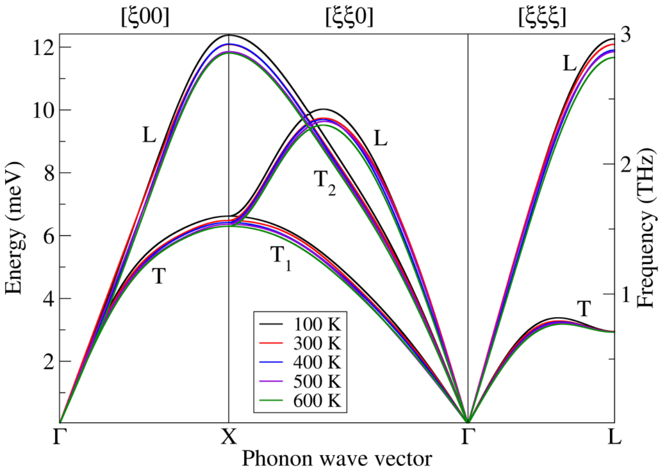

FIG. 5. SCAILD phonons for δ-plutonium at $T = 100$, 300, 400, 500, and 600 K at lattice constant 4.64 Å.

Our result on the L_T phonon, correcting for the Ga content, is 0.63 THz and that is significantly closer to the x-ray result of 0.485 THz [16] than other modeling (0.8–1.0 THz) [2,12,13]. Nevertheless, a considerable overestimation of about 30% remains. The reason for this remaining discrepancy is still being determined. Conceivably, it is related to material imperfections due to radiation self-damage in the alloy sample or a slight growth of α' phase (monoclinic α-phase alloy) in the sample. Ultimately, the softening of the [$\xi\xi\xi$] transverse mode is important to understand as it may be related to the δ to α' phase transition as discussed previously [16].

From our self-consistent phonon calculations, we can extract the thermally excited atomic mean-square displacements (mean-square vibration amplitudes) $\langle u^2 \rangle$ that can be directly compared to measured values for unalloyed δ-plutonium [31]. Most of the experimental data are taken at higher temperatures than our calculations, but at 600 K we find that theory is rather close to the observation from a powder diffractometer at the same temperature [31] (see Fig. 6). Because we calculate the temperature dependence of $\langle u^2 \rangle$, we can extract the Debye-

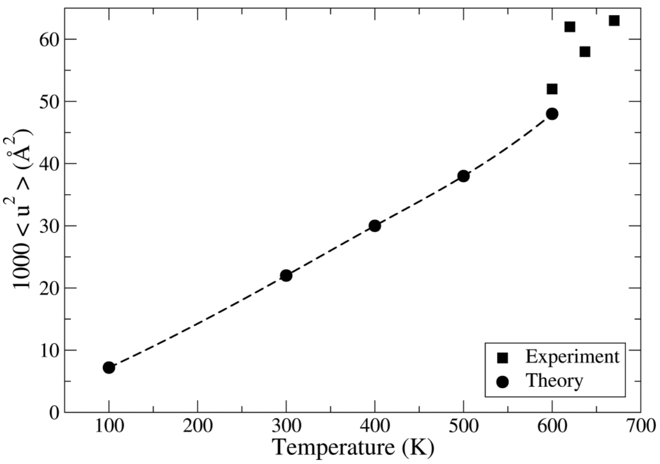

FIG. 6. Calculated (solid circles) and measured powder diffractometer [31] (solid squares) atomic mean square displacement for unalloyed δ-plutonium. The dashed line is a guide to the eye.

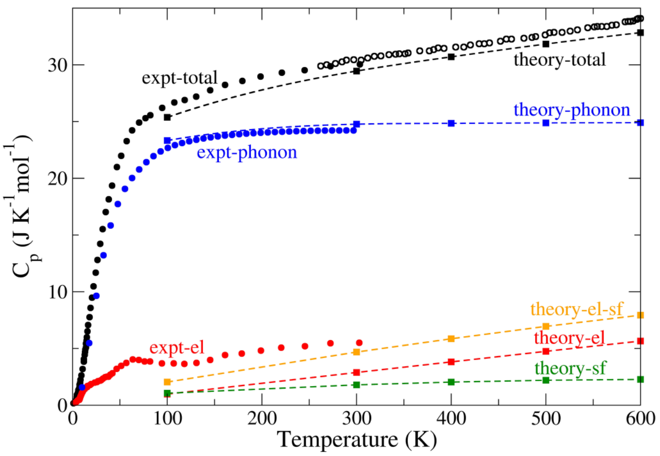

FIG. 7. Calculated (solid squares) and measured neutron scattering (solid [33] and open [27] circles) heat capacities for the δ-plutonium system. Measured samples are 5 wt. % Al [33] and 3 at.% Ga [27]. Dashed lines are guides to the eye. See main text for explanation of the various contributions.

Waller temperature Θ_{DW} that is proportional to the inverse square root of the slope of $\langle u^2\rangle$ versus temperature. Lawson *et al*. [31] report for unalloyed δ-plutonium $\Theta_{\mathrm{DW}} = 80$ K based on their measurements while our $\langle u^2\rangle$ data suggest a slightly larger value $\Theta_{\mathrm{DW}} = 83$ K. The corresponding temperatures for the gallium-stabilized δ-plutonium samples are considerably higher ($\Theta_{\mathrm{DW}} \sim 100$ K) [32].

The heat capacity is evaluated from Eq. (1) and shown in Fig. 7, together with experimental data on δ-plutonium alloys with 5 wt. % Al [33] up to 300 K and 3 at. % Ga [27] up to 600 K. The experimental electronic and phonon contributions are from the 5 wt. % Al sample [33]. The theoretical data shown in Fig. 7 are the lattice (phonon) contribution, the electronic contribution, the magnetic contribution, the sum of electronic and magnetic contributions, and finally the total heat capacity, i.e., the sum of all theoretical contributions. We notice in Fig. 7 the excellent agreement between the measured and calculated phonon heat capacity at 100 and 300 K, as expected considering that the phonons in Fig. 1 are in favorable agreement with measurements. The calculated total heat capacity is also very consistent with the two sets of measurements [27,33] from 100 to 600 K. Some minor discrepancy is anticipated because the theory considers an ideal and unalloyed plutonium material while the measured samples are alloys with natural imperfections. At higher temperatures, vacancies are produced and other imperfections may anneal contributing to the heat capacity in real materials but these effects are not addressed in our *ab initio* model. Nonetheless, the most significant difference between theory and experiment occurs at the lowest calculated temperature, 100 K. The reason appears to be that the theoretical electronic and magnetic contributions underestimate the electronic specific heat at low temperatures. The electronic specific heat [33] is not explicitly measured but deduced from subtracting the phonon contribution from the total, so it should contain any non-phonon-related parts such as that from spin fluctuation, for example. A possibility is that an α' phase is formed at lower temperatures [34], and that effect is not addressed in our calculations. We are also ignoring electron-phonon coupling which may be a factor. Finally, Lawson [27] suggests several different mechanisms at very low temperatures that are not easily computable within our first-principles approach and are consequently not addressed here.

At 300 K, however, the experimental electronic portion in Fig. 7 is actually very close to the sum of our calculated electronic and magnetic heat capacities. For the higher temperatures the phonon contribution is flat, and the temperature dependence is dominated by the electrons in our theory. The slope is essentially identical to the measurements of the total C_p at high temperatures [27], suggesting that there are no additional temperature-dependent contributions. Hence, the rather large contribution from anharmonic phonons that has been proposed [27] is inconsistent with our results.

IV. CONCLUSIONS

Our first-principles modeling (no fitting parameters) for δ-phase plutonium produces good phonons. The only significant inconsistencies with x-ray measurements, the $[\xi\xi 0]$ slope at Γ and the $[\xi\xi\xi]$ transverse phonon softening, are present in previous theoretical modeling but can mostly be explained by accounting for the 2 at. % Ga content in the measured sample. Still, a 30% discrepancy remains for the L_T phonon that may be related to imperfections and defects in the sample, growth of the α' phase, or deficiencies in our first-principles modeling.

The temperature dependence of the phonons indicates an anomalous softening with increasing temperature that, together with magnetic effects, likely explains the observed nonconventional thermal behaviors of properties such as atomic volume and bulk modulus in δ-plutonium. We emphasize that at least two mechanisms (phonons and magnetism) are probably responsible for the unique behaviors. Lawson [27] points out that the alloying dependences of the volume and the bulk modulus are entirely different: The atomic volume is strongly Ga-dependent while the opposite is true for the bulk modulus. Therefore, it seems unlikely that their respective thermal behavior is driven by only one mechanism but rather is a consequence of a combination of processes.

Our calculated thermodynamic properties, mean-square atomic displacements $\langle u^2\rangle$, Debye-Waller temperature Θ_{DW}, and heat capacity, all compare favorably with experiments considering that our calculations are performed assuming pure and pristine δ-plutonium. At the same time, the measurements are conducted on aluminum or gallium alloys with imperfections related to radiation-induced self-damage. There may also be the formation of the α' phase in the sample at low temperatures that is not addressed in our theory.

There are of course uncertainties in the calculations as well. First, for the heat capacity, the electron-phonon coupling is ignored, which may explain the slight underestimation of the theory. At low temperatures, the most significant discrepancy appears where the electronic contribution is proportional to T^2 and scales with the electronic density of states $D(E_F)$. This simple Sommerfeld electron model is consistent with the electron entropies deduced from the electronic structure but may not accurately represent low-temperature quantum effects. Additional low-temperature contributions related to electron correlation have been suggested [27] but are not easily addressed within our first-principles approach.

The accuracy and success of the present calculations hinge on magnetism. Excluding magnetic interactions leads to unrealistic bonding with unstable phonons and an underestimated lattice constant [9]. The importance of magnetism is also reflected in the heat capacity where we find good agreement with experiments only when a magnetic, spin-fluctuation, contribution is recognized. Lastly, significant anharmonic effects at high temperatures, as recently suggested [27], are not confirmed by our theory.

ACKNOWLEDGMENTS

We thank S. Hernandez, M. Surh, and A. Lawson for their valuable discussions. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. DE-AC52-07NA27344. This work was supported by the LDRD program at Los Alamos National Laboratory under Project No. 20210001DR and by the U.S. Department of Energy National Nuclear Security Administration under Contract No. 89233218CNA000001.

---

[1] P. Söderlind and G. Kotliar, in *Plutonium Handbook*, edited by D. L. Clark, D. A. Geeson, and R. J. Hanran, Jr., 2nd ed. (American Nuclear Society, La Grange Park, IL, 2019), Vol. 2, Chap. 14.
[2] X. Dai, S. Y. Savrasov, G. Kotliar, A. Migliori, H. Ledbetter, and E. Abrahams, Science **300**, 953 (2003).
[3] L. Huang and H. Lu, Phys. Rev. B **101**, 125123 (2020).
[4] M. Pénicaud, J. Phys.: Condens. Matter **9**, 6341 (1997).
[5] O. Eriksson, J. D. Becker, A. V. Balatsky, and J. M. Wills, J. Alloys Compd. **287**, 1 (1999).
[6] P. Söderlind and A. Landa, Modell. Simul. Mater. Sci. Eng. **11**, 851 (2003).
[7] A. Svane, L. Petit, Z. Szotek, and W. M. Temmerman, Phys. Rev. B **76**, 115116 (2007).
[8] B. Amadon, Phys. Rev. B **94**, 115148 (2016).
[9] P. Söderlind, A. Landa, and B. Sadigh, Adv. Phys. **68**, 1 (2019).
[10] P. Söderlind, J. M. Wills, B. Johansson, and O. Eriksson, Phys. Rev. B **55**, 1997 (1997).
[11] J. G. Tobin, P. Söderlind, A. Landa, K. T. Moore, A. J. Schwartz, B. W. Chung, M. A. Wall, J. M. Wills, R. G. Haire, and A. L. Kutepov, J. Phys.: Condens. Matter **20**, 125204 (2008).
[12] P. Söderlind, F. Zhou, A. Landa, and J. E. Klepeis, Sci. Rep. **5**, 15958 (2015).
[13] S. P. Rudin, J. Nucl. Mater. **570**, 153954 (2022).
[14] M. Janoschek, P. Das, B. Chakrabarti, D. L. Abernathy, M. D. Lumsden, J. M. Lawrence, J. D. Thompson, G. H. Lander, J. N. Mitchell, S. Richmond *et al.*, Sci. Adv. **1**, e1500188 (2015).
[15] A. Landa, P. Söderlind, and A. Ruban, J. Phys.: Condens. Matter **15**, L371 (2003).
[16] R. Xu, J. Wong, P. Zschack, H. Hong, and T.-C. Chiang, Europhys. Lett. **82**, 26001 (2008).
[17] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[18] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[19] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[20] B. Sadigh, A. Landa, A. Kutepov, and P. Söderlind, Appl. Sci. **9**, 5020 (2019).
[21] B. Sadigh, P. Söderlind, N. Goldman, and M. P. Surh, Phys. Rev. Mater. **6**, 045005 (2022).
[22] P. Söderlind, A. Landa, and B. Sadigh, Phys. Rev. B **66**, 205109 (2002).
[23] P. Söderlind and B. Sadigh, Phys. Rev. Lett. **92**, 185702 (2004).
[24] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[25] D. Alfè, Comput. Phys. Commun. **180**, 2622 (2009).
[26] P. Souvatzis, O. Eriksson, M. I. Katsnelson, and S. P. Rudin, Phys. Rev. Lett. **100**, 095901 (2008).
[27] A. C. Lawson, Philos. Mag. **99**, 1481 (2019).
[28] A. Migliori, P. Söderlind, A. Landa, F. J. Freibert, B. Maiorov, B. J. Ramshaw, and J. B. Betts, Proc. Natl Acad. Sci. USA **113**, 11158 (2016).
[29] P. Söderlind, A. Landa, J. E. Klepeis, Y. Suzuki, and A. Migliori, Phys. Rev. B **81**, 224110 (2010).
[30] P. Söderlind, A. Landa, B. Sadigh, L. Vitos, and A. Ruban, Phys. Rev. B **70**, 144103 (2004).
[31] A. C. Lawson, J. A. Roberts, B. Martinez, and J. W. Richardson Jr., in *Electron Correlations and Materials Properties 2*, edited by A. Gonis, N. Kioussis, and M. Ciftan (Kluwer Academic, New York, 2003), p. 21.
[32] A. C. Lawson, B. Martinez, J. A. Roberts, B. I. Bennet, and J. W. Richardson Jr., Philos. Mag. **80**, 53 (2000).
[33] J. C. Lashley, J. Singleton, A. Migliori, J. B. Betts, R. A. Fisher, J. L. Smith, and R. J. McQueeney, Phys. Rev. Lett. **91**, 205901 (2003).
[34] J. C. Lashley, A. Migliori, J. Singleton, R. McQueeney, R. A. Pereyra, J. L. Smith, and M. S. Blau, JOM **55**, 34 (2003).