



Electronically driven collapse of the bulk modulus in δ -plutonium

Neil Harrison^{a,1}

^aLos Alamos National Laboratory, Los Alamos, NM 87545

Edited by Zachary Fisk, University of California, Irvine, CA, and approved January 22, 2020 (received for review October 18, 2019)

Plutonium metal exhibits an anomalously large softening of its bulk modulus at elevated temperatures that is made all the more extraordinary by the finding that it occurs irrespective of whether the thermal expansion coefficient is positive, negative, or zero—representing an extreme departure from conventional Grüneisen scaling. We show here that the cause of this softening is the compressibility of plutonium's thermally excited electronic configurations, which has thus far not been considered in thermodynamic models. We show that when compressible electronic configurations are thermally activated, they invariably give rise to a softening of the bulk modulus regardless of the sign of their contribution to the thermal expansion. The electronically driven softening of the bulk modulus is shown to be in good agreement with elastic moduli measurements performed on the gallium-stabilized δ phase of plutonium over a range of temperatures and compositions and is shown to grow rapidly at small concentrations of gallium and at high temperatures, where it becomes extremely sensitive to hydrostatic pressure.

plutonium | bulk modulus | softening | electronic configurations

Plutonium (Pu) has the richest phase diagram among the metallic elements and, as a consequence, has proved to be the most challenging to grasp (1–4). In recent years, considerable advances have been made toward understanding some of Pu's unusual thermodynamic properties, such as its anomalously enhanced residual electronic heat capacity for an element (5–8) and its invar-like negative thermal expansion coefficient (9–11). The softening of the bulk modulus (12–16), by contrast, which occurs $\sim 50\%$ more rapidly with increasing temperature (relative to the melting temperature) than regular solids (17–23), has continued to remain a mystery. The increased likelihood that the entirety of the bulk modulus softening cannot be explained by phonons alone has led to the suggestion of an unconventional contribution originating from electronic degrees of freedom (16, 24).

A natural candidate for electronic degrees of freedom in Pu is provided by its unstable $5f$ -electron atomic shell, which has been shown to allow Pu to exist in a greater number of near-degenerate electronic configurations (25–27) and oxidation states (28) than other actinides and rare earths. Spectroscopic evidence for the presence of multiple near-degenerate electronic configurations in δ -phase Pu (δ -Pu) has been provided by way of X-ray (29) and neutron scattering (30) experiments. While the $5f$ electrons in partially filled shell configurations often hybridize with conduction electrons (6–8, 26, 31, 32), attempts to reconcile specific electronic structure models with the unusual temperature dependence of thermodynamic quantities such as the thermal expansion and bulk modulus have thus far been only at a qualitative level (*SI Appendix*) (10, 16, 33). The existing models have also not been shown to account for the sensitivity of elevated temperature thermodynamic quantities to the gallium (Ga) substitution used for stabilizing δ -Pu. The finding of a Ga substitution-dependent thermally activated behavior in the thermal expansion over a broad span of temperatures suggests instead that different electronic configurations can be regarded as being subject to statisti-

cal thermodynamics (9, 10). Strong support for this picture has recently been found in the magnetostriction and specific heat measurements (11).

We show here that, while the identity of the electronic configurations remains an open question (*Materials and Methods*), their compressibility is a crucial factor in considering their contribution to the bulk modulus. We show consideration of the compressibility to give rise to a previously unknown yet significant electronic contribution to the bulk modulus when different electronic configurations are thermally activated. Because this contribution is both negative and quadratic in the size of the difference in equilibrium volume (manifesting itself as a partial pressure) between the excited configurations and the lattice, it invariably leads to a softening of the bulk modulus with increasing temperature. Using a form for the free energy recently adapted from measurements of different thermodynamic quantities (10, 11), we show that the uncovered electronically driven softening of the bulk modulus is in agreement with temperature-dependent and Ga concentration-dependent resonant ultrasound spectroscopy results (12, 14–16). The softening is shown to become especially large in δ -Pu stabilized with small concentrations of Ga at temperatures well above room temperature, where it is further predicted to undergo a collapse under hydrostatic pressure.

Origin of the Bulk Modulus Softening

Studies of the thermodynamic properties of Pu have shown that their temperature dependences can be modeled by considering a partition function of the form (9–11, 16) $Z_{el} = \sum_i e^{-\frac{E_i}{k_B T}}$, where i refers to different electronic configurations with fixed energies E_i and atomic volumes V_i . Use of such a partition

Significance

A long-standing mystery in the material science of actinides concerns the question of why the bulk modulus of plutonium metal undergoes an anomalously large softening with increasing temperature compared to other metals. We show that a crucial step to understanding this phenomenon is taking into consideration the compressibility of thermally excited electronic configurations. We find this to lead to a previously unknown electronic softening contribution to the bulk modulus and a collapse of the bulk modulus when there exists a large partial pressure between different configurations.

Author contributions: N.H. designed research, performed research, analyzed data, and wrote the paper.

The author declares no competing interest.

This article is a PNAS Direct Submission.

This open access article is distributed under [Creative Commons Attribution License 4.0 \(CC BY\)](https://creativecommons.org/licenses/by/4.0/).

¹Email: nharrison@lanl.gov.

This article contains supporting information online at <https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1918281117/-DCSupplemental>.

First published February 18, 2020.

function for modeling thermodynamic quantities is warranted under circumstances where higher-energy configurations are mostly of a thermally activated nature (11, 34, 35). We find, however, that whereas the consideration of E_i and V_i as fixed and independent quantities is a reasonable approximation for modeling the thermal expansion, heat capacity, and the magnetostriction (9–11), this is not the case when considering the bulk modulus (Fig. 1). Since the relationship between E_i and V forms the basis of the definition of the bulk modulus of a material, neglect of this relationship has the potential to cause entire terms to be missing from the equation of state. Electronic structure calculations have shown that E_i and V are inextricably linked for each electronic configuration of Pu and other actinides (25, 27), making $E_i(V)$ a function of V or, equivalently, $E_i(\nu)$ a function

of the volume strain $\nu = \frac{V}{V_0} - 1$ (schematic in Fig. 2). A more generalized form

$$Z_{\text{el}}(\nu) = \sum_i e^{-\frac{E_i(\nu)}{k_B T}} \quad [1]$$

for the partition function that preserves information relating to the compressibility is therefore required.

Electronic structure calculations have shown that the $E_i(\nu)$ curves of the different configurations (illustrated in Fig. 2) are approximately parabolic (25, 27), enabling them to be represented in the reduced form (*Materials and Methods*)

$$\lim_{\nu \rightarrow \nu_i} E_i(\nu) = E_{i,0} + \frac{K_i [\nu - \nu_i]^2}{2N} \quad [2]$$

for small ν , where N is the atomic density and each of their contributions K_i to the bulk modulus is given by $K_i(\nu) = N \frac{\partial^2 E_i(\nu)}{\partial \nu^2}$ evaluated at $\nu = 0$. Here, $E_{i,0}$ is the energy minimum and $\nu_i = \frac{V_i}{V_0} - 1$ is the volume strain at the energy minimum for each configuration (Fig. 2). For the lowest-energy (ground-state) configuration, by definition $i = 0$, $V_i = V_0$, $\nu_i = 0$, and $E_{i,0} = 0$. The excited electronic configurations, by contrast, are in nonequilibrium states, causing them each to exert a statistical partial pressure $P_i(\nu) = -N \frac{\partial E_i(\nu)}{\partial \nu}$ on the surrounding lattice. In the limit of small strain, this pressure is simply

$$\lim_{\nu \rightarrow \nu_i} P_i(\nu) = -K_i [\nu - \nu_i]. \quad [3]$$

The ensemble average of the volume changes associated with these partial pressures is what ultimately drives the positive and negative electronic contributions to the thermal expansion (*Materials and Methods*) (11).

We proceed to calculate the electronic contribution to the bulk modulus by taking the second derivative $K_{\text{el}} = \frac{\partial^2 F_{\text{el}}}{\partial \nu^2} \Big|_T$ of the electronic component $F_{\text{el}} = -k_B T \ln Z_{\text{el}}(\nu)$ of the free energy with respect to the volume strain. Using the volume-dependent partition function given by Eq. 1 and $E_i(\nu)$ curves, we obtain

$$K_{\text{el}} = \sum_i p_i(\nu) K_i(\nu) - \frac{\sum_i p_i(\nu) P_i^2(\nu)}{N k_B T} + \frac{[\sum_i p_i(\nu) P_i(\nu)]^2}{N k_B T}, \quad [4]$$

where $p_i(\nu) = Z_{\text{el}}^{-1} e^{-\frac{E_i(\nu)}{k_B T}}$ is the probability of occupancy for each configuration.

The first term on the right-hand side of Eq. 4 is the probability-weighted sum of bulk moduli that has been assumed in prior models of the multiple electronic configurations in δ -Pu (9, 10, 16). While large changes in $K_i(\nu)$ with i (we discuss the extreme case where $K_i = 0$ for an excited configuration in *SI Appendix*) (10, 24) have the potential to yield significant changes in K_{el} with temperature, the individual bulk moduli contributions K_i of all of the electronic configurations obtained by density functional theory are found to all be very similar at $\nu = 0$ (25, 27). In *Materials and Methods*, we find these to have a mean value of $\bar{K}_i = 28.2$ gigapascal (GPa) and a SD of only $\sigma K_i = 5.0$ GPa. The first term in Eq. 4 is therefore not expected to lead to significant changes of the bulk modulus with increasing temperature.

The second term on the right-hand side of Eq. 4 has the potential to lead to much larger changes in the bulk modulus of δ -Pu with increasing temperature, making it the primary motivation of the present study. The origin of this term is the statistical partial pressure $P_i(\nu)$ between thermally excited configurations and the ground state that occurs as a result of their equilibrium volume strains ν_i being nonzero. For sufficiently small total strains $\nu - \nu_i$, this partial pressure is linear as shown in Eq. 3. Because

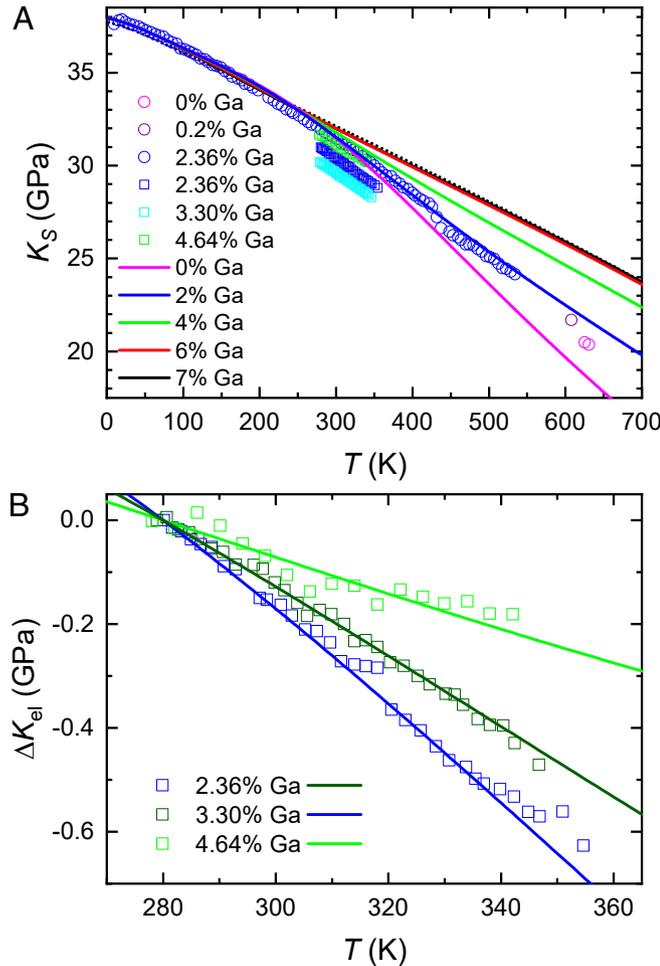


Fig. 1. (A) A comparison of experimental adiabatic bulk modulus data for different compositions x of δ -Pu $_{1-x}$ Ga $_x$ as indicated (12, 14–16) with the model calculations of $K_S = \gamma K_T$ (where $K_T = K_{\text{el}} + K_{\text{ph}}$ is the isothermal bulk modulus and γ is plotted in *SI Appendix, Fig. S2*) for different compositions, as indicated. As a point of reference, the black dotted line is the fitted functional form of K_{ph} (for $b = 18$); we have added this to $K_0 = 37.7$ GPa to bring it into alignment with the other curves at $T \approx 10$ K. (B) A comparison of the experimentally measured change in temperature-dependent electronic contribution to the bulk moduli $\Delta K_{\text{el}} = K_{\text{el}}(T) - K_{\text{el}}(280 \text{ K})$ for $x = 2.36\%$, 3.30% , and 4.64% (colored squares), having subtracted the measured values at $T = 280$ K and the calculated change $\Delta K_{\text{ph}} = K_{\text{ph}}(T) - K_{\text{ph}}(280 \text{ K})$ in K_{ph} (again for $b = 18$) relative to that at $T = 280$ K (assuming K_{ph} to be independent of x), with the equivalent change ΔK_{el} in the electronic contribution (colored lines) relative to that at $T = 280$ K calculated using Eq. 4. For noninteger values of x , calculated values of K_{el} are interpolated in x .

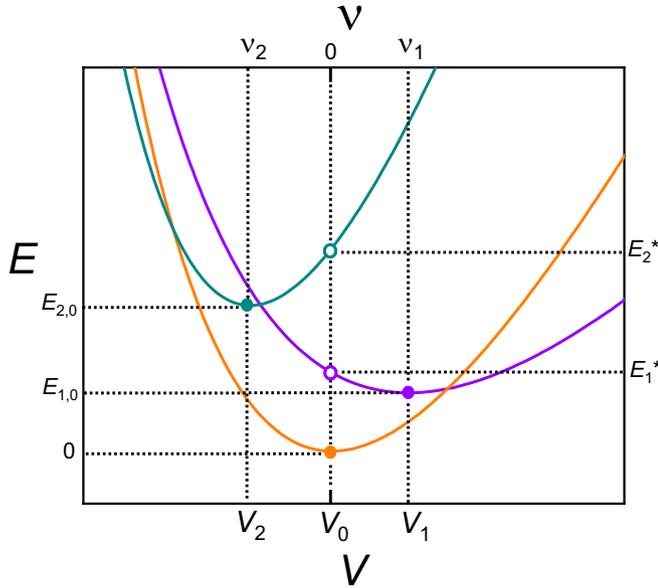


Fig. 2. Schematic $E(V)$ curves (lower axis) or $E(\nu)$ curves (upper axis) as described in the text according to Eq. 6, showing an approximately parabolic form. The energy minima $E_{i,0}$ and the energies E_i^* at $V = V_0$ or $\nu = 0$ in relation to the volumes V_i or volume strains ν_i are also indicated.

the partial pressure produces a negative quadratic contribution to the electronic bulk modulus in Eq. 4, it implies that thermally fluctuating electronic configurations invariably lead to a softening of the bulk modulus irrespective of whether $\nu_i > 0$, as for a positive contribution to the thermal expansion, or $\nu_i < 0$, as for a negative contribution to the thermal expansion (*Materials and Methods*).

The third term on the right-hand side of Eq. 4 is also determined by $P_i(\nu)$. However, because the probability factors $p_i(\nu)$ in this term are multiplied together, its overall contribution to the bulk modulus is weaker than that of the second term.

For the effect of hydrostatic pressure on the bulk modulus, this we estimate by taking the third derivative of the free energy with respect to ν and considering $\frac{\partial}{\partial P} = -K_T^{-1} \frac{\partial}{\partial \nu}$, where K_T is the isothermal bulk modulus, whereupon we obtain

$$\begin{aligned}
 K' = \frac{\partial K_{el}}{\partial P} \Big|_T &\approx \frac{1}{K_T [Nk_B T]^2} \left[\sum_i p_i(\nu) P_i^3(\nu) \right. \\
 &- 3 \left[\sum_i p_i(\nu) P_i^2(\nu) \right] \left[\sum_i p_i(\nu) P_i(\nu) \right] \\
 &\left. + 2 \left[\sum_i p_i(\nu) P_i(\nu) \right]^3 + \delta \right]. \quad [5]
 \end{aligned}$$

The first term on the right-hand side in Eq. 5, which originates from the derivative of the anomalous softening (i.e., the second term in Eq. 4), is found to dominate over the other terms. Its dominance implies that the sign and magnitude of the change in bulk modulus under pressure are determined almost entirely by the partial pressures of the electronic configurations, which in turn depend on the signs of ν_i . The cubic dependence on $P_i(\nu)$ implies K' has a more extreme sensitivity to composition than K_T . The last term on the right-hand side of Eq. 5, δ , is a correction term (*Materials and Methods*) that vanishes in the limit where the bulk moduli of the electronic configurations are the same.

Electronically Driven Softening Estimates

We proceed to estimate the electronic contribution to the bulk modulus and its pressure derivative in Fig. 3 from the multiple electronic configurations, by defining $E_i^* \approx E_{i,0} + K_i \nu_i^2 / 2N$ according to Eq. 2 and using the approximation $P_i \approx K_i \nu_i$ according to Eq. 3 (11). Low-temperature specific heat measurements have shown that the Debye temperature $\Theta_D \approx 100$ kelvin (K) remains largely unchanged as a function of the Ga concentration x used to stabilize the δ phase (11), which is consistent with the parabolic approximation given by Eq. 2. We therefore assume that the bulk modulus of the ground-state electronic configuration also remains unchanged and adopt the value $K_0 = 37.7$ GPa found in δ -Pu $_{1-x}$ Ga $_x$ for $x = 2.36\%$ (14) by way of resonant ultrasound measurements. Since the bulk moduli of the excited electronic configurations in δ -Pu are unknown, yet are predicted to fall within a narrow range of possible values, we further assume the excited configurations to have bulk moduli K_i that are similar to that of the ground-state configuration (*Materials and Methods*).

In calculating the electronic contribution to the bulk modulus, we use excitation energies E_i^* and equilibrium volume strains ν_i determined (11) (values listed in *Materials and Methods*) from fitting thermal expansion (9, 10) and temperature-dependent magnetostriction (11) measurements, the results of which were further validated using heat capacity measurements (5, 11). The resulting calculations of the electronic contribution to the bulk modulus as a function of T and x using Eq. 2 are shown in Fig. 3A. Both of the previously determined (11) excited electronic configurations (E_1^* and E_2^*) are found to lead to discernible reductions in the bulk modulus with increasing temperature. Since E_1^* leads to a positive thermal expansion (11) whereas E_2^* leads to a negative thermal expansion (9, 10), yet both lead to a softening of the bulk modulus, it is the combination of both of these terms that is responsible for the departures from simple Grüneisen scaling in δ -Pu (*Materials and Methods*).

The degree of bulk modulus softening with temperature is significantly more pronounced for the higher excitation energy $E_2^* = 125$ meV (for $x = 2\%$) at small Ga concentrations due to the large ($\approx 13\%$) difference between its equilibrium volume V_2 and the ground-state volume V_0 . Very similar results at high temperatures would therefore be obtained on neglecting E_1^* and ν_1 and considering only the excitation energy E_2^* and volume strain ν_2 determined from the invar model fits (9, 10) (*Materials and Methods*). According to our calculation, this dominant excitation is predicted to yield a reduction in the bulk modulus that is as large as ≈ 8 GPa in pure δ -Pu at 700 K; beyond this temperature the δ phase becomes unstable (2).

Turning to the effect of hydrostatic pressure on the bulk modulus, since the leading term on the right-hand side of Eq. 5 varies as the cube of the partial pressure, K' is found to be strongly dependent on x . The invar contribution, which is characterized by a negative partial pressure, clearly dominates, leading to the prediction of a dramatic collapse of the bulk modulus under pressure and at high temperatures for small concentrations of Ga in Fig. 3B.

Comparison with Experiment

To compare the calculations against experimental data, we must also include the phonon contribution to the bulk modulus, which is known to reduce the bulk modulus of most materials by $\approx 20\%$ upon reaching $T = T_m/2$ (17–23), where T_m is the melting temperature ($T_m \approx 912$ K in Pu). While a universal model able to accurately describe the reduction in bulk modulus K_{ph} attributable to phonons in all materials has yet to be developed (17–23), the model of Ida (18, 19) has been shown to provide

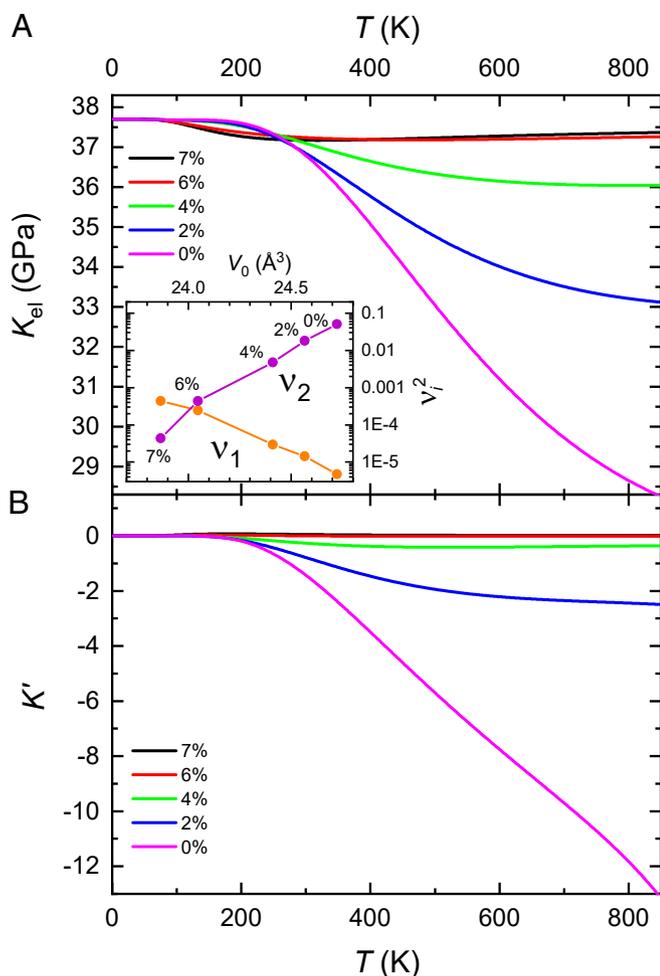


Fig. 3. (A) K_{el} of $\text{Pu}_{1-x}\text{Ga}_x$ as a function of temperature T and Ga composition x (colored lines) calculated by way of Eq. 2, using the parameters listed in *Materials and Methods* for $x = 2\%$ and $x = 7\%$, which are extrapolated for $x = 0\%$ and interpolated for $x = 4\%$ and 6% . Inset shows ν_i^2 for $i = 1$ and 2 versus V_0 , with the percentage of Ga (x) indicated for each point. It is important to note that because $P_i = 0$ for the ground-state configuration, the denominators of the second and third terms in Eq. 4 do not lead to a divergence at $T = 0$. (B) Calculated pressure derivative of the bulk modulus K' according to Eq. 5.

a good description of the heat capacity of δ -Pu at temperatures above room temperature (24)—most notably an observed upturn in the heat capacity above ~ 600 K. Since the electronic and phonon contributions to the free energy are additive, this should, to a first approximation, be similarly true for derivatives, in which case $K_T = K_{el} + K_{ph}$ (*Materials and Methods*) for the isothermal bulk modulus. To compare with the adiabatic bulk modulus K_S obtained by ultrasound measurements, we use the fact that $K_S = \gamma K_T$, where $\gamma \approx 1$ for δ -Pu (*Materials and Methods* and *SI Appendix*).

In comparing the calculation with experimental bulk modulus data, only the phonon scaling coefficient b is adjusted. The remainder of the parameters is taken from published results (*Materials and Methods*). Fig. 1A shows that on combining the electronic and lattice vibration contributions, a phonon coefficient $b = 18$ (*Materials and Methods*) yields a K_S that closely follows the temperature dependence of bulk modulus measured in δ - $\text{Pu}_{1-x}\text{Ga}_x$ (with $x = 2.36\%$) (14) over a broad range of temperatures. Establishing further confidence in the model is the finding that the value of the phonon coefficient $b = 18$ that best fits the phonon part of the bulk modulus is very similar to the

value $b = 16$ that best fits the anharmonic phonon contribution to the high-temperature heat capacity (24). For this value of b , K_{ph} also accounts for an $\approx 20\%$ reduction in K_S with temperature at $T_m/2 \approx 456$ K (the remainder coming from the reduction in K_{el}), therefore making the phonon contribution to the softening comparable to that in other materials (17–23).

Having established the approximate form of the (assumed) x -independent phonon contribution K_{ph} to the bulk modulus softening, we can proceed to subtract this contribution from measurements of K_S in other samples to isolate the electronic contribution K_{el} to the bulk modulus softening and to investigate its changes with temperature and composition x . Fig. 1B shows the T dependence of the residual electronic contribution K_{el} for samples of three different compositions (12), $x = 2.36\%$, 3.30% , and 4.64% , after having subtracted K_{ph} as well as an offset (*Materials and Methods*) to bring the measured curves into alignment at $T = 280$ K. Despite the limited range in temperature of these measurements, significant differences in the temperature dependences are clearly discernible. On comparing the model predictions of K_{el} calculated for the same x compositions using Eq. 4 with the experimental curves in Fig. 1B, we find them to be in excellent agreement—with regard to both the temperature dependence and the x dependence of the temperature dependence of the experimental data. Apart from a subtraction of the values of K_{el} at $T = 280$ K that is necessary to eliminate offsets between the experimental curves, no adjustment has been made to K_{el} calculated using Eq. 4—the parameters used are those determined elsewhere by fitting other thermodynamic quantities (11).

The other compositions, $x = 0.2\%$ and $x = 0\%$ (15, 16) in Fig. 1A, exhibit trends relative to other compositions that are consistent with the model calculations of K_S . However, the lack of temperature-dependent data for these compositions means we cannot isolate the electronic component for these compositions.

Turning once again to the effect of pressure, a fundamental question concerns whether prior measurements of a negative thermal expansion serve as a reliable predictor of a pressure-induced bulk modulus softening (10, 36). Existing experimental studies have focused only on the effect of hydrostatic pressure on the bulk modulus at ambient temperature (≈ 300 K) (37–39), the results of which are compared with the model calculations at 300 K (from Fig. 1B) in Fig. 4. Importantly, Eq. 5 is found to yield a pressure-induced change in δ -Pu whose negative sign agrees with the softening obtained experimentally; on taking an average of the δ -Pu data points in Fig. 4 (including both Ga-stabilized and americium [Am]-stabilized δ -Pu), we obtain $K' = -3 \pm 2$. The calculated value is clearly different from the positive (i.e., stiffening) $K' = +9 \pm 2$ value measured in α -Pu (plotted for comparison) (38) and the stiffening $K' = +4$ expected for a normal metal. However, the degree of scatter in the experimental data, the magnitude of the error bars, and the lack of temperature-dependent data prevent firm conclusions from being reached concerning the absolute magnitude, the doping dependence, or the volume dependence of K' (*SI Appendix*).

Figs. 3B and 4 show that a significant increase in the observable pressure-induced softening of Ga-stabilized δ -Pu could in principle be achieved by increasing the experimental temperature, which would also enable a more robust verification of the role of excited electronic configurations to be made. Access to higher temperatures would also enable such experiments to be carried out on pure δ -Pu.

Discussion

By taking into consideration the compressible nature of the previously isolated multiple electronic configurations in δ -Pu (9–11), we have discovered a previously unknown yet significant electronic contribution to the bulk modulus. We find this contribution to be primarily responsible for the excess softening of the

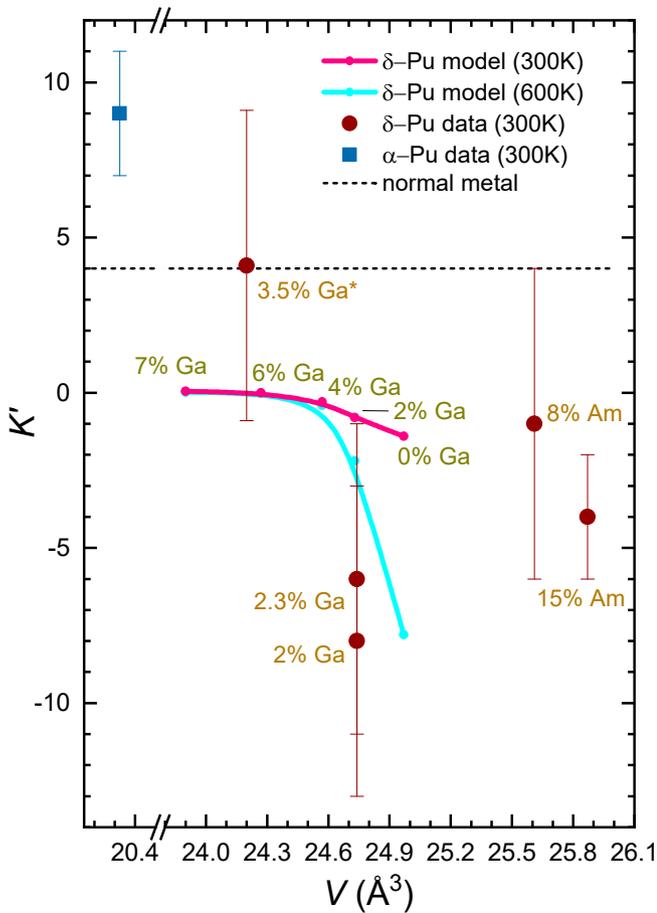


Fig. 4. Calculated pressure derivative of the bulk modulus K' of Ga-stabilized δ -Pu at 300 K (pink line and points) according to Eq. 5 versus atomic volume V at 300 K for different concentrations x of Ga as indicated. This is compared with experimental data for Ga- and Am-stabilized δ -Pu for different concentrations x as indicated (brown circles). Also shown, for comparison, are the value (light blue square) for α -Pu (2.3% Ga), the calculated Ga-stabilized δ -Pu values at 600 K (cyan line and points), and the value expected for a normal metal (black dashed line). All of the experiments were performed on ^{239}Pu with the exception of the sample with $x=3.5\%$, for which ^{242}Pu was measured.

bulk modulus in Pu, the dominant energy scale of which is the same as that previously associated with the invar effect (9, 10). The effect of the electronically driven softening is discernible in Ga composition-dependent experiments close to room temperature, but is shown to be strongly enhanced at temperatures substantially above room temperature in δ -Pu $_{1-x}$ Ga $_x$ samples with low concentrations of Ga. The bulk modulus is further shown to soften under pressure, as found experimentally (36–38), and is further predicted to undergo a collapse at low concentrations of Ga and high temperatures. Conversely, the electronic contribution to the softening is expected to be much smaller for samples with large concentrations of Ga at high temperatures, providing an opportunity for the phonon contribution K_{ph} to be more accurately isolated in future studies.

What constitutes a significant advance in the present approach to modeling the bulk modulus is that the softening is based entirely on the same free energy that has been shown to accurately describe other thermodynamic quantities as a function of temperature and Ga composition. These include the experimentally observed thermal expansion (9, 10), magnetostriction (11), and heat capacity (5, 11, 24). It also involves the same energy scale associated with the invar effect and detected in neutron

scattering experiments (30). Our results reveal the central role played by statistical thermodynamics in the equation of state in plutonium near ambient pressure.

Materials and Methods

Parameters Used in Bulk Modulus Calculations. We assume $K_0 = K_1 = K_2 = 37.7$ GPa (14). We also assume E_1^* to extrapolate linearly from 22.8 meV at $x=2\%$ to 41.0 meV at $x=7\%$ and E_2^* to extrapolate linearly from 125 meV at $x=2\%$ to 70 meV at $x=7\%$ (11). For $x=0, 2, 4, 6,$ and 7% , $\nu_1 = 0.0022, 0.0038, 0.0054, 0.016,$ and 0.021 , while $\nu_2 = -0.22, -0.13, -0.069, -0.021,$ and -0.0066 , respectively (11). According to prior invar model fits (10), $E_2^* = 121$ meV while $\nu_2 = -0.17$.

Energy versus Volume Curves. To calculate $K_i(\nu)$, we turn to a generalized model of cohesion in metals. The total internal energy for a given electronic configuration i is determined by a balance between Coulomb ($\propto \frac{1}{a}$) and kinetic ($\propto \frac{1}{a^2}$) energy terms, leading to an energy curve of the form $E_i(a) = a_0 - \frac{a_1}{a} + \frac{a_2}{a^2}$ (40), where a is the lattice spacing and $a_0, a_1,$ and a_2 are constants. One possibility in Pu is that each $E_i(a)$ curve corresponds to a different number of $5f$ electrons, $n_f = 0, 1, 2, \dots$, confined to the atomic core (25, 27). Alternative possibilities are that the different electronic configurations correspond to different correlated ground states produced by strong hybridization (10, 31), different electronic configurations with different magnetic moments (16), or different configurations within a duality picture in which the $5f$ electrons are partitioned between itinerant states and localized states subject to hybridization (26). We can obtain $E_i(\nu)$ curves in face-centered cubic δ -Pu by the substitution of $a = \sqrt[3]{4V}$ and $V = V_0 [1 + \nu]$ into $E_i(a)$, which yields

$$E_i(\nu) = E_{i,0} + \frac{9K_{i,0}}{2N} \left[1 - 2[1 + \nu - \nu_i]^{-\frac{1}{3}} + [1 + \nu - \nu_i]^{-\frac{2}{3}} \right]. \quad [6]$$

The parabolic approximation in Eq. 2 is obtained by making a Taylor series expansion of Eq. 6 about $\nu - \nu_i$. The energy minimum for each curve is given by $E_{i,0} = a_0 - \frac{1}{4}[a_1^2/a_2]$ while the bulk modulus at the minimum is given by $K_{i,0} = \frac{9}{8}[a_1^2/a_2]$.

Density Functional Theory Estimates. Double differentiation of Eq. 6 yields $K_i = K_{i,0} [5[1 + \nu - \nu_i]^{-\frac{8}{3}} - 4[1 + \nu - \nu_i]^{-\frac{7}{3}}]$. According to the results of Eriksson et al. (25), $K_i = 21.8, 34.5, 36.4,$ and 28.5 GPa for $n_f = 2, 3, 4,$ and 5 , respectively, when $\nu = 0$. According to the results of Svane et al. (27) $K_i = 26.0, 28.0, 31.0, 24.4, 20.6, 33.9,$ and 25.6 GPa for $n_f = 0, 1, 2, 3, 4, 5,$ and 6 , respectively.

The calculation of $K' = NK_i \frac{\partial^3 E_i(\nu)}{\partial \nu^3}$ from the third derivative of Eq. 6 yields $K' = 4$ at $\nu = 0$ for a normal metal. However, the absence of a discernible dependence of the Debye temperature on x (11) suggests that K' is actually closer to zero for the ground-state configuration of δ -Pu, thereby further justifying the use of a parabolic approximation for small ν in the present study.

Thermodynamics of Multiple Configurations. For the thermal expansion, one differentiates the free energy once with respect to ν to obtain $\frac{\partial F_{\text{el}}}{\partial \nu} |_{T,P} = -P = \sum_i p_i(\nu) K_i [\nu - \nu_i]$, where we have again made use of the parabolic approximation given by Eqs. 2 and 3. Since the total pressure $P \approx 0$ during experiments under ambient conditions, ν and ν_i can be separated above to yield $\nu = \frac{\sum_i p_i(\nu) \nu_i}{\sum_i p_i(\nu) K_i}$. Here, the numerator is equivalent to a summation over partial pressures, where the total pressure is ambient pressure. Meanwhile, the denominator is equivalent to the first term of Eq. 4, meaning that it is equivalent to the bulk modulus that one obtains on neglecting excitations. If we constrain the bulk moduli to be similar for all relevant configurations (i.e., $K_i = K_0$), then the denominator becomes K_0 and we obtain the much simpler form: $\nu \approx \sum_i p_i(\nu) \nu_i$. It is instructive to express Eq. 4 in a similarly reduced form by setting $K_i = K_0$ for all configurations and defining $k_{\text{el}} = \frac{K_{\text{el}}}{K_0} - 1$, whereupon we obtain $k_{\text{el}} \approx \frac{K_0}{Nk_B T} [-\sum_i p_i(\nu) \nu_i^2 + [\sum_i p_i(\nu) \nu_i]^2]$, in which the negative term inside the parentheses dominates.

Grüneisen's Law Violation. Grüneisen's law in its original form given by $\Gamma = \frac{\alpha_V V_m K_T}{C_V}$ is violated because α_V , which is the temperature derivative of ν , is proportional to the sum over ν_i contributions, whose individual values are both positive and negative, thereby giving rise to sign changes (11). By contrast, the bulk modulus softening depends on a summation over ν_i^2

contributions, causing K_{el} always to have the same negative sign. The heat capacity, meanwhile, depends only on the energies E_i , which are positive (or zero) and indirectly related to ν_i .

In the case of the pressure derivative, the last term on the right-hand side of Eq. 5 is given by $\delta = 3NK_B T [(\sum_i p_i(\nu) P_i(\nu)) / (\sum_i p_i(\nu) K_i) - (\sum_i p_i(\nu) P_i(\nu) K_i)]$, which vanishes when K_i are the same for all configurations.

Additive Electronic and Phonon Bulk Moduli. Since the isothermal bulk modulus is given by $\frac{\partial^2 F}{\partial V^2} |_T$ where the free energy $F = F_{el} + F_{ph}$ is the summation of electronic and phonon contributions, we expect that $K_T = K_{el} + K_{ph}$. The precise form of the dependence of F_{ph} leading to K_{ph} is still an area of active debate (17–23). According to Ida (18) $K_{ph}(T) = K_0 [(\frac{T}{T_0} - 1)]$, where $T_0 = 1.39 \times 10^5$ is the temperature scale associated with lattice vibrations, $(\Delta l / l)_{ph}$ is the thermal expansion of the lattice attributable to phonons (11) (SI Appendix, Fig. S1), and Q is the vibrational elongation determined by solving $Q = \frac{T}{T_0} e^{2b[(\frac{\Delta l}{l})_{ph} + Q]}$.

Calculating the Adiabatic Bulk Modulus. According to basic thermodynamics $\gamma = \frac{\alpha_V^2 V_m T K_T}{C_V} + 1$, where V_m is the molar volume and the thermal expansion

coefficient $\alpha_V = 3\alpha_l$ and heat capacity C_V values have been estimated (11), yielding the T -dependent γ in SI Appendix, Fig. S2. We find γ to be close to unity, especially for $x \approx 2\%$.

Offsets in the Measured Bulk Modulus. Significant vertical displacements between bulk moduli values for different samples of the same composition together with the absence of a trend in x near room temperature in Fig. 1A indicate that extrinsic factors unrelated to K_{el} and K_{ph} contribute random vertical offsets to the experimental data that are of order 1 or 2 GPa. Similar observations have been made in measuring control samples made of aluminum. In Fig. 1B, the extrinsic and phonon contributions are removed from the analysis of the $x = 2.36\%$, 3.30%, and 4.64% datasets by subtracting the values of the bulk moduli at $T = 280$ K.

Data Availability. Parameters for reproducing the calculated curves are included in the main text and in SI Appendix.

ACKNOWLEDGMENTS. This work was performed under the Los Alamos National Laboratory Directed Research and Development (LDRD) program, project “20180025DR.” I thank Albert Migliori, Boris Maiorov, Angus Lawson, and Paul Tobash for insightful discussions.

1. K. T. Moore, G. van de Laan, Nature of the $5f$ states in actinide metals. *Rev. Mod. Phys.* **81**, 235–298 (2009).
2. S. S. Hecker, Plutonium – an element at odds with itself. *Los Alamos Sci.* **26**, 16–23 (2000).
3. S. S. Hecker, D. R. Harbur, T. G. Zocco, Phase stability and phase transformations in Pu-Ga alloys. *Prog. Mater. Science* **49**, 429–485 (2004).
4. J. L. Smith, E. A. Kmetko, Magnetism or bonding: A nearly periodic table of the transition elements. *J. Less Common Met.* **90**, 83–88 (1983).
5. J. C. Lashley et al., Experimental electronic heat capacities of α - and δ -plutonium: Heavy fermion physics in an element. *Phys. Rev. Lett.* **91**, 205901 (2003).
6. J. H. Shim, K. Haule, G. Kotliar, Fluctuating valence in a correlated solid and the anomalous properties of δ -plutonium. *Nature* **446**, 513–516 (2007).
7. J.-X. Zhu et al., Spectral properties of δ -plutonium: Sensitivity to $5f$ occupancy, *Phys. Rev. B* **76**, 245118 (2007).
8. N. Lanatà, Y. Yao, C.-Z. Wang, K.-M. Ho, G. Kotliar, Phase diagram and electronic structure of praseodymium and plutonium. *Phys. Rev. X* **5**, 011008 (2015).
9. A. C. Lawson, J. A. Roberts, B. Martinez, J. W. Richardson, Invar effect in Pu-Ga alloys. *Philos. Mag. B* **82**, 1837–1845 (2002).
10. A. C. Lawson et al., Invar model for δ -phase Pu: Thermal expansion, elastic and magnetic properties. *Philos. Mag.* **86**, 2713–2733 (2006).
11. N. Harrison et al., Phase stabilization by electronic entropy in plutonium. *Nat. Commun.* **10**, 3159 (2019).
12. P. Söderlind, A. Landa, J. E. Klepeis, Y. Suzuki, A. Migliori, Elastic properties of Pu metal and Pu-Ga alloys. *Phys. Rev. B* **82**, 224110 (2010).
13. M.-H. Nadal, L. Bourgeois, Elastic moduli of Pu and Ga stabilized δ -Pu: Experimental data and phenomenological behavior at high temperatures. *J. Appl. Phys.* **108**, 033512 (2010).
14. Y. Suzuki et al., Temperature dependence of elastic moduli of polycrystalline β plutonium. *Phys. Rev. B* **84**, 064105 (2011).
15. F. J. Freibert, J. N. Mitchell, T. A. Saleh, A. Migliori (2012) *Instability and anharmonicity in plutonium thermo-physical properties* (Los Alamos National Laboratory, NM, 2012). <https://permalink.lanl.gov/object/tr?what=info:lanl-repo/lareport/LA-UR-12-22830>. Accessed 4 February 2020.
16. A. Migliori et al., Origin of the multiple configurations that drive the response of δ -plutonium's elastic moduli to temperature. *Proc. Natl. Acad. Sci. U.S.A.* **113**, 11158–11161 (2016).
17. M. Born, Thermodynamics of crystals and melting. *J. Chem. Phys.* **7**, 591–603 (1939).
18. Y. Ida, Theory of melting based on lattice instability. *Phys. Rev.* **187**, 951–958 (1969).
19. Y. Ida, Anharmonic effect on heat capacity of solids up to the critical temperature of lattice instability. *Phys. Rev. B* **1**, 2488–2496 (1970).
20. Y. P. Varshni, Temperature dependence of the elastic constants. *Phys. Rev. B* **2**, 3952–3958 (1970).
21. J. H. Rose, J. R. Smith, F. Guinea, J. Ferrante, Universal features of the equations of state of metals. *Phys. Rev. B* **29**, 2963–2969 (1984).
22. O. L. Anderson, D. G. Isaak, S. Yamamoto, Anharmonicity and the equation of state for gold. *J. Appl. Phys.* **65**, 1534–1543 (1989).
23. R. M. Dilglov, H. Abramovich, Temperature variation of the isothermal bulk modulus in solids: Thermo-elastic instability and melting. *J. Appl. Phys.* **125**, 065104 (2019).
24. A. C. Lawson, Thermodynamics of the bulk modulus of delta phase plutonium alloys. *Philos. Mag.* **99**, 1481–1498 (2019).
25. O. Eriksson, J. N. Becker, A. V. Balatsky, J. M. Wills, Novel electronic configuration in δ -Pu. *J. Alloys Compd.* **287**, 1–5 (1999).
26. J. W. Wills et al., A novel electronic configuration of the $5f$ states in δ -plutonium as revealed by the photo-electron spectra. *J. Electron. Spectrosc. Relat. Phenom.* **135**, 163–166 (2004).
27. A. Svane, L. Petit, Z. Szotek, W. M. Temmerman, Self-interaction-corrected local spin density theory of $5f$ -electron localization in actinides. *Phys. Rev. B* **76**, 115116 (2007).
28. C. J. Windorff et al., Identification of the formal +2 oxidation state of plutonium: Synthesis and characterization of $\{\text{Pu}^{\text{II}}[\text{C}_2\text{H}_3(\text{SiMe}_3)_2]_3\}^-$. *J. Am. Chem. Soc.* **139**, 3970–3973 (2017).
29. C. H. Booth et al., Multiconfigurational nature of $5f$ orbitals in uranium and plutonium intermetallics. *Proc. Natl. Acad. Sci. U.S.A.* **109**, 10205–10209 (2012).
30. M. Janoschek et al., The valence-fluctuating ground state of plutonium. *Sci. Adv.* **1**, e1500188 (2015).
31. S. Y. Savrasov, G. Kotliar, E. Abrahams, Correlated electrons in δ -plutonium within a dynamical mean-field picture. *Nature* **410**, 793–795 (2001).
32. P. Söderlind, A. Landa, B. Sadigh, Density-functional theory for plutonium, *Adv. Phys.* **68**, 1–47 (2019).
33. Z. P. Yin, X. Deng, K. Basu, Q. Yin, G. Kotliar, Temperature-dependent electronic structures, atomistic modelling and the negative thermal expansion of δ Pu. *Philos. Mag. Lett.* **94**, 620–628 (2014).
34. J. M. Lawrence, P. S. Riseborough, R. D. Parks, Valence fluctuation phenomena. *Rep. Prog. Phys.* **44**, 1–84 (1981).
35. D. Wohlleben, *Physics and Chemistry of Electrons and Ions in Condensed Matter*, J. V. Acrivos, N. F. Mott, A. D. Yoffe, Eds. (Reidel, Dordrecht, The Netherlands, 1984), pp. 85–107.
36. V. Klosek et al., High pressure study of $\text{Pu}_{0.92}\text{Am}_{0.08}$ binary alloy. *J. Phys. Condens. Matter* **20**, 275217 (2008).
37. P. Faure et al., “Structural investigation of δ -stabilized plutonium alloys under pressure” in *Materials Research Society Proceedings*, J. Sarrao et al., Eds. (Materials Research Society, Pittsburgh, PA, 2005), vol. 893. pp. 223–232.
38. P. Faure, C. Genestier, X-ray diffraction study δ -stabilized plutonium alloys under pressure. *J. Nucl. Mater.* **397**, 74–79 (2010).
39. J. Zhang et al., Equation of state and strain-induced stabilization of δ -phase stabilized plutonium alloys. *J. Nucl. Mater.* **524**, 54–59 (2019).
40. N. W. Ashcroft, N. D. Mermin, *Solid State Physics* (Saunders College Publishing, Orlando, FL, 1976).