Unexpected elastic softening in δ-plutonium

A. Migliori,[1] H. Ledbetter,[1] A. C. Lawson,[1] A. P. Ramirez,[2] D. A. Miller,[1] J. B. Betts,[1] M. Ramos,[1] and J. C. Lashley[1]
[1]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[2]*Lucent Technologies, Murray Hill, New Jersey 07974, USA*
(Received 27 October 2005; published 21 February 2006)

Elastic-constant measurements on a Pu-2.4 at. % Ga quasiisotropic polycrystal reveal remarkable elastic softening as temperature increases from ambient to 500 K. Unexpected softening appears in both the bulk modulus B and the shear modulus G, thus in all quasiisotropic elastic stiffnesses such as the Young modulus and the Lamé constants. The dB/dT slope gives a (lattice) Grüneisen parameter $\gamma=3.7$, much higher than a typical fcc-metallic-element value of 2.4 ± 0.5. Especially, this high γ from dB/dT measurements disagrees strongly with the $\gamma=-0.26\pm0.5$ from volume measurements. The dB/dT slope exceeds that measured previously at lower temperatures. Also, it exceeds that expected from high-temperature Debye-Waller-factor measurements. A two-level model used successfully previously to interpret this alloy's unusually low thermal expansion also describes the large dB/dT. We comment on possible explanations for plutonium's odd anharmonic behavior. These concepts include magnetism, $5f$-electron localization-delocalization, and vibrational entropy. Our measurements on the Pu-Ga polycrystal agree remarkably well with a Kröner-theory average of previous measurements on a same-composition monocrystal.

DOI: 10.1103/PhysRevB.73.052101 PACS number(s): 62.20.Dc, 63.20.Ry, 65.40.Gr

With six allotropes and irregular melting behavior, plutonium presents a perplexing array of physical properties, still much studied, both experimentally and theoretically.[1] The simplest crystal structure, δ-plutonium (face-centered cubic), displays the most puzzling properties: extreme elastic anisotropy, highest atomic volume (among the six), negative thermal expansion, strong response to dilute alloying (phase-field extension), and large volume changes during transformations to adjacent phases. Also, as described here, a δ-Pu alloy shows strong elastic softening with increasing temperature, an extreme behavior among fcc elements.

Elastic properties provide invaluable probes of other physical properties. Second-order (isothermal) elastic constants, such as bulk modulus B and shear modulus G, relate to the second derivative of the free energy with respect to strain; they determine the Debye characteristic temperature (the quintessential harmonic-lattice property); they correlate strongly with practical properties including ductility and hardness. Second-order elastic-constant temperature and pressure derivatives relate to the third-order elastic constants, thus to the quintessential anharmonic property: the Grüneisen parameter γ.

We prepared the studied alloy on 29 June 1999 from zone-refined Pu^{239} that was mixed with 99.999%-pure Ga, arc melted, quenched from the melt on a water-cooled copper hearth,[2] and homogenized for 100 h at 723 K. The material showed equiaxed 15-μm grains, absence of texture, and mass density of 15.75 g/cm^3. By usual metallographic cut-grind-polish methods we prepared a rectangular-parallelepiped specimen measuring $0.475\times0.377\times0.484$ mm. We made measurements using resonance-ultrasound spectroscopy using 32 resonance peaks to determine the two quasiisotropic effective elastic constants.[3–5] This method sweeps the frequency, drives a broadband transducer in weak contact with the specimen, and detects the macroscopic-vibration frequencies. The elastic constants B, $G,\ldots,$ result from an inverse calculation that uses the specimen mass and dimensions, known crystallographic symmetry, and the resonance frequencies. Errors arise mainly from the specimen shape, limiting absolute accuracy to about 0.3%. In this case, isotropic crystallographic symmetry was appropriate for the untextured polycrystal specimen. We used two types of measurement cells. One cell used thermoelectric cooling with piezoelectric transducers in contact with the specimen, capable of operation up to 375 K with Si-diode thermometry. The second cell (Fig. 1), built from high-temperature materials, resistively heated, can operate to 550 K. Temperature errors were approximately 2% for the thermoelectrically cooled cell and less than 1% for the resistively heated cell. Where measurements overlapped between cells, measurements agreed within their errors.

Elastic-constant results in Table I show remarkable agreement with those obtained by averaging, using Kröner's theory, the monocrystal elastic constants reported nearly thirty years ago by Ledbetter and Moment.[6] The agreement confirms both the present measurements and the specimen quality: no texture, voids, or other defects that would alter (usually lower) the elastic stiffnesses. The three Debye temperatures in Table I represent different kinds of averages. The

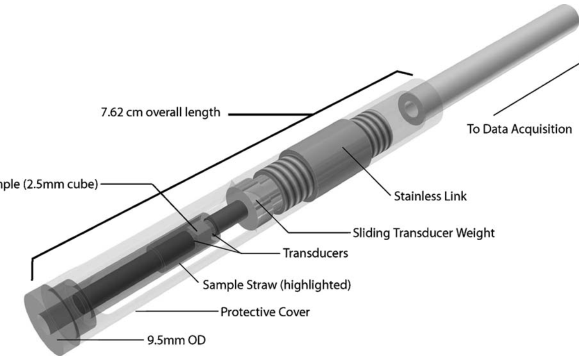

FIG. 1. Resonant-ultrasound-spectroscopy cell used for measurements. The coil-like structure is a small heater. The present specimen was about 0.5 cm on edge. Alumina buffer rods separate the $LiNbO_3$ transducers from the hot region and the specimen.

TABLE I. Elastic and related properties of Pu-2.36 at. % Ga at 298 K. B denotes bulk modulus, G shear modulus, E Young modulus, ν Poisson ratio, and Θ Debye temperature. Crystal results represent Kröner-theory averages.

	B (GPa)	G (GPa)	E (GPa)	ν	Θ (K)
Present	30.6±0.1	16.3±0.05	41.8±0.1	0.272	115±5
Crystal Avg. (Ref. 6)	29.9	16.2	41.2	0.271	115
Crystal (Ref. 6)					105
Crystal at 0 K (est.)					117

first (115 K) represents a continuum-mechanics average to obtain the effective quasi-isotropic elastic constants. The second (105 K) represents a Christoffel-Debye reciprocal-cube average over monocrystal directions to obtain the mean sound velocity. The third (117 K) follows from correcting the ambient-temperature monocrystal elastic constants to zero temperature. When measured at a low temperature, the second Debye temperature should equal the specific-heat Debye temperature. [Both depend on the (−3) moment of the phonon spectrum.]

Temperature-effect results in Fig. 2 present three surprises. First, both B and G change smoothly above 375 K (the temperature above which thermal expansion is zero), a surprise because δ-Pu is an unstable phase and elastic constants often indicate incipient phase instability.[7] Here, unstable means imminent transformation to δ'-Pu and to ε-Pu, all three being related by the Bain lattice correspondence. Second, both B and G decrease, against expectation from the alloy's small negative thermal expansion. For normal materials, in an Einstein-Grüneisen model, elastic softening arises mainly from the volume increase associated with thermal expansion. However, δ-Pu does not behave normally. In the studied temperature region, thermal expansion is small and negative; thus, one expects both B and G to change little. We see why from thermodynamics[8]

$$(\partial B_S/\partial T)_P = -\beta B_S \delta_S. \tag{1}$$

Here, β denotes volume thermal expansivity and S entropy. δ denotes a small (2–5) parameter that depends on the Grüneisen parameter γ, the logarithmic volume derivative of some characteristic energy (such as a phonon frequency). In Grüneisen's original studies, using a Mie-Grüneisen interatomic potential, he obtained the result $\delta = \gamma + 1$. A third surprise in Fig. 2 appears in the unexpectedly large decrease, especially when compared with three other representative fcc metals: aluminum, gold, lead. Figure 2 shows also the bulk-modulus change expected from the neutron-diffraction Debye-Waller Debye temperature. Here, we used the relationship $B_{\mathrm{DW}} \sim \Theta_{\mathrm{DW}}^2 V_a^{-1/3}$. The strong bulk modulus and shear modulus decrease exceeds that for any element, excepting those undergoing phase transitions. As a melting criterion, Born[9] proposed a vanishing C_{44} (a monocrystal shear modulus). Grimvall discussed melting thermodynamics.[10] δ-Pu may represent the only case where the shear modulus and the bulk modulus extrapolate to zero at the same temperature (about 300 K above the melting temperature). Plutonium's anomalously low melting temperature was ascribed to its f-electron configuration.[11,12] Lindemann's melting rule $T_m \sim \Theta^2$ predicts that δ-Pu should show a higher T_m than ε-Pu, consistent with the B, $G(T)$ extrapolation.

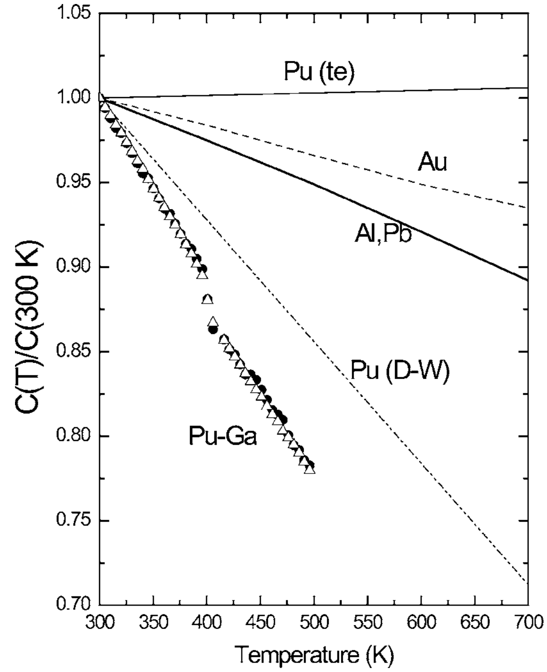

FIG. 2. Measurement results expressed as the shear modulus G and bulk modulus B. Measurements were made in two different apparatuses as described in the text, using two different thermometers. C denotes either B (open triangles) or G (filled circles). The curve labeled Pu(te) represents the bulk-modulus change expected from the alloys's small negative thermal expansion. The curve labeled D–W corresponds to the bulk-modulus change expected from Debye-Waller factors determined by neutron diffraction (Ref. 18). To show representative $B(T)$ behavior, we include "handbook" results for Al, Au, Pb. Table I gives the ambient-temperature numerical values. The jog near 400 K corresponds to a small amount of α-Pu transforming to δ-Pu.

From dB/dT, one can calculate a Grüneisen parameter. Ledbetter[13] showed that from the Leibfried-Ludwig[14] assumption about elastic constants and lattice-vibration thermal energy one obtains

$$(\partial B/\partial T)_P = -3k\gamma(\gamma+1)/V_a. \tag{2}$$

Here, k denotes the Boltzmann constant, γ the Grüneisen parameter, V_a atomic volume. Substitution gives $\gamma = 3.7 \pm 0.5$, especially large, metals showing a typical range of 1–3, and fcc metals averaging $\gamma(\text{lattice}) = 2.4 \pm 0.5$. We can compare this with the Grüneisen parameter of monoclinic α-Pu: $\gamma(\alpha) = 3.5 \pm 0.5$.[15] This surprising agreement between the α-Pu and δ-Pu Grüneisen parameters indicates that the two phases possess strong, similar overall lattice anharmonicities. Between the two phases, there exists a well-known lattice correspondence: $(111)_\delta$ parallel to $(010)_\alpha$.[16] On the other hand, a calculation for δ-Pu using Grüneisen's first rule $\gamma = B_S \beta V / C_p$ and high-temperature physical-property measurements gives $\gamma = -0.26 \pm 0.5$. [Here, B_S denotes the adiabatic bulk modulus (measured in the present study), β volume thermal expansivity, V volume, C_P constant-pressure heat capacity.]

Clearly, the Grüneisen parameter derived from dB/dT departs strongly from the thermal-expansion value, which by Grüneisen's first rule must be near zero. Figure 3 summarizes some general thermodynamics. The upper graph shows the Helmholtz free energy $F=E-TS$ at a lower temperature T_1 and a higher temperature T_2. (Here E denotes energy, S entropy.) The F-V curvatures give B. At lower temperatures (for our Pu specimen, below 375 K), state 1 dominates (lower F). At higher temperatures, state 2 dominates. The lower graphs show how volume and bulk modulus change with temperature. Effectively, upon heating, a gradual phase transition occurs from state 1 to state 2. Over a limited temperature region, volume remains approximately constant. In this same temperature region, the bulk modulus decreases strongly, giving the apparent (fictive) high Grüneisen parameter described above. Equation (2) fails because it breaks down during a phase transition. Figure 3 contains the prediction that at temperatures below and above the state-1-to-state-2 transition dB/dT (and therefore γ) should show smaller, more typical values. The phase transition may relate, as described below, to electronic-state transitions, thus to the Grüneisen parameter's electronic component.

Two previous measurements relate to our study. First, Taylor *et al.*[17] measured the low-temperature sound velocities of a Pu-5 at. % Al alloy, expected to behave similarly to our alloy. The elastic constants derived from their study showed much lower slopes dB/dT and dG/dT than we found at higher temperatures. However, our (unreported here) low-temperature slopes agree closely with those of Taylor *et al.*

Second, Lawson and colleagues,[18] for a Pu-2.0 at. % Ga alloy, measured the 0–800 K Debye-Waller factor and extracted a Debye-Waller temperature Θ_{DW} for the entire temperature range. We can calculate $B_{DW}(T)$ using the relationship $B_{DW} \sim \Theta_{DW}^2 V_a^{-1/3}$. Figure 2 shows that dB_{DW}/dT is unusually large, but smaller than $dB_{elastic}/dT$. The relationship between temperature derivatives of Θ_{DW} and Θ_e remains to be studied. Grimvall[10] described that both the heat-capacity and elastic Debye temperatures depend on the (−3) moment of the phonon spectrum, but the high-temperature thermal-displacement Θ_{DW} temperature depends on the (−2) moment, and that for many materials the difference between the (−2) and (−3) moments exceeds the difference between any other moment pairs.

Our measurements confirm an Eriksson and colleagues[19] prediction: δ-Pu should show anomalously strong elastic-constant temperature dependence. To reach this conclusion, the authors did *ab initio* Kohn-Sham density-functional calculations, including the C' elastic stiffness related to the fcc-bcc Bain strain. They found the fcc crystal structure unstable against the C' shear deformation. And they emphasized the correspondence to two-level invar systems: competing electronic configurations with different equilibrium volumes.

It seems useful to consider in more detail a two-level model summarized in Fig. 3, a model so successful in describing Pu-Ga-alloy thermal-expansion anomalies,[20] a model stimulated by its success in describing invar's remarkable thermal-expansion properties.[21] In this model, the excess-modulus/temperature slope $(dG/dT)^{ex}$ relates simply to the excess thermal expansivity β^{ex}:

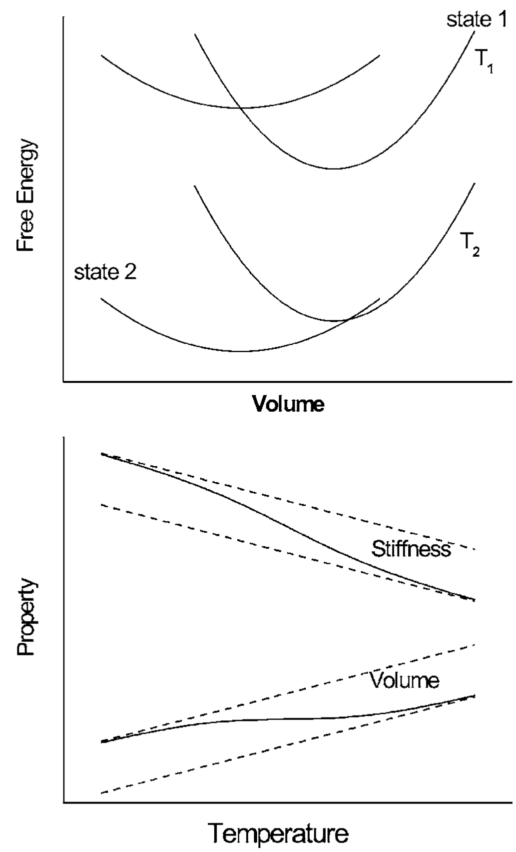

FIG. 3. Schematic thermodynamics. Upper graph shows Helmholtz free energy for two states (levels) at two temperatures. Lower graph shows temperature variation of bulk modulus and volume. The region of largest dC/dT corresponds to the region of smallest thermal expansion.

$$(dG/dT)^{ex} = \beta^{ex}(G_2 - G_1)V/\Delta V. \tag{3}$$

Here, G_1 and G_2 denote the shear moduli in states 1 and 2, and $\Delta V/V=(V_2-V_1)/V_1$ denotes the relative volume difference between the two states at zero temperature. Remarkably, this relationship omits the energy difference E_2-E_1, the degeneracy ratio g_1/g_2, and the temperature. Taking β^{ex} and $\Delta V/V$ values from Lawson *et al.*[18] gives $(dG/dT)^{ex} = -0.0023$ GPa/K. This agrees well with observation: the observed $(dG/dT)^{ex}$ of −0.002 GPa/K being given by the slope in Fig. 2 (−0.015) minus the low-temperature slope (−0.013). Here, we took the maximum G_1-G_2 by taking $G_2=0$, as suggested by the Lawson *et al.*[20] result that the state-2 Debye temperature equals zero. Thus, the two-level model describes not only the anomalous thermal expansivity, but also the large elastic-stiffness decrease.

Several recent theories consider a magnetic δ-Pu.[22–25] However, magnetism fails to explain our results. As one heats a magnetic material, magnetic interactions decrease, elastic stiffness increases,[26] against our observations. Attempts to detect magnetism in δ-Pu failed.[27]

Much current theoretical research on δ-Pu focuses on $5f$-electron localization-delocalization.[19,28–30] As the $5f$ electrons convert from itinerant to localized, volume increases. Indeed, theoretical calculations localizing four of the five $5f$ electrons account well for δ-Pu's extraordinary large atomic volume. Dynamic-mean-field-theory density-functional calculations[28] yield δ-Pu elastic constants that agree with observation, despite δ-Pu's extreme elastic anisotropy. Intuitively, we expect electron localization to reduce metallic-bond cohesion and reduce elastic stiffness. As emphasized by Gilman,[31] electron density (number of electrons per local unit volume) represents the key determiner of cohesive energy and elastic stiffness. However, not yet do these localization-delocalization theories predict the observed effects summarized in Fig. 3: upon heating, the material's state changes with the result that volume decreases (leading to near-zero or negative thermal expansion) and bulk modulus decreases strongly.

Citing the Lawson *et al.* neutron-scattering results,[18] Nadykto[32] noted large elastic softening and proposed the following explanation: upon heating, some δ-phase atoms acquire ε-phase electronic structure. Thus, Nadykto proposed an atomic-level composite. The ε-phase lower volume and lower stiffness agree qualitatively with present observations. Indeed, the bcc ε-phase relates closely to the fcc δ-phase through the well-known Bain lattice correspondence. Thus, bcc-fcc interconversion can occur by compression-extension along $\langle 100 \rangle$ axes or, nearly equivalently, shear on $\{110\}$. An important extension of these arguments and the present study is to note that as temperature rises the volume remains unchanged or decreases, while stiffness decreases, again both properties behaving atypically. Thus, the possibility appears that δ-Pu will soften under pressure, that is show a negative dB/dP, and a corresponding negative Grüneisen parameter.

Finally, we consider vibrational entropy. High entropy stabilizes a phase by decreasing its free energy. From statistical thermodynamics, we know that elastic softening decreases the effective lattice-vibration frequency and increases the phonon entropy S. Using Debye's entropy model and Lindemann's melting rule, one can show that at high temperatures, and for $T=298$ K,

$$S = 5.86R + 1.5R \ln(mr_0^2/T_m). \tag{4}$$

Here, R denotes the universal gas constant, m atomic mass, r_0 atomic radius, and T_m melting temperature. Thus, plutonium's high mass, high volume, low melting temperature all contribute to an overall high phonon entropy. Indeed, plutonium possesses the highest phonon entropy of any fcc metal.[33] It appears, then, that plutonium secures its most-stable phases not by minimizing its (small) energy with respect to crystal structure and volume, but by maximizing its (large) entropy. In summary, we reported the remarkable temperature-induced elastic softening in a dilute Pu-Ga alloy, described the thermodynamic implications, and suggested possible explanations.

The U.S. Department of Energy supported this research under Grant No. DEFG-03-86ER-45230, the U.S. National Science Foundation (NSF) under Grant No. DMR-00-72125. Research was performed under the auspices of the NSF, the State of Florida, the National Nuclear Security Administration, and the U. S. Department of Energy. For their support, the authors thank Alex Lacerda, Rob Hixson, Luis Morales, Joseph Martz, Kathleen Alexander, and Greg Boebinger.

[1] N. Cooper (unpublished).
[2] J. Lashley, M. Blau, K. Staudhammer, and R. Pereyra, J. Nucl. Mater. **274**, 315 (1999).
[3] A. Migliori and J. Sarrao, *Resonant Ultrasound Spectroscopy* (Wiley-Interscience, New York, 1997).
[4] J. Maynard, Phys. Today **49** (1), 26 (1996).
[5] A. Migliori *et al.*, Physica B **183**, 1 (1993).
[6] H. Ledbetter and R. Moment, Acta Metall. **24**, 891 (1976).
[7] B. Lüthi and W. Rehwald, in *Structural Phase Transitions I* (Springer, Berlin, 1981), p. 131.
[8] E. Grüneisen, in *Handbuch der Physik* (Springer, Berlin, 1926), p. 1, implied in Eq. (46).
[9] M. Born, J. Chem. Phys. **7**, 551 (1939).
[10] G. Grimvall, *Thermophysical Properties of Materials* (Elsevier, Amsterdam, 1999), p. 339, 89 ff.
[11] B. Matthias, W. Zachariasen, W. Webb, and J. Engelhardt, Phys. Rev. Lett. **18**, 781 (1967).
[12] E. Kmetko and H. Hill, J. Phys. F: Met. Phys. **6**, 1025 (1976).
[13] H. Ledbetter, Phys. Status Solidi B **181**, 81 (1994).
[14] G. Leibfried and W. Ludwig, Solid State Phys. **12**, 275 (1961).
[15] H. Ledbetter, A. Lawson, and A. Migliori (unpublished).
[16] C. Olsen, J. Nucl. Mater. **168**, 326 (1989).
[17] J. Taylor, R. Loasby, D. Dean, and P. Linford, in *Plutonium 1965* (Chapman and Hall, London, 1967), p. 162.
[18] A. Lawson *et al.*, Philos. Mag. B **80**, 53 (2000).
[19] O. Eriksson, J. Becker, A. Balatsky, and J. Wills, J. Alloys Compd. **287**, 1 (1999).
[20] A. Lawson, J. Roberts, B. Martinez, J. Richardson, H. Ledbetter, and A. Migliori, JOM **55**, 31 (2003).
[21] M. Acet and W. Pepperhoff, *Constitution and Magnetism of Iron and its Alloys* (Springer, Berlin, 2001).
[22] P. Söderlind, O. Eriksson, J. Wills, and A. Boring, Phys. Rev. B **48**, 9306 (1993).
[23] M. Pénicaud, J. Phys.: Condens. Matter **9**, 6341 (1997).
[24] Y. Wang and Y. Sun, J. Phys.: Condens. Matter **12**, L311 (2000).
[25] A. Kutepov and S. Kutepova, J. Phys.: Condens. Matter **15**, 2607 (2003).
[26] D. Papaconstantopoulos *et al.* (unpublished). The authors give first-principles results for bcc and fcc iron in three magnetic states: paramagnetic, antiferromagnetic, ferromagnetic.
[27] C. Olsen, A. Cornstock, and T. Sandenaw, J. Nucl. Mater. **195**, 312 (1992).
[28] X. Dai *et al.*, Science **300**, 953 (2003).
[29] V. Antropov, M. van Schilfgaarde, and B. Harmon, J. Magn. Magn. Mater. **140–144**, 1355 (1995).
[30] S. Meot-Reymond and J. Fournier, J. Alloys Compd. **232**, 119 (1996).
[31] J. Gilman, *Electronic Basis of the Strength of Materials* (Cambridge University Press, Cambridge, 2003), p. 59.
[32] B. Nadykto, J. Nucl. Sci. Technol. **3**, 221 (2002).
[33] H. Ledbetter and A. Migliori (unpublished).