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Alpha-plutonium's Grüneisen parameter

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Abstract
Reported Grüneisen parameters γ of alpha-plutonium range from 3.0 to 9.6, which is remarkable because typical Grüneisen parameter uncertainty seldom exceeds ± 0.5. Our six new estimates obtained by different methods range from 3.2 to 9.6. The new estimates arise from Grüneisen's rule, from Einstein model and Debye model fits to low-temperature $\Delta V/V$, from the bulk modulus temperature dependence, from the zero-point-energy contribution to the bulk modulus, and from another Grüneisen relationship whereby γ is estimated from only the bulk modulus and volume changes with temperature (or pressure). We disregard several high estimates because of the itinerant–localized 5f-electron changes during temperature changes and pressure changes. Considering all these estimates, for alpha-plutonium, we recommend $\gamma = 3.7 \pm 0.4$, slightly high compared with values for all elemental metals.

The Grüneisen parameter γ represents the quintessential anharmonic property. It plays a key role in describing properties that include thermal expansivity, pressure-dependent and temperature-dependent second-order elastic constants, third-order and higher-order elastic constants, thermal conductivity, sound-wave attenuation, and shock-wave propagation [1]. A dimensionless parameter, gamma varies little with temperature and usually takes values around 2. When a material shows a gamma very different from 2, we should look carefully for the possible explanation, which usually contains some new physics.

Here, we consider the Grüneisen parameter of alpha-plutonium, a monoclinic crystal with a 16-atom unit cell, stable between 0 and 388 K, where it transforms to beta-plutonium, base-centered monoclinic, with a 34-atom unit cell. Table 1 shows previous and current estimates of γ, ranging from 3.0 to 9.6 These were obtained by various methods: from $\mathrm{d}B_S/\mathrm{d}P$, where we used a well-known relationship, endorsed, for example, by Wallace [8], $\mathrm{d}B_S/\mathrm{d}P = 2\gamma + 1$; Grüneisen's rule; temperature dependence of the Debye–Waller Debye temperature $\mathrm{d}\Theta_{\mathrm{DW}}/\mathrm{d}T$; the zero-point bulk modulus; low-temperature $(\mathrm{d}V/V)_P$ (Einstein and Debye models); a $\gamma(B, V)$ relationship given by Grüneisen. The large variation in these values obtained by various physical relationships demands further discussion. Because we cannot estimate it reliably, we neglect the electronic Grüneisen parameter. This neglect could introduce a small inconsistency because some of our equations refer to the complete (lattice plus electronic) parameter, while others (based say on Einstein or Debye models) refer only to the usual lattice part.

Originally, Grüneisen defined his parameter as [9]

$$\gamma = V(\partial P/\partial E)_V. \tag{1}$$

Here, E denotes energy, P thermal pressure, and V volume. Grüneisen emphasized this equation's physical meaning: the change of thermal pressure with energy density at constant volume is temperature independent and nearly material independent. Thermal pressure can be calculated by equating the thermal-expansion volume change to the elastic volume change. As described by Brillouin [10], this internal pressure causes thermal expansion and is equivalent to Debye's thermal-expansion model based on forces nonlinear in the strains (nonvanishing third-order elastic constants). Substitution into equation (1) of the bulk modulus $B_S = -V(\partial P/\partial V)_S$ and the thermal expansivity $\beta = V(\partial V/\partial T)_P$ yields Grüneisen's familiar rule:

$$\gamma = \frac{\beta B_T}{C_V} = \frac{\beta B_S}{C_P}. \tag{2}$$

Here, T denotes temperature, S entropy, C specific heat per unit volume. Grüneisen derived this relationship in an early paper from what we now call the Mie–Grüneisen interatomic potential. Early on, Grüneisen wrote another expression:

$$\gamma = -\frac{V}{\omega_j}\frac{\mathrm{d}\omega_j}{\mathrm{d}V}. \tag{3}$$

Table 1. Alpha-plutonium's Grüneisen parameter by various methods.

	Gamma	Method	Source
1	3.0	dB/dP	[2]
2	6.8	Grüneisen's rule	[3]
3	5.1	dB/dP	[4]
4	7.0	dB/dP	[5]
5	4.1	$d\Theta_{DW}/dT$	[6]
6	9.3	dB/dP	[7]
7	3.5	Grüneisen's rule	Present
8	5.1	dB/dT	Present
9	5.2	Zero-point bulk modulus	Present
10	3.2	dV/V, Einstein-oscillator model	Present
11	3.9	dV/V, Debye-oscillator model	Present
12	9.6	$\gamma(B, V)$, Grüneisen equation (44) [11]	Present
	5.5 ± 2.2	Average of all 12	
	3.7 ± 0.4	Average of 5, 7, 10, 11	Recommended

Here, ω_j denotes the jth angular frequency of a lattice-vibration mode. For an Einstein or Debye solid, equation (3) becomes

$$\gamma = -\frac{V}{\Theta}\frac{d\Theta}{dV}. \tag{4}$$

Here Θ denotes the characteristic temperature. Originally, Grüneisen related γ also to the m, n coefficients in the Mie–Grüneisen interatomic potential $\Phi(r) = -ar^{-m} + br^{-n}$ and obtained the following expression [11]:

$$\gamma = (n+2)/6. \tag{5}$$

Thus, γ depends only on the repulsive exponent in the interatomic potential. Through this relationship, γ connects with many solid-state properties derivable from $\Phi(r)$. Considering Cu and Pb as examples, from the m, n values, Grüneisen predicted Grüneisen parameters 1.96 and 2.73, versus the modern handbook values: 1.97 and 2.84 [3]. Grüneisen's parameter also appears prominently in the well-known Mie–Grüneisen equation of state:

$$(\partial P/\partial T)_V = \gamma C_V. \tag{6}$$

Because gamma connects with so many different physical properties, the literature contains other expressions for gamma that differ considerably from those shown here [12].

Recent accurate measurements of alpha-plutonium's 0–300 K bulk modulus B [13] make possible three new estimates of γ. First, from Grüneisen's rule, equation (2), the ambient-temperature measured bulk modulus $B = 54.4$ GPa, thermal expansivity $\beta = 162 \times 10^{-6}$ K^{-1} [14], and specific heat $C_P = 30.44$ J K^{-1} mol^{-1} [15], one obtains $\gamma = 3.5$.

The $B(T)$ measurements were fit with an Einstein-oscillator-based function [16, 17]:

$$B_S(T) = B_S(0) - \frac{A}{\exp(t/T) - 1}. \tag{7}$$

Here, $B_S(0)$ denotes the adiabatic zero-temperature bulk modulus, t relates closely to the Einstein temperature Θ_E, and $A = 3k\gamma(\gamma+1)\Theta_E/V_a$, k denoting the Boltzmann constant and V_a atomic volume. At high temperatures, we obtain $dB_S/dT = -A/t$. This approach yields $\gamma = 5.1$.

The $B_S(T)$ results permit another estimate of γ from the difference between two bulk modulus values: the observed zero-temperature bulk modulus $B_S(0)$ and the harmonic bulk modulus B_h obtained by extrapolating the observed near-linear high-temperature dB/dT slope to zero temperature. For this difference, Ming and Ledbetter [18] derived the following expression:

$$B_S(\text{har}) - B_S(0) = 9k\gamma(\gamma+1)\Theta_E/V_a. \tag{8}$$

Fitted to the measurements, this relationship yields $\gamma = 5.2$.

Using an Einstein-oscillator model for thermal expansivity, Ledbetter [19] derived a relationship for the volume change upon warming from zero temperature:

$$\Delta V/V(T) = (3k\gamma\Theta_E/B_S V_a)/[\exp(\Theta_E/T) - 1]. \tag{9}$$

Fitting this relationship to $\Delta V/V$ measurements reported by Lawson *et al* [6] gives $\gamma = 3.2$. If, instead of an Einstein model, one uses a Debye model (superior at lower temperatures), one obtains $\gamma = 3.9$.

We can also calculate γ using a relationship derived by Grüneisen, which shows extreme simplicity in depending only on two physical properties: the bulk modulus B and the volume V ([11], equation (44)):

$$B_S(T) = B_S(0)(V_0/V)^{\gamma+1}. \tag{10}$$

For the four input parameters, as they appear, we used values corresponding to 0 and 300 K: 70.9 and 54.5 GPa [13], 19.4 and 19.9 Å^3 [28]. Grüneisen's simple equation yields $\gamma = 9.6$, highest (result 12) in table 1. This high value suggests that either the exponent in equation (10) deserves reconsideration, or, as described below, upon warming the bulk modulus undergoes unusual softening because of f-electron localization. The literature shows that relationships involving γ often contain small errors for three reasons: (1) many different meanings of the Grüneisen parameter; (2) different assumptions about its pressure, volume, temperature dependence; (3) looseness in what is constant (P, V, T, ...) in various thermodynamic derivatives.

Now, we discuss the twelve sets of results given in table 1, for convenience labeled 1–12. We disregard all results based

on changes in bulk modulus caused either by temperature or pressure, both involving a volume change. The basis for disregarding these is described in the next paragraph and depends on f-electron localization. We disregard result-2 because it seems too high, not traceable to original sources, and in severe disagreement with result-7, obtained from the same equation.

Before concluding, we describe problems presented by f-electrons in α-Pu. Plutonium's nominal free-atom electronic structure is $[Rn]5f^6 7s^2$. A principal problem in f-electron materials is to decide whether the f-electrons are localized (core-like, nonbonding) or itinerant (free-electron-like, bonding) [20]. More bonding electrons would increase the bulk modulus and decrease the volume. In recent years, much research, both measurement [21] and theory [22, 23], focused on the itinerant–localized 5f-electron problem in plutonium. From analyzing plutonium's $B(T)$ behavior using a simple electron theory (kinetic and potential energies), Ledbetter *et al* concluded that nearly all plutonium's 5f-electrons are localized; and that upon warming from zero to ambient temperature, about 0.25 electrons change state from itinerant to localized, thus become nonbonding, thus softening the bulk modulus more than the usual phonon softening upon warming [24]. Another important measurement study on polycrystalline α-Pu from 16 to 400 K revealed much unexpected behavior [25]: (1) upon cooling from 300 K to near 0 K, both the bulk modulus B and shear modulus G increased about 30%, *about an order of magnitude more than usual materials*; (2) because B and G represent extreme (eigenvalue) mechanical-deformation bounds, all the elastic stiffnesses (Young modulus, longitudinal modulus, . . .) must increase also about 30%. The literature shows that pressure causes f-electrons to move from localized to itinerant, thus becoming bonding electrons and raising the bulk modulus, yielding a higher apparent dB/dP [26]. Similarly, as described above, warming causes an itinerant–localized f-electron transition, thus decreasing the bonding electrons, decreasing the bulk modulus, and causing a larger apparent dB/dT. Others argued that warming elements such as Am, Pu, Np increases f-electron localization [27]. Thus both pressure and temperature changes produce higher Grüneisen parameters than intrinsic (intrinsic means absence of an f-electron phase transition, maintenance of the same thermodynamic state). From table 1, we find that the average of gammas involving either dB/dP or dB/dT (numbers 1, 3, 4, 6, 8, 9, 12) is quite high: 6.3 ± 2.4.

Thus, we conclude that the best estimate of alpha-plutonium's Grüneisen parameter is 3.7 ± 0.4, obtained by averaging results 5, 7, 10, 11 in table 1. Often, one compares plutonium with lead, a heavy fcc metal with a low bulk modulus. For lead, from a handbook, $\gamma = 2.84$ [3]. Comparison with isostructural elements is impossible because plutonium is the only metal with a monoclinic crystal structure at ambient pressure. Also, the Pb–Pu comparison can be carried only a little way because Pb is fcc, not monoclinic, has no f-electrons, and is bonded mainly by sp-electrons, its d-electrons playing little or no role. From handbook results [3], we find $\gamma = 1.4 \pm 0.3$ for alkali metals, 1.7 ± 0.1 for bcc transition metals, 1.9 ± 0.4 for c.p.h. metals, 2.4 ± 0.5 for fcc metals. Alpha-plutonium shows a significantly higher Grüneisen parameter. Thus, we expect alpha-plutonium's various anharmonic properties to exceed those of normal metals. And we believe the high reported Grüneisen parameters (5.1–9.6) are artifacts induced by temperature or pressure changes that effect a localized–itinerant f-electron transition. There remains a cogent question: why is α-Pu's 'intrinsic' Grüneisen parameter so high (3.7), the highest listed in Gschneidner's review of the metallic elements [3]?

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