Zero-temperature bulk modulus of alpha-plutonium

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Using resonant-ultrasound spectroscopy, we measured alpha-plutonium's bulk modulus B between 298 and 18 K. Fitting the measurements to an Einstein-oscillator-based function gave the zero-temperature bulk modulus $B_o = 70.9$ GPa. We compare our measurement with numerous previous measurements and with numerous theoretical estimates ranging from 41 to 227 GPa. From 0 to 300 K, $B(T)$ is regular and smooth, evincing no phase transition (electronic, magnetic, structural). The bulk modulus decreases to 54.4 GPa, about 30%, a very large change compared with typical materials. We attribute this large decrease to electron localization during warming. High-temperature dB/dT yields a Gruneisen parameter $\gamma = 5.1$, too high we believe because of temperature-induced electron localization. From the low-temperature elastic constants, averaged in the usual Debye $\langle v^{-3} \rangle$ manner, we obtain a Debye temperature $\Theta_D = 205$ K.

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Much physical-property research (measurements and theory) now proceeds on the actinides.[1] Among the actinides, plutonium receives most interest. Plutonium's ground-state (zero-temperature) equilibrium phase is the alpha phase (16-atom unit cell, monoclinic, mP16, $P2_1/m$, no. 11).[2] Along with the binding energy and atomic volume, the bulk modulus represents one of a material's three basic cohesion properties. Knowing and understanding a material's bulk modulus is important because it connects with so many other physical properties. For theorists, the (adiabatic) bulk modulus provides a favorite testing ground; it relates simply to the second derivative of energy with respect to volume. As shown below, alpha-plutonium's bulk modulus received much recent attention by theorists.

We need fresh measurements of alpha-plutonium's elastic constants for at least eight reasons. (1) Existing ambient-temperature measurements give $B = 50.1$ GPa with an 11% uncertainty. Modern measurement methods usually give elastic constants within 0.5%, better by a factor of 20. Below, we shall see that this average is low by about 8%. (2) Only one low-temperature measurement exists, by Rosen and colleagues.[3] These authors reported Young's modulus E and shear modulus G. Computing the bulk modulus B from E, G can yield large errors. For alpha plutonium, assuming 1% errors in E, G can yield an 8% error in B. This large error multiplication arises because the Young's modulus represents mainly a resistance to shear deformation. (3) Among 14 theoretical bulk-modulus studies, none support the Rosen-colleagues measurement. The theoretical studies show remarkable dispersion: 93 ± 48 GPa for the zero-temperature bulk modulus. For theoretical studies, such as the embedded-atom method, that put the bulk modulus into the calculations, the theory goes unnecessarily wrong for lacking a correct bulk modulus. Also, oddly, none of the theoretical studies cite the Rosen-colleagues results. (4) Waviness in the Rosen-colleagues $E(T)$ and $G(T)$ curves contributes to an unresolved current controversy: Does alpha plutonium undergo a low-temperature magnetic-state change?[4] (5) Accurate low-temperature measurements should resolve the large range of reported specific-heat Debye temperatures: 153–200 K. At zero temperature, elastic and specific-heat Debye temperatures are identical. (6) Accurate $B(T)$ measurements would provide a fresh estimate of alpha-plutonium's Grüneisen parameter, where reported values range from 3 to 7. (7) Knowing the $B(0)/B(300)$ ratio accurately helps scale other physical properties from ambient to zero temperature. (8) Finally, a well-known bulk modulus would eliminate spillover errors into studies that focus on bulk-modulus-related physical/mechanical properties such as melting and hardness.

To determine this fundamental property, we used resonant-ultrasound spectroscopy[5] to measure the natural macroscopic vibration frequencies of a polycrystalline (quasiisotropic) specimen. Elsewhere, we report material-measurement details.[6] Figure 1 shows the principal results.

The curve in Fig. 1 represents a function based on an Einstein-oscillator model and the assumption that elastic stiffness $C(T)$ changes with temperature T according to $C(T) = C(0)[1 - K\langle E \rangle]$, where $\langle E \rangle$ denotes the average oscillator energy and K a constant that depends on crystal structure.[7,8] For the bulk modulus, this function is

$$B(T) = B(0) - s/[\exp(t/T) - 1]. \quad (1)$$

For the three fitting parameters, we obtained $B(0) = 70.9$ GPa, $s = 11.3$ GPa, and $t = 158.8$ K. This function applies to a wide material variety,[8] including odd physical-property materials such as the negative-thermal-expansion compound ZrW_2O_8, for example.[9] In Eq. (1), t estimates roughly the Einstein temperature. The roughness arises from real solids departing strongly from a Debye model. With minor departures at lowest temperatures and above 300 K, we see smooth, regular behavior with no indication of a phase transition. Unlike Rosen and colleagues,[3] we found no irregular behavior near 65 K.

Table I shows our zero-temperature measurement result compared with several theoretical estimates. The table also shows a few theoretical estimates for neptunium. In their ground states, because they show similar Wigner-Seitz radii, and differ by a single atomic number, one expects neptunium and plutonium to possess similar bulk moduli.

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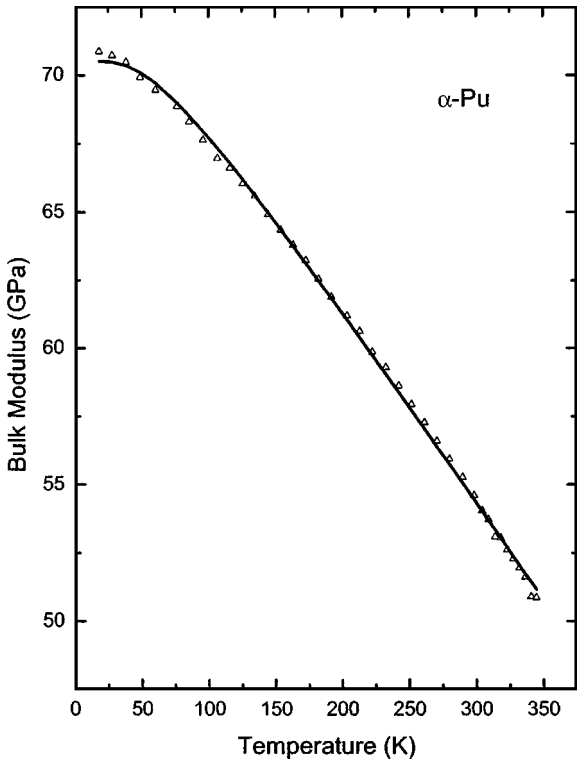

FIG. 1. Temperature dependence of alpha-plutonium's bulk modulus. Curve represents Eq. (1), based on an Einstein-oscillator model. Low-temperature departures deserve further study. Near-ambient softening may reflect behavior premonitory to the α-β transition near 400 K.

From Table I we see that, although modern theory succeeds in calculating the zero-temperature bulk modulus of many materials, modern theory remains deficient for calculating the bulk modulus of alpha plutonium. As is well known, the principal computational problem is how to handle the itinerant-localized $5f$ electrons. This problem adds to the general one of doing cohesion-property calculations for heavy metals where relativistic effects enter.

Table II shows our ambient-temperature result together with previous measurements. Among these, our value is highest. We take the general view that poor materials (impurities, lattice defects) and poor measurement methods usually yield low apparent elastic constants. Table II also shows the average value for the five highest reported measurements, an average that agrees with our result within 0.5%.

From the high-temperature slope dB/dT, one can estimate a Grüneisen parameter γ using the following relationship:[31]

$$dB/dT = -3k\gamma(\gamma+1)/V_a. \quad (2)$$

Here, k denotes the Boltzmann constant and V_a atomic volume. Substitution gives $\gamma=5.1$. There exists an alternative approach to estimating the Grüneisen parameter. We use the following relationship:[31]

$$\tilde{B} - B_0 = 3k\Theta_E\gamma(\gamma+1)/2V_a. \quad (3)$$

Here $\tilde{B}$ denotes the harmonic bulk modulus obtained by extrapolating the $B(T)$ curve linearly to zero temperature, V_a

TABLE I. Zero-temperature bulk modulus (GPa) of α-plutonium.

B (GPa)	Source
Measurement	
70.9 ± 0.5	Present
68.5[a]	Rosen *et al.* (Ref. 3)
Theory (chronological)	
55	Skriver *et al.* (Ref. 10)
40	Johansson and Skriver (Ref. 11)
152	Singh (Ref. 12)
170 ,300 (Np)	Soderlind *et al.* (Ref. 13)
130 (Np)	Soderlind *et al.* (Ref. 14)
62[b]	Wallace (Ref. 15)
53[c]	Baskes (Ref. 16)
110–124	Jones *et al.* (Ref. 17)
116–128 (Np)	
116–203[d]	Penicaud (Ref. 18)
60–92[d]	
50	Harrison (Ref. 19)
180 (Np)	Richard *et al.* (Ref. 20)
169 (NM)[e]	Robert *et al.* (Ref. 21)
101(AF)	
144–227 (NM)[e]	Sadigh *et al.* (Ref. 22)
50–189 (AF)	
50	Soderlind and Sadigh (Ref. 23)
93 ± 48[f]	Theory average

[a]Computed from extension and shear moduli.
[b]Estimated from an ambient measurement: 51 GPa.
[c]Adjusted values from ambient value: 41 GPa.
[d]Higher values from theoretical volume. Lower values from observed volume.
[e]NM denotes nonmagnetic. AF denotes antiferromagnetic.
[f]Excludes Np values.

TABLE II. Ambient measured α-plutonium bulk modulus (GPa).

B (GPa)	Source
Measurement	
48.3	Kay and Linford (Ref. 24)
53.5	Gschneidner (handbook) (Ref. 25)
51.7	Cornet and Bouchet (Ref. 26)
59.8	Rosen *et al.* (Ref. 3)
54.1	Merz *et al.* (Ref. 27)
49.1	Calder *et al.* (Ref. 28)
42.2 (static)	Roof (Ref. 29)
43 (static)	Dabos-Seignon *et al.* (Ref. 30)
54.4	Present
54.7 ± 3.0	Average of highest five

TABLE III. Bulk-modulus changes between 300 and 0 K.

Material	$B(0)/B(300)$
Al	1.075
Cu	1.036
Fe	1.030
Pb	1.104
α-Pu	1.303

atomic volume. Substitution gives $\gamma=5.1$. The handbook value from lattice specific heat is 6.8.[25] We believe these values are too high because of $5f$-electron localization that occurs during warming.[32]

Zero-temperature elastic constants provide the best estimate of Θ_D. Since Einstein's lattice-vibration studies,[33] many authors calculated the Debye temperature from the bulk modulus[21,34,35]

$$\Theta_D = K(r_0 B/m)^{1/2}. \tag{4}$$

Here, K denotes a collection of physical constants, r_0 is the Wigner-Seitz radius, and m is the atomic mass. Ledbetter showed that the bulk modulus only roughly estimates Θ_D, that one obtains a much better estimate using the shear modulus G.[36] One obtains an "exact" Θ_D from the elastic constants using a relationship given by Kim and Ledbetter[37]

$$\Theta_D = 2933.22 v_m / V_a^{1/3}. \tag{5}$$

Here, v_m denotes mean sound velocity (obtained by the usual reciprocal-cubed average) and V_a atomic volume. We calculated the mean sound velocity from a well-known relationship

$$3/v_m^3 = 1/v_l^3 + 2/v_t^3. \tag{6}$$

Here, the longitudinal and transverse wave velocities relate simply to the quasiisotropic elastic constants. This approach gives $\Theta_D=205$ K. In Eq. (5), units on v_m are centimeters/microseconds, on V_a Å^3. Θ_D (elastic) equals Θ_D (specific-heat) at zero temperature because they both depend on the same phonon moment (-3). But our Θ_D exceeds considerably most specific-heat values. This point assumes importance because Θ_D relates directly to so many physical properties. We shall give further Θ_D details elsewhere.[4–6]

The bulk modulus decrease from 0 to 300 K is particularly large, as shown in Table III, which shows handbook $B(0)/B(300)$ values for several typical metals. Usually, large changes reflect a large Grüneisen parameter. In the alpha-plutonium case, they may reflect also temperature-induced electronic changes among the $5f$ electrons. Converting itinerant electrons to localized electrons would decrease cohesion and decrease the bulk modulus.[32]

From the fitting parameters associated with Eq. (1), the bulk modulus extrapolates to zero at 1065 K, not far above the ε-phase melting point, 915 K. Although one usually discusses the elastic-constant/melting relationship in terms of a shear modulus,[38,39] some correlations exist also with the bulk-modulus/temperature behavior.[40]

In summary, through measurements we considered alpha-plutonium's bulk modulus, especially at zero temperature, for which most theoretical calculations apply. We extracted a Debye temperature Θ_D and a Grüneisen parameter γ. Smooth $B(T)$ behavior suggests strongly that in the 0–300 K interval no phase transitions occur. Especially notable is the large (30%) bulk-modulus decrease in the 0–300 K interval, which may reflect $5f$-electron localization.

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