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gamma

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Elastic properties of γ-Pu by Resonant Ultrasound Spectroscopy

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Resonant ultrasound spectroscopy was used to measure the elastic properties of pure polycrystalline ^{239}Pu in the γ phase. Shear and longitudinal elastic moduli were measured simultaneously and the bulk modulus was computed from them. A smooth, linear, and large decrease of all elastic moduli with increasing temperature was observed. We calculated the Poisson ratio and found that it increases from 0.242 at 519K to 0.252 at 571K. These measurements on extremely well characterized pure Pu are in agreement with other reported results where overlap occurs.

PACS numbers

Introduction

Plutonium (Pu) is one of the most difficult elements to study, and, second to He, one of the most interesting. At ambient pressure, Pu exhibits six distinct solid-state phases below the melting point. Despite 60 years of theoretical and experimental effort directed toward understanding its properties, open questions remain[1]. To help resolve some of those questions, it is imperative to provide accurate values for the bulk modulus in all the phases because the bulk modulus is an essential thermodynamic quantity minimally sensitive to impurities, the simplest quantity to compute from an electronic structure model, and nearly invariant between monocrystal and polycrystal specimens. This last property is relevant because it is extremely difficult to produce and measure an untwinned monocrystal of γ-Pu.

The experimental challenges are at least twofold: (i) a pure Pu sample requires considerable effort to produce, and (ii) ^{239}Pu requires special handling techniques because of its radiotoxicity. This limits the experimental investigations to techniques that can be set up in specially-designed systems that fulfill extensive safety requirements.

Resonant Ultrasound Spectroscopy (RUS) has been used extensively to determine the thermodynamic and the elastic properties of materials and to understand phase transitions. RUS measures directly the adiabatic elastic moduli; they are the second derivative of the energy (not free energy) with respect to strain, are directly related to the atomic bonding of the material, and are very sensitive to phase transitions and their order. Moduli connect to the thermal properties of solids through Debye theory. In combination with specific heat and thermal expansion measurements, elastic moduli are used to determine the equation of state and various thermodynamic functions.

RUS is described in detail elsewhere [2]. The main advantages of RUS are that:(i) all the elastic moduli are determined in a single measurement scan (ii) RUS does not require bonding of the sample to transducers (iii) it provides exceptional absolute accuracy,and,(iv) it exhibits high precision(typically at least 1 in 10^6).

We have determined the elastic moduli of pure polycrystaline Pu in the alpha (α), beta(β) and gamma (γ) phases. Here we report only the elastic moduli in the γ phase of the same Pu specimen used for all other measurements above ambient temperature. The elastic moduli of Pu in the α phase, the details of the experimental setup, the purity and preparation procedures, and a survey of outstanding problems for understanding of Pu are described elsewhere [1]. The elastic moduli of Pu in β phase will be reported separately. Because of many experimental problems, the elastic moduli of this specimen of pure Pu in the δ phase could not be determined.

The x-ray volume of γ-phase Pu (99.85% with Ag as the deliberately-introduced main impurity) from 486K to 585K was described by Zachariasen [3](analysis of available data by Wallace [4] concludes that the full range of existence of γ-Pu is 488K to 593K). To summarize Zachariasen's work, γ-Pu is face-centered orthorhombic (Fddd), with 8 equivalent atoms in the unit cell at (0, 0, 0; $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$)+ (0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0). Each Pu atom is bonded to ten others at an average distance of 3.157 A, four neighbors are at 3.026 A, two at 3.159 A, and four at 3.2888 A. However in the space group Fddd one has the choice of two origins. By placing the origin at one center of symmetry, Roof [5] pointed out that the structure can be alternatively described with the eight equivalent atoms at $\pm$ ($\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$)+ (0, 0, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0). This description is consistent with the description of other Pu phases. The unit cell dimensions in A, at 535 K, are given by Zachariasen [6] to be a=3.159 $\pm$ 0.001, b=5.768 $\pm$ 0.001 and c=10.162 $\pm$ 0.002. From x-ray experiments [6], the x-ray density was calculated to be 17.14 $\pm$ 0.01 g/cm^3 at 508 K.

The only other available data for the elastic moduli of γ-Pu were obtained from measurements of longitudinal, flexural and torsional [7] resonances, using a Young's modulus and rigidity modulus apparatus. Elastic moduli were obtained after 2 and 3 thermal cycles, a procedure we observed to produce inconsistencies in the phase of the specimen. In our measurements the sample was not cycled, but warmed only once from ambient temperature up to the γ phase boundary.

Experiment

Pure electrorefined ^{239}Pu was used for these experiments. Using chemical methods, the composition was determined to be 99.96 wt.%Pu, 115 ppm W, 49 ppm Np, 50 ppm O, 53 ppm Si, 32 ppm Am and less than 25 ppm other impurities. The parallelepiped-shaped sample was cut from a larger button that was arc melted and quenched on a copper hearth several times, until voids and metallurgical imperfections were negligible. The specimen was 0.265 cm x 0.268 cm x 0.270 cm and the immersion density at 300K was determined to be 19.55 g/cm^3 $\pm$ 0.02% [1]. This value is lower than both the density determined from mass and dimensions (19.70 g/cm^3) and the x-ray diffraction density(19.86 g/cm^3 at 294K).

The RUS system [2] used for this work is described elsewhere [1]. The experiments were carried out in vacuum. The temperature was measured using a RhFe resistance thermometer. At 400 K we obtained a temperature accuracy of 2 %. From the measured resonance frequencies we computed the elastic moduli using the Levenberg-Marquardt algoritm. These algorithms were made available for public use by us [8].

Results and Discussion

A. Resonances

Figure 1 shows the resonant spectrum from 140 kHZ to 320 kHz at two temperatures one near the low end, the other near the high end of the range of existence of γ-Pu. The high signal-to-noise ratio and the high-Q (Q was of order 1000) resonances ensure high-accuracy results for this study. The lowest resonance was observed at about 150 kHz. As the temperature was increased all resonances shifted toward lower values. Using our own algorithms, the center frequencies of 21 resonances were determined at each temperature. Each resonance corresponds to a different vibrational mode. The frequencies of each mode versus temperature were fit to a straight line. The linear fit was used to generate input frequencies for the RUS code that calculates the elastic moduli. Use of this code is described elsewhere [8]. A plot of the fitted resonances versus temperature is shown in fig. 2.

The squares of the resonance frequencies, absent small density corrections, are proportional to the elastic moduli, and therefore the observed decrease of the resonance frequencies with increasing temperature is expected.

B. Elastic Moduli

The elastic behavior of an isotropic polycrystalline material can be described completely by two independent moduli, the longitudinal (C_L) and the shear (G) modulus. The bulk modulus (B), is related to C_L and G through the following relation:

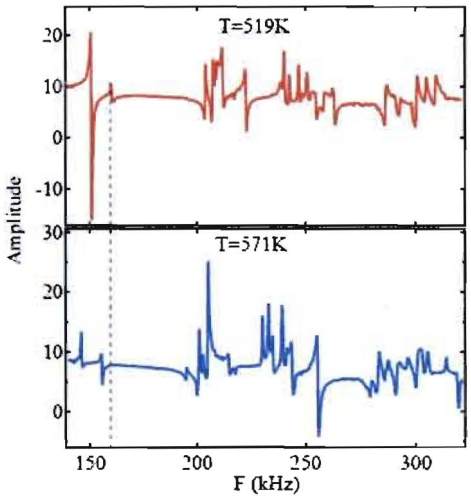

FIG. 1: Part of the resonant frequency spectrum of polycrystalline Pu shown near the low- and high-temperature ends of the γ-phase region of existence. The dashed line provides a guide to the eye to emphasize the size of the shift of the resonances with temperature.

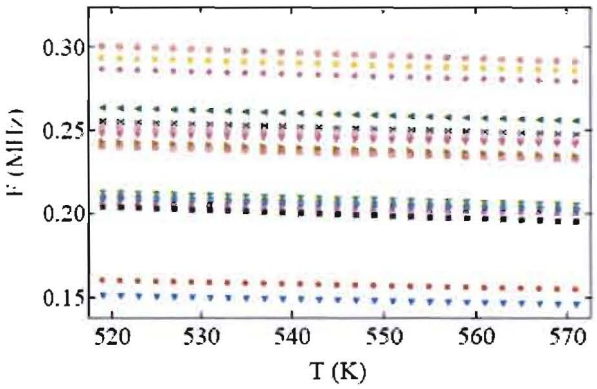

FIG. 2: Fitted resonance frequencies versus temperature. All frequencies show a smooth linear decrease with increasing temperature. These fitted values were used in the computation routine to determine the elastic moduli.

$$B = \frac{C_L - 4G}{3} \tag{1}$$

Figure 3 shows the smooth, linearly-decreasing behavior of C_L, G and, B as a function of temperature. Each elastic modulus was fitted with a straight line and the parameters of the fit are given in table I.

In using the fitting codes [8] that determine elastic moduli from measured frequencies, the algorithms can

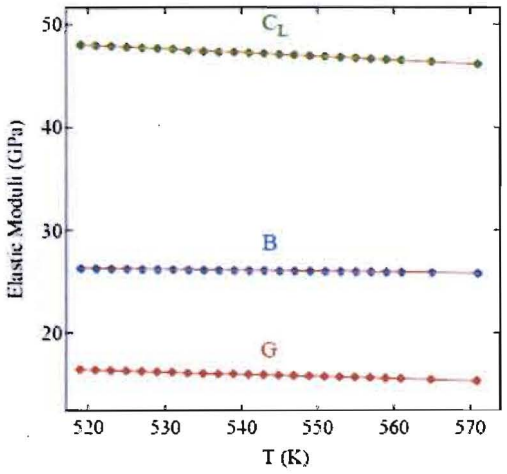

FIG. 3: Temperature dependence of bulk (B), shear (G) and longitudinal (C_L) elastic moduli of γ-Pu.

TABLE I: The parameters of the linear fits to the measurements of C_L, B, and G of the form $a + bT$.

Modulus	a (GPa)	b (GPa/K)
C_L	66.9±0.2	-0.04
B	31.02±0.02	-0.0097
G	26.9±0.1	-0.02

display small artifacts associated with modes changing relative ordering as temperature changes, introducing corresponding artifacts in what should be smooth behavior with temperature of the moduli. Using linear fits to resonance frequencies is often sufficient to block such artifacts, but the mean-square fitting error is a precise test for their presence. Small values of the fitting error are also a useful and quantitative test for isotropy of the polycrystalline specimen. This test is shown in figure 4 where we plot the mean square error of longitudinal and shear moduli versus the moduli and find no unexpected behavior, and strong evidence of isotropy manifested in the small values of the fitted errors.

C. Comparison of Elastic moduli in different phases

In figure 5 we compared the elastic moduli of pure polycrystaline γ-Pu to those of α-Pu and of Ga-stabilized δ-Pu (2.36 at. % Ga) and found, as expected that, modulus by modulus, the moduli of γ-Pu lie between those of α-Pu (highest) and Ga-stabilized δ-Pu (lowest).

We fit the elastic moduli of α-Pu and δ-Pu (2.36 at. % Ga) with a straight line, and compared the parameters of the linear fit to the ones obtained for γ-Pu in the temperature ranges indicated in the tables. Table II shows the results of the linear fit for the three phases. We found that the slope of the fit for the bulk modulus of γ is much lower than the slope of the bulk modulus of other phases.

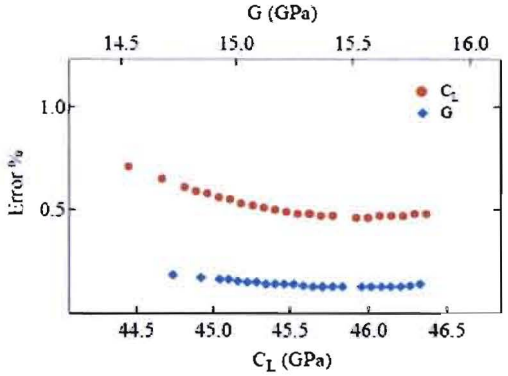

FIG. 4: Mean-square error of shear and longitudinal elastic moduli versus moduli to test for fitting and isotropy errors.

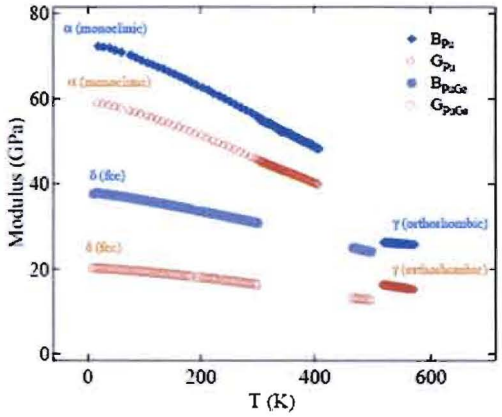

FIG. 5: Comparison of the elastic moduli versus temperature of α-Pu, γ-Pu, and δ-Pu (2.36 at. % Ga).

We compared the fitted parameters of the linear fits to the normalized temperature dependence of the shear and bulk modulus in all phases. The results are presented in table III. The fractional variation of the shear modulus with temperature is similar for α-Pu and γ-Pu, but different for Pu (2.36 at. % Ga) alloy. The fractional variation of the bulk modulus with temperature is unexpectedly small for γ-Pu compared to α-Pu and Ga-stabilized δ-Pu.

D. Poisson Ration

Poisson's ν ratio for polycrystals is defined as:

TABLE II: The parameters of the temperature fit for two elastic moduli of γ-Pu and a comparison with those for α-Pu and Ga-stabilized δ-Pu for the temperature ranges indicated.

Moduli / Phases	G (GPa)	B (GPa)
$\alpha-Pu$	$a = 62.84 \pm 0.25$	$a = 76.5 \pm 1.18$
$T = 381K - 407K$	$b = (-5.6 \pm 0.06) \times 10^{-2}$	$b = (-6.9 \pm 0.3) \times 10^{-2}$
$\gamma-Pu$	$a = 26.94 \pm 0.12$	$a = 31.02 \pm 0.02$
$T = 519K - 571K$	$b = (-2.0 \pm 0.02) \times 10^{-2}$	$b = (-0.97 \pm 0.004) \times 10^{-2}$
$\delta-PuGa$	$a = 20.50 \pm 0.19$	$a = 40.1 \pm 0.06$
$T = 466K - 496K$	$b = (-1.6 \pm 0.04) \times 10^{-2}$	$b = (-3.2 \pm 0.2) \times 10^{-2}$

TABLE III: The logarithmic temperature derivatives for the elastic moduli of γ-Pu and a comparison with those for α-Pu and Ga-stabilized δ-Pu for the temperature ranges indicated.

dlnModuli/dT / Phases	$\frac{d\ln(G)}{dT}$	$\frac{d\ln(B)}{dT}$
$\alpha-Pu$ $T: 381K - 407K$	$-1.39 \times 10^{-3} (\pm 1.1\%)$	$-1.41 \times 10^{-3} (\pm 0.9\%)$
$\gamma-Pu$ $T: 519K - 571K$	$-1.3 \times 10^{-3} (\pm 1.3\%)$	$-0.38 \times 10^{-3} (\pm 0.2\%)$
$\delta-PuGa$ $T: 466K - 496K$	$-1.19 \times 10^{-3} (\pm 0.2\%)$	$-1.32 \times 10^{-3} (\pm 5.9\%)$

$$\nu = \frac{1}{2}\frac{3B - 2G}{3B + G} \tag{2}$$

The Poisson ratio for γ-Pu (fig. 6)is unusual in that, unlike the Poisson ratio for the other Pu phases, ν for γ-Pu appears to have A normal value and increases normally with increasing temperature. Figure 7 shows a comparison of Poisson ration versus temperature of aluminum, α-Pu, γ-Pu, Pu (2.36 at. % Ga),and Pu (5 at. % Ga).

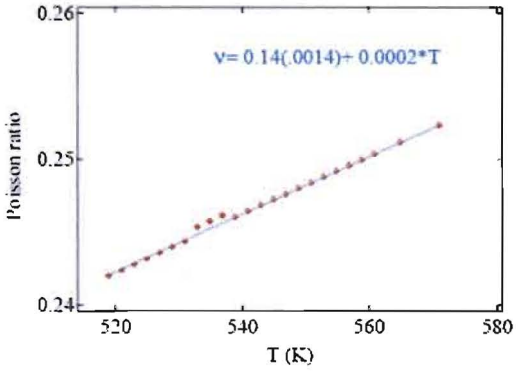

FIG. 6: Temperature variation of Poisson-ration for γ-Pu. The line represents the temperature fit and the parameters of the fit are given.

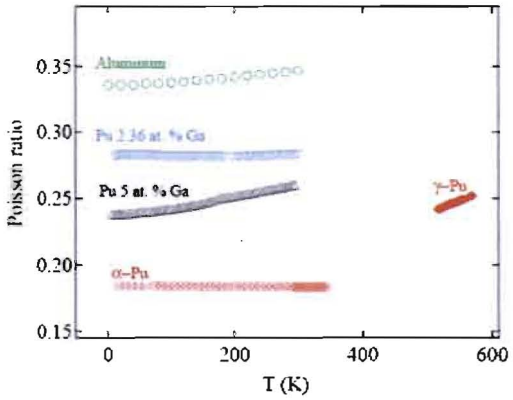

FIG. 7: Comparison of Poisson ration versus temperature of aluminum, α-Pu, γ-Pu, Pu (2.36 at. % Ga),and Pu (5 at. % Ga)

Conclusions

We report measurement of the full set of elastic moduli of a high purity, isotropic, polycrystalline specimen of ^{239}Pu throughout almost the entire range of the existence of its γ phase. We found an unusually ordinary behavior of Poisson's ratio, and unusually low variation of the bulk modulus with temperature. The measured moduli fall, as expected, below those of the lower-temperature, expectedly-stiffer α phase, and above those of the higher-temperature and expectedly-softer δ phase. The measurements pass several internal consistency tests. One previous study approximately agrees with our results.

Acknowledgment

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