Unusual Phonon Softening in δ-Phase Plutonium

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The phonon density of states and adiabatic sound velocities were measured on fcc-stabilized $^{242}Pu_{0.95}Al_{0.05}$. The phonon frequencies and sound velocities decrease considerably (soften) with increasing temperature despite negligible thermal expansion. The frequency softening of the transverse branch along the [111] direction is anomalously large (~30%) and is very sensitive to alloy composition. The large magnitude of the phonon softening is not observed in any other fcc metals and may arise from an unusual temperature dependence of the electronic structure in this narrow $5f$-band metal.

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The systematic behavior of the light actinide metals (Th-Np) is similar to the transition metal series where the $5f$ orbitals (taking the role of the d orbitals in the transition metals) are sufficiently overlapped and bonding properties are dominated by $5f$ band filling. In contrast, the heavy actinides (Am and beyond) resemble the rare earth series: the f orbitals are contracted and localized, do not participate in bonding, and display local moment magnetism. Thus, the actinide series is characterized by a transition of the $5f$ electronic structure from itinerant to localized behavior [1]. At the cusp of this transition is plutonium, where a microcosm of the $5f$ localization transition exists. Pu has six distinct crystal structures at ambient pressure that range in symmetry from simple monoclinic to face-centered-cubic (fcc) with atomic volumes differing by as much as 20%. In the dense Pu phases, the $5f$ electrons form narrow bonding bands susceptible to Peierls instabilities that cause low-symmetry structures to form (e.g., monoclinic α-Pu) [2]. Conversely, the low-density phases have high crystallographic symmetry (fcc δ-Pu) and the $5f$ orbitals are thought to be more localized [3]. Unlike the rare earths, however, the situation in δ-Pu is more complicated. For example, there is no experimental evidence for a local magnetic moment associated with the $5f$ state in δ-Pu [4]. As in related heavy fermion metals and dilute alloys at low pressure, the narrow $5f$ bands of δ-Pu exhibit behavior intermediate between weak and strong electron-electron correlation. A satisfactory theoretical description of electrons in this regime has not been found, and many properties of δ-Pu do not have obvious analogies to the properties of other metals. However, modern theoretical approaches to the problem, such as dynamical mean field theory (DMFT) [5] and density functional theory (DFT) [2] have provided specific insight into the bonding properties of δ-Pu. The very narrow $5f$ bands and subsequent electron localization in δ-Pu predispose the material to a variety of interesting lattice properties, such as negative thermal expansion and large elastic anisotropy [6]. Much can therefore be learned about the $5f$ state in δ-Pu by detailed measurements of the lattice dynamics. Recently, DMFT calculations [5] and inelastic x-ray scattering (IXS) measurements [7] of the phonon dispersion curves in δ-Pu reported an anomalously low-frequency transverse phonon branch along the crystallographic [111] direction ($T[111]$). In this Letter, we report the temperature dependence of the phonon spectrum, as observed from measurements of the phonon densities of states (DOS) and sound velocities. There is a large decrease (softening) of the phonon frequencies and sound velocities with increasing temperature, with the $T[111]$ branch softening considerably ($\Delta E/E \approx 30\%$). These results point to the necessity of elucidating strong temperature dependent effects in the electronic structure which are the root causes of such unusual lattice behavior.

Phonon DOS were obtained from inelastic neutron scattering (INS) measurements on a polycrystalline sample of δ-phase $^{242}Pu_{0.95}Al_{0.05}$. ^{242}Pu enriched to 95% isotopic purity was used because the absorption of thermal neutrons is low (18.5 b) compared to other Pu isotopes. Given the isotopic makeup of the sample, the neutron penetration depth at 25 meV is $\sim$5 mm. The δ phase is thermodynamically stable in pure Pu from 319 to 451 °C and can be stabilized at room temperature and below by small additions of aluminum or gallium [8]. A polycrystalline sample of $^{242}Pu_{0.95}Al_{0.05}$ weighing 35 g was rolled into a disk of $\sim$3 mm thickness and $\sim$30 mm in diameter and annealed after rolling. Safety concerns required the sample to be doubly encapsulated in massive Al cans, an appreciable source of scattered neutron background. Neutron diffraction measurements using the HIPPO (high-pressure preferred orientation) diffractometer at the Lujan Center at Los Alamos National Laboratory were used to determine the phase purity and crystallographic texture of the sample. No significant crystallographic texture was found. There were, however, indications of very weak Bragg peaks possibly from the α' martensitic phase. The maximum α' phase fraction

(5%) is below the detectable limit of our inelastic results. The room temperature lattice constant ($a = 4.58$ Å) and the x-ray density ($\rho = 15.75$ g/cm^3) were determined from the diffraction pattern.

INS measurements were performed using the Pharos spectrometer at the Lujan Center. The sample was mounted on a closed-cycle He refrigerator with the plane of the disk pointed at a 45° scattering angle. Measurements on the Al-encapsulated $Pu_{0.95}Al_{0.05}$ sample and also on the empty can were made at four different sample temperatures (300, 150, 65, and 27 K) over the entire detector bank ($2\theta = 2°$–$145°$) with an incident neutron energy of 36 meV. The Pu data were corrected for time-independent background, detector efficiency, aluminum scattering from the empty can (after an analytical correction for shadowing of the can by the absorbing sample), and sample self-shielding (also from absorption). Multiple scattering corrections were not necessary because such scattering processes are suppressed by the large absorption. Because of the large magnetic susceptibility of δ-Pu, we searched for evidence of magnetic scattering at low angles and found none.

The neutron energy loss data were averaged over large scattering angles $2\theta = 80°$–$145°$ to obtain the phonon spectrum of $Pu_{0.95}Al_{0.05}$. In order to isolate the intensity from single-phonon scattering, the elastic scattering was fit and subtracted, and the multiphonon intensity was calculated using a lattice-dynamical model for fcc γ-Ce [9](which has similar phonon energies). The phonon density of states, $g(E)$, is obtained after Bose thermal population factors are removed. The phonon DOS for $Pu_{0.95}Al_{0.05}$, normalized to one, are shown in Fig. 1. In general, the measured Pu phonon energies are low (less than 13 meV) but have a similar energy scale to γ-Ce [9] and to Pb [10]. Because of the large difference in the mass of Pu and Ce, the average interatomic forces are stronger in Pu ($\omega = \sqrt{K/M}$ for a simple harmonic oscillator) presumably due to involvement of $5f$ electrons in the bonding. This is corroborated by DFT calculations showing that the fcc structure of δ-Pu is stabilized by delocalizing one of the five $5f$ electrons [11].

The region of the DOS below ~1.5 meV is obscured by the elastic scattering tail (the elastic resolution half width at half maximum is 0.7 meV) but can be estimated from the elastic constants. In the limit of very low energies (the Debye or elastic limit), the DOS is quadratic [$g(E) = DE^2$] and the average sound velocity ($\bar{v}$) determines the coefficient $D = a^3/8\pi^2\bar{v}^3$. If the elastic constants are known, $\bar{v}$ is given by

$$\frac{3}{\bar{v}^3} = \sum_{j=1,3} \int \frac{1}{v_j^3(\theta, \varphi)} \frac{d\Omega}{4\pi}, \qquad (1)$$

where $v_j(\theta, \varphi)$ is the sound velocity of branch j in the crystal direction described by the spherical angles. The temperature dependence of the average longitudinal and transverse sound velocities (v_L and v_T) were measured using resonant ultrasound spectroscopy on a small polycrystalline $Pu_{0.95}Al_{0.05}$ sample (Fig. 2). Sound velocities were not corrected for thermal expansion, a small absolute effect. The small discontinuity at 175 K perhaps indicates formation of a small amount of the martensitic

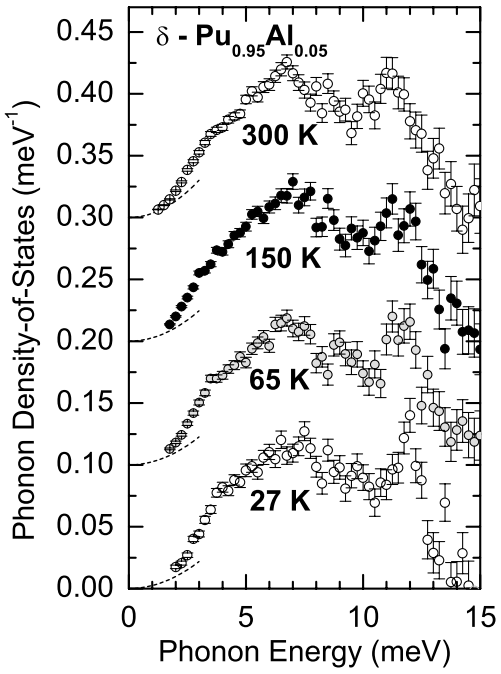

FIG. 1. Phonon densities of states of δ-phase $Pu_{0.95}Al_{0.05}$ at four temperatures: 27, 65, 150, and 300 K. The dashed line represents the quadratic part of the DOS at each temperature, as estimated by the average sound velocity obtained from resonant ultrasound measurements.

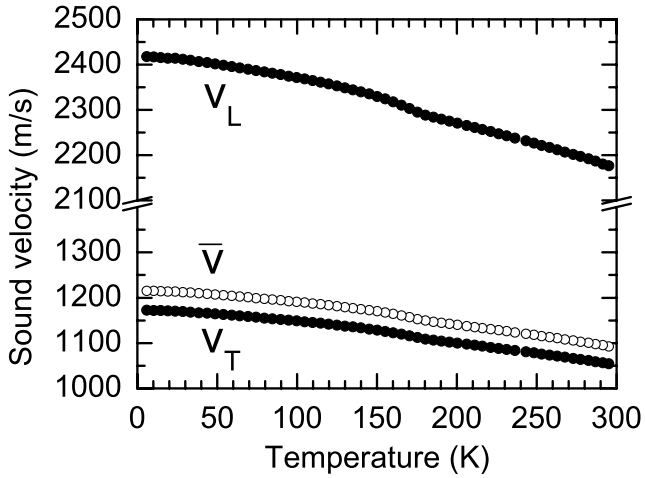

FIG. 2. Polycrystalline longitudinal, transverse, and average sound velocities versus temperature from 5 to 300 K obtained from resonant ultrasound measurements on $Pu_{0.95}Al_{0.05}$. v_L, v_T, and $\bar{v}$ decrease by about 12% upon warming to room temperature.

α' phase [3], possibly due to metastable surface formation during sample cutting. From v_L and v_T, an approximate average sound velocity ($\tilde{v}$) is estimated as

$$\frac{3}{\tilde{v}^3} = \frac{1}{v_L^3} + \frac{2}{v_T^3}. \quad (2)$$

For an isotropic elastic material $\bar{v} = \tilde{v}$; however, δ-Pu is known to have a very large elastic anisotropy [12]. We performed numerical calculations comparing the two different averaging methods [Eqs. (1) and (2)] using the elastic constants of $Pu_{0.967}Ga_{0.033}$ ($C_{11} = 36.28$ GPa, $C_{44} = 33.58$ GPa, and $C_{12} = 26.73$ GPa) [12] and estimate that $\bar{v}$ is 8% larger than $\tilde{v}$ due to anisotropy. By assuming that $Pu_{0.95}Al_{0.05}$ has similar elastic behavior to $Pu_{0.967}Ga_{0.033}$, we obtain $\bar{v}$ as a function of temperature for $Pu_{0.95}Al_{0.05}$ (Fig. 2). This averaging method was also used to calculate the curvature of the DOS at low energies seen in Fig. 1.

At low energies, the measured DOS departs drastically from Debye behavior. This is best observed by plotting $g(E)/E^2$ [Fig. 3(a)], which should be a constant equal to D in the elastic limit. Figure 3(a) shows that the DOS is not quadratic down to 1.5 meV, but has additional weight at low energies. In spite of the increased weight, the values of D seem plausible in the limit as $E \to 0$. Non-Debye behavior is seen to a lesser degree in other fcc metals such as Al, Ni, Cu, La, Ce, Au, Pb, and Th [13] and is generally due to a small nonlinearity in the dispersion at low energies. For $Pu_{0.95}Al_{0.05}$, the enhanced DOS weight arises from an anomalously low-frequency phonon branch. Furthermore, this low energy DOS feature is strongly temperature dependent. Figure 3(b) shows the difference of the 27 and 300 K DOS. The peak-to-peak softening is $\Delta E/E \sim 30\%$ in the 2–5 meV range and is completely consistent with the softening of the average sound speed $[\bar{v}\ (27\ \mathrm{K})/\bar{v}\ (300\ \mathrm{K})]^3 = 1.36$ (Fig. 2). The IXS dispersion results (Fig. 4) indicate that the strong temperature dependence seen in the DOS at ~3 meV arises from the $T[111]$ phonons. Very low energies of the $T[111]$ phonon branch in fcc lattices are commonly associated with a martensitic phase transition to the bcc phase. The softening may indicate instability to formation of bcc ε-Pu well below the transition temperature ($T_{\delta-\varepsilon} \approx 720$ K). Ce and La also have low energy $T[111]$ branches with large elastic anisotropy and a transition to bcc structure at high temperatures, but no softening is observed while approaching the fcc-bcc transition [14,15]: this behavior in Pu is atypical.

Temperature dependent softening is seen to some degree throughout the DOS with an average magnitude of $\Delta E/E \sim 10\%$ from 27 to 300 K. Modes which are identifiable as Van Hove singularities (peaks) in the DOS (see Fig. 4), such as $T[001]$ (7 meV), $L[001]$, and/or $L[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ (12 meV) also show a noticeable temperature dependence [Fig. 3(b)]. The magnitude of these energy shifts is much

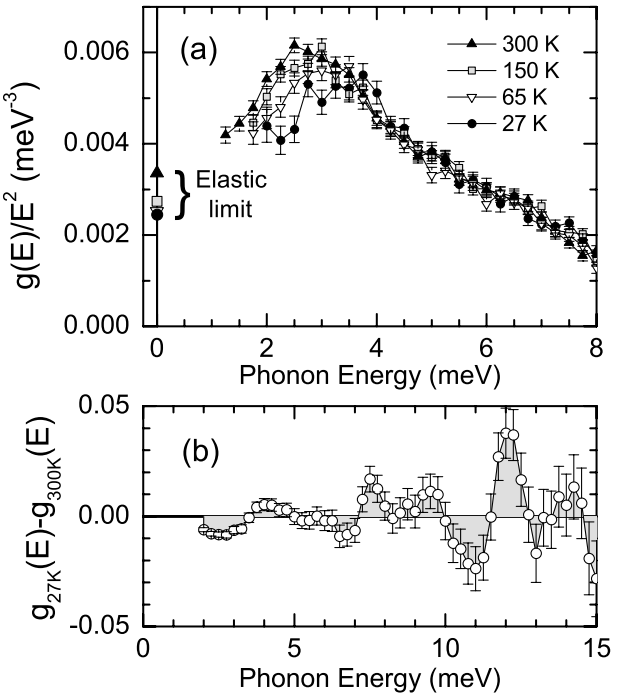

FIG. 3. (a) $g(E)/E^2$ versus E for $Pu_{0.95}Al_{0.05}$ at four temperatures: 27, 65, 150, and 300 K. The four symbols at $E = 0$ indicate the elastic limit of the DOS (D) at each temperature as obtained from the average sound velocity. (b) Difference of the densities of states of $Pu_{0.95}Al_{0.05}$ at 300 and 27 K that has been smoothed using a three-point boxcar averaging. The frequency downshifting of the main Van Hove singularities (3, 7, and 12 meV) at high temperatures are especially clear.

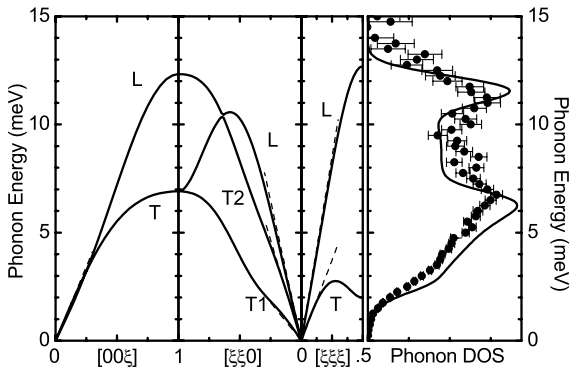

FIG. 4. The three panels on the left show the phonon dispersion curves along certain symmetry directions as calculated from a four-neighbor Born–von Kármán model for fcc $^{242}Pu_{0.98}Ga_{0.02}$ using the room temperature parameters of Wong *et al.* [6]. The dashed lines emanating from the origin reflect the slopes of the dispersion curves at low energies as obtained from the elastic constants. The rightmost panel shows the model phonon DOS for $^{242}Pu_{0.98}Ga_{0.02}$ (line), and the measured DOS of $^{242}Pu_{0.95}Al_{0.05}$ at room temperature (symbols). The calculated DOS has been convoluted with a Gaussian of standard deviation of 0.5 meV, intended to approximate the instrumental energy resolution.

larger than those of other fcc metals with similar Debye temperatures (e.g., Ce, La, and Pb) and agrees with that inferred from average lattice-dynamical properties, such as Debye-Waller factors [16]. Since the softening occurs concomitantly with energy broadening of the DOS features, anharmonicity of the interatomic potential is a possible cause. However, the lattice mode Grüneisen parameter [$\gamma_L = (\Delta E/E)/\beta\Delta T \approx 10$] is large, whereas the thermodynamic Grüneisen parameter ($\gamma_G = \beta\nu B_s/C_p \approx 0.5$) is very small because the thermal expansion, β, and isothermal bulk modulus, B_s, are small. In other words, the interatomic forces are considerably reduced with little change in the average bond length. The large electronic heat capacity of δ-Pu ($\gamma \approx$ 45–65 mJ mol^{-1} K^{-2} [17]) indicates a substantial effect of temperature on the occupancy of narrow electronic bands near the Fermi level, as would be expected for the nearly localized $5f$ states. The component of bonding between Pu atoms originating with $5f$ electrons is expected to be strongly sensitive to atom displacements (related to Peierls distortions in the low-symmetry structures), producing an electron-phonon interaction that would decrease the effective interatomic force constant with increasing temperature. These electronic effects in Pu appear to dominate the conventional sources of lattice anharmonicity, perhaps analogous to those suggested for uranium [18].

In addition to the temperature sensitivity, the lattice properties of δ-Pu should depend on pressure or alloy composition. Alloying with Al or Ga acts as an applied negative pressure, with approximately 1 at.% fully expanding the lattice by 20% to the low-density δ-phase volume. Comparison of the phonons determined from model fits to the IXS data on $^{239}Pu_{0.98}Ga_{0.02}$ [7] with our INS results on $^{242}Pu_{0.95}Al_{0.05}$ indicate a large alloying effect on the phonons (Fig. 4). The most notable difference is the higher frequency of the $T[111]$ and $T[100]$ peaks in the 5% Al stabilized alloy compared to 2% Ga. This perhaps parallels the higher degree of fcc phase stabilization in the more heavily alloyed 5% Al. The magnitude of the alloy-dependent frequency shift of the $T[111]$ mode ($\Delta E/E \sim 15\%$) is in correspondence with the variation of the transverse sound velocity with composition $[v_T(5\%\text{-Al})/v_T(2\% - \text{Ga})]^3 = 1.15$ [19]. These results indicate that the interatomic potential of Pu is extremely sensitive to pressure, alloying, and temperature unlike any other metal and most closely resembles other light actinides where bonding is progressively influenced by $5f$ bands. A full understanding of δ-Pu will require that electronic structure theories go beyond the ground state by including the effects of finite temperature and electron-phonon coupling in this narrow $5f$ band metal.

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