Unusual phonon softening in δ-Pu

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Work presented here was done while I was at Los Alamos National Laboratory
Why do we care about Pu?

- Pu is important for national security
- CTBT – how do we know nukes still work?
  - Equation-of-state (up to ridiculous P-T)
  - Electronic structure calculations (phase stability)
- Pu is extremely complicated
  - Experimental measurement of fundamental properties is essential
Atomic size of the actinides
Crystalline Pu phases

Six Distinct Solid-State Phases of Plutonium

- Body-centered orthorhombic, 8 atoms per unit cell
- Face-centered cubic, 4 atoms per unit cell
- Body-centered cubic, 2 atoms per unit cell

Anomalous Thermal Expansion and Phase Instability of Plutonium

Length change (%)

- Monoclinic, 16 atoms per unit cell
- Pure Pu

Temperature (°C)

- Pure Al

Contraction on melting
δ-Pu: Most important phase

- δ-Pu has ideal metallurgical properties….
  - fcc slip system
  - Ductile
  - Can be stabilized to RT by alloying
- But poorly understood physical properties
  - Small range of pressure-temperature-alloy stability
  - Large elastic anisotropy
  - Negative thermal expansion
  - Large low-temperature heat capacity/susceptibility
δ-Pu: Intermediate valence

- Large volume expansion compared to α-Pu
- Moderately heavy e⁻ mass (65 mJ mol⁻¹K⁻²)
- Large T-independent χ (5e⁻⁴ emu/mol)
- Negative thermal expansion (Invar)
- Unusual thermal parameters (anharmonicity)
- Largest fcc shear anisotropy (c₄₄/c*~7)
- Sensitive to alloying
Motivation for phonon work

- Phonons are normal modes of the lattice
- Phonons are a measure of the curvature of the interatomic potential
- Study of phonons can reveal anomalous bonding properties in $\delta$-Pu
Experiment setup

- Polycrystalline $^{242}\text{Pu}_{0.95}\text{Al}_{0.05}$
  - 35 grams
  - Flat-disk geometry
  - Large-encapsulation
  - Sample cost $1,000,000 !!

- Inelastic neutron scattering on Pharos (LANL)
- $T=27, 65, 150, 300$ K (Displex refrigerator)
- Resonant ultrasound, heat capacity
Pharos spectrometer

\[ h\omega = \frac{1}{2} m(v_i^2 - v_f^2) \]

\[ q = \frac{m}{\hbar} (v_i - v_f) \]
Reduced pharos data – Pu 300K

\[
g(E) = E \left(1 - e^{-E/kT}\right) \left[ \sum_{2\theta=80^\circ}^{145^\circ} S(2\theta, E) - S_e(E) - S_m(E) \right]
\]
Inelastic x-ray scattering (ESRF)

Pu$_{0.98}$Ga$_{0.02}$

Phonon Density-of-States

Several features are apparent:
- T1, T2, L van Hove singularities
- Looks like typical FCC DOS
- Very low energy DOS given by sound velocity

McQueeney et al. PRL (2004)
Phonon softening

\[ \frac{\Delta E}{E} \approx 10\% \]

\[ \frac{\Delta E}{E} \approx 30\% \]

\[ g_{27K}(E) - g_{300K}(E) \]

\[ [v(27K)/v(300K)]^3 = 1.36 \]
Non-Debye behavior & anomalous softening

\[ \frac{\Delta E}{E} \approx 30\% \]

\[ D = \frac{g(E)}{E^2} \]

Thermodynamic Gruneisen

\[ \gamma_G = \beta \nu B_s / C_p \approx 0.5 \]

Mode Gruneisen

\[ \gamma_L = \frac{(\Delta E/E)}{\beta \Delta T} \approx 10 \]

\[ \gamma_G \ll \gamma_L \text{ constant volume softening} \]
IXS – INS comparison

\[\text{Phonon Energy (meV)}\]

\[\Delta \text{E}/E \sim 15\%\]

5\%-Al

2\%-Ga

\[\xi, \xi, \xi\]
Alloy dependence

![Graph showing the relationship between solute concentration and c44, c11 properties of alloys.]

\[ \left[ \frac{v_T(5\%)}{v_T(2\%)} \right]^3 = 1.15 \]

More stable alloys have stiffer phonons
Pu magnetism ??
No evidence from neutron data
Summary

- $T[111]$ branch softens anomalously with increasing temperature seen in both INS and RUS
- No thermal expansion
- $T$-dependent potential due to intermediate valence
- $T[111]$ martensitic instability towards bcc $\varepsilon$-Pu
- Alloying stabilizes phonon softening and also $\delta$-phase
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