Unusual phonon softening in δ-Pu

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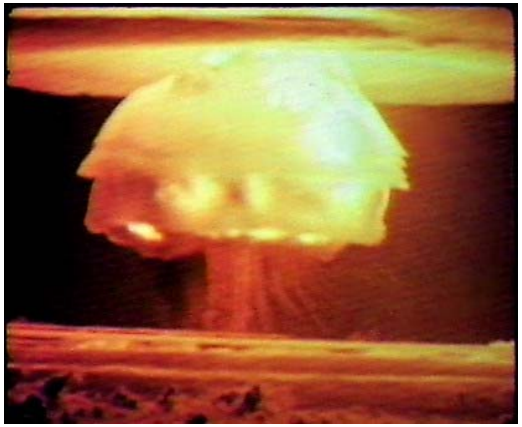
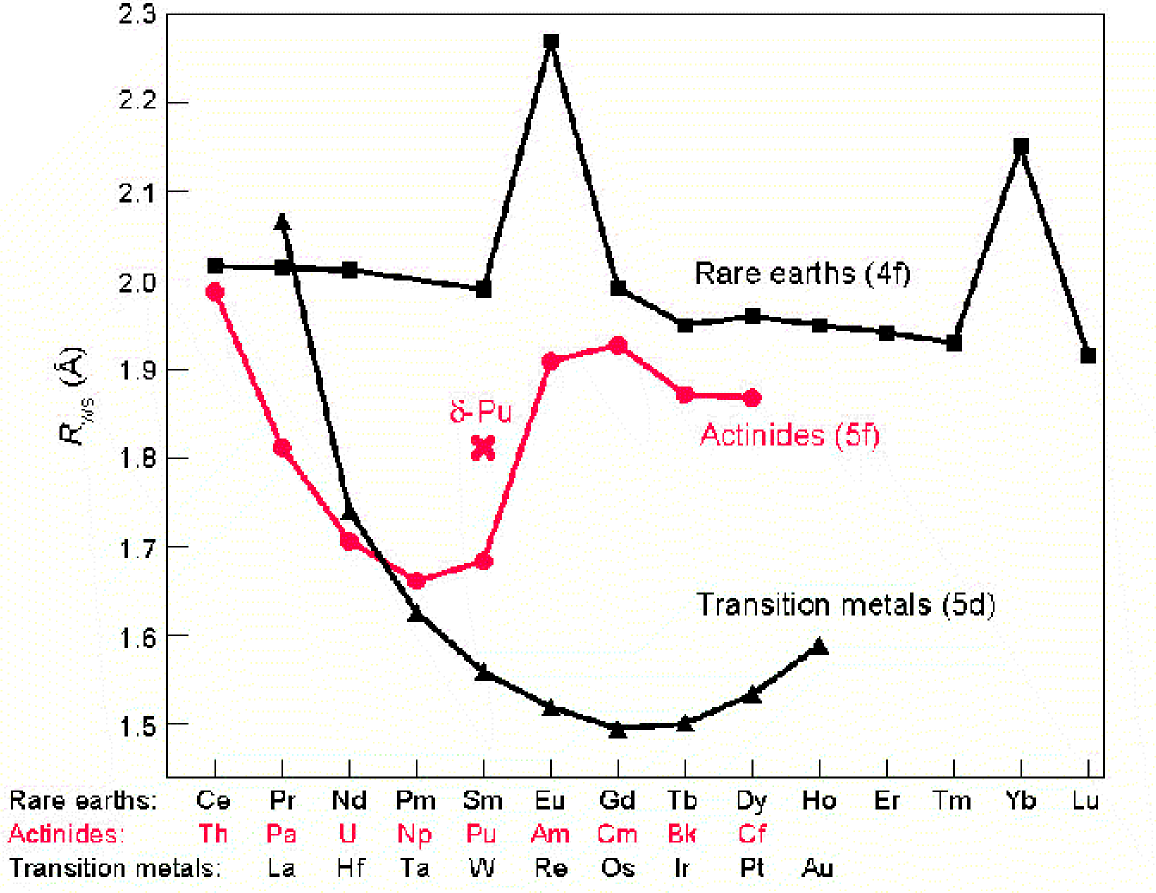
Work presented here was done while I was at Los Alamos National Laboratory

Why do we care about Pu?

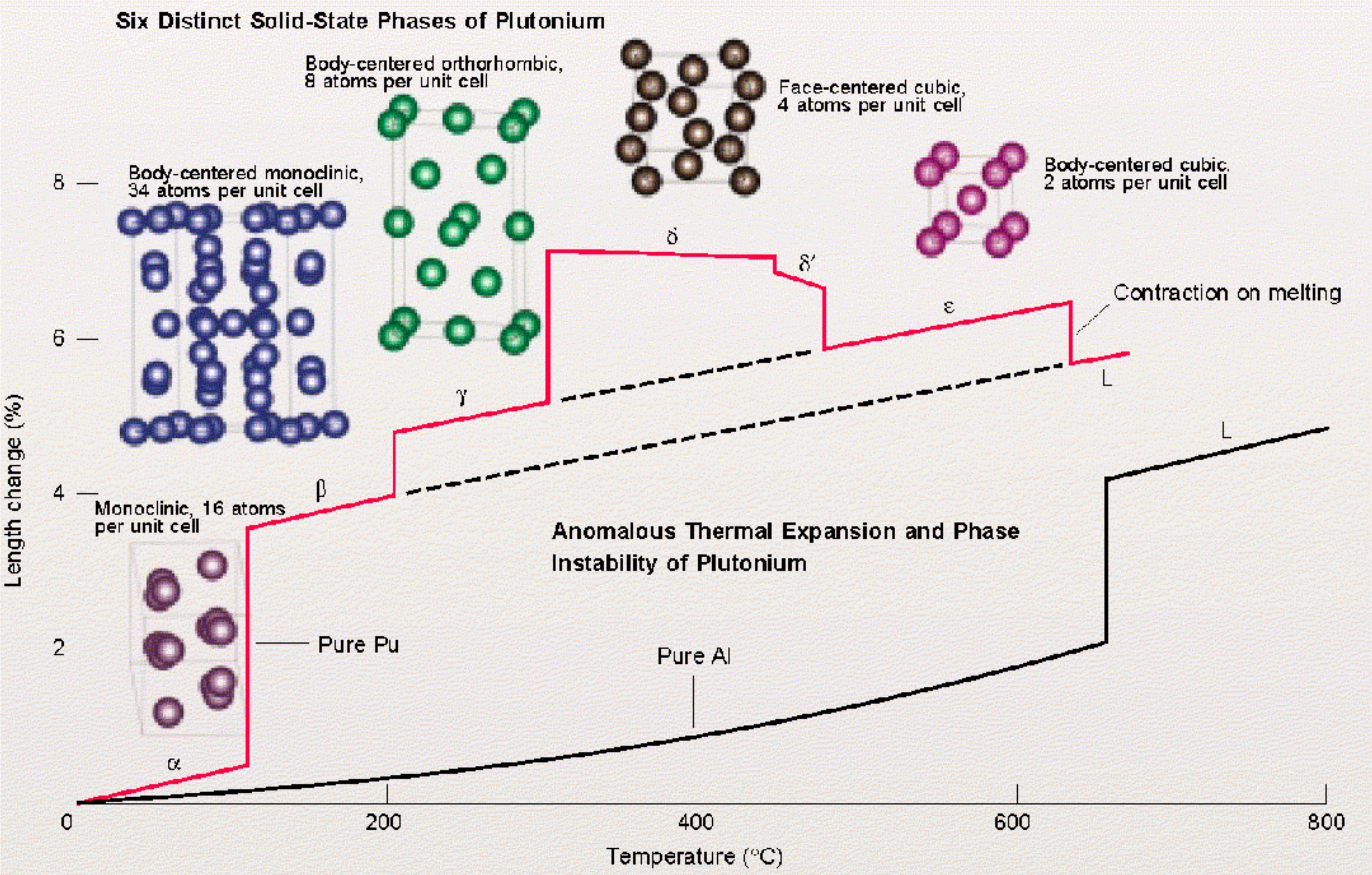
- Pu is important for national security
- CTBT – how do we know nukes still work?
  - Equation-of-state (up to ridiculous P-T)
  - Electronic structure calculations (phase stability)
- Pu is extremely complicated
  - Experimental measurement of fundamental properties is essential



Atomic size of the actinides



Crystalline Pu phases

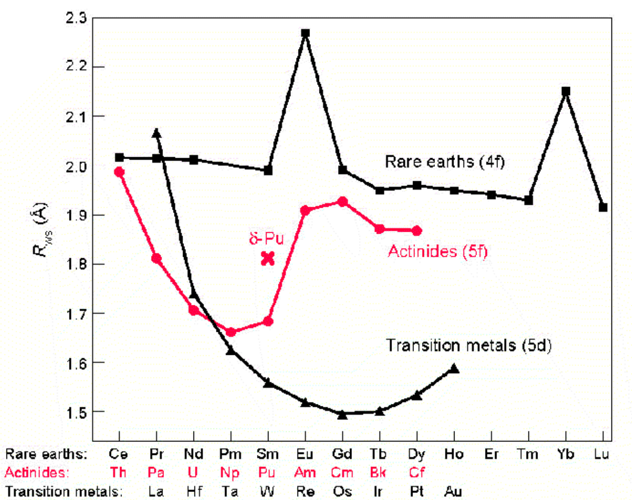


δ-Pu: Most important phase

- 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

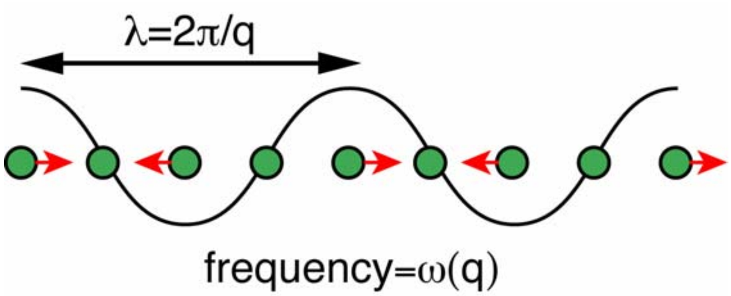
δ-Pu: Intermediate valence

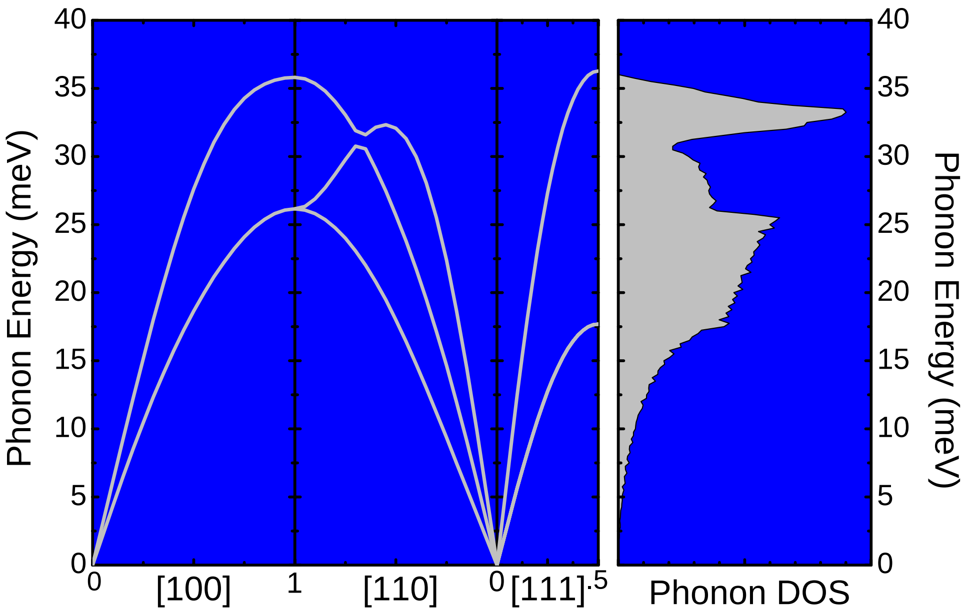
- Large volume expansion compared to α-Pu
- Moderately heavy e^- mass (65 mJ $mol^{-1}K^{-2}$)
- Large T-independent χ (5e-4 emu/mol)
- Negative thermal expansion (Invar)
- Unusual thermal parameters (anharmonicity)
- Largest fcc shear anisotropy (c44/c*~7)
- Sensitive to alloying



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 δ-Pu



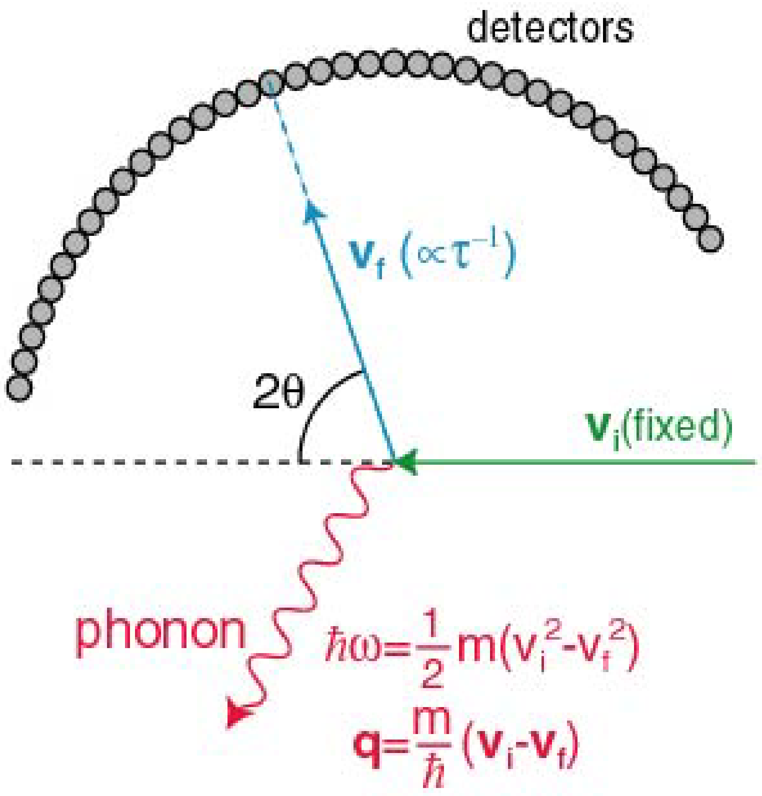


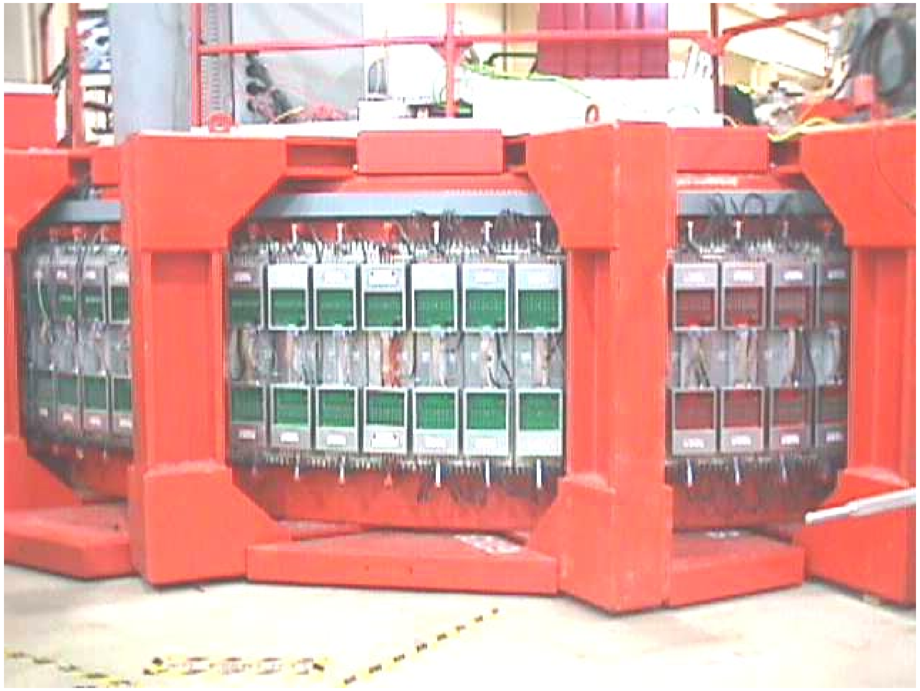
Experiment setup

- Polycrystalline $^{242}Pu_{0.95}Al_{0.05}$
  - 35 grams
  - Flat-disk geometry
  - Large-encapsulation
  - Sample cost $1,000,000 !!

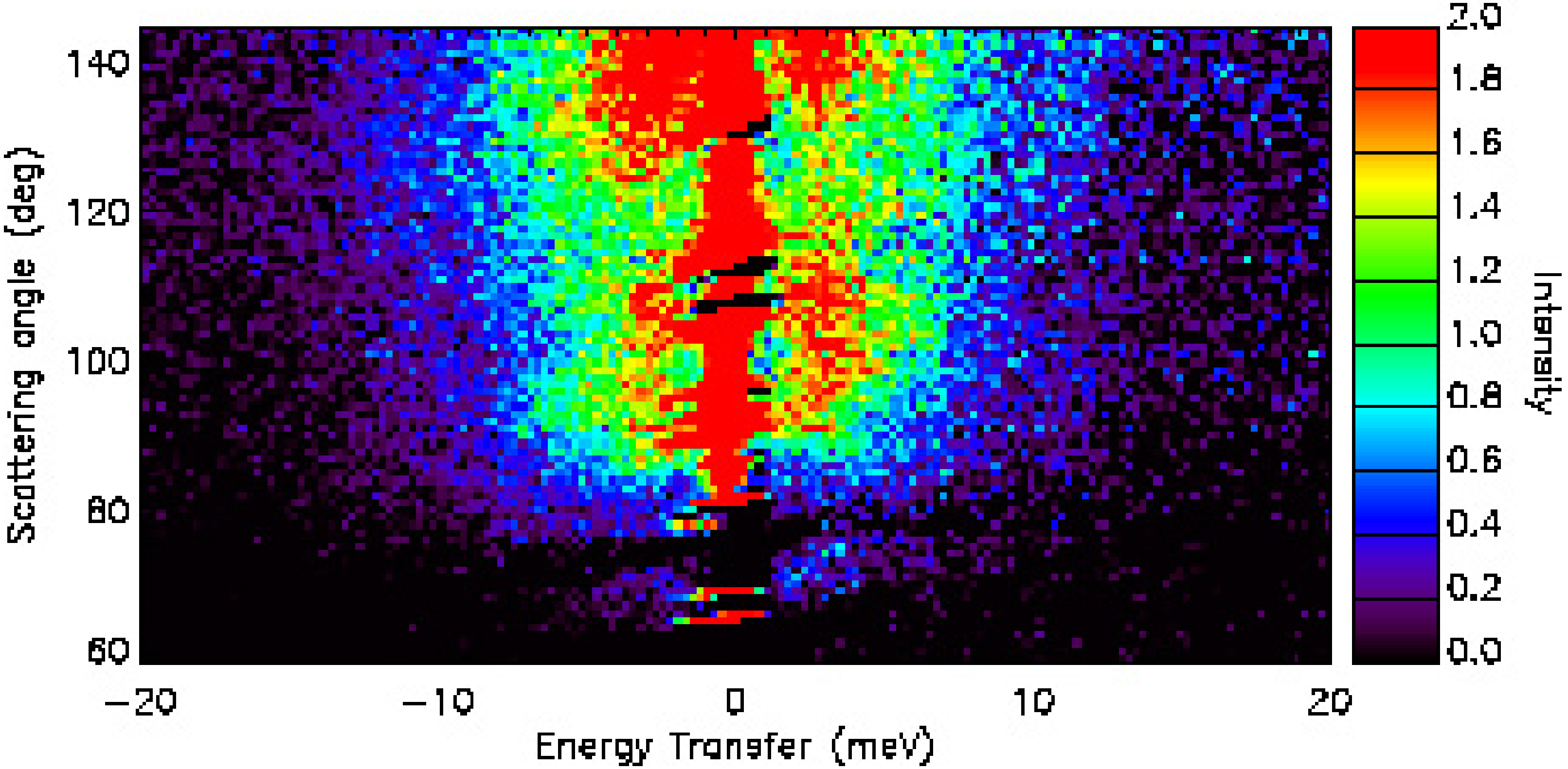
- Inelastic neutron scattering on Pharos (LANL)
- T=27, 65, 150, 300 K (Displex refrigerator)
- Resonant ultrasound, heat capacity

Pharos spectrometer





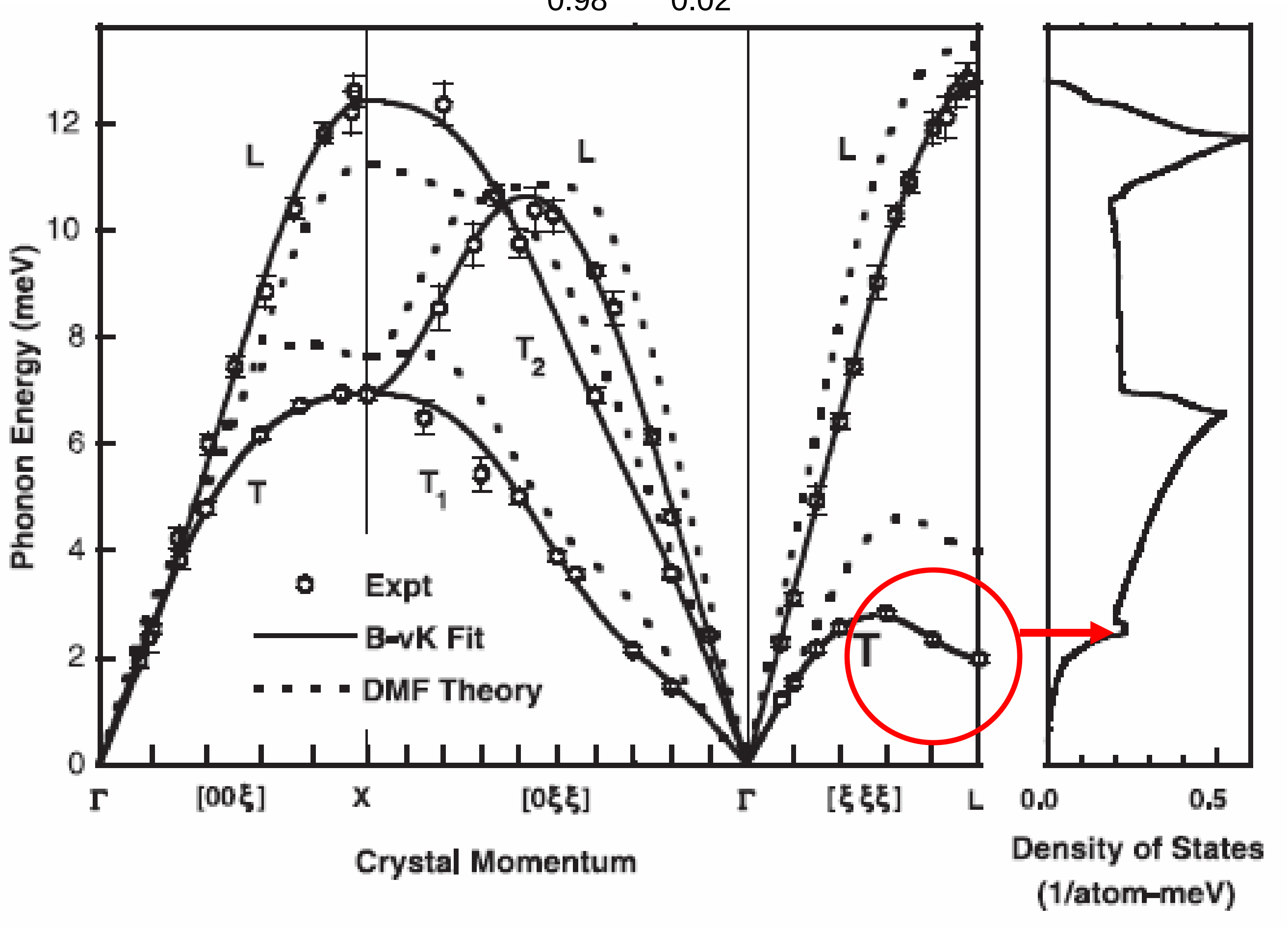
Reduced pharos data – Pu 300K



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

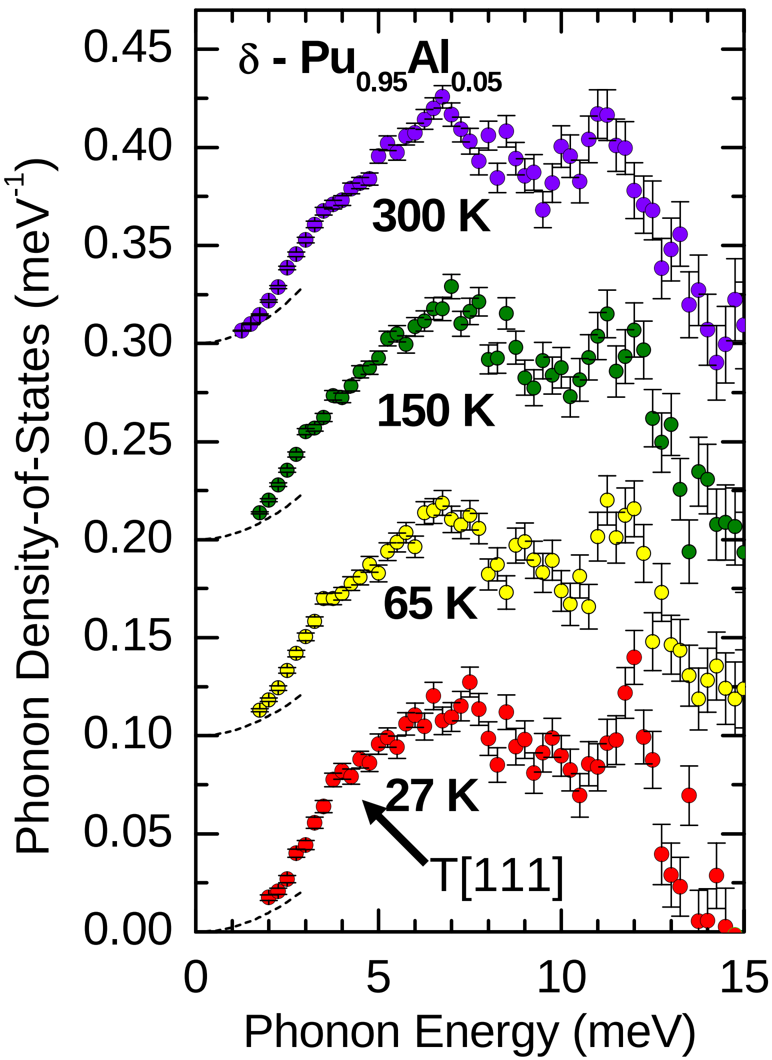
Inelastic x-ray scattering (ESRF)

$Pu_{0.98}Ga_{0.02}$



Wong, et al, Nature (2003)

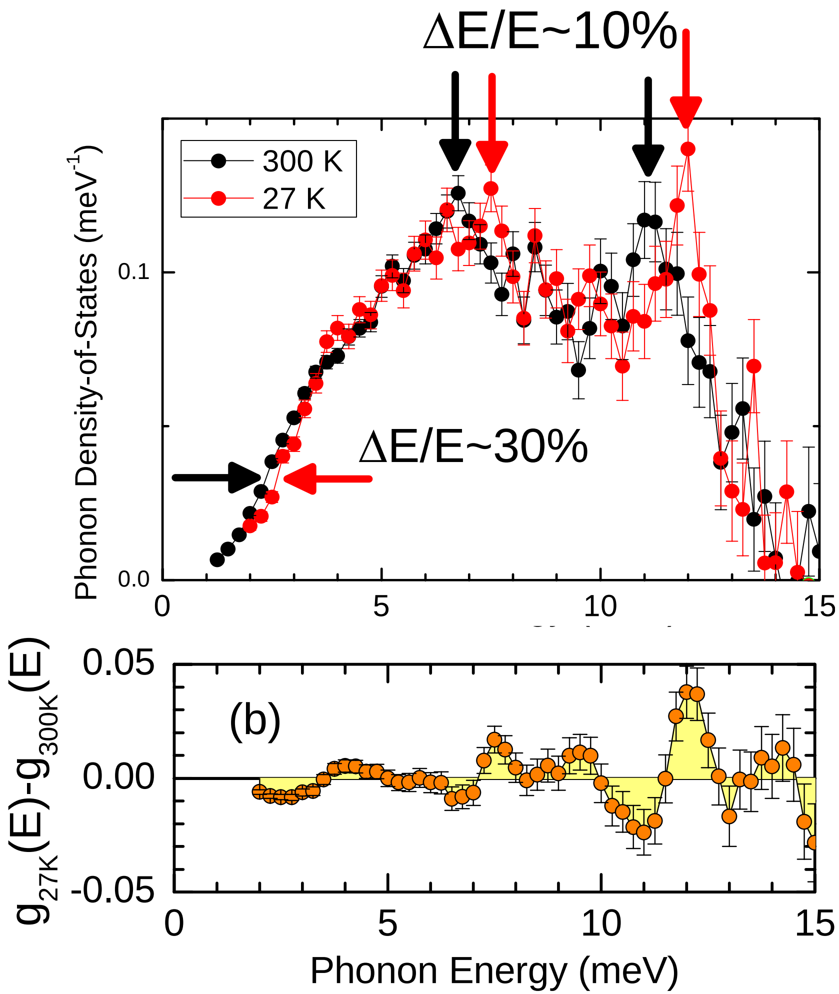
Phonon Density-of-States

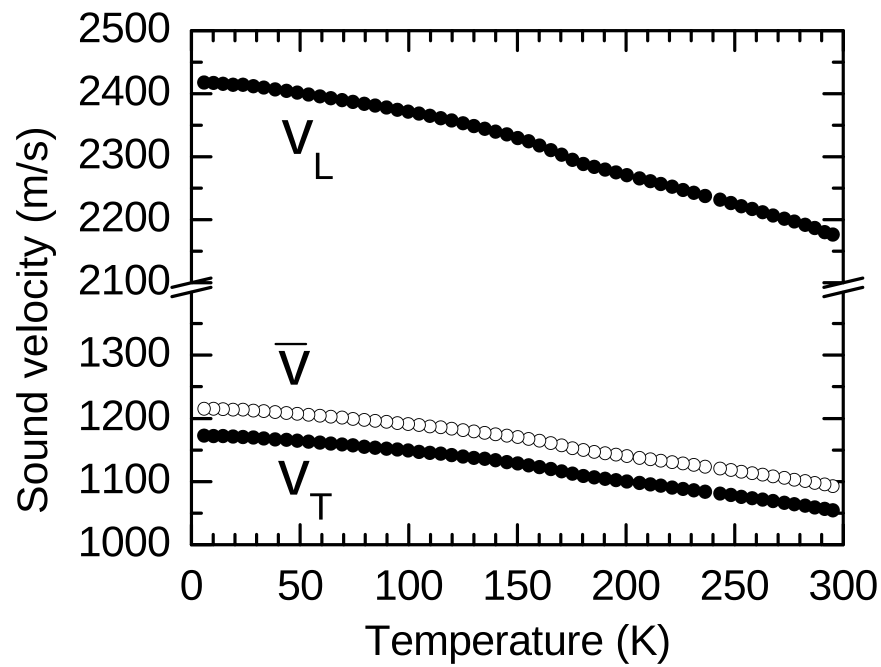


- Several features are apparent: T1,T2,L van Hove singularities
- Looks like typical FCC DOS
- Very low energy DOS given by sound velocity

McQueeney et al. PRL (2004)

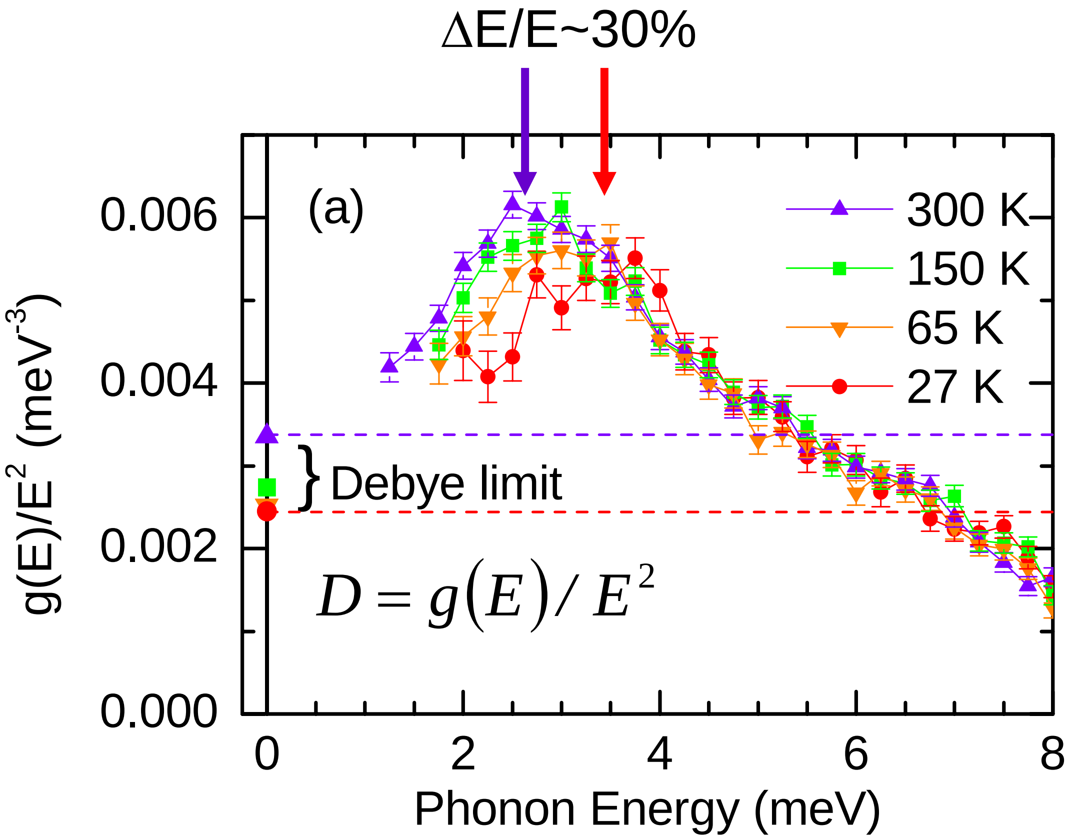
Phonon softening





$[v(27K)/v(300K)]^3=1.36$

Non-Debye behavior & anomalous softening



Thermodynamic Gruneisen

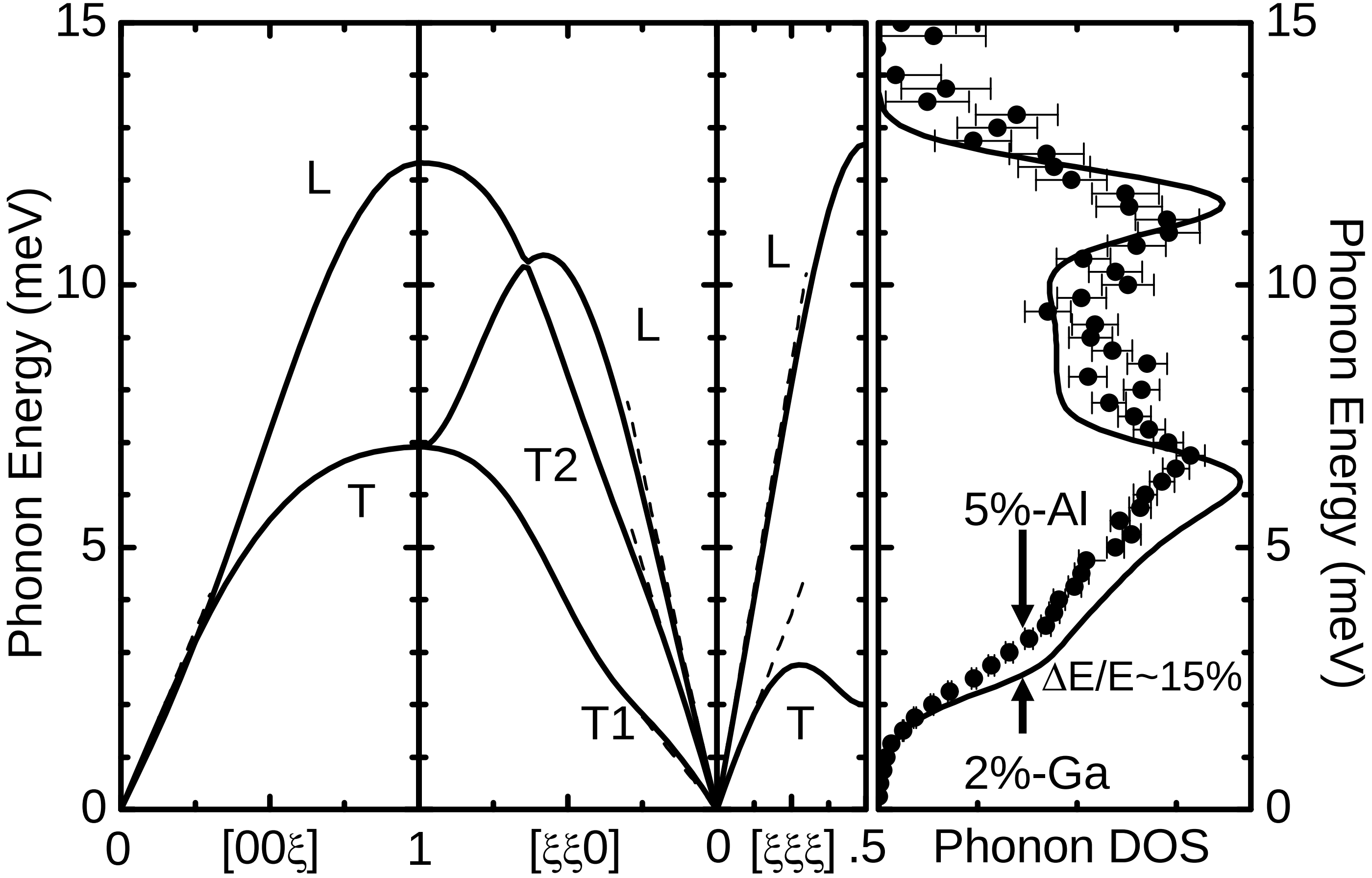
$\gamma_G = \beta \nu B_s / C_p \approx 0.5$

Mode Gruneisen

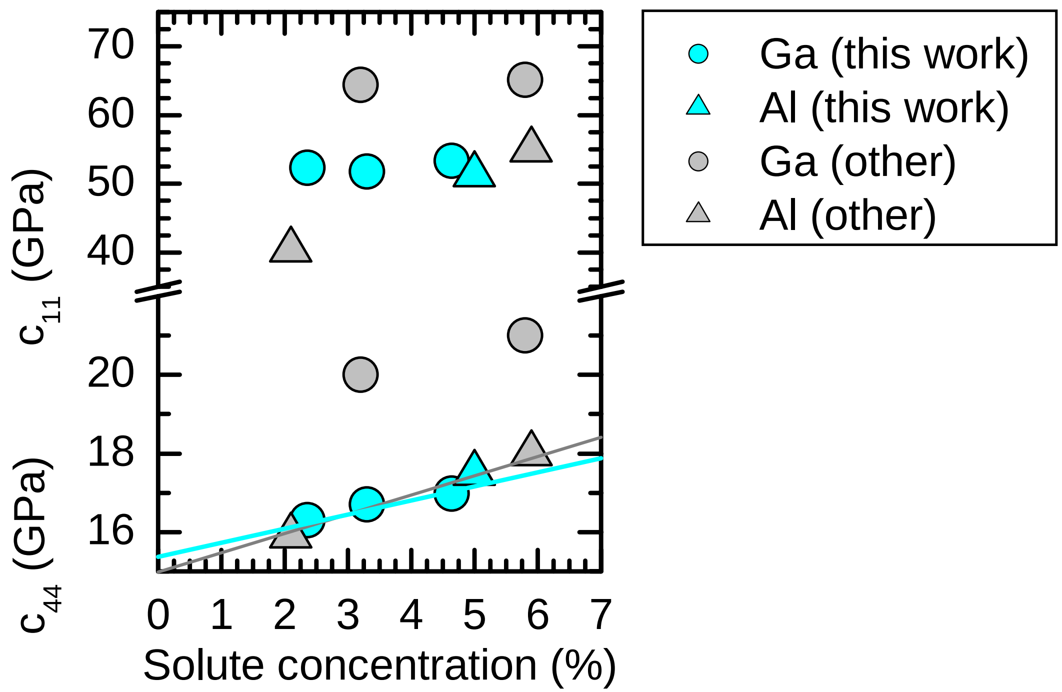
$\gamma_L = (\Delta E/E)/\beta \Delta T \approx 10$

$\gamma_G << \gamma_L$ constant volume softening

IXS – INS comparison



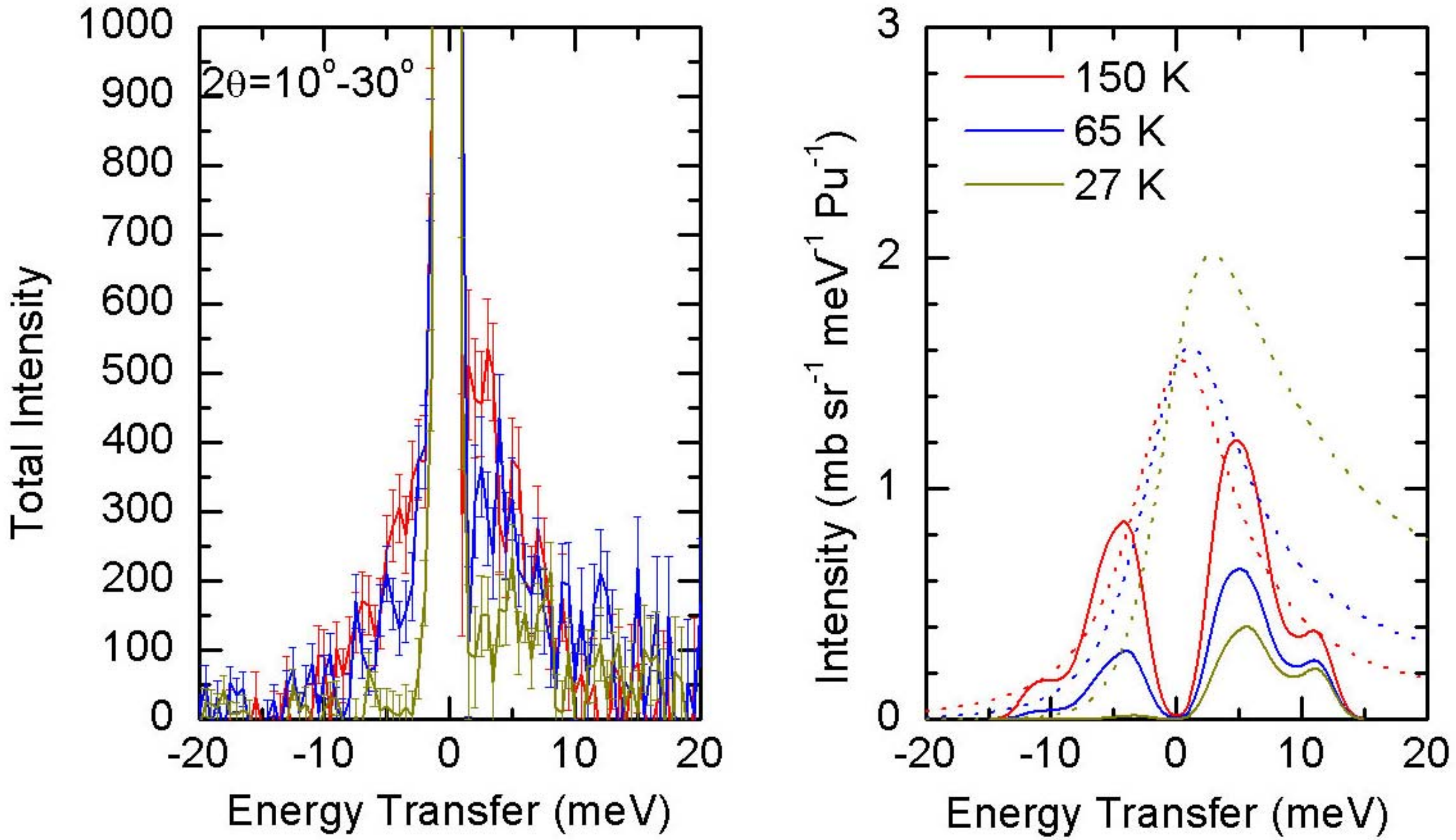
Alloy dependence



$$[v_T(5\%)/v_T(2\%)]^3=1.15$$

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 ε-Pu
- Alloying stabilizes phonon softening and also δ-phase

Acknowledgments

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