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Local Structural Investigation of Pu-7at.%Ga Alloys Using Neutron Total Scattering

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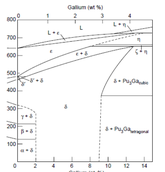
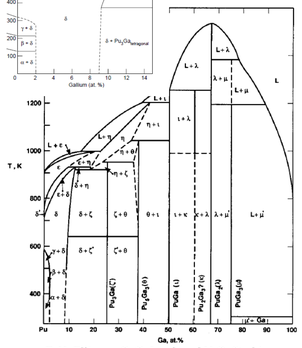
PuGa Alloys

- six phases: α, β, γ, δ, δ', and ε from 293K to 913K
- δ phase: stable 588 to 730K; Ga, Al, Ce, Am: δ-phase stabilizers down to room temperature (RT)
- ^{239}Pu-Ga lattice constants lower than the ^{242}Pu-Ga (irradiation), proportional to Ga content[1-2]
- Stability: effects on mechanical properties, microstructure, corrosion behavior, structural integrity
- stabilization mechanism not well understood



D. E. Peterson and M. E. Kassner, Bulletin of Alloy Diagrams, 9(3) 1988, 261



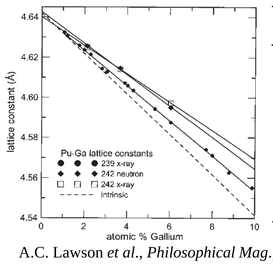
F. H. Ellinger, C. C. Land, and V. O. Strebing, The Plutonium-Gallium System, J. Nucl. Mat., 12 (1964) p. 226.

[1]. A. C. Lawson et al, Phil. Mag., Vol. 85, No. 18, 21 June 2005, 2007–2022
[2]. N. T. Chebotarev, O.N Utkina, Plutonium 1975 and Other Actinides, Elsevier, New York 1976

Synthesis and Characterization

- high purity ^{239}Pu-7at.%Ga samples
- samples cleaned, vacuum degassed, Ga homogenized in the Sievert furnace for more than 100hrs, at 525°C; cooling
- 1% D loading: furnace, 60 hours full thermodynamic equilibration; cooling

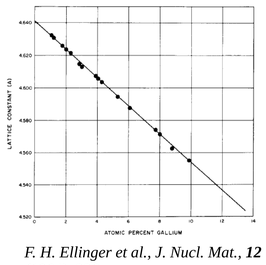
- XRD characterization (RT) Scintag XDS 2000 Powder X-ray Diffractometer MST-16, Los Alamos National Laboratory
- neutron diffraction and pair distribution function (PDF) measurements (RT) on Neutron Powder Diffractometer (NPDF) Los Alamos Neutron Scattering Center (LANSCE-LC), Los Alamos National Laboratory



A.C. Lawson *et al., Philosophical Mag.*, **85**:18, 2007-2015

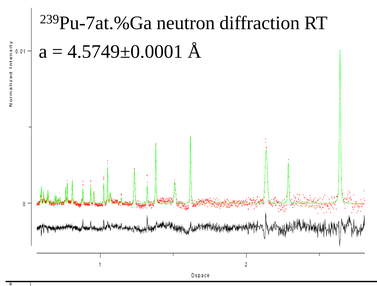
δ Phase lattice parameter/composition data

Composition by analysis (at % Ga)	Lattice parameter † (Å)	Number of samples
1.06	4.6324 ± 0.0001	2
1.19	4.6307 ± 0.0002	4
1.76	4.6259 ± 0.0002	6
1.99	4.6237 ± 0.0001	4
2.29	4.6214 ± 0.0001	5
2.82	4.6144 ± 0.0007	16
3.05	4.6128 ± 0.0002	2
3.89	4.6072 ± 0.0005	3
4.03	4.6059 ± 0.0001	5
4.28	4.6035 ± 0.0003	9
5.30	4.5943 ± 0.0003	3
6.04	4.5876 ± 0.0004	4
7.71	4.5740 ± 0.0008	16
7.99	4.5711 ± 0.0001	3
8.78	4.5626 ± 0.0002	2
9.88	4.5551 ± 0.0006	4

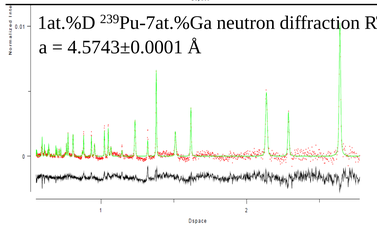


F. H. Ellinger et al., J. Nucl. Mat., 12 (1964), 226.

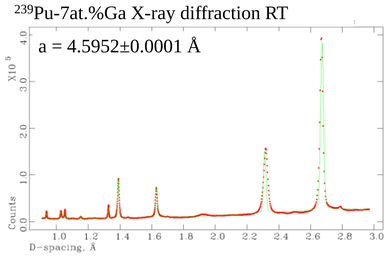
^{239}Pu-7at.%Ga neutron diffraction RT
a = 4.5749±0.0001 Å



1at.%D ^{239}Pu-7at.%Ga neutron diffraction RT
a = 4.5743±0.0001 Å



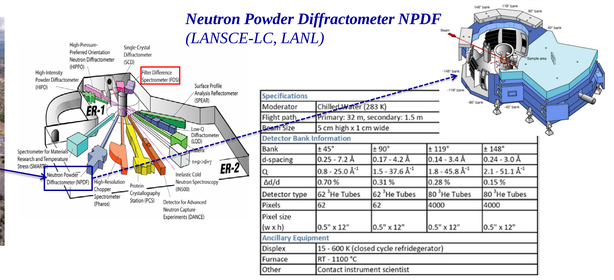
^{239}Pu-7at.%Ga X-ray diffraction RT
a = 4.5952±0.0001 Å



- no difference in lattice parameter upon D loading
- cleaner sample (compared to the ^{239}Pu-2at.%Ga): no oxides/hydrides/ carboxydes, as revealed by RT XRD

Neutron Pair Distribution Function (PDF)

Neutron Powder Diffractometer NPDF (LANSCE-LC, LANL)



Specifications					
Moderator	Chilled water (283 K)				
Flight path	Primary: 32 m, secondary: 1.5 m				
Beam size	5 cm high x 1 cm wide				
Detector Bank Information					
Bank	± 45°	± 90°	± 119°	± 148°	
d-spacing	0.25 - 7.2 Å	0.17 - 4.2 Å	0.14 - 3.4 Å	0.24 - 3.0 Å	
Q	0.8 - 25.0 Å^{-1}	1.5 - 37.6 Å^{-1}	1.8 - 45.8 Å^{-1}	2.1 - 51.1 Å^{-1}	
Δd/d	0.70 %	0.31 %	0.28 %	0.15 %	
Detector type	62 ^{3}He Tubes	62 ^{3}He Tubes	80 ^{3}He Tubes	80 ^{3}He Tubes	
Pixels	62	62	4000	4000	
Pixel size (w x h)	0.5" x 12"	0.5" x 12"	0.5" x 12"	0.5" x 12"	
Ancillary Equipment					
Displex	15 - 600 K (closed cycle refridegerator)				
Furnace	RT - 1100 °C				
Other	Contact instrument scientist				

Requirements of a good PDF

- high max momentum transfer, Q_{max}
- high Q-resolution
- good counting statistics at high Q
- low and stable instrument background

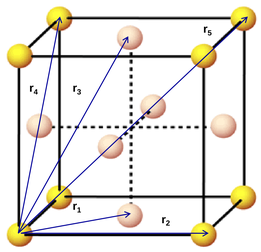
↓

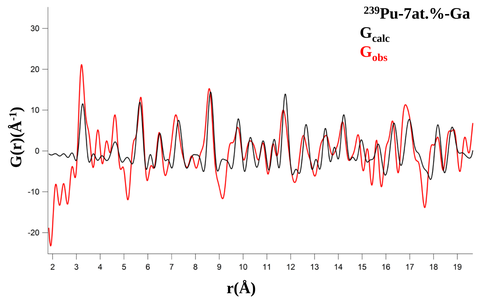
- neutron spallation sources
- synchrotron sources

Neutron advantages

- constant structure factor
- good sensitivity to deuterium/hydrogen
- low-Z elements scatter well
- good contrast between neighboring elements and isotopes
- isotopic substitution

δ ^{239}Pu-7at.%Ga

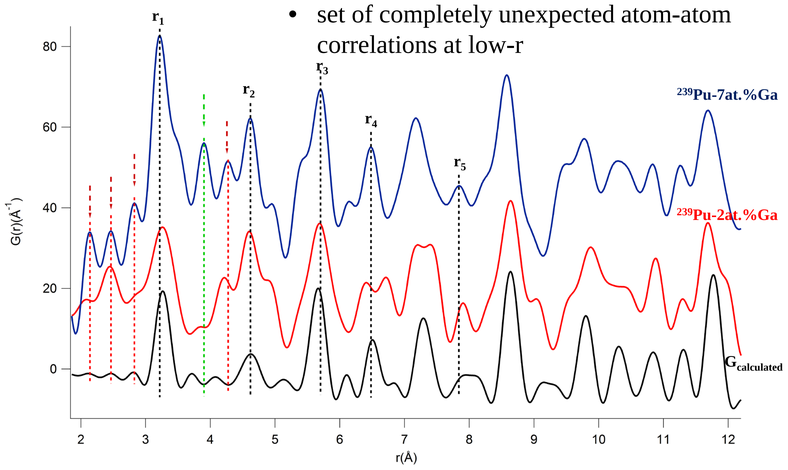




^{239}Pu-7at.%Ga

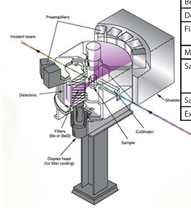
r_{calc}	r_{exp}
3.235	3.22
4.575	4.62
5.604	5.7
6.649	6.48
7.924	7.84

- lattice parameters in good agreement with previously published results
- short-range structure different from the average structure determined through conventional analysis.
- poorly described peak shapes for the expected δ-Pu local bonding
- set of completely unexpected atom-atom correlations at low-r



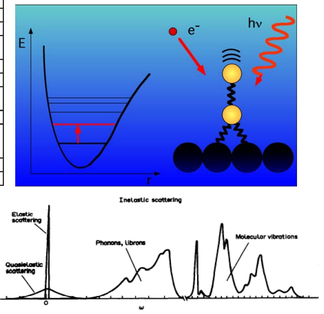
Inelastic Neutron Scattering (INS)

Filter Difference Spectrometer FDS (LANSCE-LC, LANL)



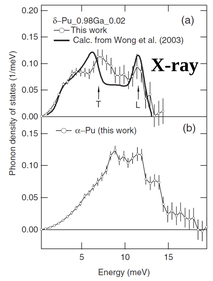
Specifications	
Energy-transfer range	50 - 5000 cm^{-1} (6 - 620 meV)
Q range	1.5 - 17 Å^{-1}
Energy-transfer resolution	2% - 5%, depending on data treatment
Beam size at sample	10-cm high x 2.5-cm wide
Detectors	60 ^{3}He (1.3 cm in diameter)
Filter analyzers	10 Be each subtending a scattering angle of 18° refrigerated
Moderators	Chilled water at 283 K
Sample environment	10 - 325 K closed-cycle refrigerator, in situ gas absorption cell; Be-Cu pressure cell to 20 kbar; 20 - 800 K, hot stage closed-cycle refrigerator
Sample size	0.5 - 100 g
Experiment duration	2 hours to 2 days

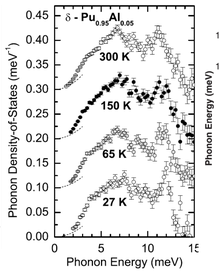
Molecular Vibrational Spectroscopy

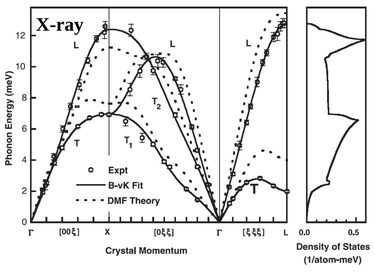


- E_i is determined by time-of-flight
- E_f is fixed at 5.22 meV by transmission of the scattered neutrons through a Be filter.
- $\hbar\omega = E_i(tof) - E_f$ (=5.22 meV)
- good intensity, lower resolution; variable $\mathbf{k_f}$
- no selection rules: torsions and librations normally not Raman- and IR-active easily seen in the neutron vibrational spectrum
- isotopic substitution

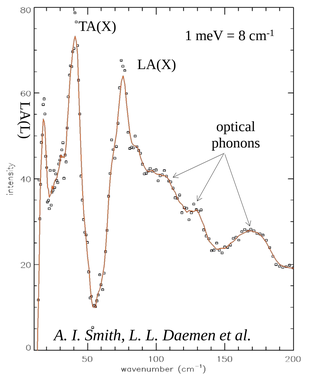
δ ^{239}Pu-7at.%Ga







M. E. Manley et al., Phys. Rev. B 79, 052301 (2009)
R. J. McQueeney et al., Phys. Rev. Lett. 92, 14, 146401-1 (2004)
J. Wong et al., Science 301, 1078 (2003)



- RT INS measurements collected on δ ^{239}PuGa samples
- 50- 4500 cm^{-1}/6.25- 562 meV
- phonon DOS in agreement with previously published inelastic X-ray scattering results by Manley et al.[1]
- sharper features
- three broad peaks observed above 100 cm^{-1} (13 meV) where Manley's et al.'s data cuts off

Acknowledgements

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