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Hidden disorder in the $\alpha' \rightarrow \delta$ transformation of Pu-1.9 at. % Ga

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Enthalpy and entropy are thermodynamic quantities critical to determining how and at what temperature a phase transition occurs. At a phase transition, the enthalpy and temperature-weighted entropy differences between two phases are equal ($\Delta H = T\Delta S$), but there are materials where this balance has not been experimentally or theoretically realized, leading to the idea of hidden order and disorder. In a Pu-1.9 at. % Ga alloy, the δ phase is retained as a metastable state at room temperature, but at low temperatures, the δ phase yields to a mixed-phase microstructure of δ- and α'-Pu. The previously measured sources of entropy associated with the $\alpha' \rightarrow \delta$ transformation fail to sum to the entropy predicted theoretically. We report an experimental measurement of the entropy of the $\alpha' \rightarrow \delta$ transformation that corroborates the theoretical prediction, and implies that only about 65% of the entropy stabilizing the δ phase is accounted for, leaving a missing entropy of about 0.5 k_B/atom. Some previously proposed mechanisms for generating entropy are discussed, but none seem capable of providing the necessary disorder to stabilize the δ phase. This hidden disorder represents multiple accessible states *per atom* within the δ phase of Pu that may not be included in our current understanding of the properties and phase stability of δ-Pu.

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I. INTRODUCTION

A phase transition requires that the free energies ($F = H - TS$) of two thermodynamic states be equal, meaning that the difference between the internal energies of the systems—usually measured as the enthalpy ΔH, which includes the pV energy required to displace the reservoir—is balanced by the difference in the entropies ΔS between the two systems: $\Delta H = T\Delta S$.[1] In a thermal process, entropy is responsible for destabilizing a low-energy ground state in favor of a high-energy, disordered state. For example, the energy of the ground state of a mean-field ferromagnet is lower than the disordered state by an amount proportional to the square of the spontaneous magnetization;[2] at the Curie temperature, the configurational entropy of the spins overcomes the reduction in energy gained by ordering, resulting in a disordered (paramagnetic) spin state. In addition to configurational entropy, there are other sources of entropy that can contribute additively to the total disorder of a system: vibrational, electronic, magnetic, etc.[3] The mechanisms responsible for order and disorder are thus critical to understanding and predicting phase transitions.

While the energetic and entropic contributions to phase stability are understood in many systems, there are numerous examples where this is not true.[3] The moderately heavy-fermion material URu_2Si_2 represents an egregious example of a system where information about the energetics of ordering is missing. At elevated temperature, URu_2Si_2 is a paramagnetic, dense Kondo system, but below 17.5 K an unconventional ordered phase develops.[4–7] This ordered phase has been denoted as the "hidden-order" state, because, even after more than 25 years of study, no microscopic model describing the order parameter or its associated reduction in energy has been confirmed.[8] The phase transformation between the α and δ phases of Pu serves as a contrary example where a typical ground state, the α phase, yields to an unconventional high-temperature state, the δ phase. The entropy stabilizing the unconventional δ phase has yet to be determined.[9] As opposed to URu_2Si_2, which exhibits a hidden-order state at low temperatures, the δ phase of Pu is stabilized by hidden *disorder* at high temperatures.

The ground-state crystal structure of elemental plutonium is the α phase, a low-symmetry monoclinic unit cell with 16 atoms positioned as pairs on eight crystallographic sites.[10,11] With increasing temperature, Pu undergoes five solid-solid phase transformations before melting at a relatively low temperature of 913 K. At elevated temperature, between the γ and ϵ phases, the face-centered-cubic (fcc) δ phase of Pu is thermodynamically stable. As may be expected, the δ phase, being fcc, is more ductile than the α phase, but there are numerous expectations typical of an fcc metal that are not met in δ-Pu. For instance, the δ phase is *less* dense than the α phase, even though the former should be a close-packed structure, but also *less* dense than the liquid.[12] The thermal expansion of δ-Pu is anomalously small, and the Grüneisen parameter is exceptionally large.[13] These and other peculiar properties are generally regarded as being manifestations of the complex bonding dictated by the 5*f* electrons of Pu and the other members of the actinide series.

With the addition of Ga, the δ phase of Pu is stabilized and can be retained down to room temperature for Ga concentrations greater than about 1.9 at. %.[14] The retained δ phase is unstable with respect to a eutectoid decomposition into α-Pu and Pu_3Ga, but this transformation is prohibited by extremely slow kinetics.[10,11,15] Instead, over a small range of Ga concentrations, retained δ-Pu is unstable towards a martensitic transformation that yields a metastable mixed-phase configuration of α'- and δ-Pu. The α' phase is crystallographically identical to α-Pu, but, by convention, the α' phase is explicitly distinguished from α-Pu due to the presence of Ga in the lattice, expanded lattice parameters, and the metastable nature of its formation. For a Pu-1.9 at. % Ga alloy, the $\delta \rightarrow \alpha'$ transformation occurs isothermally at temperatures below about 175 K, and typically results in less than 25% α' in a δ phase matrix.[16,17] The incomplete nature of this transformation is likely a result of large lattice strains associated with the 18% volume collapse that occurs upon going from the δ phase to the α' phase.

Previous measurements have determined electronic, vibrational, and anharmonic sources of entropy in the α and δ phases of Pu.[9] These measured sources of entropy provide about 0.9 k_B/atom, but theoretical modeling using the calculation of phase diagrams (CALPHAD) approach suggests that the $\alpha' \rightarrow \delta$ reversion entropy is 1.3 k_B/atom, leaving a significant fraction of the theoretical entropy unexplained.[18] If the calculations represent the true entropy stabilizing the δ phase in favor of the α' phase, then there is a large source (or sources) of entropy that is unaccounted for. This would mean that there are additional accessible states in δ-Pu that are excluded from our current understanding of the δ phase and its unusual properties. Herein we report a combined calorimetry and diffraction experiment aimed at determining experimentally the enthalpy of the $\alpha' \rightarrow \delta$ transformation in a Pu-1.9 at. % Ga alloy. These measurements permit a quantitative comparison of the previously measured and potential entropic sources that stabilize the δ phase in this alloy.

II. EXPERIMENTAL DETAILS

Differential scanning calorimetry measurements were performed on a 178 mg, 3-mm-diameter disk of Pu-1.9 at. % Ga; the isotopic and chemical compositions of this sample and the preparation techniques have been previously reported.[19] The sample was loaded into a hermetically-sealed, gold-plated, stainless-steel pan that was subsequently installed in a power-compensated differential scanning calorimeter (DSC). The calorimeter was calibrated below and above room temperature with adamantane, indium, and zinc. A smooth background was subtracted to reveal the sample's contribution to the heat transport.

The sample was subjected to nine consecutive and identical thermal cycles (see Fig. 1) in order to ensure a precise determination of the enthalpy: (a) the sample was annealed for 4 h at 650 K, (b) cooled to 300 K at 100 K/min, (c) conditioned at 300 K for 8 h, (d) cooled to 150 K at 100 K/min, (e) held at 150 K for 10 h, and then (f) heated to 650 K at 20 K/min. Step (a) served to anneal out any previous damage and permit repeatable transformations,[20] whereas step (c) served to promote more α' formation.[21,22] The isothermal hold in step (e) was chosen to be near the nose of the upper-C of the time-temperature-transformation diagram for this Pu-Ga alloy,[16] thus evoking a near maximal amount of the α' phase at the end of this step. The $\alpha' \rightarrow \delta$ reversion occurred during step (f).

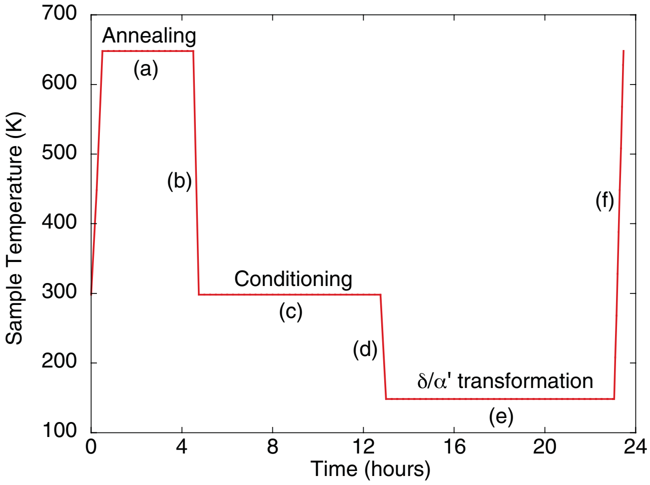

FIG. 1. (Color online) Schematic representation of the DSC thermal cycles, sample temperature vs time, consisting of (a) annealing, (c) conditioning, (e) a hold to allow the $\delta \rightarrow \alpha'$ transformation, and (f) a final heating to elicit the $\alpha' \rightarrow \delta$ reversion.

After nine consecutive DSC cycles, the sample was removed from the DSC pan and prepared, following previously reported methods,[23] into a 90-μm-thick, 3-mm-diameter disk ($\approx$6 mg) suitable for transmission-geometry x-ray diffraction experiments. Once prepared, the sample was then loaded back into the same DSC pan and reinstalled into the DSC. The sample then was subjected to a final thermal treatment that included (a)–(e) above. Instead of heating through the $\alpha' \rightarrow \delta$ reversion, as described in step (f) above, the sample was only heated to room temperature. This procedure ensured temperature conditions identical to those used to extract the heat of transformation, but avoided the $\alpha' \rightarrow \delta$ reversion, leaving the sample with a mixed phase microstructure of α'- and δ-Pu. X-ray diffraction measurements were performed to identify the volume fraction of the α' phase formed only after this final thermal procedure. To avoid oxidation of the surface, the sample was hermetically sealed in a dry nitrogen atmosphere in a specially designed sample holder. The sample holder consisted of three nested volumes separated by Kapton windows (25–50 μm thick) and sealed with indium o-rings.

Given the propensity for Pu to oxidize even in low-oxygen environments, high-energy x-ray diffraction was performed in order to probe the bulk of the system as opposed to the surface where an oxide layer may contribute to a large fraction of the signal (a typical Cu x-ray source would scatter only from the first few μm of a Pu metal or oxide sample). Angle-dispersive x-ray diffraction measurements were performed at the HPCAT beamline 16 BM-D of the Advanced Photon Source at Argonne National Laboratory. A 5×15 μm incident beam with wavelength $\lambda_{\mathrm{inc}} = 0.4055$ Å(30.58 keV) was rastered over several overlapping 1×1 mm areas of the sample, generating a powder average. Two-dimensional (2D) diffraction data were acquired with a Mar345 image plate using 300 s exposure times. 2D diffraction patterns were collapsed to 1D intensity versus 2Θ plots using the program FIT2D.[24] Lattice parameters and relative weight fractions of the phases present in the sample were extracted from the diffraction patterns via refinements using the EXPGUI/GSAS package.[25,26] Volume fractions were calculated from the refined weight fractions.

III. RESULTS

The results of the DSC measurements are summarized in Fig. 2, which highlights the heat flow versus temperature in the region around the $\alpha' \rightarrow \delta$ reversion. Each of the nine consecutive thermal cycles is represented and labeled (a)–(i) (left side of figure); the traces (b)–(i) are shifted vertically for clarity. The exothermic peak centered near 338 K corresponds to the $\alpha' \rightarrow \delta$ reversion, and the oscillations seen on the

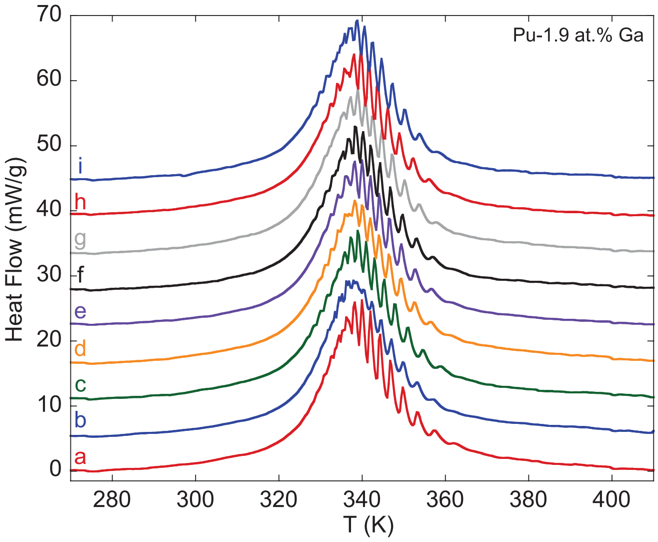

FIG. 2. (Color online) Differential scanning calorimetry traces, heat flow vs sample temperature T, for nine consecutive thermal cycles [(a)–(i), see text]. The individual traces [(b)–(i)] have been shifted vertically for clarity. The $\alpha' \to \delta$ reversion is clearly evident as the peak centered near 338 K; the oscillations on the high-temperature side of the reversion peak are characteristic of the burst nature of the $\alpha' \to \delta$ reversion.

high-temperature side of the peak are characteristic of the burst nature of the transformation.[27]

The $\alpha' \to \delta$ reversions look substantially equivalent for each thermal cycle, implying an excellent reproducibility and allowing for a quantitative analysis of the enthalpy of the $\alpha' \to \delta$ reversion for this particular thermal cycle, ΔH_0. The enthalpies of reversion are calculated by integrating the areas under the reversion peaks of each thermal cycle; in this case, the integrals have been carried out from 288 to 388 K (i.e., 50 K on either side of the center of the peak). The integrations of each DSC trace in Fig. 2 yield $\Delta H_0 = 1.73 \pm 0.06$ J/g; the error corresponds to 3.49%.

An example x-ray diffraction pattern is shown in Fig. 3, where the black crosses represent the observed diffraction pattern, the red line running through the data represents the refinement, and the light blue line below the data represents the difference between the observed and calculated pattern. The tick marks below the data demarcate the positions of the Bragg reflections of the phases used in the refinement: δ-Pu (red), α'-Pu (blue), and PuO$_2$ (orange) (fluorite-type structure). The three-phase refinement excellently reproduces the observed data with $R_{wp} = 3.5\%$, and provides a quantitative measure of the weight fraction of α'-Pu in the sample. The weight fractions (w) returned from the refinements yield volume fractions (v) through

$$v_{\alpha'} = \frac{w_{\alpha'}\rho_\delta}{w_{\alpha'}\rho_\delta + (1 - w_{\alpha'})\rho_{\alpha'}},$$

where ρ_δ and $\rho_{\alpha'}$ are the mass densities of the δ and α' phases, respectively. From the six overlapping diffraction patterns analyzed, $v_{\alpha'} = 10.37 \pm 1.50\%$ for the thermal cycle employed.

From the enthalpy ΔH_0 and volume fraction $v_{\alpha'}$ measured by DSC and x-ray diffraction, respectively, the enthalpy of transformation for the $\alpha' \to \delta$ reversion in Pu-1.9 at. % Ga can be determined: $\Delta H_{\alpha' \to \delta} = 16.67 \pm 1.82$ J/g. For comparison, the enthalpy change between α- and δ-Pu in pure plutonium is $\Delta H_{\alpha \to \delta} = 19.70$ J/g (note that in pure Pu, the α and δ phases are separated by β and γ).[28] The reduction in ΔH with increasing Ga content is consistent with the stabilization of the δ phase seen in the Pu-Ga phase diagram. In fact, for Pu-1.9 at. % Ga, the δ phase is stable approximately 90 K below that of pure Pu, a reduction in the minimum stable temperature of about 15%. Similarly, ΔH between the α and δ phases changes by about 15% between pure Pu and Pu-1.9 at. % Ga.

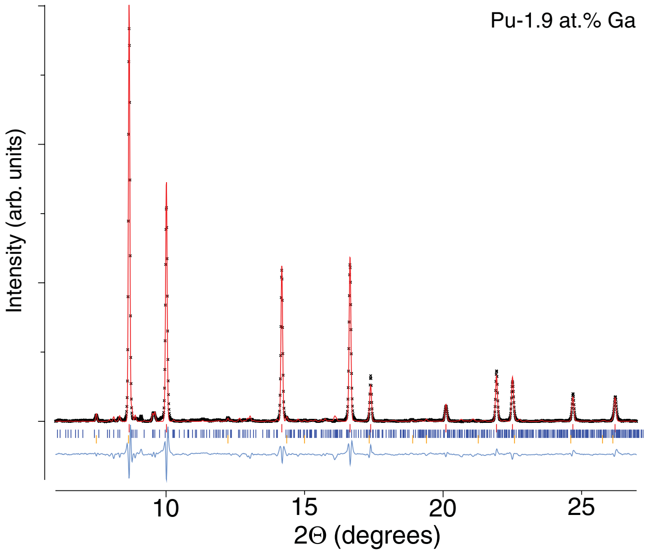

FIG. 3. (Color online) Representative x-ray diffraction pattern (background subtracted) of a partially transformed Pu-1.9 at. % Ga alloy. The red line through the black (observed) data points is the refinement, while the blue line below the pattern is the difference between the calculated and observed patterns. The vertical tick marks below the pattern mark the positions of the Bragg peaks of the phases included in the refinement: δ-Pu (upper, red), α'-Pu (middle, blue), and PuO$_2$ (lower, orange).

IV. DISCUSSION

Given the $\alpha' \to \delta$ reversion temperature—about 338 K—the entropy associated with the transformation is calculated to be $S_{\alpha' \to \delta} = 1.41 \pm 0.16\ k_B$/atom. This experimental value is very close to the CALPHAD modeling result of $S^{\text{model}}_{\alpha' \to \delta} = 1.3\ k_B$/atom (Ref. 18) and close to previous specific-heat measurements comparing pure α-Pu with an Al-stabilized δ-Pu sample, 1.36 k_B/atom.[32] The experimental value of $S_{\alpha' \to \delta}$ also confirms the previous idea of missing entropy associated with the $\delta \to \alpha'$ transition.[9]

The differences in the phonon density of states between α- and δ-Pu contribute only 0.36 k_B/atom to the total entropy,[9] while unconventional phonon softening, potentially driven by temperature-dependent electronic structure effects, accounts for about 0.40 k_B/atom.[13,29–31] At low temperatures, specific-heat measurements reveal a distinct difference between the electronic contribution to entropy from the α and δ phases of Pu (note that the δ phase was stabilized with 5 at. % Al).[32] Up to 10 K and driven entirely by the enhanced Sommerfeld coefficient γ, in the δ phase, the electronic contribution to the entropy difference between phases amounts to about 0.1 k_B/atom. Above 10 K, however, defining the electronic contribution to the entropy is not straightforward. In α-Pu, the specific heat can be fit up to 300 K using a conventional electronic term, γT;[9] however, in δ-Pu, it is clear that a simple γT dependence is not sufficient to describe the observed data. The phonon-subtracted specific heat of Ref. 32 exhibits nonmonotonic behavior with the 300 K value being lower than the extrapolated zero-temperature value. This type of behavior is typical in many heavy-fermion materials, where a heavy Fermi-liquid state "condenses" out of a Kondo lattice at low temperatures.[33] However, the electronic entropy as a function of temperature in this Kondo lattice scenario is not well formulated, nor is it clear that this scenario is applicable to δ-Pu. Including only the low-temperature electronic contribution to the entropy, the sum of these previously measured entropic contributions falls short of the measured entropy by about 0.5 k_B/atom, implying that there exists another source (or additional sources) of entropy that accounts for a significant amount of the entropy stabilizing the δ phase in favor of the α' phase.

Sadigh and Wolfer have proposed, based on density functional theory calculations, that it is energetically favorable for Ga atoms in the α' phase of Pu-Ga alloys to substitute onto a specific lattice site, namely, site 8.[34] If the Ga is randomly distributed within the δ phase of Pu-Ga alloys, then there could be an entropy associated with the disordering of the Ga atoms upon transforming from α'- to δ-Pu. However, the entropy contributed by Ga disordering in the δ phase is likely small for two reasons: (1) a full order-disorder transition in a Pu-1.9 at. % Ga alloy would contribute, as an upper bound, less than 0.1 k_B/atom of entropy to the system; (2) Sadigh and Wolfer suggest that the formation of the α' phase results in a random distribution of Ga on the eight lattice sites of the α-Pu structure,[34] implying that at least some degree of disorder is present in the α' phase, thus reducing the entropy difference from this contribution between the α' and δ phases.

In other *f*-electron systems, magnetism plays an important role in stabilizing different crystallographic phases.[35,36] For instance, the isostructural volume collapse in dilute Ce-La-Th alloys is driven almost entirely by electronic degrees of freedom, including the spin state of the Ce atoms.[37–39] Theoretical descriptions of elemental Pu have been able to reproduce the general energy landscape of the crystallographic phases by including magnetic moments;[40,41] however, for Pu, experimental evidence thus far indicates a lack of local moments.[42,43] More recent theoretical calculations suggest that it is possible to achieve the correct phase stability in Pu while simultaneously reducing the moment via an on-site spin and orbital cancellation.[44] It is unclear at this point, especially in light of the vanishingly small measured moments, how such a cancellation might contribute magnetic entropy to the α' or δ phases.

The temperature dependence of the lattice constant of a δ-phase Pu-2 at. % Ga alloy is anomalously flat over a wide range from about 400–800 K.[45–48] This flat thermal expansion has been relatively well explained by invoking an Invar model,[47,48] which is a model developed to describe the invariant thermal expansion of an Fe-Ni alloy in which this effect was first discovered. The Invar model for Fe-Ni explicitly assumes two magnetically disparate Fe-Ni states with different atomic volumes.[49] However, the success of the model is dependent on the different atomic volumes of nominally identical atoms, therefore, the genesis of these different volumes is not required to be magnetic in order to invoke the model. The Invar model applied to the thermal expansion data of Pu suggests two states with atomic volumes of 25 and 21 Å^3 separated by 1400 K (the low-volume state is the excited state).[48] The Invar model of δ-Pu, being a two-state model, should have an associated entropy; the model effectively breaks the crystallographic symmetry of the fcc δ phase, lifting the restriction that each Pu be identical. The exact details, specifically the origin of the different atomic volumes, governing this Invar model for δ-Pu would be necessary to unambiguously quantify its entropic contribution, but the entropy associated with this two-level Invar system can be estimated. Assuming that the two states, the high- and low-volume Pu sites, are noninteracting (i.e., there is no tendency for ordering on nearest-neighbor, next-nearest-neighbor, etc. sites), these two sites can be treated analogously to a disordered alloy system, where each species may randomly occupy crystallographic sites. The concentration of the low-volume (excited) state is then governed by the thermal population of a two-state system with an energy gap.[1] At the $\alpha' \rightarrow \delta$ transformation—which is at a low temperature with respect to the 1400 K gap—the low-volume state would make up only about 2% of the Pu atomic sites. Therefore, the entropic contribution from the Invar model in δ-Pu would contribute, like the Ga disorder above, less than 0.1 k_B/atom toward the $\alpha' \rightarrow \delta$ transformation.

V. CONCLUSIONS

The δ phase in Pu-Ga alloys is an atypical excited state, being stabilized over the α' phase by multiple entropic contributions with none of those contributions contributing a majority share of the entropy. Current measurements indicate that an entropy $S_{\alpha' \rightarrow \delta} = 1.41 \pm 0.16$ k_B/atom is necessary to stabilize the δ phase; however, the previously measured sources of entropy account for only about 65% of the disorder driving the $\alpha' \rightarrow \delta$ transformation. There is thus a significant missing entropic contribution to the transformation, which suggests that there are unknown or poorly understood factors in δ-Pu that engender its complexity and properties. None of the previously proposed mechanisms seem capable of accounting for the missing entropy by themselves. More experimental and theoretical work is necessary to balance the fundamental thermodynamic driving forces behind the stabilization of the δ phase in Pu-Ga alloys.

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