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Cerium isomorphism and the δ–α transformation in plutonium

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Abstract

We use the thermodynamic model introduced by Aptekar' and Ponyatovskiy for the γ–α transformation in cerium metal to study the properties of plutonium metal. The model describes the δ–α transformation in Pu and explains the minimum in the melting versus pressure curves for both materials. Ga stabilization of the δ-phase of Pu is explained in terms of a first order transition between the two phases. The model parameters found for Pu are similar to those found earlier for Ce.

Keywords: Metals; Thermodynamic properties; Phase diagrams; Phase transitions

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1. Introduction

A long time ago, Bridgman discovered a pressure-induced solid–state transition in cerium metal [1], and subsequently Lawson and Tang [2] found that the transition was isostructural: both phases are FCC. Ponyatovskiy [3] found evidence for a critical point in the solid state, and Jayaraman [4] published a phase diagram that showed a correlation between the critical point and the pressure-induced depression of the melting point.

Aptekar' and Ponyatovskiy [5] created a model for the isomorphous γ–α transformation in cerium metal that is based on a notional binary phase equilibrium between the α and γ phases described by regular solution theory. The phases are supposed to have energy difference ΔE, entropy difference ΔS, volume difference ΔV and energy of mixing U, all of which are materials parameters to be found from experiment. The difference in free energies of the two phases is:

$$\begin{aligned}&\Delta G(C, p, T, \Delta E, \Delta S, \Delta V, U)\\&\quad = RT[C\ln C + (1-C)\ln(1-C)]\\&\qquad + (\Delta E - T\Delta S + p\Delta V)C + \mathrm{UC}(1-C)\end{aligned}$$

The relative concentration of the phases $C(p,T)$ is found by minimization of ΔG. Excellent agreement with experiment is found for the choices $\Delta E = 505$ cal/mol, $\Delta S = 3.69$ cal/mol K, $\Delta V = 3.4\,\mathrm{cm}^3$/mol and $U = 2200$ cal/mol. In agreement with experiment, the A–P model predicts critical behavior, with phase separation along a line in the pressure–temperature plane defined by points $p = 0$ and $T_0 = \Delta E/\Delta S$, and the critical point $p_{\mathrm{crit}} = [U(\Delta S/2R) - \Delta E]/\Delta V$ and $T_{\mathrm{crit}} = U/2R$. For the parameters given, $p_{\mathrm{crit}} = 19$ kbar and $T_{\mathrm{crit}} = 550$ K.

Fig. 1 shows a contour map of the calculated compressibility superimposed on a phase diagram based on [4]. The behavior of the calculated compressibility χ was confirmed at room temperature by Voronov et al. [6]. Minimum melting point is correlated with divergent χ in accord with the Lindemann rule.

From the point of view of chemical periodicity, one expects a close similarity between the properties of cerium and plutonium, as discussed, for example, by Johansson [7]. In this paper we use the Aptekar' and Ponyatovskiy (A–P) model to describe the physical properties of plutonium metal.

2. Plutonium model

Fig. 2 shows the molar volume of cerium metal calculated with the A–P model versus temperature and pressure, together with the measured molar volume of unalloyed plutonium versus temperature only. The principal feature of the cerium plot is the volume collapse that is the quintessence of cerium physics. Below the critical pressure, the high temperature cerium γ-phase

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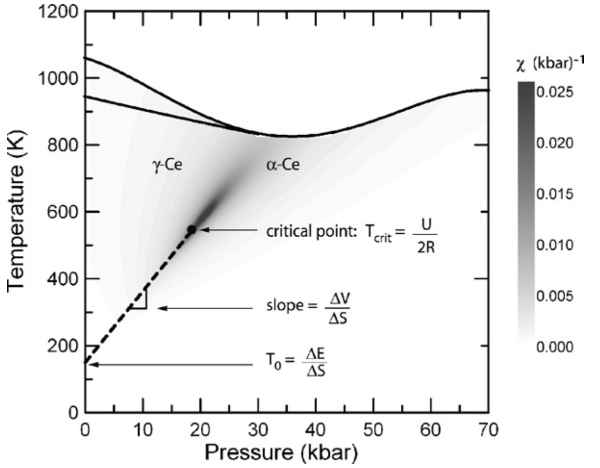

Fig. 1. Cerium phase diagram with coexistence curve from Aptekar' and Ponyatovskiy (A–P) model. The dashed line shows the locus of first order transformations ending in a critical point. A contour map of the compressibility χ is superimposed, and expressions from the A–P model for diagram features are shown.

shows negative thermal expansion at temperatures high enough for the free energy to be dominated by the entropy of mixing: in that case, minimum free energy is found for $C = 1/2$. Plutonium shows a progression of phases from high to low temperature. At high temperature the δ and ε phases have simple FCC and BCC structures, respectively, while the α, β and γ phases have complicated structures. The high-temperature plutonium δ-phase also shows negative thermal expansion. The essential feature of the plutonium data is the large volume collapse between the δ and α phases. We propose that the A–P model be applied to plutonium with the identifications Pu δ-phase ≡ Ce γ-phase and Pu α-phase ≡ Ce α-phase. We ignore the plutonium β-, γ-, δ′- and ε-phases, just as the original A–P model ignores the cerium β- and δ-phases.

The structure of α-Pu is famously complicated. From powder X-ray data, Zachariasen and Ellinger [8] found eight pairs of structurally unique atoms per monoclinic cell. A close relationship between the monoclinic structure and the close-packed hexagonal structure is shown in Fig. 3. It is known that the addition of a few per cent gallium or aluminum stabilizes plutonium FCC δ-phase to room temperature, and that stabilized δ-phase transforms to α′-phase via a martensitic mechanism with low temperature or high pressure. (The α′ structure is the same as α, but includes retained solute.) Fig. 3 may be helpful in understanding how this transformation occurs: it involves a change of stacking from three layers to two (FCC to HCP) and an intralayer distortion. (We are neglecting the difference between the HCP and FCC close packed structures, which are very close in energy.) In our model, the δ–α′ transformation in plutonium is the analog of the γ–α transformation in cerium.

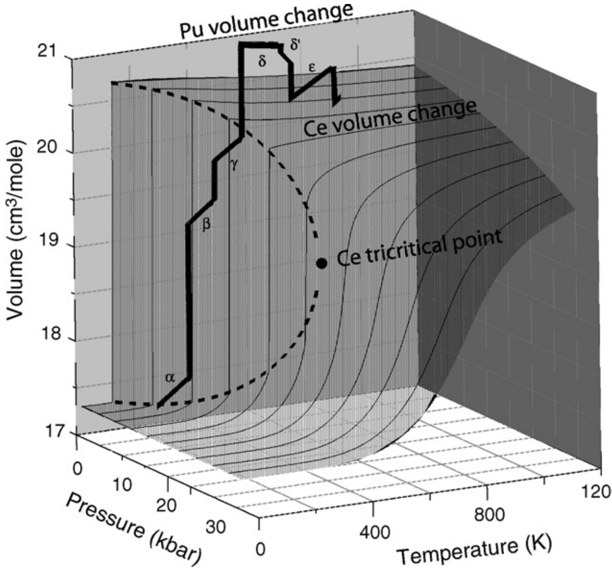

Fig. 2. Cerium volume vs. pressure and temperature from A–P model using parameters from [5]. Experimental plutonium volume vs. temperature at $p = 0$ is embedded in the low-pressure region of the cerium surface.

3. Plutonium model properties

We now evaluate the plutonium parameters ΔE, ΔS, ΔV and U for the A–P model. This occurs in two stages. ΔV and ΔE come from consideration of the δ–α′ transformation, assuming that ΔS is known. ΔS and U come from fitting the measured temperature dependence of the lattice constant, assuming ΔV

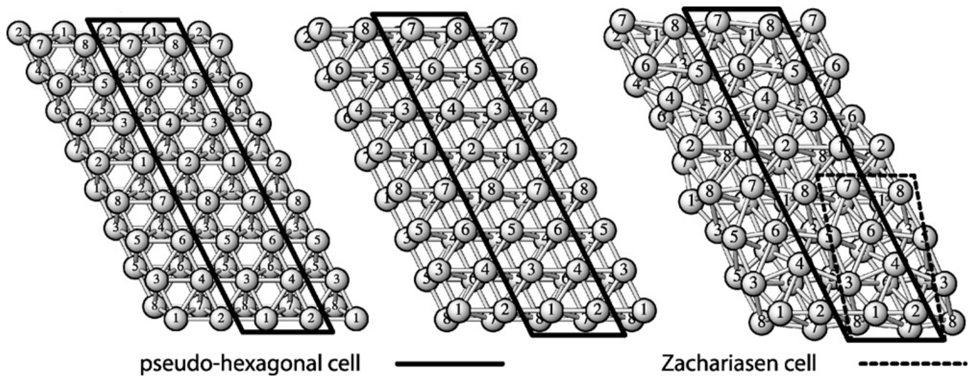

Fig. 3. Left panel: two layers of hexagonal close-packed structure. Center: HCP with interlayer shift of ~1.5 Å. Right: two layers of the α-Pu structure. In all cases a large pseudo-hexagonal cell containing 32 atoms is shown. In the third case, the conventional monoclinic cell for α-Pu is also shown: the inscribed numbers correspond to the atomic designations of Zachariasen and Ellinger [8].

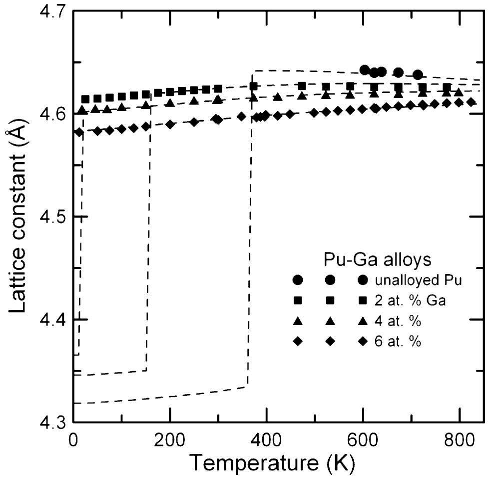

Fig. 4. Lattice constants vs. temperature for Pu–Ga alloys fit with the A–P model.

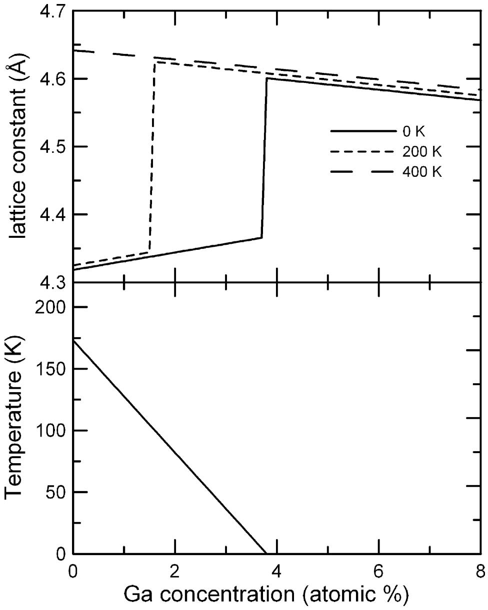

Fig. 5. Upper panel: lattice constants from the A–P model vs. Ga concentration. Lower panel: δ–α transition temperature T_0 from the A–P model vs. Ga concentration.

and ΔE are known. Some iteration is required, as the two stages are weakly coupled through the value of ΔS.

For Pu–Ga alloys, we know that ΔV at room temperature is linear with atomic Ga concentration x from data for the α′-phase tabulated by Hecker [9]: $\Delta V = (3.05 - 0.197x)$ cm^3/mol. We assume that ΔE is linear with x and use the known transformation temperatures at zero pressure of 1.4 and 1.9 at% Ga alloys given by Deloffre et al. [10] of 223 and 163 K. We find $\Delta E = (646 - 172x)$ cal/mol. As a check, we calculate the transformation pressure at 300 K for Pu–2 at.% Ga and find 5.1 kbar; Hecker et al. [11,12] report an onset pressure of 4 kbar for Pu–2 at.% Al.

We next assume that ΔS and U are independent of x and fit the ^{242}Pu–Ga lattice constants measured by Lawson et al. using neutron diffraction [13] to find $\Delta S = 1.96$ cal/mol K and $U = 3280$ cal/mol. In this stage of the fitting process, the low temperature data also determine the phonon Grüneisen constant $\gamma = 0.49$, which is needed to correct the measured lattice constants for ordinary vibrational thermal expansion [13]. The fits, which are shown in Fig. 4, are somewhat poorer than those obtained with an earlier, simpler invar model [13,14], but they are satisfactory considering the much broader scope of the A–P model. The value of U is in fair agreement with the energy difference of 2780 cal/mole found by the invar model. It is unnecessary to assume anomalous properties of liquid plutonium to explain its melting behavior. The calculated compressibility is similar to that of cerium, consistent with the observed minimum in the plutonium-melting curve. The fitted parameters are collected in Table 1 in both molar and atomic units. The critical point for plutonium happens to fall in the liquid state and cannot be observed directly.

Lattice constants calculated with the A–P model are plotted versus Ga concentration in the upper panel of Fig. 5. In agreement with experiment, Ga suppresses the first order transition between the δ- and α-phases by driving the zero-pressure transformation temperature T_0 negative, via the linear Ga dependence of ΔE. The lower panel shows the δ–α transition temperature (T_0) versus gallium concentration. The behavior of T_0 is in general agreement with the experimental Pu–Ga phase diagram, but the calculated transition temperatures are too low by a factor of 3. We are unable at present to account for this discrepancy, but a possible problem is the neglect of the β-, γ- and δ′-phases in the A–P model.

4. Discussion and summary

The results of this paper clarify the close relationship between cerium and plutonium by providing a quantitative basis for comparing the properties responsible for their unusual behaviors. We have used the correspondence γ-cerium ≡ δ-plutonium and α-cerium ≡ α-plutonium and neglected the other phases. The model explains the unusual temperature dependence of the thermal expansion and elastic stiffness of δ-Pu and the minimum in

Table 1
A–P parameters for Ce, Pu and Pu 2 at% Ga

	ΔE		ΔS		ΔV		U		T_{crit}	P_{crit}
	cal/mol	meV/atom	cal/mol K	k_B/atom	cm^3/mol	Å^3/atom	cal/mol	meV/atom	K	kbar
Ce	505	21.9	3.69	1.86	3.4	5.6	2200	85.6	550	19
Pu	646	28.1	1.96	0.99	3.05	5.1	3280	143	829	13.4
$Pu_{0.98}Ga_{0.02}$	302	13.1	1.96	0.99	2.66	4.4	3280	143	829	20.7

the melting curve, and it provides a basis for describing gallium stabilization.

Johansson et al. [15] created a model for cerium based on the Mott transition that leads to conclusions very similar to those drawn from the A–P model. Comparison of the two models should provide a physical basis for interpretation of the parameters of the A–P model, but is beyond the scope of the present paper. We note also that V.M. El'kin and his colleagues have recently applied the A–P model to plutonium and obtained results similar to ours [16,17].

Future work is indicated: microscopic interpretation of A–P model parameters, identification of the microscopic order parameter associated with the critical transition in Ce and Pu, an improved understanding of the role of complex Pu phases, and a search for negative thermal expansion in γ-cerium (including careful accounting for Grüneisen effects.) Electronic theories of cerium and plutonium should be constrained by the findings of this paper.

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