

Instability of the electronic structure of actinides under the high pressure

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Abstract

The paper discusses phase transitions in Pu–Ga alloy under the pressure up to 1 GPa and analyzes electronic phases of unalloyed actinides using data of static experiments at pressure of 100–300 GPa.

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1. Introduction

The analysis of the experimental data on static and shock compression of materials suggests that many materials change their properties under the compression due to changes of the states of electrons in the atomic cell of the solid. The diversity of electronic phases in solids relates to the large variations of the energy of excited states that are observed in the atomic spectroscopy. While atomic spectroscopy deals with energy levels of free atoms, the energy levels observed in solids are the energy levels of atoms whose volume is fixed.

2. Phase transition in δ plutonium alloy

Studies [1,2] present experimental data on transformations of four plutonium-gallium alloys with 1, 1.7, 2.5 and 3.5 at.% Ga under isostatic pressure at 25 °C in the Bridgman dilatometer. Large-volume δ phase expectedly collapses at quite low pressures and it transforms directly from δ to α' phase with possible traces of γ' -phase. All the observations indicate that $\delta \rightarrow \alpha'$ transformation occurs through the martensite transformation which is similar to the martensite mechanism in cooling.

The data [1,2] show that the change in the specific volume of the δ -phase alloy under the positive pressure is accompanied by the work which is expended for the $\delta \rightarrow \alpha'$ transformation.

This means that the energy level of the alloyed δ -phase is lower than that of the α' phase. On the other hand, it is well known that the unalloyed α phase is more favorable energetically than the unalloyed δ phase and that $\alpha \rightarrow \delta$ phase transition at the room temperature occurs when a tensile stress of 0.35 GPa is applied [3].

Curves presented in Fig. 1 allow for the explicit determination of the $\delta \rightarrow \alpha'$ transformation energy as a function of gallium concentration in the alloy through the calculation of $\int P dV$ integral at the inelastic segment of the compression curve. Energy per gallium mole in alloy is almost independent of the gallium content. This shows on the existence of a stable gallium complex in δ plutonium that exists in alloys with the Ga content ranging from 1 at.% to 3.5 at.%. The energy of such complex can be expressed as

$$\Delta E = 67 - 100x \text{ kJ/mole Ga}, \quad (1)$$

where x is the molar fraction of Ga in Pu–Ga alloy. In this case, the enthalpy of intermetallic compound Pu_3Ga is 42 kJ/mole that is close to the value of Pu_3Ga enthalpy reported in [4].

The pattern of the transition of gallium-alloyed δ -plutonium under the high pressure to the α' -phase state can be seen from the plot of the Helmholtz free energy as a function of the specific volume. Internal energy of different phases of plutonium is given by

$$E_i(\sigma) = \frac{9B_i}{2\rho_i}(\sigma^{1/3} - 1)^2 + C_i, \quad (2)$$

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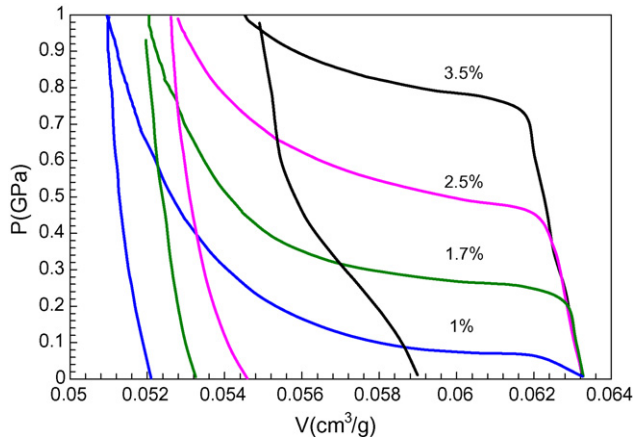


Fig. 1. Pressure vs. specific volume of Pu–Ga alloy with different contents of Ga (at.%) in loading and pressure release.

where B_i and ρ_i are the bulk modulus and equilibrium density for each phase at $P=0$ and $T=0$, respectively, and C_i are constants determining the minimum energy for each phase [9]. Curves in Fig. 2 have been calculated using bulk modulus $B_1 = 30$ GPa for the δ phase, $B_2 = 50$ GPa for the α' phase and experimental equilibrium densities of either phase. The slope of the common tangent to curves $F(V)$ for the two phases determines the pressure of the phase transition at the thermodynamically equilibrium state.

Curves in Fig. 1 show that the transition occurs with changing pressure. This is concrete evidence of the absence of the thermodynamic equilibrium. The presence of hysteresis also indicates the absence of thermodynamic equilibrium. It is well known that at temperatures of 130–150 °C the remaining δ phase gets enriched in gallium during the $\delta \rightarrow \alpha'$ transformation. This kinetic process may be responsible for the formation of the thermodynamically non-equilibrium state.

The tension of $P = -0.35$ GPa applied to α -plutonium [3] corresponds the $\alpha \rightarrow \delta$ transformation in unalloyed plutonium at standard temperature with phase energy difference of 1.2 kJ/mole. This value is much less than $T\Delta S$ in the $\alpha \rightarrow \delta$ transformation (3.6 kJ/mole at 300 K and $\Delta S = 12$ J/mole). Lack of the information about the $\alpha \rightarrow \delta$ transformation in tension

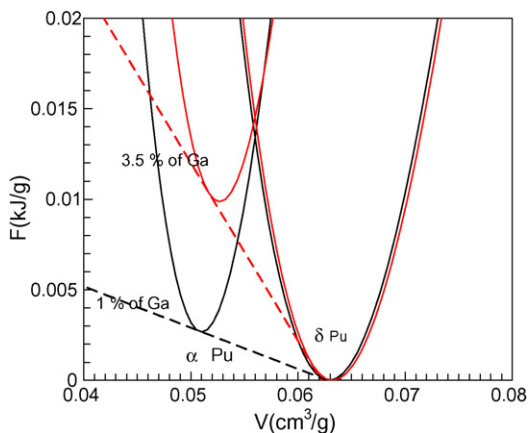


Fig. 2. Energy of α' and δ plutonium alloys as a function of the specific volume.

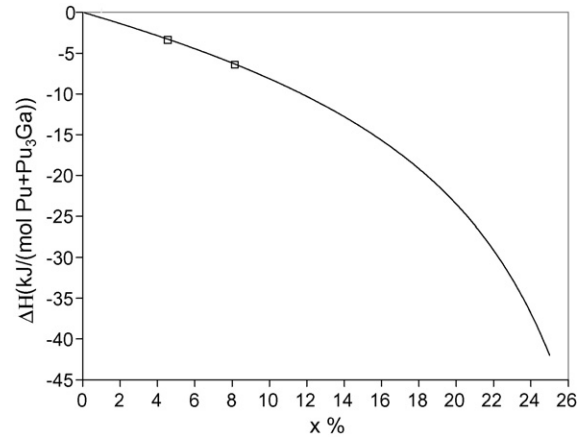


Fig. 3. δ Plutonium alloy formation enthalpy (kJ/(mole of Pu + Pu₃Ga)) vs. Ga concentration in Pu–Ga alloy.

do not allow a direct comparison of the transition energies in pure and alloyed plutonium because the fraction of δ phase that therewith results is unknown. The transition from the α' phase to the pure α phase may be accompanied with the energy release of 3.6–10 kJ/mole, depending on the gallium concentration. This energy is likely the energy of pure α -phase lattice deformation in α' -phase formation due to the capture of gallium atoms in random sites of the α -phase lattice.

Assuming that in gallium-stabilized δ phase gallium and plutonium are bonded forming in Pu₃Ga and that this bond in the α' phase disappears, one can determine from the $\delta \rightarrow \alpha'$ transformation under pressure at constant temperature the Helmholtz free energy difference. This difference appears to be close to the plutonium–gallium alloy formation enthalpy. Fig. 3 shows the δ plutonium alloy enthalpy calculated using expression (1), divided by mole of the sum of nuclei of plutonium and complexes Pu₃Ga as a function of the molar fraction of gallium in Pu–Ga alloy. Two experimental points obtained with the method of drop calorimetry [5] fall on this calculated curve. This means that results of the calorimetric measurements and experiments on the $\delta \rightarrow \alpha'$ transformation under pressure are in agreement. The experimental Pu–Al alloy formation enthalpy is given in [6].

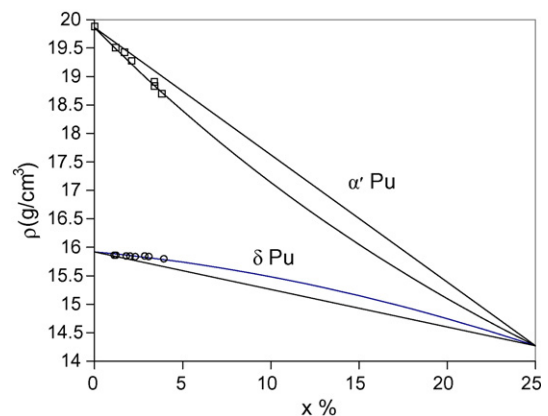


Fig. 4. Density of plutonium in the form of δ and α' alloy vs. Ga concentration in Pu–Ga alloy.

Our study suggests that the formation of δ -phase plutonium alloy can be represented as the incorporation of chemical Pu–Ga complexes into the crystalline lattice of metallic plutonium. Based on this model, we can determine the dependence of the alloy density on the gallium content as the density of the metallic plutonium and Pu₃Ga mixture. Alloy densities versus Ga concentration calculated using the above-mentioned model are given in Fig. 4. The straight lines “obey” the Vegard rule.

3. Electron phase transitions in actinides with compression

The concept of the electronic phases in solids appeared in the late 1940s, when it was found from the X-ray diffraction measurements in samples under pressure [7] that different cerium phases had the same crystalline lattice type. E. Fermi suggested that different phase characteristics appear due to different electron structure of solid atoms in different phases [8]. Electron positions in the atomic shells alter during the phase transition, while the crystalline structure remains unchanged.

The solid phase state attained under pressure can be characterized using the energy of outer electrons of the unit cell of the solid atom. This energy is calculated with taking into account their interaction by inner electrons and atomic nucleus. This approach leads to the equation of state of solids (energy and elastic compression pressure) that accurately describes the experiment data [9].

Recent experiments performed using diamond anvils and synchrotron radiation sources gave important information about the crystalline and electronic structure of actinides under the megabar pressures [10–14].

Recent study [12] presents compressibility of Pa at $P < 129$ GPa. The theoretical analysis shows that at pressure up to ≈ 95 GPa the experimental points fall on the theoretical curve with parameters $\rho_0 = 15.37$ g/cm³ and $B_0 = 115$ GPa. At higher pressures the experimental points deviate significantly from the theoretical curve and they can be described by another electronic phase of Pa with parameters $\rho_0 = 19.827$ g/cm³ and $B_0 = 400$ GPa. It has been found [12] that at $P = 77$ GPa the tetragonal structure of protactinium changes to low-symmetry orthorhombic structure of α uranium. At $P = 77$ GPa there is no noticeable change in slope of the $P(\rho)$ curve. This evidences that the initial electronic structure of Pa remains unchanged. The slope and electronic structure change suddenly at 95 GPa, while orthorhombic crystalline structure remains unchanged. It has been noticed [15] that the experimental data on compressibility of thorium and uranium also indicate the existence of a stiff phase (with $B_0 = 400$ GPa) at pressure above 100 GPa.

Compressibility of metallic curium to 100 GPa pressure has been studied in [14]. The parent phase of Cm (of equilibrium density 13.3 g/cm³) has bulk modulus $B_0 = 40$ GPa, which is somewhat higher than that of metallic americium and δ -phase plutonium. At pressure about 10 GPa the electronic structure of Cm changes. The new phase parameters are $\rho_0 = 13.96$ g/cm³, $B_0 = 60$ GPa. According to [14], at 17 GPa the initial dhcp

Table 1

Energy of states (eV) of atoms with different number of outer electrons for 5f elements

Element	Number of outer electrons				
	2	3	4	5	6
Th	17.8	37.8 50.7	66.5 69.5	131	211 209
Pa	17.6	37.4	80		217
U	18.1	38	70.4 69.5	106	196
Np	18.0	38.7	72.3 72.3		
Pu	17.8	39.4 32.4	74		
Am	18 23.4	40.1 48.4	76.3	161	
Cm	18.4	39.4 34	76.2 60	157	

The bold type denotes energies of outer electrons of atoms of 5f metals under ambient conditions.

structure changes to fcc structure. In the 10–37 GPa pressure range, the experimental points are described well as states of a single electron phase. No non-monotonicity of $P(\rho)$ function has been observed during the crystalline rearrangement at 17 GPa. CmIII phase (monoclinic structure) has slightly lower bulk modulus ($B_0 = 53$ GPa) at the same equilibrium density ($\rho_0 = 13.96$ g/cm³). At $P > 57$ GPa, the experimental points for CmIV and CmV phases can be described as states of single electronic phase with $\rho_0 = 20.35$ g/cm³, $B_0 = 280$ GPa. The parameters of this electronic phase are close to those of Am IV phase at pressures of 55–100 GPa. The experiments suggest the existence of phases of close bulk module, $B_0 = 340$ –400 GPa, at pressures higher than 50–150 GPa in all actinides (Th, Pa, U, Am, and Cm).

Table 1 presents energies of outer electrons of solid atoms of actinide metals obtained with method described in [9] using compressibility data (lower number) [10–14]. The upper number is the sum of free atom ionization potentials. From the spectroscopy data the multiple ionization potentials of free atoms of actinide elements are known for thorium and uranium only. Sums of ionization potentials of free atoms have been calculated using four sequential ionization potentials for actinides reported in [4]. As seen from Table 1, the theoretical energies of different actinide phases are close to the sum of the free atom ionization potentials. This clearly shows that quantum states of atoms in solids are identical to quantum states of free atoms. This behavior has been found in the case of transition metals [16], for which the ionization potentials of free atoms are well defined. At ambient conditions, there are three electrons in the outer shell in metal thorium and four in metal uranium. In compression, the electron structure rearrangement takes place leading to the increase in the number of outer electrons to five or even six. In metal americium and curium under pressure the number of outer electrons increases to five.

4. Conclusion

The analysis of the experimental data on $\delta \rightarrow \alpha'$ transformation under pressure suggests that alloyed δ phase has a lower energy level compared to the thermodynamically non-equilibrium state of α' phase. Energy per gallium mole in alloy is almost independent of the gallium content. This indicates the presence of a stable gallium complex (probably Pu_3Ga) in δ plutonium that exists in alloys with the Ga content ranging from 1 at.% to 3.5 at.%.

Our study shows that the experimental data on material compressibility bear significant information about the electronic structure of materials. We have shown that energies of outer electrons of different actinide phases are close to the sum of free atom ionization potentials. This means that the quantum states typical for free atoms can also be found in solids.

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