Electronic structure of actinides

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This paper shows that the variety of actinide properties relates to a change both in the actinide crystal structure and electronic structure with changing temperature and pressure. The change in plutonium properties during the transition from α to δ phase can correspond to the rearrangement in inner electron shell (either 5f or 6d) with the electronic configuration of outer electrons remaining unchanged. However, the electronic structure of the outer electron shell of the ε - phase dramatically differs from that of α and δ phases. Outer electron energy of the ε -phase is 4.3 eV which corresponds to the one-electron configuration of outer electrons.

KEY WORDS: actinides, plutonium, compressibility, electronic structure

1. Introduction

At standard pressure actinide elements have several different crystal phases in various temperature ranges up to melting point^{1,2)}. Actinide properties and structure also change under pressure. In compounds actinides appear as elements of a variable valence¹⁾. Owing to complex behavior of actinides thus far there is no commonly accepted viewpoint of the electronic structure of their outer electron shell. In this paper an attempt is made to obtain additional information about the electronic structure of actinides reasoning from the experimental data on their compressibility.

2. Compressibility and electronic structure of actinides

A method for calculating the energy of a compressedatom state was proposed in^{3,4)}. When the volume per atom is limited, the calculated set of energy levels differ from the energy levels of a free atom. This model explicitly includes the quantum nature of electron motion and allows us to clearly explain behavior of many elements under pressure⁴). The model of^{3,4)} provides approximate analytical expressions describing elastic energy and pressure in compression:

$$E(\sigma) = \frac{2E_n N_A}{A} \left(\frac{\sigma^{2/3}}{2} - \sigma^{1/3} \right), \quad (1)$$

$$P(\sigma) = \frac{2E_n N_A \rho_n}{3A} \left(\sigma^{5/3} - \sigma^{4/3} \right) \quad (2)$$

The parameters of the equation of state are material equilibrium density ρ_n (at P=0, T=0) and outer electrons energy E_n of atoms in the equilibrium state; A is atomic mass, N_A is the Avogadro number, $\sigma=\rho/\rho_n$ is compression degree.

In expression (2) $2E_nN_A\rho_n/3A=3B_0$, where B_0 is bulk modulus at $\sigma=1$. For a known bulk modulus B_0 this allows us to estimate outer electrons energy state $E_n=9AB_0/2N_A\rho_n$.

Table 1 presents parameters for various actinide phases

obtained from the experimental data on compressibility. In the table, N is the number of outer electrons.

Table 1. Parameters of actinide atomic cell states

Material	ρ _n ,	B ₀ ,	E_n	N
	g/cm ³	GPa	eV	
Th	11.72	55	50.7	4
Th	12.2	78.3	69.5	4
U	19.1	115	69.5	4
U	19.25	153	88	4
U	19.6	187	106	5
U	22.3	400	196	6
Np	20.4	134	72.3	4
Pu-α	19.98	58	32.4	3
Pu-β	18.18	47	32.4	3
Pu-ε	16.2	6.2	4.3	1
Pu-liquid	16.6	24	16	2
Pu-α	20.1	83	46	3

The bulk modulus value obtained with ultrasonic measurements⁵⁾ is 115 GPa. Uranium compression by static pressure was studied by P.Bridgman to pressure P=10 GPa⁶⁾. Uranium compression in static experiments with the diamond anvil method is studied to pressures P~50 GPa in ref.⁷⁾. Parameters of the equation of state of uranium initial phase, $\rho_n=19.08$ g/cm³, $B_0=115$ GPa, describe the data of static measurements up to 5 GPa pressure quite well. The computed dependence and experimental points are shown in Fig. 1. At high pressures the experimental points clearly deviate from the computed dependence for the initial phase. At pressure P=5-20 GPa the measured data⁷⁾ lies on the computed curve with the parameters of equation of state (1), (2) $\rho_n=19.25$ g/cm³, $B_0=153$ GPa.

Using experimental physical values following the shock front in uranium presented in⁸, the parameters for equation of state (1), (2) were selected to describe the experiment. The first segment to P=80 GPa is described by the parameters $B_0=187$ GPa, $\rho_n=19.6$ g/cm³. The data of static measurements⁹ at P>20 GPa also lie on this computed curve. The 80-150 GPa pressure range is described by equation of state (1), (2) with the parameters $B_0=400$ GPa, $\rho_n=22.6$ g/cm³. There is an explicit kink in curve $P(\rho)$ at



Fig. 1. Dependency $P(\rho)$ on uranium normal isotherm.

Thus, the analysis conducted indicates existence of four different uranium phases in the pressure range studied: the initial phase and three high-pressure phases. They considerably differ in outer electron energies (67 eV, 88 eV, 106 eV, and 196 eV, respectively) and, hence, are different electronic phases.

At room temperature and standard pressure (in the α phase state) neptunium which is next to uranium in the periodic table is of the highest density (20.4 g/cm³) and the highest bulk modulus (119 GPa at temperature 298 °K and 132 GPa at T=77 °K) among actinides⁹. The atomic cell outer electron energy ($E_n=73$ eV) for neptunium is also higher than that for α phase of uranium.

Under standard conditions plutonium exists in the form of the α phase. As temperature increases, the transition to the β , γ , δ , ε phase and to the liquid state occurs. Under standard conditions the α plutonium bulk modulus is 53.5 GPa ¹⁰. At room temperature the bulk modulus of δ plutonium with 1% of *Ga* by weight is 28.9 GPa^{11,12}. The ε phase parameters are B_0 =6.2 GPa, ρ_0 =16.2 g/cm³, Poisson ratio is μ =0.20±0.02¹³. The bulk modulus for the ε phase is ~4 times lower than that for the δ phase and ~8 times lower than that for the α phase of plutonium. Reasoning from this bulk modulus value, the ε - phase plutonium atomic cell outer electron energy is 4.3 eV which corresponds to the one-electron configuration of outer electrons.

For liquid plutonium measured sound speed¹⁴⁾ is 1200-1220 m/s at T=650-950 °C. This sound speed value is correspondent with the bulk modulus of $B_0=24$ GPa which is considerably higher than that of ε phase plutonium and liquid plutonium atomic cell energy of 16 eV corresponding to the two-electron configuration. The different electronic structure of the ε phase and liquid seems to be a reason for the abnormal plutonium behavior during melting (increasing density during melting). Apparently, plutonium melting is attended with an electronic phase transition with increasing number of outer atomic electrons. Disappearance of the long-range order which usually results in decreasing density of the liquid phase is accompanied in this case with a transition to a denser state in the short-range order and the sum of these two changes leads to the abnormal melting.

1945 measured α -plutonium In P.Bridgman compressibility at room temperature up to 10 GPa pressure¹⁵⁾. Bridgman performed the measurements with two devices of different types: one of them which ensured quite a good measurement accuracy was used up to $P \sim 4$ GPa pressure and the other of a lower accuracy was used up to P~10 GPa. Plutonium compressibility was also estimated up to $P \sim 5$ GPa from measured sound speed in¹⁶). This data is presented in Fig. 2. In this figure solid curves show $P(\rho)$ computed by relation (2). The plutonium initial α phase parameters describe the static measurement data^{15,16} only to $P \sim 1.7$ GPa pressure. At higher pressures the slope of $P(\rho)$ increases by a factor of ~ 1.4 .



Fig. 2. Dependency $P(\rho)$ on plutonium normal isotherm.

The phase diagram of plutonium is known up to pressure $P \sim 12 \text{ GPa}^{17}$. At standard temperature no transition from the crystal structure of the α phase (simple monoclinic) to any other crystal lattice type has been detected. An abrupt change in compressibility at P=1.7 GPa can be accounted for by an electronic phase transition relating to a change in the energy state and the number of plutonium outer electrons. At high temperatures the phase equilibrium line for these electron phases of α plutonium may pass through the phase equilibrium line maximum of the α - β phases $(dT/dP \sim 150 \%/GPa)$. Such a slope corresponds to approximately constant plutonium density at the electronic phase transition at various temperatures.

P.Bridgman's data¹⁵⁾ indicate a noticeable change in the $P(\rho)$ slope at P=7.5 GPa as well. Evidently, this is also an electronic phase transition without any change in the crystal structure as the transition pressure is within the experimentally studied phase diagram of plutonium¹⁷⁾.

According to the analysis of the plutonium compressibility data, the number of atomic cell outer electrons in the α phase is 3, in the ε phase is 1, and in liquid plutonium is 2. At the same time, from the data for atomic radii²⁾ it follows that in the α and ε phases the valence is 5. This contradiction can be avoided assuming that in plutonium valent electrons are not equivalent. They can be considered as positioned in two valent subshells. The outer subshell is responsible for material compressibility. Both the

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subshells are responsible for density of solid. Electron redistribution among subshells can account for both compressibility change under pressure and complex behavior of plutonium density during heating.

B. Cooper¹⁸⁾ suggests that in homogeneous material, like pure α plutonium, two species of atoms with a different number of localized *f* electrons (i.e. those localized in inner shells) can exist. It is therewith suggested that for one crystal lattice site the number of the localized *f* electrons is fixed (f⁵), while for another it fluctuates (between f⁴ and f⁵). This suggestion is used as a basis for an attempt to account for the plutonium behavior features, including the effect of the IIIB group elements on the δ phase stabilization at low temperatures.

Another model of d- and f-electron metals composed of two species of atoms with a different number of inner d and felectrons can be considered. Formation of positively and negatively charged ion pairs differing in the number of inner d and f electrons from neutral metal atoms with five localized 5f electrons, with the electron configuration of outer (valent) electrons remaining the same, can prove energetically dominating. For example, a positive ion with localized f⁴ electrons and a negative ion with localized f⁶ electrons can form instead of the localized f^5 electrons in the neutral atom. This phenomenon is similar to disproportionation, where chemical compound changes and produces a mixture of compounds with valence higher by one and that lower by one.

The change in plutonium properties during the transition from α to δ phase can correspond to the rearrangement in inner electron shell (either 5f or 6d) with the electronic configuration of outer electrons remaining unchanged. However, the electronic structure of the outer electron shell of the ε - phase dramatically differs from that of α and δ phases. The changes occur in plutonium at standard pressure with changing temperature. Bridgman's experiments indicate that the change in the outer electron shell of plutonium metal atoms occurs under relatively moderate pressures.

According to the experimental data on neutron scattering¹⁹⁾, with temperature increasing from 320 °C to 440 °C the bulk modulus of the δ phase decreases by 25%.

The physical model is considered that treats a change in δ - phase plutonium elastic characteristics as temperature increases due to a change in the electronic structure of some plutonium atoms with the crystal structure of the δ - phase remaining unchanged.

Assume that in solid plutonium the number of atoms of different electronic structure changes as temperature increases. In the δ phase these can be atoms with the electronic structure of δ phase and ϵ phase. The volume of ϵ phase atoms is less by 3.7% than that of δ phase atoms and the bulk modulus of the ϵ -phase is B₀=6.2 GPa against B₀=30 GPa for the δ phase. Let α be contribution of the new phase to the mixture, ρ_2 be equilibrium density. The following expression is valid for the bulk modulus of the mixed phases:

$$B_{0} = B_{01} \frac{1 - \alpha + \alpha \frac{\rho_{01}}{\rho_{02}}}{1 - \alpha + \alpha \frac{\rho_{01}B_{01}}{\rho_{02}B_{02}}} .$$
 (3)

When the bulk modulus of the new phase dramatically differs from that of the initial phase, the average modulus can also considerably differ from the initial modulus. For example, when the ε -phase atoms make 7% within the δ -phase, the bulk modulus of the mixed phases is 1.25 times less than the bulk modulus of the initial δ phase. This value is close to neutron scattering data¹⁹ obtained for decrease in elastic constants of δ -phase plutonium with temperature increasing from 320 °C to 440 °C. The bulk modulus decrease may be essentially the same, if the volume of the ε -phase is considered as free volume (i.e. the material is considered as porous material with k=1.07) because of high ε phase compressibility.

Conclusion

Under action of pressure and temperature plutonium experiences a change in electronic structure of atoms in solid. The change in plutonium properties during the transition from α to δ phase can correspond to the rearrangement in inner electron shell (either 5f or 6d) with the electronic configuration of outer electrons remaining unchanged. However, the electronic structure of the outer electron shell of the ϵ - phase dramatically differs from that of α and δ phases. The changes occur in plutonium at standard pressure with changing temperature. Bridgman's experiments indicate that the change in the outer electron shell of plutonium metal atoms occur under relatively moderate pressures.

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