

The unique high-pressure behavior of curium probed further using alloys

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Received 27 October 2006; received in revised form 6 December 2006; accepted 7 December 2006

Available online 22 January 2007

Abstract

The changing role of the 5f electrons across the actinide series has been of prime interest for many years. The remarkable behavior of americium's 5f electrons under pressure was determined experimentally a few years ago and it precipitated a strong interest in the heavy element community. Theoretical treatments of americium's behavior under pressure followed and continue today. Experimental and theoretical findings regarding curium's behavior under pressure have shown that the pressure behavior of curium was not a mirror image of that for americium. Rather, one of the five crystallographic phases observed with curium (versus four for americium) was a unique monoclinic structure whose existence is due to a spin stabilization effect by curium's 5f⁷ electronic configuration and its half-filled 5f-shell. We review briefly the behavior of pure curium under pressure but focus on the pressure behaviors of three curium alloys with the intent of comparing them with pure curium. An important experimental finding confirmed by theoretical computations, is that dilution of curium with its near neighbors is sufficient to prevent the formation of the unique C2/c phase that appears in pure Cm metal under pressure. As this unique C2/c phase is very sensitive to having a 5f⁷ configuration to maximize the magnetic spin polarization, dilution of this state with adjacent actinide neighbors reduces its stability.

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Keywords: Actinides; High-pressure structures; High-pressure behaviors

1. Introduction

The abrupt change in atomic volumes and structural behavior observed in going from plutonium to americium in the actinide series is well documented and discussed in the literature. This change is attributed to a change in bonding going from itinerant electrons to localized 5f electrons at the plutonium to americium region. The report of the remarkable delocalization of americium's 5f electrons under pressure [1] initiated subsequently a number of theoretical analyses of its behavior [2–5]. Subsequently, experimental and theoretical studies performed on curium demonstrated that curium's behavior under pressure [6] was not identical to that for americium.

Curium normally has a half-filled shell with seven 5f electrons spatially residing inside its radon core, and the element lies at the

center of the actinide series. This half-filled 5f⁷ state for curium and its higher nuclear core charge from its higher atomic number compared to americium, would be expected to increase curium's resistance to undergoing delocalization of its 5f electrons. This was found to be the case. Compared to the behavior of americium to 100 GPa, curium exhibits one additional, unique structural form (identified as a Cm-III phase, having a C2/c monoclinic symmetry) that occurs between 37 and 56 GPa [6].

Findings from ab initio electronic structure calculations performed on curium agreed with the observed experimental structural sequence [6], and established that it is the spin polarization and magnetism of curium's 5f electrons that are responsible for the formation and the stabilization of this rare, C2/c (Cm-III) pressure phase. With additional pressure, curium subsequently adopts the Fddd and then the Pnma structures, which are phases observed in americium under pressure [1]. The Fddd and Pnma structures appear in these actinide metals because of their acquiring participation of 5f electrons into their bonding due to pressure [1–6]. The Pnma structure, observed for

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americium at 16 GPa and for curium when approaching 100 GPa [6], is accepted as reflecting that full delocalization of these two metals' 5f electrons has occurred from the application of pressure [2–6].

In the effort reported here, the objective was to examine the pressure behaviors of three curium alloys formed with curium's near neighbors to determine if the unique C2/c phase of curium would form under pressure. The three curium alloys consisted of: (1) 50 at.% americium; (2) 30 at.% berkelium; and (3) 54 at.% berkelium. The three alloys alter significantly the pure 5f⁷ state found in curium which reduces the potential for formation of the C2/c phase under pressure.

2. Experimental and computation efforts

The experimental approach used for the high-pressure alloy studies has been described [1] and will not be discussed in detail here. The studies used diamond anvil cells and X-ray diffraction techniques. The calculations for the crystal structures under pressure for the three alloys with curium were performed by the generalized full potential, linear muffin-tin orbital (FP-LMTO) method together with the generalized gradient approximation as suggested by Perdew, Burke and Ernzerhof within density functional theory (DFT) [7]. The detailed computational approach is described in our work on curium [6]. The virtual crystal approximation and the spin-orbit coupling of the 5f electrons were both considered in the calculations for these alloys. Calculations for both antiferromagnetic and ferromagnetic states were performed; the antiferromagnetic states were always found to be lower in energy.

3. Results

We initiated studies of the pressure behavior of three curium alloys to enlighten further the influence of spin polarization for formation of the Cm-III phase and the extent of the influence of curium's 5f⁷ electronic configuration for forming the C2/c phase. These curium alloys were formed with curium's near neighbors, americium and berkelium: specifically, an Am_{0.5}Cm_{0.5} alloy [8] and two Cm,Bk alloys (Cm_{0.7}Bk_{0.3} and Cm_{0.46}Bk_{0.54}). The experimental relative volume (V/V_0) behaviors of these alloys are shown in Figs. 1 and 2, while Fig. 3 compares the pressure behaviors of the two Cm,Bk alloys to those of pure americium and curium.

The pressure behavior and the phase transitions for the Am_{0.5}Cm_{0.5} alloy [8] are similar to that observed with pure Am (see Figs. 1 and 3). However, the important point to note is

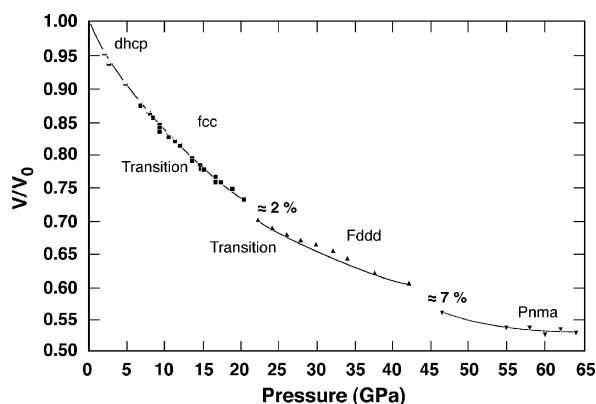


Fig. 1. Relative volume behavior versus pressure for an Am_{0.5}Cm_{0.5} alloy.

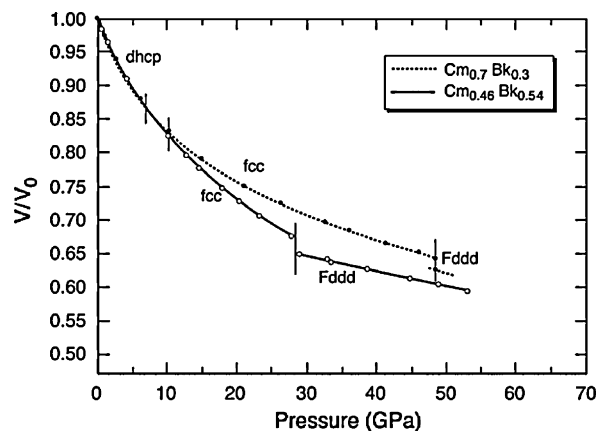


Fig. 2. Relative volume behavior vs. pressure for two Cm,Bk alloys.

that the unique C2/c phase is not observed for this alloy under pressure. Instead, the phases progress from a double hexagonal close packed (dhcp) to cubic (fcc) and to orthorhombic (Fddd) structures and then to another orthorhombic structure (Pnma). The transitions for the alloy are shifted to higher pressures than found for pure americium: dhcp–fcc at 10 versus 6 GPa; the fcc–Fddd at 20 versus 9 GPa; and the Fddd to Pnma at 43 versus 16 GPa.

Likewise, the pressure behaviors of the two Cm,Bk alloys under pressure also do not show the formation of the C2/c phase, and the structural forms observed for these alloys are again similar to those for americium [1] and the Am_{0.5}Cm_{0.5} alloy. The phases for these two Cm,Bk alloys also progress from a dhcp to fcc to an orthorhombic (Fddd). As the intent here was to probe for the potential formation of the intermediate (between fcc and Fddd) C2/c phase, the data shown do not go to pressures high enough for the Fddd to Pnma transitions to occur in the two Cm,Bk alloys. This topic will be the subject of future work, as it will be important to also incorporate a discussion of the behavior of pure berkelium under pressure.

In the present studies, the dhcp–fcc and the fcc–Fddd transitions for the Cm_{0.7}Bk_{0.3} alloy were observed at 10 and 48 GPa, respectively, while for the Cm_{0.46}Bk_{0.54} alloy the respective transitions were at 7 and 28 GPa. Again, the significant finding is

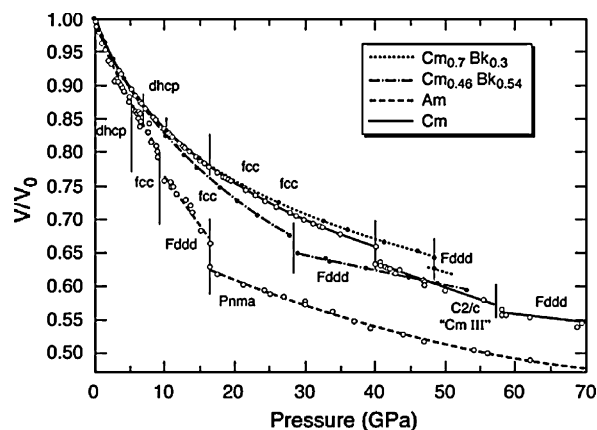


Fig. 3. The relative volume behavior as a function of pressure for two curium-berkelium alloys, plus americium and curium.

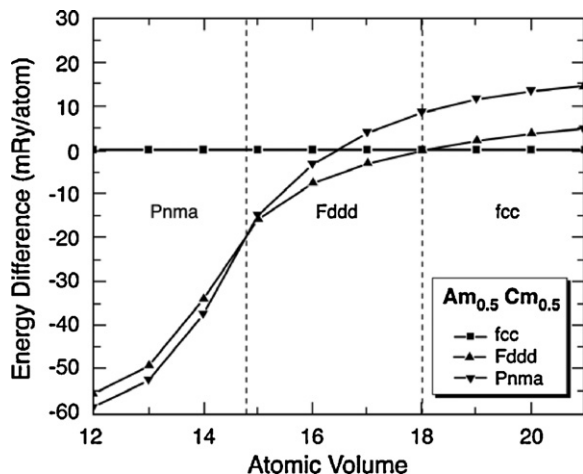


Fig. 4. Calculated total energy differences vs. the fcc structure for selected structures of $\text{Am}_{0.5}\text{Cm}_{0.5}$ as a function of atomic volume.

that for these two alloys under pressure, the unique C2/c phase was not observed as a result of “diluting” curium’s $5f^7$ configuration by the alloying elements. A secondary finding is that comparable transition pressures for the alloys occur at lower pressures than for pure curium. This is in accord with the resistance of curium to depart from a $5f^7$ configuration—e.g., curium resists the incorporation of its $5f^7$ electrons into a bonding mode under pressure, and it requires higher pressures to accomplish this delocalization process.

The atomic volume of pure curium is 29.98 \AA^3 and that of pure americium is 29.27 \AA^3 at 298 K and one atmosphere [10]. For the alloys, the atomic volumes for these same conditions were 29.6 \AA^3 for the americium–curium alloy; 29.4 \AA^3 for the 70 at.% curium–berkelium alloy; and 28.9 \AA^3 for the 46 at.% curium–berkelium alloy. Americium, curium and berkelium all exhibit the dhcp structure at 298 K and 1 atm.

The calculated energy versus atomic volume plots for the $\text{Am}_{0.5}\text{Cm}_{0.5}$ [9] and the $\text{Cm}_{0.7}\text{Bk}_{0.3}$ alloys are shown in Figs. 4 and 5. The calculated fcc to Fddd phase transition in $\text{Cm}_{0.7}\text{Bk}_{0.3}$ takes place at an atomic volume of 17 \AA^3 , while

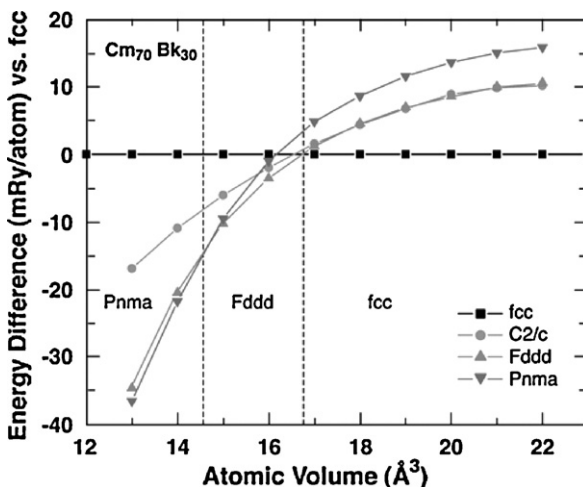


Fig. 5. Calculated energy difference for selected structures vs. the fcc structure for selected structures of $\text{Cm}_{0.7}\text{Bk}_{0.3}$ as a function of volume.

experimentally the transition volume was 19 \AA^3 . The experimental transition for $\text{Cm}_{0.46}\text{Bk}_{0.54}$ (data not shown) also occurs at a larger volume (e.g., 20 \AA^3) compared to a calculated volume of 18 \AA^3 . With the $\text{Am}_{0.5}\text{Cm}_{0.5}$ alloy, this same fcc to Fddd transition is observed experimentally at 21 \AA^3 but the calculated volume 18 \AA^3 . The differences between the experimental and calculated volumes arise due to a common situation in the calculations that is associated with the simulation of the core states for the actinides; this generates somewhat smaller transition volumes in the calculations.

The important findings were that addition of both americium and berkelium to curium reduce the pressures necessary to bring about comparable transitions versus the case of pure curium, and that the three alloys do not form the C2/c phase under the pressures reported. Although the calculated transition pressures differ slightly from the experimental findings, it is important to recognize that the fcc to Fddd transitions in the alloys occur in the correct sequence when compared to the experimental findings. Specifically, that the dhcp to fcc transition occurs followed by the fcc to Fddd transition, and that the respective transitions occur at larger volumes than observed for alloys with reduced curium concentrations. Thus, the overall behaviors and the order of the appearance of the structure types found experimentally with the three alloys are in good agreement with those calculated by theory.

4. Concluding remarks

An important experimental finding from this work is that a dilution of curium metal with either americium or berkelium in the amounts studied prevents the formation of the unique C2/c phase that appears in pure curium. Thus, the formation of this C2/c phase has been shown to be very sensitive to having a significant $5f^7$ configuration present for achieving the necessary magnetic spin polarization of the 5f electrons. In addition, computations have shown that the energies for the structures support the sequential appearance of the phases in the alloys under pressure, as well as the relative stabilities of the different phases as a function of atomic volume. In short, theory and experiment are in good accord with regard to the behaviors of these three alloys under pressure. The limits of dilution by adjacent elements necessary to prevent formation of curium’s C2/c phase will be explored further with alloys having greater Cm concentrations.

Acknowledgements

Support was from the European Commission, JRC, the Division of Chemical Sciences, Geosciences and Bioscience, OBES, DOE with ORNL (DE-ACO5-00OR22725, UT-Battelle), the CEA and the Swedish Research Council & Swedish Foundation for Strategic Research.

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