Pressure Induces Major Changes in the Nature of Americium's $5f$ Electrons

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(Received 13 June 2000)

Americium occupies a pivotal position in the actinide series with regard to the behavior of $5f$ electrons. High-pressure techniques together with synchrotron radiation have been used to determine the structural behavior up to 100 GPa. We have resolved earlier controversial findings regarding americium and find that our experimental results are in discord with recent theoretical predictions. We have two new findings: (1) that there exists a critical, new structural link between americium under pressure and its near neighbor, plutonium; and (2) that the $5f$ electron delocalization in americium occurs in two rather than one step.

PACS numbers: 61.50.Ks, 64.70.Kb

Over the past decade there have been several studies of lanthanide metals pursuing the occurrence of f electron delocalization by pressure, where these new investigations employ advancements in experimental techniques. The reader is referred to reviews [1,2], as well as recent efforts on cerium [3] and neodymium [4] metals. Some early lanthanide ($4f$) metals in the first half of this series delocalize under pressure and can adopt low-symmetry structures exhibited by the early actinide metals.

The involvement of f electrons in bonding, at normal or high pressure, is a function of the extension of the wave functions and the comparable energies of hybrid states relative to electronic levels without f character. These conditions change with increasing nuclear charge, type of f orbital (e.g., $4f$ or $5f$), etc. The $5f$ electrons of americium (the element following plutonium) are nonbonding (localized) at normal pressure, as are the $5f$ electrons for the remaining elements in the actinide series. In this sense, americium occupies an important pivotal position in the $5f$ series, which is in part reflected in the sudden change in atomic volume in going from plutonium, which has itinerant $5f$ electrons, to americium (see Fig. 1 inset) at atmospheric pressure. The smaller atomic volumes of the protactinium through plutonium metals result from the additional bonding supplied by $5f$ electrons.

Americium also displays significant structural differences at atmospheric pressure between its near neighbor, plutonium and its lanthanide homolog, europium. Its localized $5f$ electrons and special nonmagnetic $5f^6$ ($J = 0$) configuration lead to superconducting properties at low temperatures [5].

Previous results with americium were obtained at lower pressures [6–8] than here. Our data are in general agreement with the fact that the double hexagonal close-packed phase (dhcp, Am I phase) transforms at low pressure to a face-centered cubic phase (fcc, Am II phase). However, important differences are found at higher pressures, both in structural assignments and more importantly, in the interpretation of electronic behavior for the structures at higher pressure.

The intent of the present study was to understand correctly the behavior of americium up to 100 GPa. This is the first time the structural behavior of americium under pressure using synchrotron radiation has been reported.

Foils of americium [^{243}Am isotope ($t_{1/2} = 7 \times 10^3$ yr)] metal were prepared by vacuum vapor deposition after reduction of americium dioxide with lanthanum metal. Mass spectrographic analysis indicated purity of >99.9% and x-ray analysis showed the metal exhibited a double hexagonal close-packed structure [$a_0 = 3.467(4)$ and $c_0 = 11.240(8)$ Å, where 10 Å = 1 nm] in excellent accord with literature values [6–8]. Small pieces (5–10 μg each) were taken for the studies.

Diamond anvil cells are now widely used for studying minute quantities (a few μg) of materials up to and beyond the megabar range [9]. In our experiment both Syassen-Holzapfel (up to 60 GPa) and Cornell-type (up to 100 GPa) pressure cells have been used. The experiments were performed at room temperature at the European Synchrotron Radiation Facility (ESRF) ID30 beam line in the angular dispersive mode. Nitrogen was

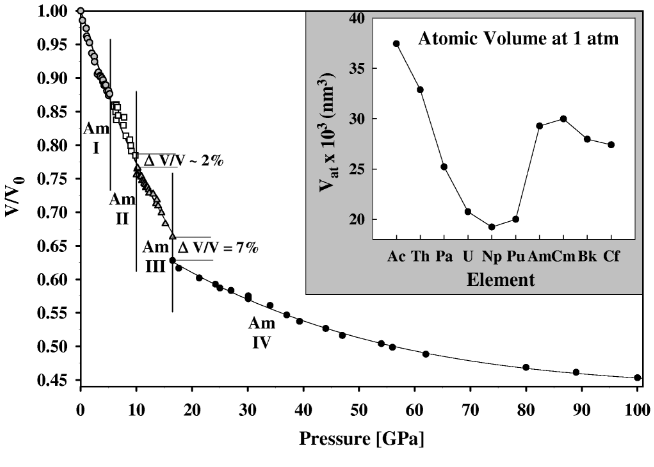

FIG. 1. Relative volume vs pressure curve for americium. The inset shows the atomic volume at ambient pressure across the actinide series.

used as the pressure transmitting medium in the Syassen-Holzapfel cells enabling hydrostatic conditions between 0 to 18 GPa where the first three high-pressure phases were observed. Silicone oil was used as the pressure medium for the Cornell cells in the experiments up to 100 GPa. Pressure markers were ruby (fluorescence technique [9]) or platinum metal (via its equation of state [9]). Diffraction images were captured with a Fastscan image plate detector [10]. The diffraction images were then processed using the ESRF FIT2D program [11] and interplanar distances for the data collected were calculated. Indexing programs were employed to suggest possible structures, which were then refined with Rietveld analysis [12].

With the application of pressure, the dhcp form ($P6_3/mmc$, Am I) of americium converts to a fcc structure ($Fm3m$, Am II) at 6.1(2) GPa. This fcc phase is identical to the high-temperature phase reported for americium metal above 650 °C. This dhcp to fcc transformation requires little energy and probably indicates an increase in the *d* character of the bonding. In Fig. 1, one observes a smooth transition for the Am I to Am II structural change and that the fcc compression curve is a continuous extension of the dhcp compression curve, which suggests each phase has a comparable bulk modulus.

With additional pressure, the fcc Am II phase transforms to a third Am III phase at 10.0(2) GPa. The structure of this phase has been most controversial in past studies of americium. It has been assigned previously as a monoclinic structure [7] and a distorted, face-centered cubic structure [8]. In neither of these earlier works was delocalization of americium's *f* electrons considered in conjunction with this Am III phase.

As a result of the larger number of high quality diffraction data, we successfully arrived at the correct assignment for the Am III phase. The structure has a face-centered orthorhombic cell (space group *Fddd*, Am on the 8*a* sites, all position parameters fixed by symmetry) and exists between 10 and ~17 GPa (see later section on the Am IV phase). A Rietveld refinement of the data is shown in Fig. 2.

A crucial, and new, aspect is that this Am III structure is the same as is known for the gamma phase of plutonium metal, which is a slightly distorted hexagonal, close-packed structure considered to have 5*f* electrons involved in its metallic bonding. Thus, under pressure the electronic energy levels of americium are altered sufficiently so that it adopts one of the structures established for its near neighbor, plutonium, and the bonding in americium now has *f* electron character. This finding provides new insight into the role of the 5*f* electrons in americium as pressure is applied. A small "collapse" (~2%) in relative volume can be extracted from the data shown in Fig. 1.

The next phase, Am IV, was observed as early as 16(1) GPa but was the exclusive phase by 17.5 GPa. It was retained up to 100 GPa, the highest pressure for which we report data. Both of the previous groups reporting an Am IV phase assigned it to an alpha-uranium structure, and suggested that the appearance of this structure reflected itinerant 5*f* electrons in the metallic bonding.

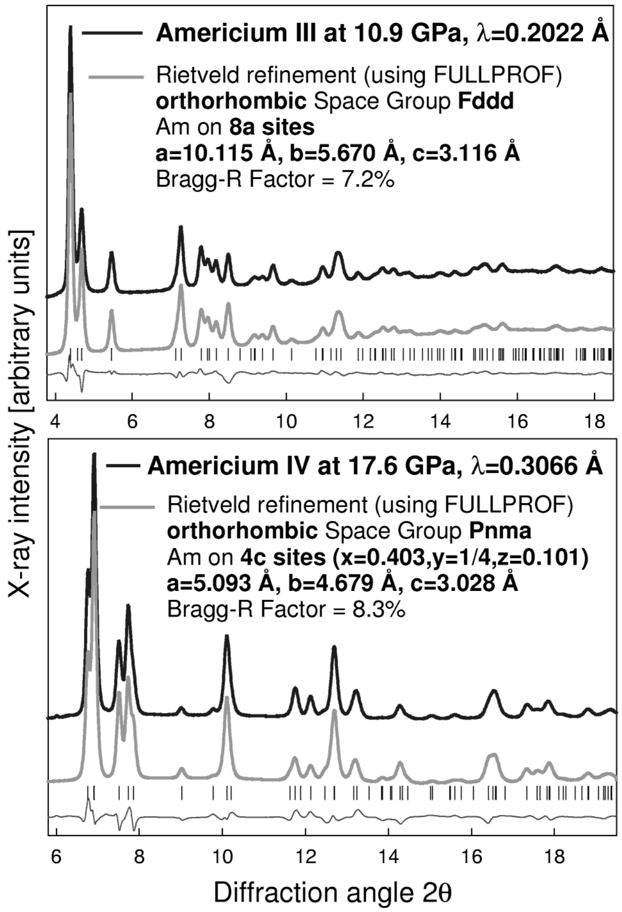

FIG. 2. Rietveld fits for the Am III and Am IV structures at 10.9 and 17.6 GPa showing the observed (top lines) and calculated (center lines) diffraction patterns, reflection tick marks, and difference profiles (lower trace).

A Rietveld refinement for our Am IV data (Fig. 2) establishes that Am IV has an orthorhombic structure similar to the base-centered alpha-uranium structure (*Cmcm*), but with a different space group (*Pnma*, primitive orthorhombic). The lattice parameters and atomic positions at 17.6 GPa are given in the figure.

Our Am IV structure represents a modified alpha-uranium structure. If the *z* value of the 4*c* sites in the *Pnma* structure is placed at zero, one then obtains the higher-symmetry, alpha-uranium structure with the base-centered orthorhombic unit cell. This is depicted in Fig. 3, where the change in structure is demonstrated. Given the excellent quality of our data and the Rietveld fit (Fig. 2), we believe that the *Pnma* structure is the correct assignment for the Am IV phase.

The four different structures observed for americium in this study are shown in Fig. 4. The structural transformations can be envisioned as occurring from a shift and distortion of the planes and a change in stacking sequence. This structural progression, which results from

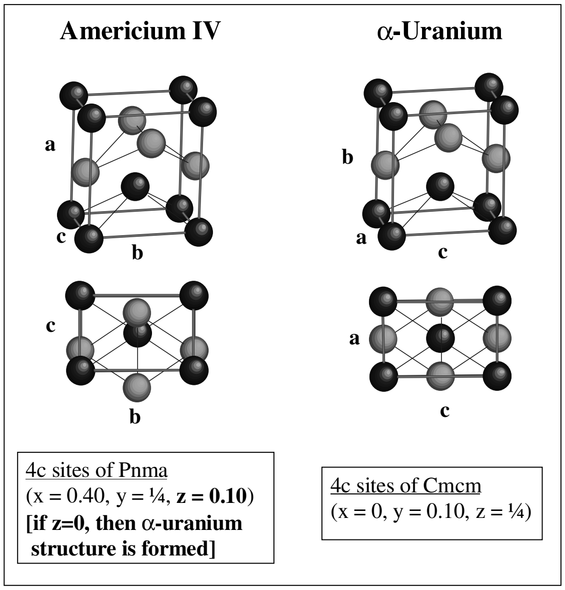

FIG. 3. Orthorhombic cells for the Am IV and alpha-uranium structures. Setting the z value of the $4c$ sites in the *Pnma* structure (left) to 0 means a shifting of the planes with the light atoms relative to the dark ones in the c direction so that one obtains the alpha-uranium structure (right).

changes in the metallic bonding, provides an increase in the crystal density.

In Fig. 1 a plot of the relative volumes (V/V_0, where V_0 is the volume at atmospheric pressure) versus pressure is shown, where the different structural regions and the relative volume changes are shown. We attribute both the 2% Am II to Am III transition and the 7% Am III to Am IV transition to f electron delocalization processes.

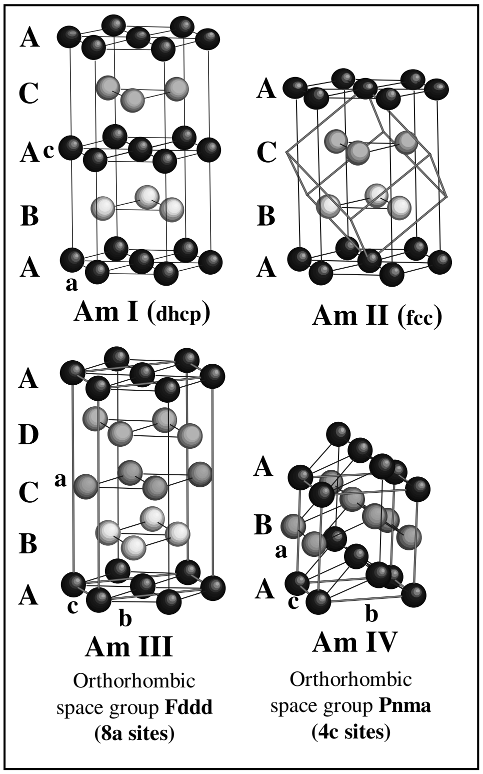

FIG. 4. The four structures observed for americium under pressure.

The collapse of 7% observed here is lower than the 25% change suggested in the recent theoretical predictions for americium metal under pressure [13]. The theoretical treatment also assigns the volume collapse as being due to the incorporation of f electrons in the metallic bonding of americium. Two conclusions were reached in this theoretical work: (1) that the high-pressure phase of americium was predicted to be the monoclinic alpha plutonium structure; and (2) that a volume collapse of 25% should accompany the incorporation of f electrons into the metallic bonding. Our experimental findings are in discord with both of these suggestions.

The isothermal bulk moduli and their pressure derivatives were obtained by fitting the Birch and Murnaghan equations of state [14,15] to the low-pressure phases (regions of localized f electrons) to obtain the bulk modulus B_0 and its pressure derivative B_0'. Both calculations gave similar values, which were $B_0 = 29.7 \pm 1.5$ GPa and $B_0' = 3.7 \pm 0.2$, and $B_0 = 29.9 \pm 1.5$ GPa and $B_0' = 3.5 \pm 0.2$, respectively. These americium moduli are in line with values for the light lanthanide metals [1], but considerably smaller than the modulus of alpha plutonium (45 GPa), which has additional bonding from its itinerant f electrons.

Obtaining high quality experimental data for the structural behavior of americium metal under pressures up to 100 GPa (one megabar) permits the proper identification of the Am III and Am IV phases. New insights into the behavior of americium's $5f$ electrons under pressure and a mechanistic picture for the sequential conversion of americium from one phase to another under pressure are also obtained.

In addition to resolving the controversy regarding the structural behavior of americium in the 10–30 GPa region, this work has established two critical findings about the Am III and the Am IV structures. First, that the Am III phase is a face-centered orthorhombic structure (space group *Fddd*), which is the same structure displayed by gamma plutonium (atmospheric pressure between 206 and 319 °C), and the bonding now involves itinerant $5f$ electrons. Second, the Am IV structure appears to be a primitive orthorhombic structure (*Pnma*), rather than the base centered alpha-uranium structure as reported previously [1,16]. The Am IV structure shows a smaller compressibility with pressure (being more similar to that of uranium), as expected for a metal with appreciable $5f$-electron character in its bonding.

This work provides important new insights for understanding the pivotal position of americium in the actinide series with regard to the involvement of $5f$ electrons in metallic bonding. The quality of these data establishes firmly the experimental behavior of americium under pressure, and should promote the convergence of experimental and theoretical views regarding the volume collapse and the $5f$ electron delocalization in americium under pressure.

This work was supported by the European Commission and by the Division of Chemical Sciences, Geoscience and Biosciences, Office of Basic Energy Science, USDOE, under Contract No. DE-ACO5-00OR22725 with Oak Ridge National Laboratory, managed by UT-Battelle, LLC. The ^{243}Am isotope used in the study was supplied by the DOE Transuranium Production Program at Oak Ridge National Laboratory. A. L., K. L., and Y. M. wish to thank the "Training and Mobility of Researchers" program of the European Union and the Austrian Science Foundation FWF (Project No. P-11581-PHY). The authors acknowledge useful discussions with G. H. Lander of ITU.

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