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High-pressure studies of americium metal: Insights into its position in the actinide series

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Americium metal occupies a pivotal position in the actinide series, displaying localized f electron bonding while the four preceding members are recognized for their itinerant f electron behavior. Important insights into the nature of americium's f electrons with regard to metallic bonding and the relationship to that in the γ form of plutonium have been acquired through studies of americium up to 100 GPa. Synchrotron radiation and other experimental advances were used to obtain data of high quality and resolution to resolve fully the high-pressure crystal structures of americium metal. We have resolved controversial findings reported earlier for americium in the 10–30 GPa region, and also addressed the significant differences that exist between the reported theoretical and experimental volume collapses. In this work we found that the normal pressure double hexagonal close packed ($P6_3/mmc$) structure transforms at 6.1 GPa to a face centered cubic ($Fm3m$) phase. At 10.0 GPa, the latter converts to a face centered orthorhombic ($Fddd$) structure, which with additional pressure undergoes a further transformation to form a primitive orthorhombic structure ($Pnma$) at 16 GPa. The $Pnma$ structure is stable up to at least 100 GPa, the maximum pressure reported here. By identifying correctly the structural forms of the Am III and IV phases, the mechanisms for sequential conversion of the structures with pressure have been established. A critical aspect of these data is that the Am III phase is now believed to reflect the first involvement of americium's f electrons in the metallic bonding; additional involvement occurs in the Am IV phase. This work provides important insights for understanding the pivotal position of americium in the actinide series and should bring about the convergence of experimental and theoretical views regarding its pressure behavior.

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I. INTRODUCTION

In recent years there has been an increased interest in the effect of high pressure on materials. Geologists have probed the behavior of materials under pressure and/or temperature for learning the physicochemistry of materials near the center of the earth. There has been a continued advancement and interest in studies involving the lanthanide and actinide (the two f electron series) metals under pressure. The advancement has been due to the development of different designs of diamond anvil pressure cell (DAC), detectors, use of synchrotron radiation, and, in the case of the actinides, authorization to perform studies at synchrotron sites with elements more radioactive than thorium or natural uranium. With a modern DAC, it is possible to reach pressures of 100 GPa routinely, and pressures of 500 GPa or higher are achievable. At such pressures, materials are reduced to fractions of their original volumes. With this reduction in interatomic distances, significant changes in bonding and structure as well as other properties take place. Given this potential, there has been significant scientific interest in investigating pressure-induced changes in the chemistry and physics of the two f series of elements. A central point of interest in this regard is whether pressure can force delocalization of f electrons in metals where they are normally not involved in the metallic bonding.

Over the past few decades there have been several studies of lanthanide metals designed to pursue the above question, and investigations continue. The reader is referred to reviews[1–4] in this regard, and to a recent study of cerium metal.[5] There is strong evidence that the $4f$ electrons of some early lanthanide metals do indeed delocalize under pressure and the metals then adopt low-symmetry structures, exhibited by the early actinide metals having itinerant $5f$ electrons. There have been significant disagreements about the high-pressure structures formed. It is clear that the pressure required for delocalizing the $4f$ electrons rapidly increases across the series, and in the region of neodymium or samarium 100 GPa or more is required. This delocalization phenomenon has not been reported for members in the second half of the $4f$ series. In contrast, the spatial extension of the $5f$ electrons permits the delocalization and/or hybridization process to occur at lower pressures with transplutonium metals, even though they contain an even higher number of f electrons. For example, this process has been reported for californium metal, but not for dysprosium metal.[6]

The physicochemical properties of the actinide metals at normal pressure vary widely across the series, due largely to the changing nature of the $5f$ electrons. In principle, the filling of $5f$ orbitals begins after thorium. It is generally accepted that the $5f$ electrons are involved to varying degrees in the bonding (itinerant $5f$ electrons) for protactinium, uranium, neptunium, and plutonium. These four elements display quite different properties from the transplutonium elements that have localized $5f$ electrons. Itinerant $5f$ electrons arise due to their more extended wave functions than those of the $4f$ electrons, and the comparable energies of hybrid states relative to other electronic levels without f character. With increasing nuclear charge the extension and energies of these $5f$ levels and/or hybridized states change. The $5f$ electrons of americium, the element following plutonium, are now nonbonding (localized) at normal pressure, as are the $5f$ electrons for the remaining elements of this series. In this sense americium occupies a pivotal position in the $5f$ series.

Given this pivotal position of americium, its behavior under pressure becomes especially interesting. Americium displays significant structural differences at atmospheric pressure both from its near neighbor plutonium and from its lanthanide homolog europium. Its localized f electron state and nonmagnetic $5f^6$ $(J=0)$ configuration, which lead to superconducting properties at low temperatures,[7] reflect a changing internal pressure for this element.

Several structural studies of americium have been performed previously at lower pressures[8–15] than obtained in the present work. Results from previous workers and this work are in agreement that the double hexagonal close packed phase (dhcp, Am I phase; $P6_3/mmc$ space group) transforms at a low pressure to a face centered cubic phase (fcc, Am II phase; $Fm3m$ space group). The latter phase is also obtained when the dhcp phase of americium is heated above 650 °C.[16] Differences are noted between previous structural assignments at increased pressures, especially for the Am III phase.[14] The Am IV structure has been assigned to be an α-uranium, orthorhombic structure, first by Roof *et al.*[11] and then by Benedict *et al.*[14] Both groups reported that delocalization of the $5f$ electrons of americium occurs in conjunction with the appearance of the Am IV phase.

There has also been one study to measure the resistivity of americium metal under pressure up to 25 GPa.[17] This experimental approach added another dimension in seeking an understanding of the pressure behavior of americium and its underlying causes. The main finding in this work was that the superconducting T_c of americium became elevated under pressure but the work provided additional evidence to support the onset of $5f$ delocalization due to the application of pressure.

The intent of the present study was to examine the behavior of americium under pressure using both synchrotron (angle dispersive mode) and conventional x-ray (energy dispersive mode) radiation sources in order to acquire the best possible data for resolving its pressure behavior. It is believed that this is the first time that americium has been studied under pressure using synchrotron radiation. The exceptional brilliance afforded by the European Synchrotron Radiation Facility, a third generation machine, allowed us to work with only a few micrograms of americium in each DAC. The companion studies using an energy dispersive mode allowed additional details of the behavior of americium to be obtained.

In the present structural study, we also observed the hexagonal $P6_3/mmc$ and the cubic $Fm3m$ phases, in accord with the structures reported in earlier work, but an important finding was that the Am III and Am IV structures previously reported were incorrect. We have now assigned structures for the Am III and Am IV phases, that provide additional understanding of the behavior of americium metal under pressure, as well as allowing a viable mechanistic picture for the structural progression under pressure. A very important finding was that under pressure americium adopts a known structural form of plutonium, its near neighbor in the series, considered to have itinerant $5f$ electrons. From our data we have also established transition pressures for the different structural forms and a more reasonable bulk modulus for Am. Major factors in obtaining these findings are the experimental advances employed in the work, which includes the use of synchrotron radiation. Given the lower symmetry of the structures encountered, especially at higher pressures, it is imperative that data of the highest quality be used in determining the behavior of americium.

The data obtained permitted us to resolve the previous controversy concerning the Am III and Am IV structures, while confirming that pressure forces the $5f$ electrons of americium to become itinerant. It was important to determine the correct structures obtained under pressure, and to acquire accurate relative volume data, to understand correctly the changes occurring with pressure. The insights obtained from these studies permit (1) interpretation and correct understanding of the behavior of americium under pressure; (2) a comparison of americium's structure/bonding behavior with that of its near neighbor plutonium; and (3) establishment of trends expected in future studies of transamericium metals and alloys under pressure.

These results also address differences noted between experiment and theory, especially regarding the magnitude of the volume collapses in americium. These data should now permit the convergence of experimental and theoretical concepts for the pressure behavior of americium. Reported here are the results of our experimental studies on americium and a discussion of the implications of the changes in structure and atomic volumes observed following the application of pressure. A short account of this work has recently been published elsewhere.[18]

II. EXPERIMENT

A. Materials

Foils of americium metal were prepared by vapor deposition following the reduction of americium dioxide by lanthanum metal. The ^{243}Am isotope ($t_{1/2}=7\times10^3$ years; specific heat generated by the radioactive decay$=6\times10^{-3}$ W/g) was employed in these studies. Mass spectrographic analysis indicated a high purity (99.94% based on metal ion content) and x-ray analysis showed that the metal exhibited the double hexagonal close packed structure ($a_0=3.467\pm0.004$ Å, $c_0=11.240\pm0.008$ Å), in excellent accord with the accepted literature values for it.[19] Small pieces (5–10 μg each) of this foil were cut in a helium atmosphere glove box for placing into the different diamond anvil cells used in the studies.

B. Diamond anvil cells

The high-pressure studies of americium were performed at room temperature using two different diamond anvil cell designs. One was of the Syassen-Holzapfel design (lever-type design) capable of routinely reaching up to 60 GPa. The second was the Cornell-type cell (Ruoff design). The Syassen-Holzapfel cell is best suited for small pressure steps, while the Cornell cells are designed for megabar pressures.

The Syassen-Holzapfel cell was used both in the energy dispersive mode with tungsten radiation produced via a conventional x-ray generator and in the angle dispersive mode with synchrotron radiation. In this cell, the diamonds had a 400 μm flat and the Inconel gasket had a nominal 200 μm hole for the sample. Two Bragg angles (nominal 5° and 7°) were employed in the energy dispersive measurements. The method has been described in the literature.[15] The Cornell-type cells used diamonds with a 95–120 μm flat and a T-301 steel gasket with a 40–70 μm diameter hole for the sample. The Cornell cells were used only in the angle dispersive mode with synchrotron radiation.

The pressure transmitting medium in the cells was either nitrogen or silicone oil. Pressure markers were either ruby (ruby fluorescence technique[20]) or platinum metal using its equation of state.[21] For the synchrotron studies, the cells were prepared at Oak Ridge National Laboratory (ORNL) and shipped to the European Synchrotron Radiation Facility (ESRF) at Grenoble, France. Using in-house developed techniques, the closed cells (few kbar pressure) free of any radioactive contamination were double sealed and placed in special holders for use at the ESRF synchrotron. For additional confinement, beryllium foils and plastic films (Melinex® and/or Kapton®) were used. These plastic films were selected based on their transparency to x rays and the laser wavelength used for the ruby fluorescence technique. After the studies at the ESRF, the sealed cells were returned to ORNL for unloading. The emptied cells were found to be free of radioactive contamination and were reused for other experiments.

Studies involving the energy dispersive technique were performed at the European Institute for Transuranium Elements (ITU) in Germany. In this work, americium was transported from ORNL to ITU. The DAC's were loaded and studied in nitrogen atmosphere glove boxes at ITU.

C. Synchrotron diffraction

Several different experimental parameters were used in the diffraction work at the ESRF synchrotron (beamline ID30). A typical arrangement for the Syassen-Holzapfel cell was to use a 100×100 μm^2 monochromatic collimated beam in the 32-bunch machine mode (100 mA) with an exposure time of ≈1 min. For the Cornell cells, a microfocused beam of 25×25 μm^2 (two bent mirrors in conjunction with a 30 μm pinhole filter) was used. A 15 s exposure was sufficient (2/3 fill machine mode, 200 mA) to obtain excellent diffraction data. Diffraction images were captured with a Fastscan image plate detector[22] and the images viewed within seconds. This permitted making a number of diffraction images under different parameters (wavelength, sample to detector distance, etc.) in a short time frame. The diffraction images were then processed using the FIT2D program,[23] which produced the diffraction results used for data analysis.

III. RESULTS

A. Am I and II structures

The initial structure of the americium used in the high-pressure studies was the normal dhcp form ($P6_3/mmc$;Am I) that has been reported as the stable ambient temperature/pressure phase. This dhcp form is isostructural with several of the early lanthanide metals through neodymium.[4] Although the actinide metals display smaller lattice parameters than the lanthanide metals, the transplutonium metals through californium and most of the lanthanide metals (except europium and ytterbium) are considered as being trivalent metals having localized f electrons.

With the application of pressure, the dhcp form of americium converts to a fcc structure ($Fm3m$; Am II) at 6.1 ±0.2 GPa. The lattice parameter at 6.5 GPa is $a=4.613$ Å. This fcc phase is identical to the high-temperature phase that has been observed for americium metal above 650 °C. Benedict *et al.*[14] reported this dhcp →fcc transition to occur at 9.5 GPa, a higher pressure than observed in this work. A third high-temperature phase, believed to be a body centered cubic phase but not confirmed by x-ray analysis,[24] has not been observed as a pressure phase.

Combined results from both angle and energy dispersive mode studies in the form of interplanar distances versus pressure are plotted in Fig. 1 (up to 15 GPa) and Fig. 2 (10 to 65 GPa). Four distinct phases were observed in the work and these are shown as dhcp (Am I), fcc (Am II), Am III, and Am IV in Fig. 1 and Fig. 2.

B. Am III structure

With additional pressure, we observed that the fcc Am II phase transformed to the Am III phase at 10.0 ± 0.2 GPa, which was retained up to 16 ± 1 GPa. In the work of Benedict *et al.*[14] the Am III phase is reported to start at 13.5 GPa and was retained up to 23 GPa. It is the structure of this phase that has been controversial in past studies of americium under pressure.[9,12–14] Knowledge of the exact structure of the Am III phase is critical in order to understand correctly its behavior under pressure.

The Am III phase has been assigned previously as a monoclinic structure,[12,13] a triple hexagonal closed packed structure,[9] and a distorted, face centered cubic structure.[14] The highest pressure obtained with Am prior to our work (52 GPa) was reported by Benedict *et al.*,[14] while other efforts were limited to 20 GPa. Benedict *et al.*[14] argued that the monoclinic indexing reported in Refs. 12 and 13 was incorrect, and would require an expansion of the volume with pressure. The assignment of a trigonal distortion[14] (distorted fcc) of the cubic Am II phase removed this contradiction and provided a 6% volume collapse when the Am III phase converted to a proposed α-uranium Am IV phase. Theoretical

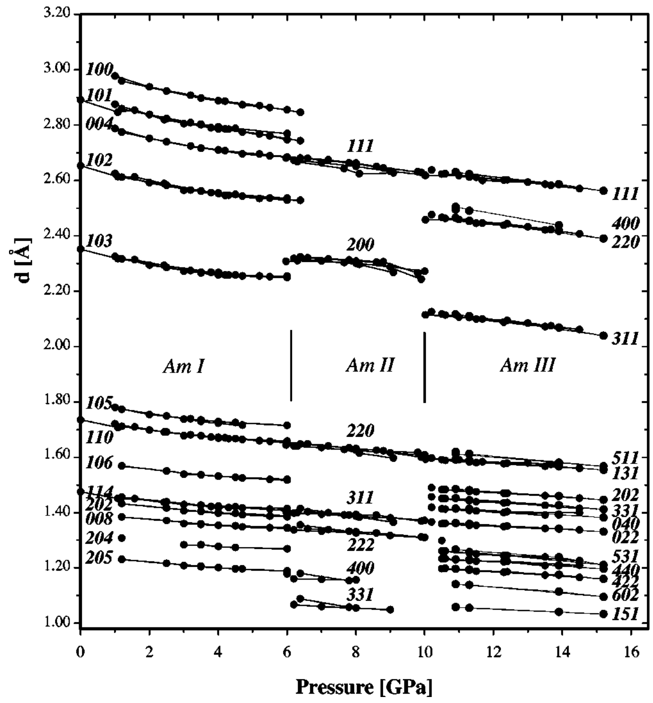

FIG. 1. Interplanar distances in americium metal as a function of pressure up to 15 GPa. (Miller indices *hkl* are indicated for the phases.)

calculations[25,26] at that time suggested a volume collapse of 22%. Subsequent estimations suggest that a collapse of 34% (Ref. 27) or 25% (Ref. 28) would be observed. A significant difference exists between these earlier experimental findings and the theoretical expectations.

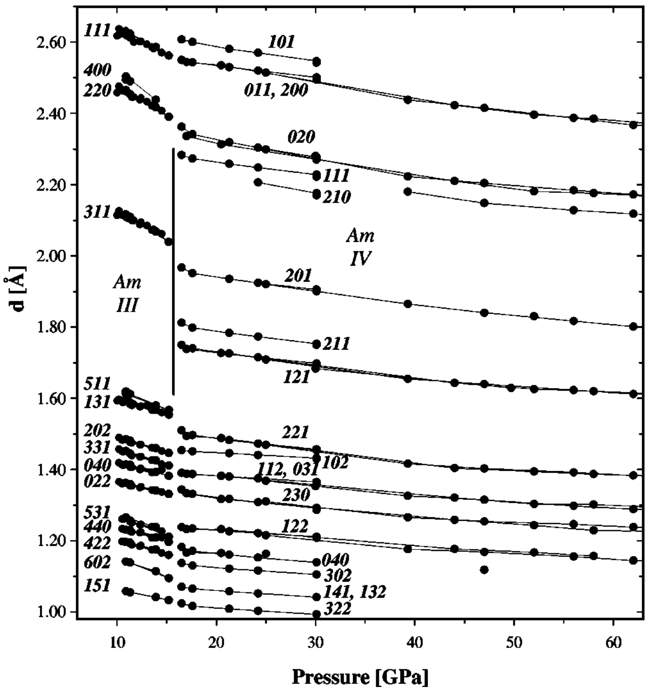

FIG. 2. Interplanar distances for the Am III and Am IV high-pressure phases of americium as a function of pressure from 10 to 65 GPa. (Miller indices *hkl* are indicated for the phases.)

In our study, extensive efforts were made to determine correctly the structure of this Am III phase. Nine diffraction spectra were collected at different pressures and multiple indexing programs, TREOR,[29]DICVOL91,[30] and ITO,[31] were employed to extract the structure type. Initial attempts suggested a monoclinic symmetry (e.g., $I2/m$, $C2/m$, etc.) but it was not possible to assign unequivocally all the diffraction peaks observed for the americium III phase. Deviations were especially notable at the higher diffraction angles for the $I2/m$ assignment and Rietveld refinements with the $C2/m$ space group indicated an unsatisfactory correlation with intensities at lower diffraction angles.

Given the quality and reproducibility of our diffraction data collected from multiple samples of Am and different DAC's, we were finally successful at arriving at the correct assignment of the structure of the Am III phase. We have determined that the structure has an unexpectedly high symmetry with a face centered orthorhombic cell (space group $Fddd$, Am on the $8a$ sites, all position parameters fixed by symmetry). The lattice parameters at 10.9 GPa are $a=10.115$, $b=5.670$, and $c=3.116$ Å ($\rightarrow b/c\approx\sqrt{3}$, i.e., the structure consists of slightly distorted close packed hexagonal planes; this is discussed in detail in a later section). Our findings for the Am III phase do not agree with the previous structural assignments[12–14] or pressure range for this Am III phase. A trigonal distorted Am III phase[14] was reported to exist between 13.5 and 23 GPa, while Roof[12,13] suggested that a monoclinic Am III phase started at 10 GPa. We observed the orthorhombic $Fddd$ structure between 10 and 16 GPa.

C. Am IV structure

In our work the Am IV phase was observed to form at 16 ± 1 GPa and was retained up to 100 GPa, the highest pressure for which we report data. Close examination of our data suggested evidence for the beginning of the Am IV phase already at 13 GPa ($\approx 10\%$ Am IV) and that Am IV was the exclusive phase by 17.5 GPa. We also observed a gradual separation of the first three diffraction lines for this structure with pressure, and a definite separation was noted at 60 GPa. Roof *et al.*[11] first reported the appearance of the Am IV phase at 15.2 ± 0.2 GPa and assigned it as being an α-uranium structure (orthorhombic), while Benedict *et al.*[14] found that the phase formed at 23 GPa and reported it was stable up to 52 GPa.

Using Rietveld refinement (see below) we were able to assign this Am IV structure as being primitive orthorhombic (space group $Pnma$, Am on $4c$ sites with $x=0.403$, $y=1/4$, $z=0.101$ at 17.6 GPa, and $x=0.406$, $y=1/4$, $z=0.118$ at 89 GPa), in contrast to the base centered orthorhombic α-uranium structure (space group $Cmcm$, U on $4c$ sites with $x=0$, $y=0.102$, $z=1/4$). The lattice parameters for the Am IV structure are $a=5.093$, $b=4.679$, $c=3.028$ Å at 17.6 GPa and $a=4.607$, $b=4.288$, $c=2.737$ Å at 89 GPa.

This structure for Am IV is closely related to the α-uranium structure. If the atomic position parameter z of the $4c$ sites of the $Pnma$ structure is placed at zero, one obtains the higher-symmetry α-uranium structure with the

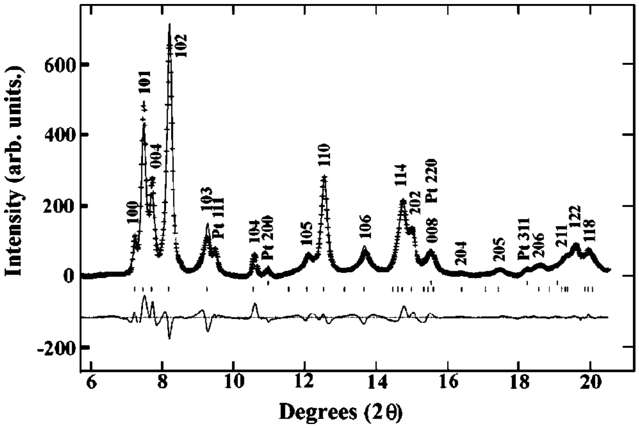

FIG. 3. Rietveld fit of the dhcp (space group $P6_3/mmc$) Am I phase at 1.2 GPa ($\lambda=0.3738$ Å, pressure transmitting medium nitrogen) showing the observed (crosses) and calculated (line) diffraction patterns, reflection tick marks, Miller indices of the principal reflections, and difference profile. (Pt pressure calibrant used.)

base centered orthorhombic unit cell (only the definition for the three lattice parameters is different). We have found that the fit of the data is better with the *Pnma* structure type and propose this as the correct identification of the Am IV phase.

D. Rietveld analyses of data

The Rietveld analyses of the angle dispersive synchrotron data were made using FULLPROF and GSAS.[32,33] It is often difficult to make a Rietveld analysis for very small samples, since bad grain statistics lead to unrepresentative intensities of the integrated diffraction lines. However, the grain size of our polycrystalline Am samples was small enough to produce perfect diffraction rings and reproducible intensities of the integrated patterns. It was only necessary to take into account the potential for preferred orientation. The Rietveld fits are shown in Figs. 3–7 for the observed phases of americium, where Figs. 6 and 7 represent two pressures for the Am IV phase. The refinements for the Am III and Am IV phases are especially important in this regard, as the first two phases were already well established. Figures 5–7 show very good agreement between the experimental and calculated data points. The Bragg *R* values of the Rietveld refinements shown are 7.2% for Am III at 10.9 GPa, 8.3% for Am IV at 17.6 GPa, and 4.9% for Am IV at 89 GPa.

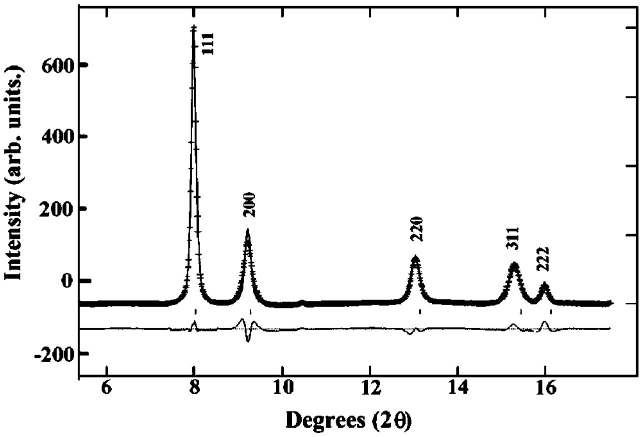

FIG. 4. Rietveld fit of the fcc (space group $Fm3m$) Am II phase at 6.5 GPa ($\lambda=0.3738$ Å, pressure transmitting medium nitrogen) showing the observed (crosses) and calculated (line) diffraction patterns, reflection tick marks, Miller indices of the principal reflections, and difference profile.

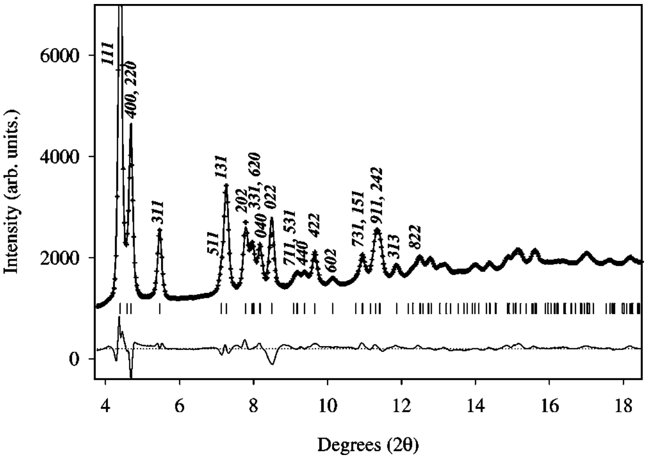

FIG. 5. Rietveld fit of the orthorhombic (space group $Fddd$) Am III phase at 10.9 GPa ($\lambda=0.2022$ Å, pressure transmitting medium nitrogen) showing the observed (crosses) and calculated (line) diffraction patterns, reflection tick marks, Miller indices of the principal reflections, and difference profile.

IV. DISCUSSION

A. Volume and bulk modulus

In Fig. 8 the relative volumes (V/V_0, where V_0 is the volume at normal pressure) are plotted against pressure. The changes occurring when changing from one pressure to another for the different phases are evident in the figure. Two abrupt changes in volume can be observed: one small one ($\approx 2\%$) at the Am II to Am III transition and a larger change ($\approx 7\%$) at the Am III to Am IV transition. These distinct

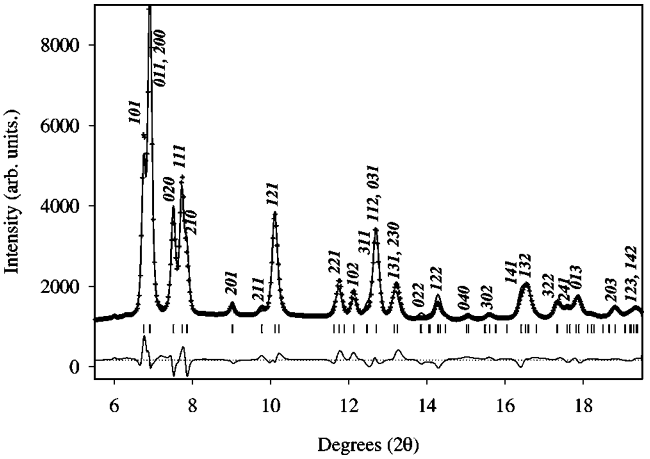

FIG. 6. Rietveld fit of the orthorhombic (space group $Pnma$) Am IV phase at 17.6 GPa ($\lambda=0.3066$ Å, pressure transmitting medium: nitrogen) showing the observed (crosses) and calculated (line) diffraction patterns, reflection tick marks, Miller indices of the principal reflections, and difference profile.

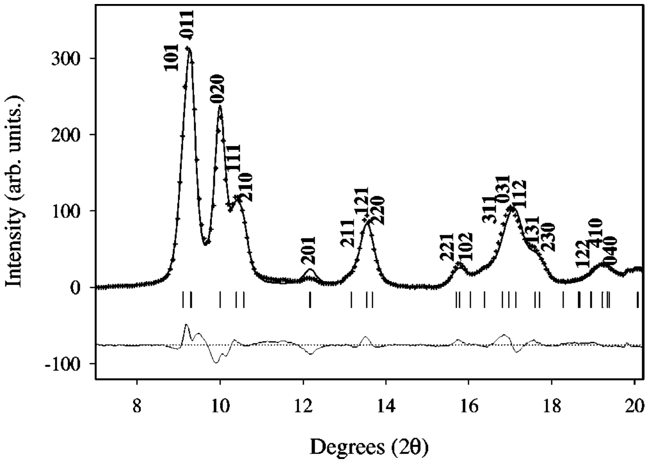

FIG. 7. Rietveld fit of the orthorhombic (space group *Pnma*) Am IV phase at 89 GPa ($\lambda = 0.3738$ Å, pressure transmitting medium silicone oil) showing the observed (crosses) and calculated (line) diffraction patterns, reflection tick marks, Miller indices of the principal reflections, and difference profile.

volume ''collapses'' are attributed to the onset of *f* electron contribution to the metallic bonding. A major difference in this work compared to former studies is the assignment of *f* electron character to the Am III phase, rather than only to the Am IV phase, and a second volume change for the Am III to Am IV transition. However, the change in volume is lower than the 25% change predicted by the most recent theory.[28] This onset of *f* electron itinerancy in americium metal due to pressure is discussed further in a subsequent section.

The isothermal bulk moduli and their pressure derivatives were obtained by fitting the Birch[34] and Murnaghan[35] equations of state to the experimental curve of the lower-pressure phases Am I and Am II (localized *f* electrons) to obtain the bulk modulus B_0 and its pressure derivative B_0' (the subscript zero indicates ambient pressure). The following values were obtained: Birch equation, $B_0 = 29.7 \pm 1.5$ GPa, $B_0' = 3.7 \pm 0.2$, and Murnaghan equation, $B_0 = 29.9 \pm 1.5$ GPa, $B_0' = 3.5 \pm 0.2$. These moduli are consistent with values reported for the light lanthanide metals.[1] The modulus reported by Benedict *et al.* for americium metal is 45 GPa,[14] appreciably higher and close to the value of 43 GPa reported for α-plutonium.[36] The modulus for plutonium with itinerant *f* electrons would be expected to be higher than that for americium metal with three non-$5f$ conduction electrons. That is, the lattice for α plutonium should be ''stiffer'' than that of the dhcp form of americium metal.

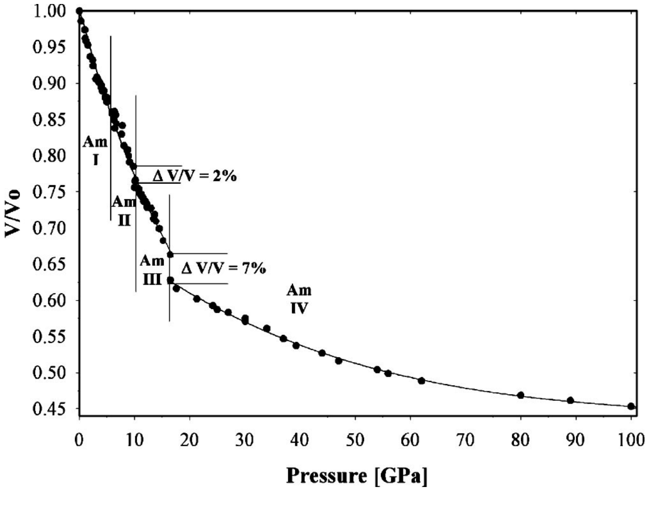

FIG. 8. Relative volume of americium metal as a function of pressure up to 100 GPa.

Another point is that some hysteresis is observed upon the release of the applied pressure (not shown). In the energy dispersive studies, the Am IV phase was retained down to ≈ 11 GPa and a mixture of Am III and Am IV was observed down to ≈ 6 GPa. The Am II phase was retained after the total release of the pressure. The retention of the fcc phase has been observed before[9,37] and was used to obtain ''pressure quenched'' lattice parameters for this cubic phase. However, the retention of the Am III and Am IV phases was surprising, as it was expected that *f* bonded structures forced by pressure would quickly revert back to stable, localized *f* electron structures with the release of pressure.

B. Compressibility of the Am IV phase

In the previous section the bulk modulus of americium metal obtained from this pressure study was discussed. The modulus can be obtained via the compression behavior of the Am I and Am II phases using established equation of state relationships. The bulk modulus of 30 GPa found for americium in this work is consistent with moduli established for several lanthanide metals that have localized *f* electrons.[2] The steep portion of the compression curve for Am I and Am II in Fig. 8 is in accord with a smaller bulk modulus—that is, a metal with a softer lattice that can be readily compressed. In contrast, the modulus of α uranium is much larger (reported as 100 to 152 GPa by various methods[2]) and under pressure uranium shows a much ''flatter'' compression curve.

In Fig. 8 it can be observed that the compression of the Am IV curve is also much ''flatter'' than for the Am I, Am II, or Am III phases, which suggests, that the Am IV phase has a much higher bulk modulus. It is not fully appropriate to calculate a bulk modulus for the Am IV phase using our data, but a pseudomodulus can be extracted from it by extrapolation. By this approach, we obtained a bulk modulus for the Am IV phase and estimate a value approaching 100 GPa. Such a value is in full accord with a rather ''stiff'' or ''rigid'' lattice, which has $5f$ electron involvement in the metallic bonding. This pseudo bulk modulus for the Am IV phase suggests that this phase's compressibility falls between those of α uranium and α neptunium, two actinide metals with itinerant $5f$ electrons. The difference in compressibility for the Am III and the Am IV phases (e.g., the compression curves in Fig. 8) also supports the contention that the Am IV phase has a higher degree of $5f$ involvement in its bonding.

C. Relationship between structures

The four different americium structures observed in this work are shown in Fig. 9, which permits one to envision the

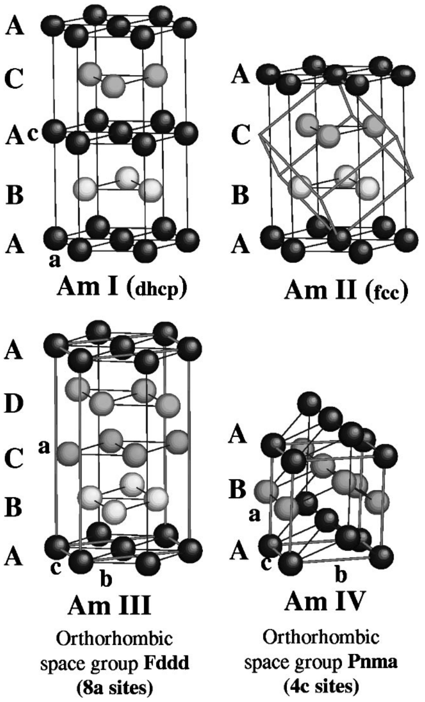

FIG. 9. Models for the four structures of americium metal under pressure.

transformation process occurring under pressure. In principle, the structures can be viewed as being composed of close packed hexagonal (Am I, Am II) or distorted close packed hexagonal planes (Am III, Am IV) with a stacking sequence that changes in going from one structure to the next. Thus, for the dhcp Am I structure, the sequence is $(A\text{-}B\text{-}A\text{-}C\text{-}A)$, which changes to $(A\text{-}B\text{-}C\text{-}A)$ for the fcc Am II phase by shifting planes. The fcc then converts to an $(A\text{-}B\text{-}C\text{-}D\text{-}A)$ arrangement by a shift and distortion of planes to produce the Am III phase (b/c differs only by 5% from the ideal $\sqrt{3}$ value for close packed hexagonal planes). Finally, a shift, distortion, and zigzag bending of the hexagonal planes yields $(A\text{-}B\text{-}A)$ for the Am IV phase. As shown in Fig. 9, this bending requires a shifting of the planes parallel to the a-c faces, which are perpendicular to the close packed hexagonal planes.

For the Am I and Am II structures, there are 12 nearest neighbors with the same interatomic distances (six in the same plane, three in the plane above, and three in the plane below). For the Am III phase there are also six neighbors in the same plane, but now four in the plane below and four in the plane above. Two of these four are the nearest neighbors, whereas the other two have the largest distance of all neighbors. This means that the Am III structure provides 14 neighbors with distances between 3.0 and 3.72 Å (at 10.9 GPa). There is then a distance gap and the next atom is at 4.85 Å.

The Am IV structure also has 14 neighbors with distances between 2.61 and 3.51 Å (at 17.6 GPa). Then there is again a gap with the next atom being at 4.44 Å. The atomic sites in the Am III structure have high point symmetry 222, while the sites in the Am IV structure have a lower point symmetry m.

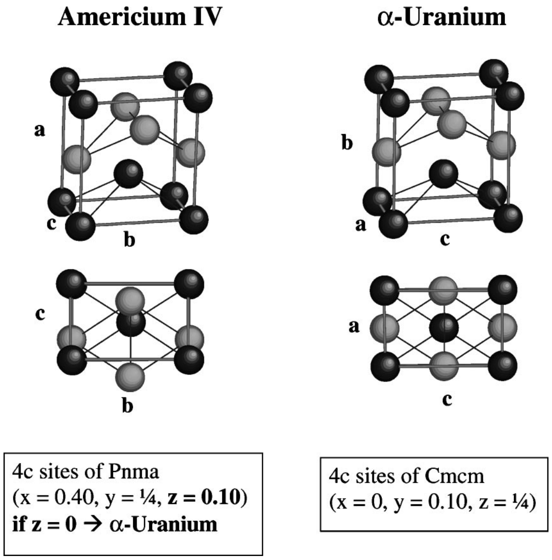

FIG. 10. Orthorhombic cells for the Am IV and α-U structures. Setting the z value of the $4c$ sites in the $Pnma$ structure of Am IV (left) to 0 means a shifting of the planes with the light atoms relative to the dark ones in the c direction so that one obtains the α-U structure (right).

What is most significant here is that this Am III structure is the same as that known for the γ phase of plutonium,[38] considered to have $5f$ electron involvement in its metallic bonding. Thus, under pressure the electronic nature of americium is altered and the metal adopts one of the structures established for its preceding neighbor, plutonium.

As discussed earlier, the structure proposed here for the Am IV phase is similar to the α-uranium structure previously assigned to the Am IV phase.[11–14] The orthorhombic cells of the two structures are shown in Fig. 10. If the atomic position parameter z (≈ 0.10) of the $4c$ sites of the Am IV $Pnma$ structure is set to zero, the second zigzag like bent plane (light colored atoms) of Am IV in Fig. 9 or Fig. 10 is shifted in the c direction so that one obtains centered rectangular a-c planes, i.e., the base centered orthorhombic α-uranium structure ($Cmcm$) is formed. The latter has a higher symmetry than the $Pnma$ structure (only the definition of the lattice parameters is different in the $Cmcm$ space group). If the α-uranium structure were the right structure of Am IV, then it would be possible to identify these centered rectangular planes as distorted close packed hexagonal planes. This means that the α-uranium structure could be obtained from the Am III structure by only shifting (without bending) the distorted close packed hexagonal planes. This argument leads also to a second possibility for the transformation path from Am III to the right Am IV structure: Instead of bending the close packed hexagonal planes of Am III one must shift the atoms within the plane, so that one no longer has hexagonal planes. This means that the a-c faces of Am IV in Fig. 9 have to be assigned to the b-c faces of Am III.

Evolution of the lattice parameters for the four Am pressure phases is shown in Fig. 11. These parameters have been multiplied by the factors shown in the figure and assigned to each other in a way which enables the changes in pro-

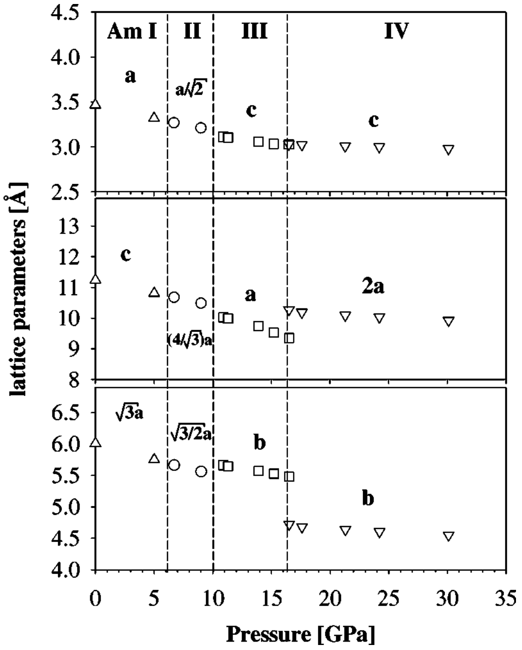

FIG. 11. Evolution of the lattice parameters for the four Am pressure phases with pressure. (See text for detailed explanation.)

gressing from one phase to another to be followed. Figure 11 helps to illustrate the mechanism of the structural changes which are shown in Fig. 9. Let us take, for instance, the first lattice parameter in Fig. 11, which shows the evolution of the interatomic distance defined by the hexagonal lattice parameter a of Am I through all the structural transitions. It is clearly evident that there is a smooth evolution of this parameter, which one would expect from looking at Fig. 9. On the other hand, the third parameter in Fig. 11 shows the evolution of the interatomic distance defined by the orthorhombic lattice parameters b of Am III and Am IV. This parameter shows a sharp pronounced decrease at the transition between Am III and Am IV, which is due to the bending of the hexagonal plane in the case of Am IV.

D. Discussion of structure and bonding

The involvement of $5f$ electrons in the metallic bonding of the actinides gives rise to several special physicochemical properties. The unique behavior of plutonium, the near neighbor of americium, is an example of the effects brought about by having itinerant $5f$ electrons. Plutonium is perhaps the most complex metal in the periodic table, displaying six structural forms between ambient temperature and its melting point of 640 °C. Below 155 °C, the pure metal displays a complex monoclinic (α phase, simple monoclinic, $P2_1/m$) structure, rather than the more symmetrical structures (cubic, hexagonal, etc.) found for most metals in the periodic table; for the transition metals it is the *d*, *s*, and *p* electrons that are responsible for the metallic bonding and hence the structures.

For americium and the subsequent actinide metals in the series that have localized f electrons, symmetrical crystal structures and a simpler phase behavior is observed. In this regard, the transplutonium metals are similar in their behavior to the lanthanide metals, the $4f$ series of elements. In essence, plutonium is trying to become a trivalent metal but its situation is complicated by a number of electronic states of similar energy. On the other hand, americium is a trivalent metal but not far removed from the electronic situation of plutonium. Perturbations like pressure therefore may alter its electronic nature more readily than for a higher member of the actinide series.

For the actinides, based only on atomic volume, α neptunium could be considered as having the maximum degree of *f* bonding, whereas the complex phase behavior of plutonium metal suggests a maximum multiplicity of energy levels of similar stability. The more complex behavior of actinide metals with itinerant *f* electrons is due to the latter's involvement in the metallic bonding. These different electronic configurations can yield atoms of different sizes, which affects packing and can give rise to denser metallic structures. For example, the ambient temperature form of plutonium (monoclinic α phase) has a calculated density of 19.86 $\mathrm{g/cm^3}$, whereas the dhcp form of americium under comparable conditions has a density of 13.61 $\mathrm{g/cm^3}$.

The important point is that there is a potential for generating multiple electronic levels of similar energy by incorporating *f* character in the bonding. This often leads to distorted structures of low symmetry. It is the symmetry of the *f* electrons' orbitals that disfavors the traditional close packed, high-symmetry structures and produces the distorted plutonium structures instead of a hexagonal-type structure. The appearance of such low-symmetry structures can be used to infer the partial infusion of *f* electron character into the metallic bonding. A low-symmetry structure, especially one displayed by the early actinide metals known to have itinerant *f* electrons, then becomes a ''fingerprint'' for the involvement of *f* electrons in metallic bonding. In conjunction with the formation of a low-symmetry structure, the appearance of a volume collapse (sharp decrease in relative volume at a given pressure) is also taken as a sign that *f* electrons may have been forced into the metallic bonding.

Given that americium is the near neighbor of plutonium, it seems reasonable that by adding *f* character Am would adopt one of the plutonium structures, a neptunium structure, or the α-uranium structure. There may be only small differences in the *f* electron character and energy levels between these structures. It is significant that the γ phase of plutonium has the same structure cited here for the Am III phase formed under pressure. The facts that plutonium is the near neighbor of americium and that Am adopts under pressure the γ-Pu structure make it worthwhile to note some specific characteristics about the behavior of plutonium.

The behavior of the crystal structure of plutonium with temperature is well established.[39,40] Beginning with the α phase of plutonium and increasing the temperature (which should increase the interatomic distances, as opposed to the effect of pressure), there are six reported phases, the third being the γ phase (the same structure as the Am III structure). With expansion there may be some reduction in *f* electron involvement in the bonding. However, there seems to be little question that *f* electron bonding is still present in these higher-temperature phases—it is likely that some *f* character even remains in the molten state.[40]

There are some important aspects of plutonium with reference to americium. One is that the largest atomic radius for plutonium metal[40] (1.64 Å calculated for both the δ and the δ' phases at 25 °C)[40] is smaller than the atomic radius of americium at the same temperature (1.73 Å). This is as expected given the type of bonding present in each metal at atmospheric pressure (plutonium, at least partial f character; americium, localized f electrons). Second, the atomic radius of americium near the Am II →Am III transition point is close to that for f electron bonded plutonium. The shortest distance of the Am III phase just after the transition is 1.50 Å and it is accepted that f bonding is still present in δ-plutonium at 25 °C, where the calculated radius is as large as 1.64 Å.[40] Further, the atomic radius for curium, the other near neighbor of americium in the series (for the fcc, Cm II phase), just before the onset of delocalization of its $5f$ electrons occurs, is ≈1.52 Å.[41] The important point of these comparisons is that they show the interatomic distances for americium III are (1) smaller than those in plutonium where f interactions are present; and (2) close to the value where f interactions take place in curium. The existence of localized versus itinerant f electron states is important in defining/understanding chemical and/or physical properties. The above comparisons of interatomic distances for Am and Pu also support the concept proposed here that, given the smaller interatomic distances in Am, the bonding in the Am III phase has acquired f electron character.

The above discusses americium's pressure behavior in conjunction with aspects of its neighbors plutonium and curium and it is worthwhile to make some more comparisons with the behavior for curium under pressure. Curium is reported to undergo two phase transitions with pressure.[41] The sequence is dhcp→fcc→orthorhombic, α-uranium structure (which is presumed to have itinerant $5f$ electrons). The transitions occur at much higher pressures and an intermediate phase is not observed between the fcc and the α-uranium phases. The volume collapse at the fcc to orthorhombic transition is 21%, much greater than observed for americium. The 21% for curium is much more in line with the theoretical estimates of 25–34 % for the volume collapse in americium.[27,28] If the overall volume change for americium between the fcc Am II structure (at 10 GPa) and the orthorhombic Am IV structure (at 16 GPa) is taken, without compensation for compression, the volume change appears to be 20%. Thus, the appearance of the additional Am III phase makes an important difference in the apparent behavior of americium. Americium appears to change in multiple steps rather than one much larger collapse, as observed for curium. Whether the Cm III phase is truly an α-uranium structure, or perhaps a $Pnma$ structure as found here for Am IV, must be determined in future studies of curium with synchrotron techniques.

V. CONCLUSIONS

Obtaining high-quality experimental data for the structural behavior of americium metal under high pressure up to 100 GPa permitted the proper identification of the Am III and Am IV phases. It was possible to acquire these data by using synchrotron radiation and other experimental advances. The findings provide important insights into the behavior of americium's $5f$ electrons under pressure and permit a mechanistic picture for the sequential conversion of americium from the Am I phase through the Am IV phase.

In addition to resolving a previous 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 Am IV structures formed under pressure. First, the Am III phase is now properly identified as a face centered orthorhombic structure (space group $Fddd$, Am on $8a$ sites), which is the same structure displayed by the γ phase of plutonium where the bonding involves itinerant $5f$ electrons. Second, the Am IV structure is now shown to be a primitive orthorhombic (space group $Pnma$, Am on $4c$ sites) structure, rather than the very similar base centered orthorhombic α-uranium structure as reported previously, and it is stable up to at least 100 GPa.

An important finding in this work is that the delocalization of americium's $5f$ electrons forced by pressure occurs in two rather than a single step. The first process involves partial delocalization and an accompanying 2% volume collapse (Am II→Am III transition). The belief that the bonding in the Am III phase has $5f$ electron character is supported by both the magnitude of the interatomic distances in this phase (relative to those in f electron bonded Pu structures) and the fact that Am III is isostructural with γ-Pu. This is based on the concepts of critical distances for f electron involvement and that f bonding is responsible for the formation of lower-symmetry structures. In the second delocalization step the involvement of $5f$ electrons becomes more prominent and this change is accompanied by a larger collapse in volume (Am III→Am IV transition). It is not known if all or just a greater portion of americium's $5f$ electrons are now involved in the Am IV phase. The Am IV phase is a more ''rigid'' structure, as evident by its apparent lower compressibility that reflects the behavior of α-uranium. The lower compressibility also supports the concept that the Am IV phase has a greater involvement of its $5f$ electrons in the metallic bonding than the Am III phase.

These experimental findings are not in accord with theoretical projections suggested recently for the pressure behavior of americium,[28] where the α-plutonium structure was believed to represent the high-pressure structure of americium.

Overall, this work provides important insights for understanding the pivotal position of americium in the actinide series, especially with regard to the involvement of its $5f$ electrons in metallic bonding. The quality of these data firmly establish the experimental behavior of americium under pressure up to 100 GPa. It is hoped that these findings for americium will promote the convergence of experimental and theoretical views regarding the volume collapse and $5f$ electron delocalization in americium metal under pressure.

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