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Pressure-induced changes in protactinium metal: Importance to actinide-metal bonding concepts

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Protactinium occupies an important position in the actinide series of elements, as it represents the first of four elements (Pa-Pu) having $5f$-electron character in their bonding at atmospheric pressure. We have determined in experimental studies with synchrotron radiation to 130 GPa, that the tetragonal structure of protactinium (space group $I4/mmm$) converts to an orthorhombic, alpha-uranium structure (space group *Cmcm*) at 77(5) GPa, where the atomic volume has been reduced by ~30%. This structural change is interpreted as reflecting an increase in $5f$-electron contribution to the bonding in protactinium over that initially present, becoming more similar to that present in alpha-uranium metal at atmospheric pressure. We determined experimentally that this structural transformation occurred at significantly higher pressures and at a smaller atomic volume than predicted by theory. The experimental results reported here represent the highest pressures under which protactinium metal has been studied.

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I. INTRODUCTION

In the f series of elements, it has been established that metals having localized f electrons exhibit greater atomic volumes and have more symmetrical structures than those whose f electrons are involved in their bonding. Reviews are available covering the occurrence of f-electron delocalization in lanthanide and actinide metals accompanying decreased interatomic distances forced by pressure.[1–3] Interestingly, after acquiring $4f$-electron character in their bonding from applying pressure, lanthanide metals adopt some of the same, low-symmetry structures exhibited normally by the protactinium through plutonium elements at atmospheric pressure. Cerium, neodymium, and praseodymium are three examples of $4f$-electron elements that display this behavior.[4–6] The structures of these four light actinides arise from $5f$-electron participation in their bonding. Recently there has been increased interest in the pressure behavior of f elements given the capability to predict theoretically potential structural changes with pressure[7–11] and the ability to now acquire experimental information to very high pressures (e.g., hundreds of GPa).

Studies of protactinium in general have been sparse, due in part to its limited availability and radioactivity, but some of its known properties have been reviewed.[12] Its superconducting properties[13] and high enthalpy of vaporization[14–16] in part established that its bonding has $5f$-electron character at atmospheric pressure (i.e., itinerant $5f$ electrons).[17]

Protactinium being the first of four actinide metals having itinerant $5f$ electrons at atmospheric pressure occupies an important position in the series. The energies of the empty $5f$ orbitals of the preceding actinide element, thorium, are sufficiently high, and it behaves as a $6d$-block transition metal with $6d^2 7s^2$ bonding electrons. With increasing nuclear charge, the energies of the $5f$ orbitals relative to the $6d$ and $7s$ orbitals change dramatically. The $5f$ orbitals of the next four elements (protactinium through plutonium) are increasingly occupied, and participate to varying degrees in the metallic bonding.[17–21] It is this influx of f-electron character into their bonding that generates rare polymorphism, low-symmetry crystal structures, and smaller compressibility, facets not displayed by other metals in the Periodic Table. This itinerancy of $5f$ electrons at atmospheric pressure disappears when reaching americium, with it and the subsequent elements, their $5f$ electrons are fully localized. The transplutonium elements' crystal structures resemble mainly those displayed by the $4f$ series of elements that have fully localized $4f$ electrons.

Theoretical calculations in conjunction with experimental findings have provided important fundamental insights into the behavior of the structures, bonding, and energy levels of these f-electron elements as a function of pressure, when their interatomic distances are significantly reduced. Both fully relativistic, linear muffin-tin orbital and/or full-potential, linearized plane-wave methods have been used in these predictive calculations. Of particular interest here is the computational work on americium,[7] praseodymium,[8] thorium, uranium, neptunium, plutonium, and americium metals.[9–11] Results from recent experiments have provided important insights into the bonding and behavior of americium under pressure,[22–24] altering previous conclusions reached by experiments[1–3] and theory.[7,21] The more recent experimental findings with americium have relevance to the present work on protactinium, and for this reason some aspects are cited here.

The delocalization of americium's $5f$ electrons by pressure occurs in two steps, with the progressive formation of two lower-symmetry structures. In the first step, a γ-plutonium-type structure (*Fddd*) is formed, which is followed by a primitive orthorhombic structure (*Pnma*). The latter has a close relationship to the *Cmcm*, α-uranium structure.[22–24] An important finding was the establishment of structural links of americium with other actinides: first, between the Am-III phase and γ-Pu (its near neighbor) and then between the Am-IV phase and α-U. In the present work, structural links are established between the high-pressure phase of protactinium and its near neighbor, uranium, and with the high-pressure Am-IV phase.

Our focus in the present work was to ascertain the effect of pressure on the structural and electronic behaviors of protactinium. The pressure behavior of protactinium has been addressed previously, first experimentally[25] and then by theory.[26] This earlier experimental work examined protactinium metal up to 53 GPa, using energy dispersive x-ray diffraction. A subsequent calculation for the pressure behavior of protactinium under pressure using first-principles theory[26] suggested that several potential structural transformations may occur under pressure.

The experimental work reported here examined the structural behavior of protactinium to 130 GPa, using diamond-anvil pressure cells (DAC's). The exceptional brilliance provided by the European Synchrotron Radiation Facility (ESRF) allowed us to acquire high quality, angle dispersive x-ray data, and to analyze its behavior using only a few micrograms of metal. In addition to determining comprehensively the behavior of protactinium under pressure, we have also derived a different experimental bulk modulus. Our value is considerably smaller than that derived from a previous study,[25] but higher than the modulus extracted by calculations.[26–28] We present here our detailed experimental findings for the pressure behavior of protactinium, together with discussions on the implications of these findings and the reported theoretical predictions for its pressure behavior.

II. EXPERIMENT

A. Materials

Small bulk forms of protactinium (Pa-231 isotope, $t_{1/2} = 3.28\times10^4$ yr) metal were obtained by the thermal reduction of protactinium iodide[29–31] and was prepared at the Institute for Transuranium Elements (ITU). Just prior to the loading of the DAC's for the subsequent diffraction studies, the protactinium was annealed at 1200 °C under 10^{-8} torr.

Analyses of the material confirmed total impurities were below 2000 ppm (atomic; major contaminants were 500 ppm oxygen and nitrogen, 600 ppm silicon, and <500 ppm of iron, titanium, and tungsten). Conventional x-ray analyses of the metal showed it existed in the bct structure at atmospheric pressure, and its lattice parameters were within error bars of the published literature values.[31–33] We used lattice parameters of $a_0 = 3.925(3)$ Å and $c_0 = 3.238(4)$ Å in calculating the relative volumes shown in the different figures. Small pieces (~2 μg each) were cut from the protactinium stock for insertion into each of the different DAC's used.

B. Diamond-anvil cells

Diamond-anvil cells are widely used for studying very small quantities (multiple micrograms) of materials under high pressures (i.e., hundreds of GPa). In our experiments, both Syassen-Holzapfel-type[1] (to 60 GPa) and Cornell-type (Ruoff design[24] to 130 GPa) DAC's were used. Liquid nitrogen was used as the initial pressure-transmitting medium in the Syassen-Holzapfel cells, enabling reasonable hydrostatic conditions to be retained during important pressure regions. Silicone oil (Dow Corning D-205) was used as the pressure medium for the Cornell cells. At higher pressures, the hydrostatic nature of the two transmitting media is about equivalent.

The Syassen-Holzapfel cell functions better for small pressure steps and for employing liquefied gases (e.g., nitrogen, argon) as the pressure-transmitting medium, while the Cornell-type design is better suited for higher pressures. The Cornell-type cells used beveled diamonds with nominal 120 μm flats and steel gaskets with 40–70-μm-diameter holes. The Syassen-Holzapfel cells used beveled diamonds with 400-μm flats and inconel gaskets with holes of ~200-μm diameter. Pressure "markers" were ruby (the fluorescence technique[34]) or copper metal (via its equation of state[35]).

The pressure cells were pre-conditioned at the Institute for Transuranium Elements (ITU), and then loaded with samples and provided with the proper containment at Oak Ridge National Laboratory (ORNL). Using in-house techniques developed at ORNL, the cells with the samples (under a few tenths GPa and free of any radioactive contamination) were "double contained" and placed in special housings for use at the ESRF. For containment, beryllium foils and plastic films (Melinex) were used in conjunction with the special metal housings[24] for the DAC's. Melinex was selected based on its transparency to x rays as well as to the argon laser output used for the fluorescence analyses. The cells were then shipped to the ESRF for the diffraction studies. After the diffraction studies at the ESRF, the cells were returned unopened to ORNL for decommissioning.

C. Synchrotron diffraction

The high-pressure studies of protactinium metal were performed at room temperature using the two different DAC designs. The experiments were done at the ESRF (ID30 beamline) in an angular dispersive mode using synchrotron radiation of a selected monochromatic wavelength (mainly, 0.3738 Å). A microfocused beam of 10×15 μm^2 full width at half maximum (FWHM) (two bent mirrors in conjunction with a 30-μm pinhole filter) was used. A 5–15-sec exposure ($\frac{2}{3}$ fill machine mode) was sufficient to obtain the desired diffraction data. A few data points for the high-pressure phase were also acquired using a shorter wavelength (0.202 15 Å) together with a collimated beam of 40×40 μm^2.

Diffraction images were captured with a Bruker 6500 charge coupled device (CCD) detector, and the diffraction images processed using the ESRF FIT2D program[36] to provide interplanar distances for structural calculations. The experimental data were then refined with Rietveld analysis using the FULLPROF program.[37]

III. RESULTS

A. Pa-I structure

The initial structure of the protactinium used in the high-pressure studies was the body-centered-tetragonal form

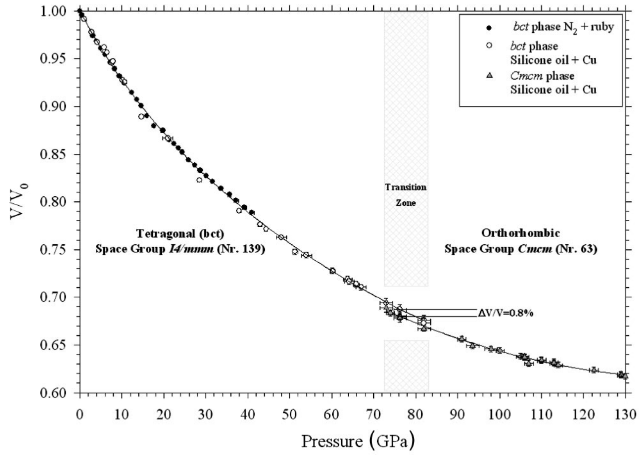

FIG. 1. Relative volumes for protactinium. The 0.8% change at 77 GPa for the Pa-I to Pa-II transition is attributed to an increase in 5*f*-electron itinerancy.

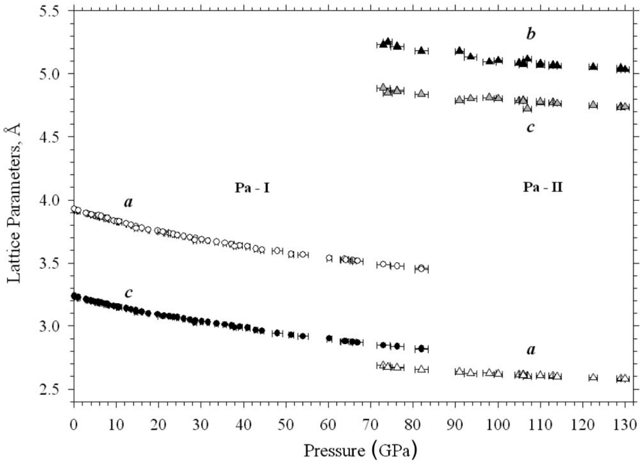

FIG. 2. Variation of the lattice parameters with pressure for the Pa-I and Pa-II structures. The transition zone is assigned as being 72–82 GPa.

(space group $I4/mmm$, number 139) reported for the metal.[32] It is assigned here as the Pa-I structure. This form is the stable, STP phase of the metal. A potential high-temperature form ($Fm3m$) has been reported[29] but was not observed in this work. The bct structure is unique in comparison to other *f*-element metals at atmospheric pressure, but is adopted by selected lanthanide and actinide metals under high pressure,[1–3] presumably following the partial acquisition of *f*-electron character in their bonding.

We found this Pa-I form to be stable up to 77(5) GPa, where it converts to an orthorhombic structure. This latter structure is assigned here as Pa-II. The pressure behavior of protactinium is shown in Fig. 1, where the relative volumes (V/V_0, where V and V_0 are the atomic volumes under pressure and at atmospheric pressure, respectively) are plotted against pressure. Thus under pressure the metal undergoes a single structural transition (Pa-I to Pa-II), which is accompanied by a small (0.8%) volume change (''collapse'').

The relative volume of the Pa-I phase decreased smoothly from atmospheric pressure down to a volume ratio of ~0.7, before transforming to the Pa-II phase. The bulk modulus for protactinium is derived from the compression behavior of this Pa-I phase. The compression curve for Pa-II, which is less compressible than the Pa-I phase, then also proceeded smoothly down to a relative volume of ~0.62 at 130 GPa.

The points in Fig. 1 were established from multiple experimental studies, which employed different experimental variables and the DAC designs. Data obtained under these different conditions are combined in the figure, where it can be seen they are in excellent agreement with one another.

We are in agreement with the findings from the earlier experimental study by Benedict *et al.*[25] that the bct structure of protactinium is the stable structure up to at least 53 GPa, the highest pressure reached in that work. We determined further that the Pa-I form is stable up to ~77 GPa, which accounts for the fact that the Pa-II phase was not observed in the earlier study. We also noted an important difference in the compressibility (i.e., reflection of the metal's bulk modulus) of protactinium. The difference in bulk modulus will be addressed in a subsequent section, but we observed a greater compressibility (i.e., a smaller bulk modulus) for it than had been reported.[25]

The variation and progression with pressure of each of the lattice parameters for the Pa-I phase are shown in Fig. 2. There is a smooth decrease with pressure in the ''*a*'' and ''*c*'' parameters of the tetragonal Pa-I structure up to the transformation point, where the ''*c*'' parameter then becomes the ''*a*'' parameter of Pa-II, and the ''*a*'' parameter converts to the ''*b*'' and ''*c*'' parameters of the orthorhombic structure. These changes result in the formation of the lower symmetry Pa-II phase.

B. Pa-II structure

At ~77 GPa, experimental evidence for the Pa-II structure of protactinium was acquired (see Fig. 2), and it was determined to be isostructural with that for α-U; specifically, an orthorhombic (space group *Cmcm*, number 63) structure. This Pa-II structure remained the stable structure to 130 GPa. At this pressure, the relative volume was 0.62 (the atomic volume had changed from the initial value of 24.94 Å^3 down to 15.40 Å^3).

Theoretical calculations[26] have predicted a transition from the bct phase to the orthorhombic phase at an atomic volume of slightly greater than 20 Å^3 and at a pressure of 25 GPa. From our experimental data, we place the start of the transformation to the Pa-II phase at an atomic volume of ~17.2 Å^3 and assign the transition zone from 17.2 Å^3 at 72 GPa to 16.4 Å^3 at 82 GPa.

Accompanying the structural transition was a small but definitive volume ''collapse.'' Such a volume change is normally accepted as reflecting a change in the metals' bonding,[1–3] but the magnitude of the change for the Pa-I to Pa-II transformation was smaller than expected. This collapse is much smaller than either of the two collapses (2% and 7%) found with americium metal.[22–24] This ramification of protactinium's behavior will be addressed further in a subsequent section.

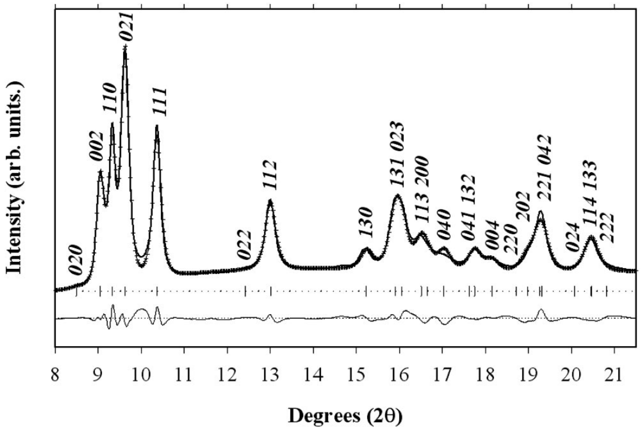

FIG. 3. Rietveld fit of the orthorhombic (space group *Cmcm*) Pa-II phase at 129 GPa ($\lambda = 0.3738$ Å), where the Bragg *R* value $= 2\%$. (Experimental and calculated profiles, reflection tick marks, difference profile, and Miller indices are shown.)

The rather large transition zone shown for the Pa-I to Pa-II conversion, covering ~10 GPa, may result from a more gradual change in the relative energy of the structures, reflected in part by the magnitude of the change. It may also reflect a kinetically hindered transition, as it involves the formation of the more complex, lower symmetry, Pa-II structure. These factors and together with the data led us to assign a ±5-GPa error bar for the transition pressure.

Examination of the compressibility curves for the Pa-I and Pa-II structures (see Fig. 1) indicates a smaller compressibility for the orthorhombic structure, expected if additional bonding had been acquired. The compressibility curve for the Pa-II phase appears similar to that observed for isostructural uranium, which is stable from atmospheric pressure to at least 100 GPa.[1,2,38–40] Extrapolation of the Pa-II compressibility curve (Fig. 1) back to atmospheric pressure generates a hypothetical volume for the Pa-II form, which is smaller than the atmospheric pressure volume of the Pa-I phase but larger than the atomic volume of uranium. That is, bonding changes forced by high pressure (if retained at atmospheric pressure), would provide only a slightly depressed atomic volume.

C. Rietveld analyses of data

The Rietveld analyses of the angle dispersive synchrotron x-ray data for protactinium metal under pressure were made using the FULLPROF program.[37] Although it is frequently difficult to perform Rietveld analyses on such very small samples, due to several factors (poor statistics, low intensities, incomplete "diffraction rings," etc.), the grain sizes and crystallinity of our materials were of sufficient quality to produce perfect diffraction rings and therefore reproducible intensities. Excellent Rietveld fits for the experimental and calculated values were obtained for the new Pa-II structure of protactinium metal, and one set of data for 129 GPa is shown in Fig. 3. The agreement in the Rietveld fit (Bragg *R* value for the refinement is 2%) provides a high degree of confidence in the structural assignment. Lattice parameters determined for the Pa-II structure at 110 GPa are: $a = 2.609$ Å, $b = 5.077$ Å, and $c = 4.771$ Å, where the free atomic position "y" is 0.118. At 129 GPa, the values are: $a = 2.584$ Å, $b = 5.046$ Å, and $c = 4.740$ Å, and $y = 0.119$. These represent the first parameters for the high-pressure, Pa-II phase of protactinium.

TABLE I. Bulk moduli for the Th through Cf metals.

Element	Range of moduli reported, GPa[a]	References
Th[b]	50–72	1, 2
Pa[c]	100–157	1, 2, 25, 26
Pa[c]	118	this work
U[c]	100–152	1, 2, 38, 39, 42, 43
U[c]	104	40
Np[c]	74–110	1, 2
Pu[c]	40–55	1, 2
Am-Cf[d]	38–50	1, 2, 22–24, 54

[a] Includes experimental and calculated values.
[b] No 5*f* electrons in bonding.
[c] Itinerant 5*f* electrons.
[d] Localized 5*f* electrons.

IV. DISCUSSION

A. Volume and compressibility

From the compression behavior of Pa-I, values for the isothermal bulk modulus and its pressure derivative for the metal were obtained by fitting the experimental data to the Birch-Murnaghan[41] equation of state. The values obtained for the Pa-I compression behavior in this work were 118 (1) GPa for the modulus (B_0), and 3.4 (0.2) for the derivative (B_0').

In the earlier study of protactinium up to 53 GPa,[25] the bulk modulus and first derivative were reported as being 157 (5) GPa and 1.5 (0.5), respectively. This modulus is significantly larger than found here. In contrast, theoretical calculations have suggested a modulus of about 100 GPa.[26–28]

The moduli and first derivatives for selected actinide and lanthanide metals[1,2] are shown in Table I. Values for the modulus of thorium metal range from 50 to 72 GPa (B_0' from 2.5 to 6.6), from 100 to 152 GPa for uranium metal (B_0' from 2.8 to 6.2), and from 40 to 55 GPa for plutonium (B_0' from 10 to 16). The elastic and structural properties of uranium have also been calculated by total-energy theory, where bulk moduli were given as 133 GPa from theory,[42] and 130 (Ref. 42) and 115 GPa (Ref. 43) from considerations of elastic constants. Recent diffraction work on uranium metal[40] has re-evaluated its pressure behavior and modulus, using precise experimental data acquired in synchrotron experiments. A value of 104 (2) GPa for the modulus and 6.2 (2) for the pressure derivative were found.[40] In comparison, moduli for the americium through californium metals, and many of the lanthanides with localized 4*f* electrons, are below 40 GPa.[1,2]

It is recognized that some correlation exists between values for the bulk modulus and its pressure derivative; the exact relationship being defined in the Birch-Murnaghan equation.[41] The value of 1.5 (0.5) (Ref. 25) reported previously for protactinium's pressure derivative is anomalously low, whereas our value of 3.4 (0.2) is in better accord with average values of 4–6 found for such metals.[1,2] It appears that with the thorium through plutonium metals, high bulk moduli are accompanied by low-pressure derivatives, and vice versa.[1] This was observed in comparing our protactinium values with those previously reported.[25]

We believe that our modulus for protactinium metal is a more realistic value. We shall not dwell on the specific aspects for the differences in values reported previously for the modulus or its derivative, but note that nonhydrostatic experimental conditions (i.e., the solidification of the transmitting media, especially in the critical, lower pressure segments of the compression data) can lead to significant errors. In addition, angle dispersive x-ray data using higher intensities available at synchrotrons, together with a liquefied gas, pressure transmitting medium (which was used here) can provide superior data with less scatter, smaller error bars and therefore more reliable moduli. We believe the differences between our experimental data and that reported earlier data[25] arise mainly from the improved precision and accuracy of our data, the much larger number of experimental data points acquired (especially in the early compression stages) and the more accurate pressure measurements. These improvements allow a very precise compression curve to be generated, which in turn yields more precise values.

A comparison can be made between the volume behaviors of protactinium, uranium, and americium with pressure, which permits one to arrive at some conclusions regarding the materials having the same or closely related structure. The relative volume of the Am-IV phase at 100 GPa is 0.46, whereas with the Pa-II phase at 100 GPa, the relative volume reaches 0.64. The relative volume of α-U at 100 GPa is $\sim$0.7,[40] but the particular value depends on which bulk modulus and pressure derivative is considered. This reflects that overall protactinium metal is less compressed than americium metal at 100 GPa. This is due largely to the compression behavior of the Am-I and Am-II forms (which have localized $5f$ electrons) before formation of the Am-IV phase. Overall, the Pa-I phase is less compressible, as it initially has a ''stiffer'' lattice from $5f$-electron itinerancy. A significant degree of compression in americium is encountered with its ''softer'' Am-I and Am-II phases. The compression behavior[1,2,38–40,42] and atomic volume of uranium suggest a more dominant level of $5f$-electron involvement in its bonding and a rigid structure. The α-U structure is accepted as providing a fingerprint for *f*-electron involvement in bonding.

A general correlation between bulk moduli (compressibility), atomic volumes, and cohesive energies of the metals with bonding would seem appropriate. However, a correlation with cohesive energies for the *f*-electron elements is complicated by differences that exist in the electronic energies of the solids and free atoms.[20] In general, correlations with these properties would reflect the degree of interatomic interaction (bonding) present. It should be more difficult to compress a dense, rigid structure that would arise from increased bonding. The compression behavior of these metals is determined by both their bulk modulus and pressure derivative, so a comparison of moduli alone may be limiting in reflecting the compression curve and the degree of bonding present. Atomic volumes (see Sec. IV D) and interatomic distances may be better indicators of the latter. The occurrence of phase transitions during compression is a complicating factor in the compression behavior.

The more dominant level of $5f$-electron participation in uranium's electronic structure (high density of f states at the Fermi level[44]) is likely to be responsible for the stability of its structure and the absence of phase transitions up to 100 GPa. Its compression behavior is much ''flatter'' than for the softer, more compressible trivalent metals with localized f electrons.[45] Although it is not appropriate to calculate a modulus for the Pa-II phase from our data, the nature of its compression curve (see Fig. 1) appears similar to that of α-U (Refs. 1, 2, 40, 45) and the Am-IV orthorhombic phase.[22–24,45] This is in accord with the fact that these three phases have either identical or closely related structures. Our experimental bulk modulus of 118 GPa for the Pa-I phase is reasonable with that expected for a metal having some $5f$-electron itinerancy, which would produce a more rigid lattice than found for a metal with only localized $5f$ electrons. That is, the modulus of protactinium is significantly higher than would be expected for metals having only ''*s,p,d*'' bonding electrons, and which display more symmetrical structures (fcc for thorium, dhcp for Am-Cf). These metals have moduli <72 GPa (see Table I) and may display similar physical properties.

B. Nature of the Pa-I and Pa-II structures

In the Pa-I bct structure at atmospheric pressure, the c/a ratio is 0.825, optimum from an energy standpoint and relatively close to a ratio of 0.816 ($\sqrt{2/3}$). Zachariasen[32] had suggested this Pa-I structure can be ''derived'' from a bcc structure by compressing one of the three fourfold axes, so that the axial ratio decrease from 1 to 0.825. In the ''ideal'' case when the ratio is 0.816, each protactinium metal atom would have ten equidistant neighbors. The Pa-I structure at atmospheric pressure is therefore very ''slightly distorted,'' in that there are eight neighbors at 3.213 Å and two at 3.238 Å (average$=$3.218 Å). The next four near neighbors are at a greater distance (3.925 Å). This slight ''distortion'' produces a more favorable energy state for the metal.

The variation of the a/a_0 and c/c_0 axial ratios for the Pa-I with pressure is shown in Fig. 4, where there is a ''restricted'' movement of the atoms along the ''a'' axis as compared to the ''c'' axis (the c/c_0 ratio decreases more rapidly than the a/a_0 ratio). The change in the c/a ratios for Pa-I with pressure is shown in Fig. 5, which shows a diminishing c/a ratio, especially in the 45–65-GPa region. This c/a ratio reaches a value of $\sim$0.816 near 65 GPa, and is retained when entering the Pa-I to Pa-II transition zone. Thus pressure eventually forces changes in protactinium's atomic positions and leads to an arrangement of each atom having ten equidistant neighbors in achieving a lower energy state.

Eventually, pressure forces parameters of the Pa-I structure to convert to those of the Pa-II structure. The Pa-II

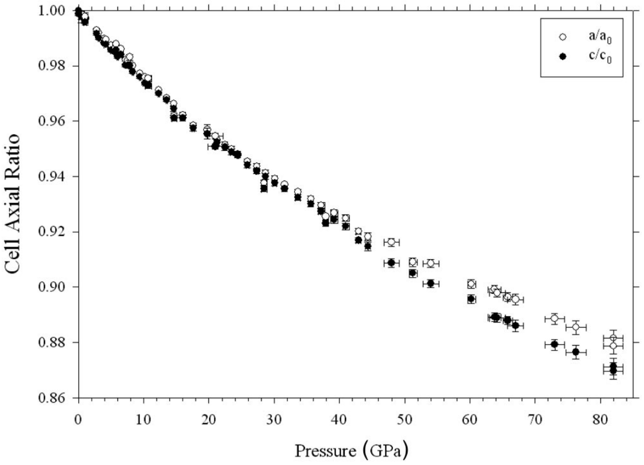

FIG. 4. Variation of the a/a_0 and c/c_0 ratios with pressure for the Pa-I structure.

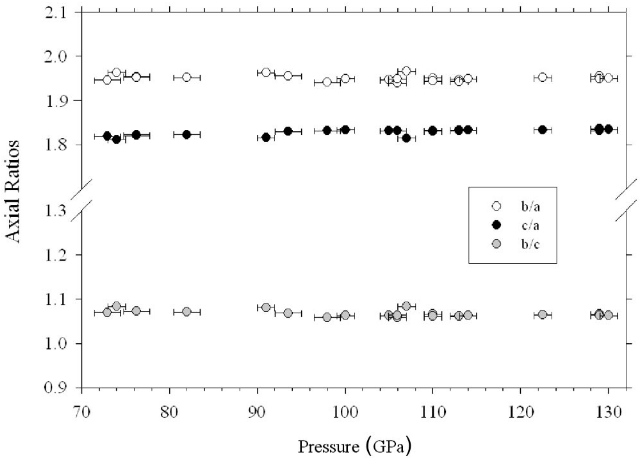

FIG. 6. The effect of pressure on the b/a, c/a, and b/c ratios of the Pa-II structure.

orthorhombic structure has four atoms per unit cell [at equivalent positions (0, y, $\frac{1}{4}$)]. The 12 atoms are at the vertices of a polyhedron, which represents a distorted type of hexagonal close packed structure.

Variations in the three lattice parameters of the Pa-II structure with pressure are shown in Fig. 2. The three parameters of Pa-II decrease more slowly with pressure than those of the Pa-I form, which reflects the lower compressibility of the Pa-II phase. The decrease in individual parameters of the Pa-II phase with pressure appears very similar, and gives rise to essentially parallel curves for the three parameters, when they are plotted as a function of pressure. The a/a_0, b/b_0, and c/c_0 axial ratios (not shown) as a function of pressure all show a comparable decrease with pressure. The b/a, c/a, and b/c ratios for the Pa-II form (see Fig. 6) are also quite similar to one another, showing only a small or negligible decrease with pressure.

In the case of Pa-II, the near neighbors at 110 GPa are: two at 2.609 Å; two at 2.269 Å; four at 2.854 Å; and four at 3.483 Å (lattice parameters for Pa-II are given in Sec. III C). It has a c/a ratio of 1.829 at 110 GPa. For comparison, the isostructural α-U form at atmospheric pressure has the parameters: $a_0 = 2.8537$ Å, $b_0 = 5.8695$ Å, and $c_0 = 4.9548$ Å.[46] These give a c/a ratio of 1.736. The nearest neighbors in uranium at atmospheric pressure are: two at 2.753 Å, two at 2.854 Å, four at 3.263 Å, and four at 3.343 Å.

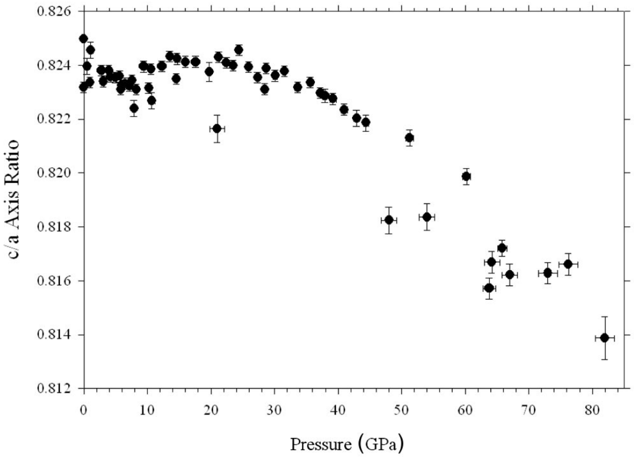

FIG. 5. Variation of the c/a ratio with pressure for the Pa-I structure. At a ratio of 0.816, each metal atom has ten equidistant neighbors, as compared with two distances at atmospheric pressure (8 at 3.213 Å and 2 at 3.238 Å).

Of interest here is the Pa-II form's behavior relative to that of the isostructural α-U phase, regarding changes in the c/a, b/a, and b/c ratios and the positional parameter "y" with pressure. The c/a ratio for the Pa-II structure (see Fig. 6) with pressure is nearly constant (~1.82, with a slightly detectable rise with pressure in the 77–130 GPa range). The b/a and the b/c ratios for Pa-II are also essentially constant with pressure. The c/a ratio for α-U between atmospheric pressure and ~100 GPa was reported to increase from 1.75 to 1.82 (1.82 at a relative volume of 0.70, which occurs at ~100 GPa).[38] Newer work on uranium from synchrotron studies[40] shows in greater detail a similar rise with pressure for the c/a ratio, a nearly constant b/a ratio and a slightly decreasing b/c ratio with pressure. The b/a ratio for uranium is ~6% higher and the b/c ratio about 4% higher than those for the Pa-II phase at 100 GPa.

Only a small difference is observed between the α-U and the Pa-II structures in their positional y coordinate. In α-U at atmospheric pressure, y is 0.1025,[46] and it appears to vary less than a few percent up to 100 GPa.[38,40] The y parameter for the Pa-II phase was determined as 0.118(1) at 110 GPa, and it did not vary significantly with pressure (at 129 GPa, it was 0.119), in accord with the behavior of uranium. A slight difference in actual value is observed between Pa-II and α-U (0.118 versus 0.1025 at 100 GPa). The axial ratios and the y value of uranium are also addressed from calculational considerations of uranium, which are compared to experimental data.[40,42]

The behavior and variation of these different values likely contribute to the stability of this particular structure at high pressure. Finally, the compressibility of the Pa-II phase and α-U phase is similar,[45] in line with the fact they are isostruc-

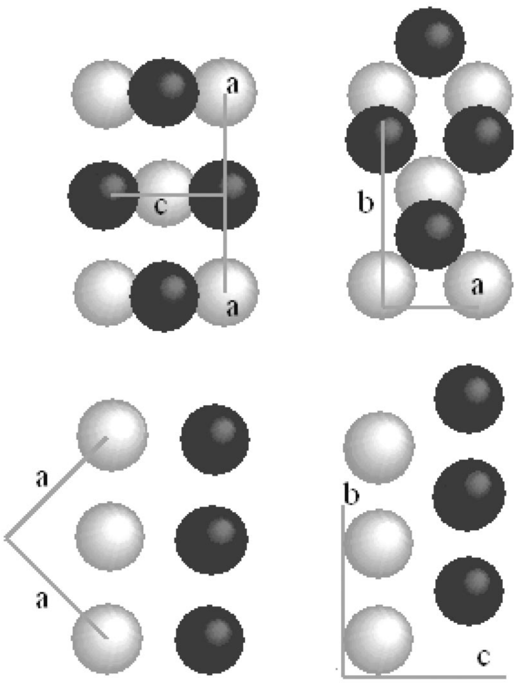

FIG. 7. Structural sketches of the Pa-I and Pa-II (high-pressure) phases of protactinium (left side is for Pa-I; right side is for Pa-II).

tural phases. In contrast, the Pa-I phase is less ‘‘rigid’’ and slightly more compressible than the Pa-II phase.

C. Structure and bonding in protactinium

The two protactinium structures (Pa-I and Pa-II) encountered in this study are depicted in Fig. 7, which can aid in perceiving the transformation process. The Pa-I bct structure can be described as stacking of hexagonal-close-packed layers, with the second lying on the first, so that each atom touches two rather than three in the first layer. With distortion, which can occur by the sliding/buckling of planes in the lattice under pressure, the lower-symmetry, orthorhombic Pa-II form is obtained. Additional shifting of planes with respect to one another could generate the proposed hexagonal structure, predicted to occur at ultrahigh pressures.[26] In the same vein, the Am-IV structure (*Pnma*) is derived readily from the α-U structure by a small buckling of certain planes.[23] Thus there is considerable commonality for the Pa-II, α-U, and Am-IV structures. Both the Pa-I to Pa-II change and the transition to Am-III and Am-IV phases in americium[22–24] are attributed to alternations in the metallic bonding that occur with pressure. The involvement of the $5f$ electrons in the bonding (which already exists at atmospheric pressure in protactinium), gives rise to the less-symmetrical structures observed.

Using a calculational approach, Söderlind and Eriksson[26] predicted a series of phase transitions for protactinium under pressure, which are shown in Fig. 8. The approach of these authors was to employ thermodynamic Gibbs free energies for evaluating different potential structures of protactinium at absolute zero, to predict which structure would be stable at different atomic volumes. It was suggested that *s,p,d* bonding without $5f$ character would prevail at these very small atomic volumes,[26] and thus produce a hexagonal structure, as these orbitals in protactinium would offer a lower energy state. Thus the nature of the bonding is expected to change significantly with volume, as electrostatic interactions and relative energy levels are altered, with the net effect determining which structure(s) are the most stable at a given pressure.

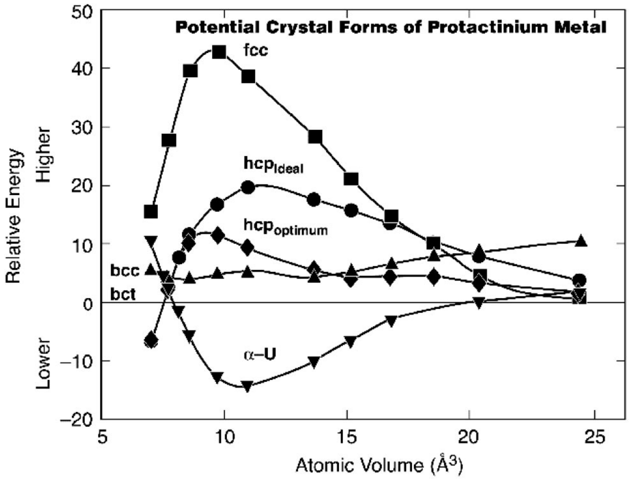

FIG. 8. Calculated stability of different protactinium structures as a function of atomic volume. (Adapted from Ref. 26). Experimentally, the Pa-I to Pa-II transformation occurred 77 GPa (rather than the proposed 25 GPa), and at a volume of 17 Å^3.

The energy of Pa-I (bct) in Fig. 8 is represented by the straight line at zero relative energy, and structures located below this line (negative values) would be more stable. This plot suggests that the Pa-I structure is the most stable under pressure until an atomic volume of ~20 Å reached, after which the α-U structure would have a lower energy. The plot suggests further that additional pressure would generate the hexagonal form, but with a potential for a re-appearance of a bct structure as an intermediate phase. The volume at which the hexagonal phase is predicted to occur is much smaller than the 15.4 Å^3 reached by us at 130 GPa, and this is consistent with the fact that we did not observe another transition—the Pa-II structure remained the stable phase to the highest pressure studied. We have made an extrapolation to estimate the pressures needed to reach a volume of ~8 Å^3 (see Fig. 8) and have concluded that at least several hundred GPa would be needed. Such pressures are difficult to reach, and not readily attainable with present day DAC technology.

With reference to Fig. 8, overall we observed the appearance of the Pa-II structure at a higher pressure (77 versus 25 GPa) and at smaller atomic volume (17 Å^3) than predicted, suggesting the energy difference between the Pa-I and Pa-II structures is larger, or changed more slowly with pressure, than calculated. The considerable difference noted between the transition pressures determined by experiment and calculations may have arisen from the modulus used for the Pa-I phase's compressibility.

Another important point shown in Fig. 8 is that two hexagonal structures with different c/a axial ratios can have different stabilities. One structure has the ‘‘ideal’’ c/a ratio

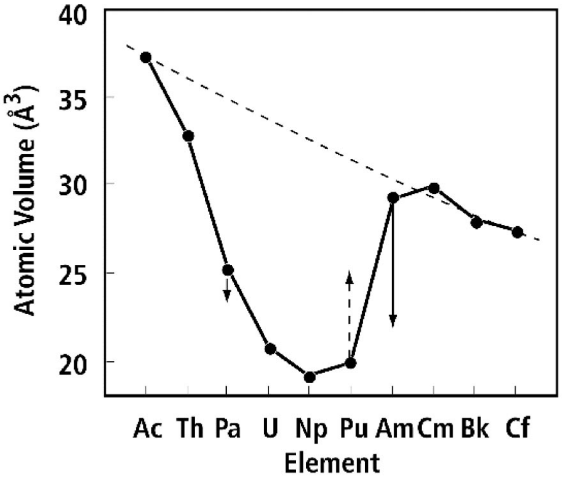

FIG. 9. Atomic volumes at one atmosphere. [Dotted line represents volumes when the $5f$ electrons are not itinerant. Arrows represent ‘‘altered’’ volumes for bonding changes due to pressure (Pa and Am) and heating (Pu).]

(often found in hexagonal structures), while the ‘‘optimum’’ form (from the energy standpoint) is generated by distortion. This demonstrates how distortion, brought about by pressure, can lower a system's energy, and alter facets of the crystal structure. A form of ‘‘distortion’’ was observed in the changes of the Pa-I structure under pressures (Fig. 5), where the c/a ratio for the stable form changed from 0.825 to 0.816.

D. Atomic volumes and bonding

The change in electronic behavior and bonding at atmospheric pressure across the actinide series results in very dramatic anomalies. One of these is seen in a plot of the atomic volumes of the actinides (see Fig. 9), where a type of ‘‘well’’ is formed by the smaller volumes exhibited by the Pa-Pu metals at one atmosphere. The element following plutonium, americium, displays a ~50% larger atomic volume than plutonium, as a result of the change to fully localized $5f$ electrons. Thus protactinium is the first actinide to have itinerant $5f$ electrons, and americium the first with fully localized $5f$ electrons. For these reasons there is a special interest in the high-pressure behaviors of both americium and protactinium.

We have incorporated certain aspects of the volumes associated with changes for americium and protactinium under pressure. The arrows in Fig. 9 associated with protactinium, plutonium, and americium represent the effect of adding (americium and protactinium) or removing (plutonium) $5f$-electron participation in the bonding. The arrow at plutonium points to the volume of the gamma phase [parameters corrected to 25 °C (Ref. 47)], acquired by heating its alpha form. The pseudovolumes for americium and protactinium in the figure were obtained by simple extrapolations of the pressure-volume curves for these high-pressure phases back to one atmosphere, if the additional contribution to bonding under pressure would be retained after the pressure was released. The different volumes projected by the arrows (Fig. 9) then represent values expected for bonding changes from heating (plutonium) or applying pressure (americium and protactinium).

The degree and nature of $4f/5f$ delocalization processes has not been quantified for the actinides and the topic for the extensively studied (theoretically and experimentally) case of plutonium is of considerable current debate.[48–51] It has been suggested that the volume change in plutonium with temperature reflects different degrees of localization and bonding of its $5f$-electron states[52] and that the localization of its $5f$ states is crucial for describing the important δ-plutonium phase. Söderlind[26] has discussed some aspects of the $5f$-electron count in the different protactinium structures. We make no attempt to quantify or describe the processes occurring in protactinium under pressure, but clearly they involve some aspect of $5f$ electron change with pressure. It is also clear that in the actinide series, phase stability is driven by the role of $5f$ electrons.

It is also relevant to point out that thorium metal (cubic, [Rn core] d^2s^2 configuration) under high pressure has been reported to acquire $5f$ electrons in its bonding, as its unfilled $5f$ levels become occupied as their relative energy levels change with pressure. With such an acquisition, thorium at very high pressures (~100 GPa) adopts a bct structure.[53] Similarly, cerium, neodymium, and praseodymium also acquire a bct structure under high pressures.[4–6] These findings are consistent with the concept that acquisition of $4f$- or $5f$-electron character into the metallic bonding, or the filling of empty $5f$-electron levels in the case of thorium (i.e., arising from promotion of thorium's bonding $6d$ electrons to the $5f$ band[53]), can lead to these lower symmetry structures. Theoretical discussions of the behavior of praseodymium[8] and thorium[11] under pressure have been given.

V. CONCLUDING REMARKS

The objective of our experimental study of protactinium was to determine if pressure would alter the $5f$-electron contribution to the metal's bonding and bring about a structural transformation. Obtaining high quality synchrotron diffraction data up to 130 GPa permitted us to achieve this goal and we observed an important structural transition at 77(5) GPa, which had not been observed previously. The Pa-I to the Pa-II transformation was found at a considerably higher pressure than the calculated value of 25 GPa, and it occurred at smaller atomic volume (17.4 versus ~20 Å^3). These differences imply a greater resistance to transformation than predicted, possibility due to kinetics and/or the influence of temperature, as the calculations have been made for absolute zero.

From our experiments, we established a lower bulk modulus for protactinium of 118(1) GPa. This value will remove deviations encountered in actinide systematics encountered with previously measured (157 GPa) and calculated values (~100 GPa).

We propose that pressure on protactinium forced a small, increase in the $5f$-electron content of its band structure, acquired in conjunction with transformation to the Pa-II structure. On the basis of theory,[26] the Pa-I to Pa-II transition represents a transition of *spd* states to $5f$ states. Indeed,

''$sp \rightarrow d$'' promotions alone are not accompanied by abrupt volume changes, or the generation of lower symmetry structures, as found for the Pa-II phase.

The surprisingly small (only 0.8%) accompanying ''volume collapse'' at the Pa-I to Pa-II transformation suggests a small additional influx of $5f$-electron character into protactinium's bonding under pressure. An extrapolation of the Pa-II compression curve back to atmospheric pressure indicates a larger pseudoatomic volume would exist for it than for alpha uranium, signifying only a small acquisition of additional $5f$-electron content in the Pa-II form under pressure. In contrast, the incorporation of $5f$-electron character into americium's bonding occurs at lower pressures and produces an overall larger (9%) volume change, and represents a change from fully localized to itinerant $5f$ states.

The compression behavior of the Pa-II phase between 77 and 130 GPa appears quite similar to that of both α-U (*Cmcm*) and the Am-IV (*Pnma*) phases under pressure. As with the Am-IV phase, the Pa-II structure reverts back to its initial, atmospheric pressure structure (Pa-I) after pressure is released (reversible phase transition). This confirms that protactinium had not been converted to another material (i.e., oxide or other compound), and that the additional bonding acquired under pressure was lost when its interatomic distances returned to those in the initial Pa-I structure.

The results in conjunction with structural considerations permit a simple mechanistic picture for the conversion of Pa-I to Pa-II; the change represents mainly the shifting/buckling of lattice planes due to pressure. The pressure behavior of protactinium is of particular interest, as it is the first of the four actinides having some degree of $5f$-electron itinerancy at atmospheric pressure. Our experimental pressure limit of 130 GPa prevented us from reaching even smaller atomic volumes, where new bonding facets are expected to produce more symmetrical structures.

We believe our experimental results will allow an improved understanding not only of the bonding and electronic nature of protactinium, but also for generating important systematics concerning the actinides. These interesting experimental data should also allow a platform from which to evaluate and fine tune theoretical predictions and/or understanding of these metals.

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[1] U. Benedict, in *Handbook on the Physics and Chemistry of the Actinides*, edited by A. J. Freeman and G. H. Lander (Elsevier Science, Amsterdam, 1987), Vol. 5, Chap. 3, pp. 227–269.

[2] U. Benedict and W. B. Holzapfel, in *Handbook on the Physics and Chemistry of the Rare Earths*, edited by K. A. Gschneidner, Jr., L. Eyring, G. H. Lander, and G. R. Choppin (Elsevier Science, Amsterdam, 1993), Vol. 17, Chap. 113, pp. 245–300, and references therein.

[3] R. G. Haire, in *Rare Earths, Resources, Science Technology and Applications*, edited by R. Bautista and N. Jackson (TMS, PA, 1991), pp. 449–462, and references therein.

[4] M. I. McMahon and R. J. Nelmes, Phys. Rev. Lett. **78**, 3884 (1997).

[5] G. N. Chesnut and Y. K. Vohra, Phys. Rev. B **61**, 3768 (2000).

[6] G. N. Chesnut and Y. K. Vohra, Phys. Rev. B **62**, 2965 (2000).

[7] Per Söderlind, R. Ahuja, O. Eriksson, B. Johansson, and J. M. Wills, Phys. Rev. B **61**, 8119 (2000).

[8] Per Söderlind, Phys. Rev. B **65**, 115105 (2002).

[9] M. Pénicaud, J. Phys.: Condens. Matter **12**, 5819 (2000).

[10] M. Pénicaud, J. Phys.: Condens. Matter **14**, 3575 (2002).

[11] Per Söderlind, Adv. Phys. **47**, 959 (1998).

[12] H. Blank, J. Alloys Compd. **343**, 108 (2002).

[13] J. L. Smith, J. C. Spirlet, and W. Müller, Science **205**, 188 (1979).

[14] M. H. Bradbury, J. Less-Common Met. **78**, 207 (1981).

[15] J. W. Ward, P. D. Kleinschmidt, R. G. Haire, and D. Brown, in *Vapor Pressure and Thermodynamics of Actinide Metals*, ACS Symposium Series Vol. 131, edited by J. Comstock (American Chemical Society, Washington, DC, 1980), pp. 199–220.

[16] J. W. Ward, P. D. Kleinschmidt, and D. E. Peterson, in *Handbook on the Physics and Chemistry of the Actinides* (Ref. 1) (Elsevier Science, Amsterdam, 1986), Vol. 4, pp. 309–412.

[17] J. J. Katz, L. R. Morss, and G. T. Seaborg, in *The Chemistry of the Actinide Elements*, 2nd ed., edited by J. J. Katz, L. R. Morss, and G. T. Seaborg (Chapman and Hall, New York, 1986), pp. 1121–1195.

[18] A. Michael and J. L. Smith, LANL, Report No. LA-UR-00-4100, 2000 (unpublished), pp. 90–127.

[19] J. M. Fournier and L. Manes, in *Structure and Bonding*, edited by L. Manes (Springer-Verlag, Berlin, 1985), Vols. 59/60, pp. 1–57.

[20] M. S. S. Brooks, B. Johansson, and H. L. Skriver, in *Handbook on the Physics and Chemistry of the Actinides* (Ref. 1), Vol. 1, Chap. 3, pp. 227–269.

[21] B. Johansson, Phys. World **13**, 26 (2000).

[22] S. Heathman, R. G. Haire, T. Le Bihan, A. Lindbaum, K. Litfin, Y. Méresse, and H. Libotte, Phys. Rev. Lett. **85**, 2961 (2000).

[23] A. Lindbaum, S. Heathman, K. Litfin, Y. Méresse, R. G. Haire, T. Le Bihan, and H. Libotte, Phys. Rev. B **63**, 214101 (2001).

[24] R. G. Haire, S. Heathman, T. Le Bihan, and A. Lindbaum, NEA Publication, ISBN 92-64-18485-6 (2002), p. 147.

[25] U. Benedict, J. C. Spirlet, C. Dufour, I. Birkel, W. B. Holzapfel, and J. R. Peterson, J. Magn. Magn. Mater. **29**, 287 (1982).

[26] P. Söderlind and O. Eriksson, Phys. Rev. B **56**, 10 719 (1997).

[27] H. L. Skriver, O. K. Andersen, and B. Johansson, Phys. Rev. Lett. **41**, 42 (1978).

[28] B. Johansson and H. L. Skriver, J. Magn. Magn. Mater. **29**, 217 (1982).

[29] H. K. Kirby, in *The Chemistry of the Actinide Elements*, edited by J. J. Katz, G. T. Seaborg, and L. R. Morss (Chapman and Hall, New York, 1986), Vol. I, pp. 126–128, and references therein.

[30] J. Bohet, European Commission Report No. EUR-5882, 1977; and J. Less-Common Met. **57**, 185 (1978).

[31] R. D. Baybarz, J. Bohet, K. Buijs, L. Colson, W. Müller, J. Reul, J. C. Spirlet, and T. Toussaint, in *Transplutonium Elements*, edited by W. Müller and R. Lindner (North-Holland, Amsderdam, 1976), pp. 61–68.

[32] W. H. Zachariasen, Acta Crystallogr. **5**, 19 (1952).

[33] W. H. Zachariasen, Acta Crystallogr. **12**, 698 (1959).

[34] H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).

[35] W. J. Carter, S. P. Marsh, J. N. Fritz, and R. G. McQueen, in *NBS Special Publication 326*, edited by E. C. Lloyd (U.S. Gov. Printing Office, Washington, DC, 1971), p. 147.

[36] A. P. Hammersley, FIT2D, V9.129, Reference Manual V3.1, European Synchrotron Radiation Facility, 1998.

[37] J. Rodriguez-Carvajal, Physica B **192**, 55 (1993).

[38] J. Akella, S. Weir, J. M. Wills, and P. Söderlind, J. Phys.: Condens. Matter **9**, L549 (1997).

[39] J. Akella, G. S. Smith, R. Grover, Y. Wu, and S. Martin, High Press. Res. **2**, 295 (1990).

[40] T. Le Bihan, S. Heathman, M. Idiri, G. H. Lander, J. Wills, A. Lawson, and A. Lindbaum, Phys. Rev. B (to be published).

[41] F. Birch, Phys. Rev. **71**, 809 (1947).

[42] P. Söderlind, Phys. Rev. B **66**, 085113 (2002).

[43] C.-S. Yoo, H. Cynn, and P. Söderlind, Phys. Rev. B **45**, 13 879 (1998).

[44] M. V. Nevitt and M. B. Brodsky, in *The Chemistry of the Actinide Elements* (Ref. 17), pp. 1388–1416.

[45] A. Lindbaum, S. Heathman, T. Le Bihan, R. G. Haire, M. Idiri, and G. H. Lander, J. Phys. Condens. Matter (to be published).

[46] C. S. Barrett, M. H. Müeller, and R. L. Hitterman, Phys. Rev. **129**, 625 (1963).

[47] W. H. Zachariasen and F. H. Ellinger, Acta Crystallogr. **8**, 431 (1955).

[48] S. Y. Sarasov, G. Kotliar, and E. Adams, Nature (London) **410**, 793 (2001).

[49] J. Boucher, B. Siberchicot, F. Jollet, and A. Pasturel, J. Phys.: Condens. Matter **12**, 1723 (2000).

[50] Yi Wang and Y. Sun, J. Phys.: Condens. Matter **12**, L311 (2000).

[51] P. Söderlind, Europhys. Lett. **55**, 525 (2001).

[52] B. R. Cooper, LANL, LA-UR-00-4100, 2000 (unpublished), p. 154.

[53] Y. K. Vohra and J. Akella, Phys. Rev. Lett. **67**, 3563 (1991).

[54] T. Le Bihan, R. G. Haire, S. Heathman, M. Idiri, and A. Lindbaum, J. Nucl. Sci. Technol., Suppl. 3, 45 (2002).