Pressure-induced phase transitions in Pa metal from first-principles theory

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Protactinium metal is shown to undergo a phase transition to the α-U orthorhombic structure below 1 Mbar pressure. At higher pressures, the bct phase reenters in the phase diagram and at the highest pressures, an ideal hcp structure becomes stable. Hence, Pa undergoes a sequence of transitions; bct→α-U→bct→hcp, with the first transition taking place at 0.25 Mbar and the subsequent ones above 1 Mbar. The bct→α-U transition is triggered by the pressure-induced promotion of the spd valence states to $5f$ states. In this regard, Pa approaches uranium which at ambient conditions has one more $5f$ electron than Pa at similar conditions. At higher compression of Pa, the $5f$ band broadens and electrostatic interactions in combination with Born-Mayer repulsion become increasingly important and this drives Pa to gradually more close-packed structures. At ultrahigh pressures, the balance between electrostatic energy, Born-Mayer repulsion, and one-electron band energy stabilizes the hcp (ideal packing) structure. The electrostatic energy and Born-Mayer repulsion rule out open crystal structures under these conditions in Pa and between the close-packed structures, the hcp structure is shown to be stabilized by filling of the $5f$ band. [S0163-1829(97)05541-0]

The polymorphism found in the crystal structures of the actinide series of metals is without doubt the richest among all metallic elements. Throughout this series of metals, the complexity of the crystal arrangement is increasing, with plutonium having the most distorted crystal structure. The actinides beyond Pu, however, show a more rare-earth-like behavior, with close-packed structures, due to the localization of their $5f$ electrons. In the light actinides, as opposed to the heavier ones, the $5f$ states are delocalized. Moreover, the occupation of the $5f$ states increases with about one electron for each element traversing the series.

Experimental work by Vohra and Akella[1] and theoretical calculations by Eriksson *et al.*[2] showed that thorium, the metal preceding Pa, undergoes a phase transition from fcc→bct just below 1 Mbar. It was explained[2] that the promotion of primary $6d$ electrons to the $5f$ band pushed this transition. In terms of $5f$-band occupation, Th under pressure approaches Pa which at ambient conditions has roughly one more $5f$ electron than Th. In light of the importance of the $5f$ electrons for the crystal structures, it was not surprising to find that Th adopted the same type of structure as Pa when compressed, namely bct. Here we apply the same arguments for Pa; the increase of the $5f$ population with pressure would push Pa closer to uranium's $5f$ occupation as Pa is compressed. This fact raised the question that perhaps Pa will undergo a phase transition to the same structure as U has, namely, an orthorhombic (α-U) structure. In the present paper we investigate this possibility by means of electronic-structure, total-energy calculations.

The theoretical method,[3] briefly described below, is developed in the framework of density functional theory, with the application of the generalized gradient approximation (GGA) for the exchange and correlation potential.[4] Moreover, we have used an electronic structure method where the self-consistent potential contains no geometrical approximations.[3] This so-called full-potential method[3] has previously been applied to many systems, also for the actinides,[5–8] proving its reliability. We refer to these studies for a more thorough description of the computational technique, except that we here mention that our calculations take the relativistic effects (including the spin-orbit coupling) into account. The electronic structure and total energy are thus calculated from first-principles theory with the atomic number and the crystal structure as the only input. The approximations used in the theory are the approximation for the exchange and correlation energy functional (GGA), truncation of the expansion of the wave function ($6s$, $6p$, $7s$, $7p$, $6d$, and $5f$ atomic orbitals), density, and potential, as well as the Born-Oppenheimer approximation (no nuclear motion is accounted for). The expansion of the potential and density inside the muffin-tin spheres contained angular momentum up to $l=8$. The sampling of the Brillouin zone was done using the special k-point method[9] and involved 160 or more k points in the irreducible wedge.

For Pa, we chose to calculate the total energy differences, as a function of volume, for typical actinide crystal structures, α-Np, α-U, and bct. We anticipate higher symmetry crystal structures at elevated pressures and for that reason we also included bcc, fcc, and hcp in our investigation. For the most complicated structure, the α-Np structure, we only did a few test calculations. This phase was considerably higher in energy than any of the other and we conclude that for Pa, the α-Np structure is not important. The remaining five structures are less complicated than the α-Np phase. For the hcp and the bct crystal structures, the c/a axial ratio was optimized as a function of pressure. The α-U structure is, however, considerably harder to optimize in practice. This structure can be described as follows. It has a face centered orthorhombic arrangement with 2 atoms/cell, with atomic positions (0,0,0) and $(1-2y,1-2y,0.5)$ in units of the Bra-
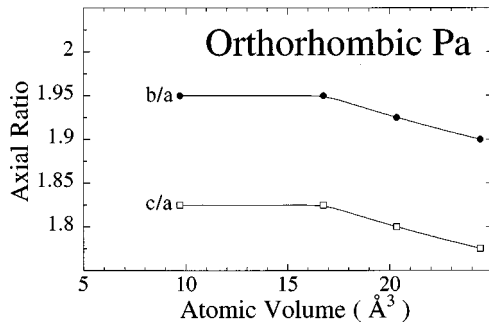
FIG. 1. Calculated axial ratios for orthorhombic (α-U) Pa as a function of volume. The atomic coordinate (y; see text) was optimized to about 0.125 within the studied volume interval.

vais lattice vectors ($-a/2,0,c/2$), ($a/2,0,c/2$), and ($0,b,0$). Hence, three parameters (b/a, c/a, and y) have to be optimized for each studied volume. The search for an energy minimum in the parameter space was simplified by the fact that (i) b/a, c/a, and y have a local minimum in the electrostatic Madelung energy for $b/a = 1.825$, $c/a = 1.98$, and $y = 0.14$, as was pointed out in Ref. 10, and (ii) for uranium (at equilibrium), $b/a = 1.73$, $c/a = 2.06$, and $y = 0.1025$. The electrostatic energy becomes relatively more important for higher densities and we therefore expect the parameters to approach values that minimizes that contribution at higher pressures. In practice the optimization was done for each parameter separately; starting with the c/a ratio, and then the b/a ratio and finally the least important parameter, y. Our optimized structural parameters for the α-U structure are shown in Fig. 1 as a function of volume. At the equilibrium volume we obtained the values; $b/a = 1.775$, $c/a = 1.90$, and $y = 0.120$. Both the b/a and c/a axial ratio are increasing with compression and at about 17 Å^3 their values are stabilized to 1.825 and 1.95, respectively. Note that those values are indeed very close to the values (1.825 and 1.98) obtained simply by optimizing the Madelung energy. We do not show the very weak pressure dependence of the y parameter; it was close to 0.125 within this volume range. It should be mentioned that keeping c/a, b/a, and y fixed to the values that give the lowest total energy at the equilibrium volume for Pa would make the bct$-\alpha$-U energy difference always positive. Hence, it is uttermost important to optimize these parameters as a function of volume to detect the phase transition.

In Fig. 2 we show the main results from our calculations. The total energy, relative to the bct (α-Pa) energy is plotted as a function of atomic volume. Notice that at the equilibrium volume we find the bct structure to be stable, in good comparison with experiment[11] and previously published theory.[5] Here we optimized the c/a axial ratio to be about 0.82 in agreement with experimental observations and Ref. 5. Throughout the studied volume range the optimized c/a ratio remained the same for bct Pa, showing that this c/a ratio is either an absolute minimum or at least a local minimum. At about 20 Å^3 we observe a phase transition, bct$\rightarrow\alpha$-U structure and at about 8 Å^3 the bct phase reenters into the phase diagram to be followed by the hcp (ideal c/a) at about 7.5 Å^3. We thus predict the following structural sequence for Pa as a function of pressure; bct$\rightarrow\alpha$-U $\rightarrow$bct$\rightarrow$hcp.
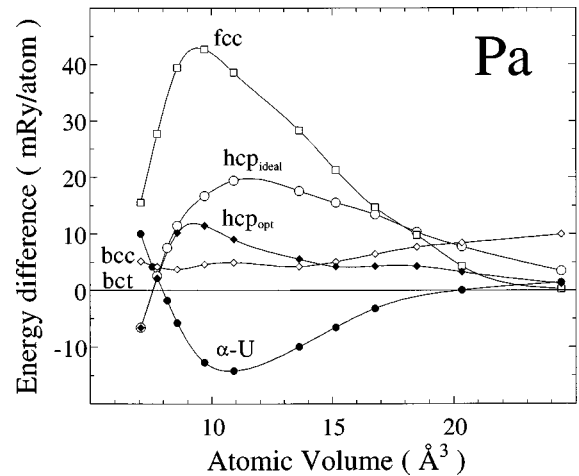

FIG. 2. Total energies for Pa in the bcc, fcc, hcp, and α-U structures relative to the bct structure energy. Three phase transitions are shown, bct$\rightarrow\alpha$-U$\rightarrow$bct$\rightarrow$hcp. The c/a axial ratios at the transitions are 0.82 (bct), 1.633 (hcp), and 1.95 (α-U). The other two crystal structure parameters for the α-U phase are optimized to 1.825 (b/a) and 0.125 (y).

The first of these transitions occur at a pressure that could be obtained in the diamond-anvil cell. The thermodynamic quantity associated with a phase transition in this case is pressure and in our study of the the bct$\rightarrow\alpha$-U transition we calculated Gibbs free energy for the two phases

$$G = E + PV - TS = H - TS.$$

H, S, and E are the enthalpy, entropy, and the internal energy of the system, respectively. The entropy term vanish for our zero temperature calculations and it suffices to study the enthalpy as a function of pressure for the two phases. The enthalpy for the bct and the α-U phase coincide for the transition pressure, 0.25 Mbar but no other transitions could be found below 1 Mbar. For higher pressures we only studied the energy differences between Pa in the various crystal structures. Hence, the transition volumes for these are approximations; we assume that both phases have the same volume at the transition. This is most likely a good approximation since transitions in the light actinide series, as opposed to the heavier ones beyond Pu, do not involve any appreciable volume collapse.

The high pressure phase, hcp Pa, was also studied in some detail. Figure 3 shows the volume dependence of the axial c/a ratio. This parameter was optimized as a function of volume and interestingly its value is first increasing with decreasing volume and reaches a maximum at a volume of about 14 Å^3 before its value rapidly approaches the ideal value at a volume close to 8 Å^3. At this volume, bct Pa is still lower in energy but at higher compression hcp Pa, with an ideal c/a ratio, is the stable phase. This high pressure phase of Pa was first proposed by Söderlind et al.[6] who argued for its existence by using a simple model involving canonical f bands.[12] Now we try to shed light on the peculiar behavior of the c/a ratio as a function of volume for hcp Pa (Fig. 3). In a simple model, we isolate the one-electron contribution to the total energy, by means of the structure energy difference theorem[13] in combination with canonical bands,[12]
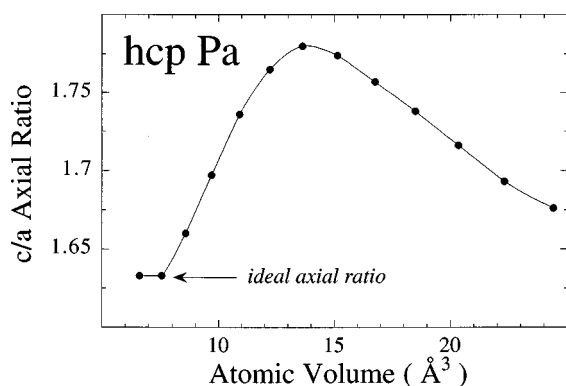
FIG. 3. Calculated axial c/a ratio for hcp Pa as a function of volume. At high compression c/a approaches the value corresponding to ideal close packing of the hcp crystal structure (1.633).

FIG. 4. Calculated energy versus c/a ratio for hcp Pa using Pettifors structural energy difference theorem[13] in combination with canonical bands.[12] The energies have arbitrary units. The solid circles represent a $5f$ occupation of 1.5 and the open squares a $5f$ occupation of 2.0. The curves connecting the points are fitted polynomials and serve as a guide to the eye.

and calculate the energy versus c/a ratio of hcp Pa. In Fig. 4 we show our model results for two different $5f$ band fillings (n_{5f}), which are close to the filling of Pa at ambient conditions ($n_{5f}=1.5$) and at elevated pressures ($n_{5f}=2.0$). The lowest energy for $n_{5f}=1.5$ occurs for $c/a=1.72$ whereas for $n_{5f}=2.0$ the optimal c/a ratio has increased to about 1.77. Hence, our simple model reproduces the trend of the full potential results in that an increased $5f$ occupation stabilizes a hcp structure with larger c/a ratio. For increasing compression, electrostatic interactions, and Born-Mayer repulsion will eventually dominate, stabilizing the ideal c/a ratio, as is found in the calculations of Fig. 3. We thus have two contending mechanisms driving the trend of c/a ratio in Fig. 3. First, the shape of the $5f$ density of states results in a one-electron contribution which favors larger c/a ratios when the pressure, and thus $5f$ occupation, increases, and secondly the electrostatic energy in combination with the Born-Mayer repulsion favors an ideal c/a axial ratio.

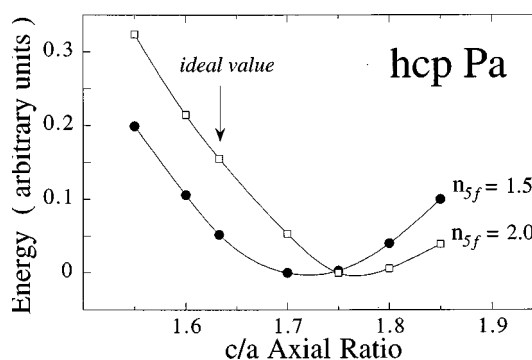In summary we predict a sequence of structural phase transitions with increasing pressure, which hopefully may be verified experimentally. We show that in the hcp phase the c/a ratio varies with pressure in a rather intricate way, increasing at first, then reaching a maximum of about 1.78 before decreasing to an ideal value. We make use of canonical bands[12] in combination with Pettifors structural energy difference theorem[13] to demonstrate that the one-electron contribution gives rise to the initial increase and then a decrease. We argue that the decrease is due to electrostatic (Madelung) interactions and Born-Mayer repulsion. It would be interesting to investigate if these simple interactions could explain also some of the more intricate structural phases of the actinides phase diagrams. Such studies are underway.

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