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USING A DIAMOND-ANVIL CELL**

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STATIC ULTRA-HIGH PRESSURE STUDY OF LANTHANIDE AND ACTINIDE METALS USING A DIAMOND-ANVIL CELL

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Structural phase transformations in lanthanides and actinides were investigated as a function of pressure up to 300 GPa at room temperature. Except in Ce and Pr, no large volume changes were noticed for these metals as they went through several phase changes. The appearance of a bct ultra-high pressure phase in Ce, Sm, Th, and possibly in Np, raises the possibility that the ultimate high pressure structure for the 4f and 5f metals may be the bct structure. On the other hand, it is also possible that this is a precursor to another close-packed structure at even higher pressure.

INTRODUCTION

The rare-earth series of elements (lanthanum through lutetium) are characterized by a gradual filling of the 4f shell in the atom. This shell is located deep within the atom and thus the associated magnetic moments are highly localized.¹ The lanthanide elements form a long series whose physical properties vary smoothly with 4f occupancy. Since the outer regions of the different lanthanide atoms are very similar to each other one may expect a broadly related behavior in their solid modifications.^{2,3,4} If so, the lanthanide phase diagrams may be fitted into a single universal phase diagram in which the same sequence of changes could be represented either with decreasing atomic number or with increasing pressure. This possibility has stimulated both theoretical and experimental studies on lanthanides.

In the actinide series (actinium through lawrencium) the 5f shell is gradually filled and according to Johansson and Rosengren,¹ although the 5f wave function is fairly localized, it is more extended than the lanthanide 4f. Kmetko and Hill⁵ have shown, from energy-band calculations on actinides, that the earlier actinide metals (Pa-Pu) give good evidence for an itinerant character of the 5f electron. On the other hand, the 5f electrons in heavy actinides (Am and above) are localized and their properties resemble those of the rare-earth elements which have localized 4f electrons; so another important motivation to

electrons; so another important motivation to study both lanthanides and actinides is to understand any similarities between these two groups of elements. This has led experimentalists to examine the high pressure structural changes in actinides and lanthanides. In this paper we present a short review of data that were collected at LLNL both on lanthanides and actinides and briefly compare salient differences between our data and that of other workers.

EXPERIMENTAL PROCEDURE

We used the Mao and Bell⁶ type diamond-anvil cell (DAC) with the diamond anvils that were beveled with 7°–8.5° bevel angle, 300–400 μm culets, and 50–150 μm central flats. Depending on the size of the flat, a 35–100 μm hole was drilled in a pre-pressed rhenium gasket into which a 20–50 μm piece of sample along with 99.999% pure platinum powder or a ruby chip as an internal pressure calibrant were loaded. X-ray diffraction data were obtained by the film technique (to ~50 GPa) and by the energy dispersive method from few GPa to ~300 GPa at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. At NSLS the incident x-ray beam was collimated to 25–10 μm and the diffracted x-ray beam was collected with a germanium detector. Accuracy

in the calculated volumes from the crystallographic data ranges between 1–2%, the latter being at the highest pressure. Pressure measurements are accurate to 1.0 to 2.0 GPa (the latter being at ~250 GPa).

RESULTS

Rare-Earth Metals

Structural phase transformation data for the rare-earth elements that were investigated by us are presented in Table 1. At lower pressures Jayaraman and Sherwood⁷ have reported a systematic behavior in the phase transformations in the lanthanides as a function of pressure. Their suggested structural sequence with increased pressure is hcp–Sm type–dhcp–fcc. Beyond the face-centered cubic (fcc) phase a six-layered structure was discovered^{8,9} and at still higher pressures an orthorhombic (α -U type) phase was reported for Pr^{10,11} and the accompanying volume change is attributed to the delocalization of the 4f electron. In the post-fcc regime, present data differs from that of Grosshans, Holzapfel and Benedict.^{12,13}

Benedict *et al* proposed that the 4f electron delocalization is accompanied by a large volume change and the structure of the new phase at that pressure will have a lower symmetry (monoclinic); which they called the “collapsed phase.” For Sm they proposed that this phase could appear at about 36.0 GPa but our data do not substantiate their pressure and the predicted large volume change. Secondly, we differ from them in that the post-fcc phase in the lanthanides is a distorted form of the fcc phase.¹⁴ We argue on theoretical grounds¹⁵ and on the interpretation of our X-ray diffraction patterns collected by the angular dispersive technique on film, that it could be a six-layered hexagonal packing of ABCACB repeat called triple-hexagonal-close-packed (thcp) structure.⁹ However, it is important to note that both interpretations for the post-fcc phase have some drawbacks, and much more precise x-ray diffraction data are required to resolve this issue. For this reason instead of calling this phase dfcc or thcp, we are calling it hex/6 phase. Benedict *et al*¹³ also suggest in their generalized phase

diagram that in the heavy rare-earths holmium through lutetium, the high-pressure dhcp phase changes directly to the dfcc phase without the intermediate fcc phase [the general sequence is hcp–Sm type–dhcp–fcc–dfcc–collapsed (?) phase (monoclinic)]. Our studies on Gd¹⁶ and Tb (in preparation) suggest that at high pressure there would be a stability field for fcc holmium contrary to the observation of Benedict *et al*. The modified phase diagram proposed by Krüger *et al*¹⁷ is in general agreement with our observed data and is similar to the tentative phase diagram proposed by us for the rare-earth elements (actual publication of this is deferred until we finish investigation of holmium).

Actinides

Among the actinides, we studied the phase changes in Th, U, Np, Pu, Am, and Cm under elevated pressures while Roof^{18,19} studied Pu and Am. Benedict²⁰ recently published a review of the experimental work done on the actinides at Karlsruhe.

Data on thorium published by Akella *et al*²¹ suggested no phase change up to 100 GPa; however, a more recent detailed study²² with Pt as an internal pressure calibrant rather than Ag (which interfered with the sample reflections) has clearly shown that indeed Th does go through a phase change from fcc to bct (body-centered tetragonal structure at about 70 GPa with very little volume change. No other structural change was noticed even up to 300 GPa. A possible structural change at 70 GPa was suggested for uranium from a preliminary investigation²³; however, further study of uranium to 100 GPa²⁴ has dismissed this possibility. From our recent study to still higher pressure,²⁵ we are convinced that there is no phase change in U at 70 GPa, but at least one of the two extra reflections that previously led us to that suggestion is due to the flipping of the relative compressibilities of *a* and *b* axis. In all three investigations so far on U, we could not index the other reflection (which appears at low energy), and even at the highest pressure, the intensity of that reflection does not change.

A detailed investigation of Np is underway at present which will help us better understand the behavior of the lighter actinides; however, in our preliminary investigation we observed a trend

for the *a* and *b* axis becoming equal, which suggests a phase change from orthorhombic to body-centered tetragonal (bct) structure. On the other hand, alpha plutonium, which has a complex monoclinic crystal structure with 16 atoms in the unit cell at one atmosphere, changes to a simple hexagonal-close-packed (hcp) structure at elevated pressure.²⁶ Dabos²⁷, in her doctoral thesis work on plutonium, reported a high pressure structural transformation for this metal to an orthorhombic structure with 21% volume change, the largest ever reported for an actinide or lanthanide metal. If her identification of the structure is correct then the high pressure behavior of plutonium is reminiscent of the trivalent rare-earth elements (as pressure increases the structures of lower *Z* elements appear; see phase diagram for actinides by Benedict²⁰). On the contrary, if the high pressure structural form for plutonium is hcp, then one is tempted to presume that it may behave like the localized *f*-electron metals of heavy actinides as pressure is increased; yet in a more recent paper, Dabos *et al*²⁸ changed their structural identification for this high pressure phase from orthorhombic to primitive hexagonal with only 1-2% volume change. Both the identifications for the high pressure form of plutonium need further clarification. More detailed experimental and theoretical work need to be considered to understand the high pressure behavior of this complex metal.

At room pressure americium has a double hexagonal close-packed (dhcp) structure. As pressure is increased, Am goes through three structural transformations^{29,30,31}: AmI dhcp-AmII fcc-AmIII monoclinic (α " uranium like)-AmIV orthorhombic (?). The transformation pressures were 5.0 ± 1.0 , $\sim 11.0 \pm 1.0$, and ~ 15.0 GPa. Roof *et al*³² have also observed structural changes at similar pressures but they assigned AmIII to have a body-centered monoclinic structure and AmIV as an orthorhombic structure. Benedict assigned different structures for AmIII and AmIV phases in his earlier reports, but recently (review paper)²⁰ he proposed that AmIII had trigonal and AmIV orthorhombic structures. According to him, the AmIII to IV transformation occurs at a slightly higher pressure than that reported by Smith *et al* and Roof *et al*.

Akella *et al*³³ reported data on Cm up to 20.0 GPa in which they mentioned a possible structural change around 18.0 GPa from an ambient dhcp phase. No further details of this work could be published. Benedict also worked on Cm and published his data to 50.0 GPa and the structures are CmI dhcp-CmII fcc-CmIII orthorhombic at 23.0 and 43.0 GPa, respectively. Benedict and his associates also investigated the high pressure properties of californium and berkelium. Their data are given in detail in a recent publication by Benedict.²⁰

CONCLUSION

The appearance of a bct phase in lanthanides (Ce and Sm) and actinides (Th and Np) at very high pressures is noteworthy; especially in Th, where the fcc phase changes to a bct phase and remains stable even at 300 GPa. The proposal for a bct high pressure phase in uranium based on theoretical calculations³⁴ raises the possibility that the ultimate high pressure phase for 4*f* and 5*f* metals could have the bct structure; or it is also possible that this is a precursor to another close-packed structure even at still higher pressures.

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Table 1. Structural phase changes in the rare-earth elements at elevated pressures.

Pr	dhcp $\rightarrow$ fcc (3.8)*; fcc $\rightarrow$ hex/6 (6.2); hex/6 $\rightarrow$ orthorh (21.0)
Nd	dhcp $\rightarrow$ fcc (3.3 < 4.5); fcc $\rightarrow$ hex/6 (~17.3); hex/6 $\rightarrow$?
Sm	Sm type (ortho) $\rightarrow$ dhcp (3.2); dhcp $\rightarrow$ fcc (13.0); fcc $\rightarrow$ hex/6 (32); hex/6 $\rightarrow$ bct
Gd	hcp $\rightarrow$ Sm type (1.5); Sm type $\rightarrow$ dhcp (6.5); dhcp $\rightarrow$ fcc (>24<29); fcc $\rightarrow$ hex/6 (>44<55) 106 hex/6 continues
Tb	hcp $\rightarrow$ Sm type (5.0); Sm type $\rightarrow$ dhcp (~11.8); dhcp $\rightarrow$ fcc (~30) up to (100) fcc continues
Dy	hcp $\rightarrow$ Sm type (~8.9); Sm type $\rightarrow$ dhcp (~17.0); dhcp $\rightarrow$ fcc (~>32.0<42.7) to 57.0 fcc continues

* Values in () pressure in GPa where approximately the phase changes have occurred.

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