5*f* Bonding in Thorium Metal at Extreme Compressions: Phase Transitions to 300 GPa

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The 5*f* element thorium has been studied in a diamond-anvil cell to pressures of 300 ± 8 GPa (volume fraction $V/V_0 = 0.40$) at 300 K by energy-dispersive x-ray diffraction using a synchrotron source and platinum pressure standard. Thorium undergoes a phase transition from its ambient fcc phase to a body-centered-tetragonal (bct) phase near 100 GPa. This bct high-pressure phase of thorium is similar to the one found previously in the 4*f* lanthanide element cerium above 12 GPa. We suggest that the 5*f* band which lies above the Fermi energy in thorium at ambient conditions is occupied at megabar pressures and significantly contributes to bonding.

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Thorium (Th) metal occupies a unique position in the periodic table as being a transition metal with strong *s*-*d* hybridization and on the threshold of being a regular 5*f* band light actinide element. Th is the only element which has an unoccupied 5*f* band as near as 1.5 eV above the Fermi level [1], and at ambient conditions with four valence electrons is regarded as a regular tetravalent transition metal like titanium, zirconium, and hafnium. The Fermi surface of Th at ambient conditions is indeed simple [2] and its pressure dependence [3] can be explained within the tetravalent transition-metal framework [1]. Electronic band-structure calculations to 30 GPa [1] indicate that the 5*f* band is still approximately 1.25 eV above the Fermi level to these pressures. However, occupation of the 5*f* band is expected at higher pressures because of the broadening of the electronic bands and their relative motion as the volume is decreased. This relative motion of the electronic bands at high pressures gives rise to electronic transfer between the bands (*sp* to *d* bands in transition metals [4–6]) and, in addition, we expect in Th that electrons will be transferred from the *spd* bands to the *f* band at ultrahigh pressures. Th crystallizes in the fcc structure at ambient conditions and no phase transition indicative of *f*-electron bonding has yet been seen to pressures of 100 GPa [7] (1 Mbar), to which it has been studied. Diamond-anvil-cell devices can now generate calibrated static pressures in the range of 250–400 GPa and structural studies have been carried out on several materials [8–10]. The multimegabar pressure capability of diamond-anvil cells is expected to uncover new phenomena in transition metals and *f*-electron systems like rare earths and actinides [11].

In this Letter, we report our structural investigations on Th metal to pressures of 300 ± 8 GPa at 300 K in a diamond-anvil cell and show that it is isostructural with cerium at high pressures. We discuss our results in terms of the 5*f* bonding in Th at high pressures. Cerium (Ce) metal is a 4*f* counterpart of Th in the periodic table and crystallizes in the fcc(γ) phase near ambient conditions. However, unlike Th, Ce has one *f* electron which is localized at ambient conditions in addition to its three valence electrons. Ce displays a classic example of an isostructural phase transition (γ to α) at a high pressure of 0.8 GPa with 16% volume change (see Ref. [12] for a compilation of high-pressure research on Ce). The γ to α phase transition in Ce has been explained by the 4*f* delocalization (Mott transition) model [13] and also by the "Kondo-collapse" model [14]. Some features of this phase transition are still not completely understood and have received considerable theoretical and experimental attention (for a recent review see McMahan [15]). The α(fcc) phase of Ce shows further transformations to a body-centered-monoclinic phase at 5 GPa and finally to a body-centered-tetragonal (bct) phase at 12 GPa [16]. The bct phase of Ce has a very wide stability range from 12 to 46 GPa [12], in which it has been studied.

Th metal was studied in the diamond-anvil cell by the energy-dispersive x-ray-diffraction (EDXD) technique [17] using a synchrotron source. Type-Ia diamond anvils with 30 μm central flat size with 8.5 deg bevel angle to culet size of 350 μm were used in the present experiments. The diamond geometry was particularly chosen to study samples of 25 μm in diameter to pressures of 300 GPa and to minimize the pressure gradients across the x-ray sampling region of 10 μm. The sample hole of 25 μm in diameter was filled with 1-μm-grain-size Pt powder (pressure calibrant, 99.9% purity) and 5-μm-grain-size Th powder (99.9% purity). The energy-dispersive x-ray diffraction spectra were collected at the superconducting wiggler white beam line [8] X-17C at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Excellent quality diffraction patterns were obtained to 300 GPa with the 10-μm collimated x-ray beam. The pressure was calculated from the measured lattice parameter of Pt using the equation-of-state Pt measured to 660 GPa by shock wave methods [18].

The EDXD spectrum of the Th and Pt mixture in the diamond-anvil cell at low pressure (1.6 GPa) showed both Th and Pt in the fcc structures based on the twelve diffraction peaks from Th and the six diffraction peaks from the pressure marker Pt. No extra diffraction peaks due to any impurity phase in the sample were detected. The concentration of the Pt standard in the Th sample varied across the 25-μm sample region and several 10-μm regions were x rayed at each pressure. Near the phase transition, we also recorded the Th spectra with no interference from the marker material to solve for the crystal structure. The fcc phase of the Th sample is found to be stable to pressures near 100 GPa. A phase transition to a new phase was observed with the appearance of several new diffraction peaks. Figure 1 shows the diffraction pattern for Th at a pressure of 102 ± 3 GPa; the pressure is measured by the Pt standard by positioning the x-ray beam at the Th and Pt mixture region at the same pressure. The diffraction pattern is excellent and all nine diffraction peaks index very well to the bct structure with two atoms in the unit cell. The other known structures of transition metals, rare earths, and actinides do not fit the diffraction data. The Th metal is soft and very compressible and does not support large shear stresses or pressure gradients. Therefore, we do not expect that shear stresses play any major role in the fcc to bct transition and we believe that this transition is electronically driven. Furthermore, the fcc Pt pressure standard that is squeezed along with Th does not show any distortion in the unit cell. The measured lattice parameters for Th at 102 GPa are $a = 2.822$ Å and $c = 4.411$ Å with $c/a = 1.563$ (volume fraction $V/V_0 = 0.534$). There is no measurable volume change at the fcc to bct phase transition (< 1%). Similar results were reported for Ce where no volume discontinuities were detected at the phase transitions after the formation of the α phase. The fcc structure can be expressed as a bct unit cell as $a_t = a_c/\sqrt{2}$ and $c_t = a_c$ with $c_t/a_t = 1.414$, where c_t and a_t are lattice parameters for the bct phase and a_c is the lattice parameter for the fcc phase. It is interesting to point out that the Th crystal structure at high pressures is considerably distorted from this ideal value.

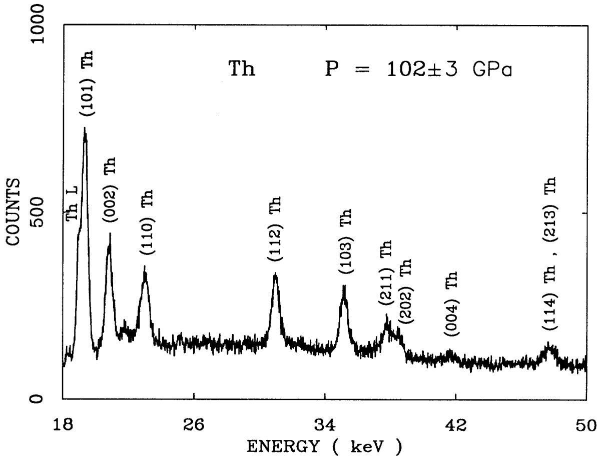

FIG. 1. Energy-dispersive x-ray diffraction spectrum of thorium (Th) at a pressure of 102 GPa taken from the Th-rich region of the sample. The product of energy E and interplanar spacing d for this spectrum is $Ed = 45.859 \pm 0.007$ keV Å. All nine diffraction peaks of Th are indexed to a body-centered-tetragonal (bct) structure. The pressure is measured by the Pt standard by positioning the x-ray beam at the Th and Pt mixture region at the same pressure. The lowest-energy peak marked Th L is the fluorescence peak of Th.

This distortion from the fcc structure, in fact, increases rapidly with increasing pressure. Figure 2 shows the plot of axial ratio (c/a) as a function of pressure for various phases of Th. There is a rapid increase in c/a between 100 and 200 GPa pressure. The c/a value tends to saturate around 1.65 between 200 and 300 GPa. It is interesting to point out that a similar behavior of c/a in the bct phase has been observed in Ce between 12 and 46 GPa.

The bct phase of Th is found to be stable to the highest pressure of 300 ± 8 GPa achieved in the present experiments. The diffraction pattern of the Th and Pt mixture at this pressure is shown in Fig. 3. The Pt calibrant is in the fcc structure at this pressure and Th is in the bct phase. The uncertainty of 8 GPa at 300 GPa is due to the random errors in the measurement of the lattice parameter of Pt and does not include possible errors in the shock wave equation of state [18]. The diffraction data at 300 GPa are summarized in Table I. The eight diffraction peaks of Th, (101), (002), (110), (112), (103), (211)/(202), and (004), give an excellent fit with the bct structure as shown in Table I. The lattice parameters for Th at 300 GPa are $a = 2.525$ Å and $c = 4.178$ Å with $c/a = 1.655$ (volume fraction $V/V_0 = 0.405$). The pressure of 300 GPa is obtained by fitting the (111), (200), and (220) diffraction peaks (Table I) of Pt ($V/$

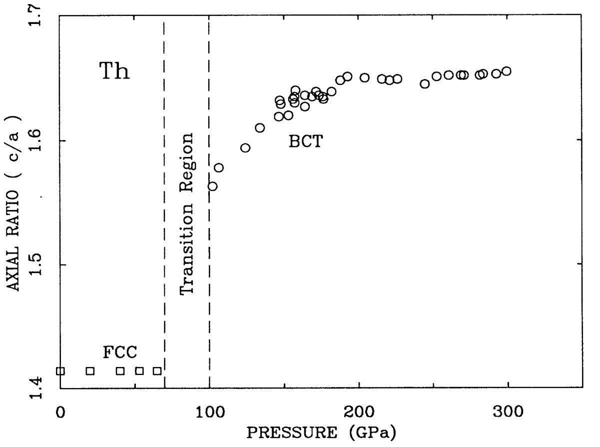

FIG. 2. The measured axial ratio (c/a) as a function of pressure for the body-centered-tetragonal (bct) phase of thorium (Th). The ideal value of 1.414 for the fcc structure of Th below 70 GPa is also indicated. The dashed lines define the 70–100-GPa transition region.

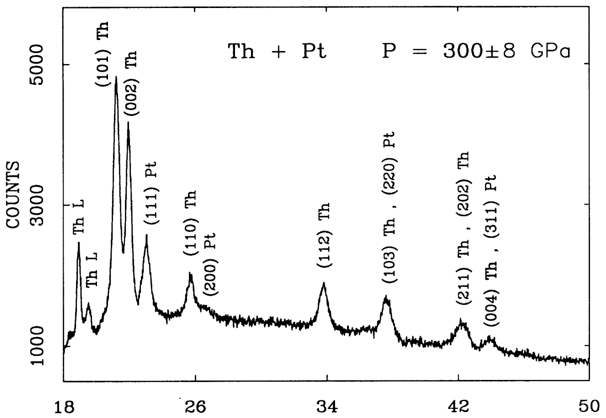

FIG. 3. Energy-dispersive x-ray-diffraction spectrum of the thorium (Th) and platinum (Pt) mixture at 300 ± 8 GPa. The product of energy E and interplanar spacing d for this spectrum is $Ed = 45.859 \pm 0.007$ keV Å. All Th peaks are indexed to the bct structure while the Pt peaks are indexed to the fcc structure. The two lowest-energy peaks marked Th L are the fluorescence peaks of Th.

$V_0 = 0.679$) and using the room-temperature shock equation of state [18].

The change in crystal bonding in Th is reflected by the lowering of symmetry from cubic to tetragonal and also by the formation of short bonds characteristic of f electrons. Th at 300 GPa pressure has four nearest neighbors at 2.525 Å and eight next-nearest neighbors at 2.748 Å. This should be contrasted with the twelve nearest neighbors at 2.661 Å for an assumed fcc structure of the same density. The low-symmetry crystal structures are known to exist in metallic systems where f bonding is dominant, like the light actinides from protactinium to plutonium [13], and in some lanthanides under high pressures, i.e., Ce [12], Pr [19,20], and recently Sm [21]. The present experiments on Th clearly indicate the formation of a bct structure near 100 GPa due to participation of $5f$ electrons in bonding which give rise to formation of four short bonds in this structure. Furthermore, very interesting similarities between the phase diagrams of Ce and Th at high pressures have been discovered. We plan now to closely examine the pressure range between 70 and 100 GPa in Th to look for evidence for the formation of the intermediate body-centered monoclinic phase. This monoclinic phase is known to exist in Ce in a narrow pressure range between 5 and 12 GPa [12].

TABLE I. The observed (d_{obs}) and calculated (d_{calc}) interplanar spacings for the diffraction data for Th and Pt at 300 ± 8 GPa. The calculated interplanar spacings are based on the lattice constant $a = 3.449$ Å for fcc Pt and the lattice parameters $a = 2.525$ Å and $c = 4.178$ Å for bct Th.

Peak	d_{obs} (Å)	d_{calc} (Å)	(hkl)
1	2.161	2.161	(101) Th
2	2.089	2.089	(002) Th
3	1.991	1.991	(111) Pt
4	1.784	1.785	(110) Th
5	1.730	1.724	(200) Pt
6	1.357	1.357	(112) Th
7	1.219	1.219, 1.219	(103) Th, (220) Pt
8	1.086	1.090, 1.080	(211) Th, (202) Th
9	1.044	1.044, 1.040	(004) Th, (311) Pt

The situation for thorium and cerium can be summarized as follows.

(1) The actinide element thorium is shown to be isostructural with the corresponding $4f$ lanthanide element cerium at high pressures. Th above 100 GPa adopts the bct structure known for Ce above 12 GPa. This is remarkable from the point of view that the ambient-condition electronic structure of the two elements is radically different. Ce has a localized $4f$ shell with one f electron while the itinerant $5f$ band of Th is unoccupied and is at 1.5 eV above the Fermi level.

(2) We suggest significant occupation of the $5f$ band in Th from our experiments at megabar pressures with electrons transferred from the s and d bands to the f bands. Detailed band-structure calculations are needed for quantitative comparison of Ce and Th at high pressures. However, in view of the high atomic number, fully relativistic calculations and electron-electron correlation for f electrons must be included in an adequate theoretical description of these systems.

(3) The bct phase of Ce and Th has a very wide range of stability. For Ce, the bct phase is stable in the range from 12 to 46 GPa pressure in which it has been studied. For Th, the bct phase is stable from 100 to 300 GPa, the range covered in the present experiments. The interesting possibility of the bct phase being the ultimate high-pressure phase of the f-band systems needs to be confirmed in other elements of the periodic table.

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