PHYSICAL REVIEW B **74**, 104107 (2006)

X-ray diffraction study of elemental thulium at pressures up to 86 GPa

Michael Pravica,* Zachary Quine, and Edward Romano
High Pressure Science and Engineering Center, Department of Physics, University of Nevada Las Vegas, Las Vegas, Nevada 89154-4002, USA

(Received 2 June 2006; published 14 September 2006)

We have performed a high-pressure synchrotron x-ray diffraction experiment on elemental thulium in a diamond anvil cell to 86 GPa. A series of phase transitions was observed as a function of pressure that follow the expected hexagonal-close-packed → Samarium-type → double hexagonal-close-packed → distorted distorted face-centered cubic sequence. In particular, we present evidence for the predicted double hexagonal close packed → distorted face-centered cubic phase transition near 68 GPa. Equation of state data for thulium are also reported up to 86 GPa.

DOI: 10.1103/PhysRevB.74.104107 PACS number(s): 64.30.+t, 62.50.+p, 61.10.Nz, 61.66.Bi

I. INTRODUCTION

There is much scientific interest in better understanding the lanthanide metals (also known as "rare earth" metals) which possess unique electrical, magnetic, thermal, and material properties that are frequently poorly understood because of the complex interactions of $4f$ electrons within the lattice, especially when subjected to high pressures when interatomic interactions increase. The partially filled $4f$ electron shells are mostly localized in the atoms and, therefore, contribute only slightly to the bonding or crystal structure at ambient pressure. Consequently, lanthanides have similar chemical properties and are often difficult to separate from one another.[1]

The lanthanides (from La through Lu) exhibit crystal structures at atmospheric pressure that vary with increasing atomic number as follows: double hexagonal-close-packed (dhcp) {La → Pm with the exception of Ce}; samarium-type (Sm-type)/rhombic {Sm}; hexagonal-close-packed (hcp) {Gd → Lu with the exception of Yb}.[1] Of these elements, only Eu and Yb are divalent. Ce, Pr, and Tb can be tri- or tetravalent.[1] The rest of the rare earths are trivalent at ambient pressure and temperature. With increasing pressure, the metals below and including Dy adopt crystal structures as follows: hcp → Sm-type → dhcp → face-centered cubic (fcc) → distorted fcc, reverting to the prior crystal structure in the lanthanide series.[1] Above Dy, the elements transform directly from dhcp → distorted fcc, skipping the fcc phase.[2] It is believed that application of pressure causes delocalization and an increase in hybridization of the unfilled $4f$ shell and may induce electron transfer among subbands of conduction electrons near the Fermi surface such as $s,p \rightarrow d$ and $s,p,d \rightarrow f$ electrons.[2–5]

The current paper represents a continuation of our efforts[6] to better understand the high-pressure properties of the lanthanide metals, especially the distorted fcc phase. Our interest in studying thulium (electronic configuration: $4f^{13}5d^{0}6s^{2}$, atomic number 69[7]) originated from the paucity of high-pressure data in the literature about the element beyond about 40 GPa[2,8–10] (though TmTe was studied to 49 GPa[11]) and a desire to verify that the material indeed undergoes the anticipated dhcp → distorted fcc transition somewhere above 70 GPa.[2] Thulium possesses interesting magnetic properties at ambient[12] and high pressures.[10] The metal also has useful electrical properties[13] and optical properties, especially in transparent doped-glass ceramics/fibers for laser applications.[14–16] Thus, better understanding of the high-pressure properties of the element would be very beneficial.

II. EXPERIMENTAL METHOD

Elemental thulium (packed in argon) with 99.9% purity was obtained in powder form (−40 mesh size) from Aldrich Chemical. Due to the slow oxidation of thulium in air, we promptly dropped the metal grains (in the presence of flowing argon gas) into a mortar containing cyclohexane (99.9% purity, Aldrich Chemical) and gently ground the material with a pestle. Rhenium (10 mils thick) served as the gasket material and was preindented to a thickness of ~48 μm with two 300 μm culet type I diamonds. A hole of diameter ~130 μm was electric discharge machined. The completed gasket was secured to the base diamond of a Mao Bell diamond anvil cell and then cleaned ultrasonically in cyclohexane, acetone, and then optical-quality methanol. The entire assembly was immersed in a beaker filled with cyclohexane liquid, which also served as our chemically inert, quasihydrostatic medium.[17] The beaker was placed underneath a stereoptical microscope for convenient sample viewing. A few 10-μm ruby crystals were sprinkled into the sample chamber to measure pressure.[18] After some thulium chips were introduced into the gasket by a hypodermic syringe, the other half of the Mao Bell cell was installed, and the sample was sealed in the beaker. Room temperature angular-dispersive x-ray diffraction (XRD) patterns were recorded at the 16 ID-B x-ray facility of the High Pressure Collaborative Access Team (HPCAT) of the Advanced Photon Source at Argonne National Laboratory. The focused monochromatic x-ray beam was spatially collimated with a 30-μm pinhole. Sample pressure was measured via a diode-pumped 532 -nm wavelength laser near the HPCAT beamline. Typical diffraction patterns were collected with 20 s exposures. Figure 1 illustrates typical XRD patterns taken at various represen-

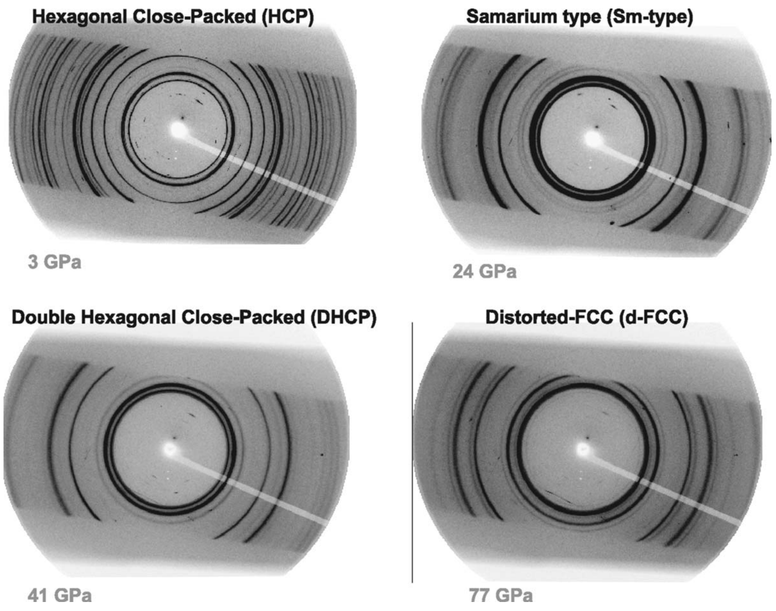

FIG. 1. Thulium powder XRD patterns at various indicated pressures illustrating the polycrystallinity of the sample and the major phase transformations seen in thulium. All patterns were collected at the Advanced Photon Source, Argonne National Laboratory (λ=0.411 047 Å).

tative pressures illustrating the different phase transitions. The patterns were recorded by a MAR345 image plate. For this experiment, the x-ray wavelength was 0.411047 Å.

III. RESULTS

Very little interference in the XRD patterns was observed from the pressure medium because the hydrocarbon (C_6H_{12}) consists of atoms with much lower Z than thulium (6 and 1 compared to 69). The low scattering cross section of the cyclohexane allowed us to easily locate and to center the thulium sample in the synchrotron beam to prevent any contamination from the rhenium gasket. During the entire experiment, there was no evidence of any sudden sample contraction while increasing pressure.

Two-dimensional (2D) ring patterns from the image plate were converted into intensity vs 2θ plots using FIT2D.[19] Unit cell structure determinations were then attempted using the JADE[20] data processing program. Figure 2 shows the intensity vs 2θ plots for thulium at various pressures studied.

At ambient pressure, the accepted structure for thulium is hcp (hP2) with $Z=2$, $a=b=3.534\pm0.005$ Å, $c=5.573\pm0.008$ Å,[8] and thus, a calculated volume per atom of 30.13 Å^3($=\sqrt{3}/4a^2c$). Lattice parameters garnered from the Jade fits are displayed in Table I. Below 14 GPa, patterns were easily fit using the hcp (hP2, space group 194)[2] structure. Between 18 and 33 GPa, the patterns therein were all easily fit using the Sm-type (hR9) structure, $Z=9$, space group 166.[2] Between about 41 GPa and 68 GPa, the patterns were easily fit using the dhcp structure (hP4, $Z=4$). Both hcp and dhcp structures belong to the same space group (194, $P6_3/mmc$).[21] The pattern at 67.9 GPa is a phase mixture where the distorted fcc phase begins to appear. Above 68 GPa and to the highest pressure studied (86 GPa), the distorted fcc phase appears. The diffraction lines were most easily fit to the C_{mmm} (space group 65, $Z=8$) orthorhombic unit cell[2,22] and the trigonal $R\bar{3}m$ (space group 166, $Z=8$) structure,[3] the two leading candidates for the yet-unknown distorted fcc structure. Both space groups fit to our highest pressure data very well, though it was difficult to distinguish which was the more accurate pattern. In that spirit, we include fit results from both structures in Table I and in Fig. 3. Assuming that our sample was very polycrystalline, if we consider the relative intensities plotted in Ref. 22 (particularly the first two peaks which are around 10° in our data), we would then draw the conclusion that the distorted fcc structure is probably $R\bar{3}m$.

Figure 3 shows a plot of the volume per atom (V) versus pressure [equation of state (EOS)] as obtained from the fits. This data was then fit using the Modified Universal Equation of State (MUEOS),[23,24]

$$\ln H = \ln B_0 + \eta(1-x) + \beta(1-x)^2,$$

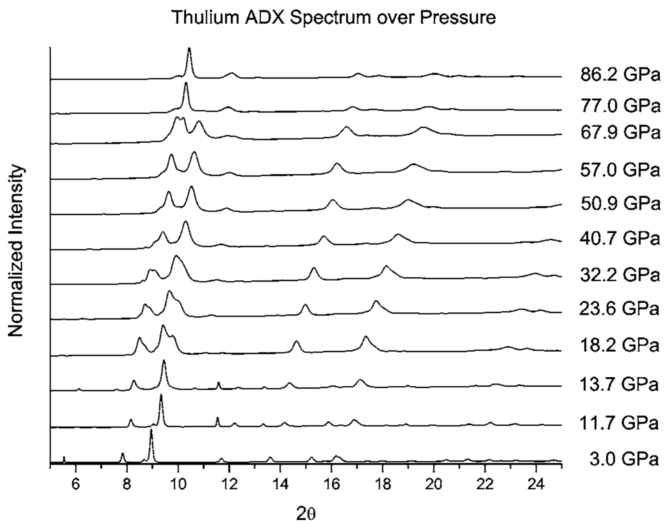

FIG. 2. Intensity vs 2θ plots of thulium in cyclohexane at the various pressures studied. λ=0.411 047 Å.

TABLE I. Results from the JADE fits for thulium.

Pressure (GPa)	Cell packing	Structure	Space group	a (Å)	σa (Å)	b (Å)	σb Å	c (Å)	σc (Å)	Volume per atom (Å^3)	σV (Å^3)
3.0	hcp	$p6_3/mmc$	194	3.488	0.001	3.488	0.001	5.463	0.001	28.775	0.001
11.7				3.348	0.001	3.348	0.001	5.239	0.002	25.415	0.001
13.7				3.311	0.005	3.311	0.005	5.186	0.010	24.620	0.024
18.2	Sm-type	R-3m	166	3.253	0.006	3.253	0.006	23.311	0.052	23.742	0.033
23.6				3.170	0.001	3.170	0.001	23.020	0.003	22.240	0.000
32.2				3.100	0.007	3.100	0.007	22.350	0.029	20.668	0.022
40.7	d-hcp	$P6_3/mmc$	194	3.010	0.013	3.010	0.013	9.700	0.050	19.028	0.156
50.9				2.969	0.012	2.969	0.012	9.501	0.031	18.130	0.091
57.0				2.919	0.008	2.919	0.008	9.425	0.010	17.385	0.021
67.9				2.863	0.004	2.863	0.004	9.230	0.011	16.385	0.011
77.0	d-fcc	$Cmmm$	65	7.965	0.010	5.632	0.004	2.816	0.004	15.789	0.004
		R-3m	166	5.629	0.023	5.629	0.023	13.797	0.006	15.783	0.016
86.2		$Cmmm$	65	7.868	0.018	5.560	0.014	2.778	0.030	15.206	0.045
		R-3m	166	5.57	0.024	5.57	0.024	13.63	0.016	15.272	0.047

where $H=Px^2/[3(1-x)]$, $x^3=V/V_0$, $\eta=1.5\ (B_0'-1)$; and V_0, B_0, B_0' are the atomic volume, isothermal bulk modulus, and the pressure derivative of the bulk modulus at ambient pressure, respectively. The values obtained were $V_0=30.8881\pm0.6823$ Å^3; $B_0=44.5\pm11.5$ GPa; $B_0'=2.7119\pm1.4534$; and $\beta=2.5631\pm6.0263$.

As discussed in our recent study of erbium to 70 GPa[6] and other studies,[25] up to 86 GPa, the EOS of thulium appears more or less continuous up to the highest pressures investigated. This may be due to the fact that the hcp, Sm-type, dhcp, and distorted fcc phases represent different stacking sequences of already space-efficient hexagonal close packed layers and thus the present level of resolution, transition hysteresis, and/or quality of fits may obscure observation of any discontinuity in the transitions.[9] Also, recent x-ray studies of Fe-Sn intermetallics[26] have reported observing sharp discontinuities/kinks in the EOS when using poor quasihydrostatic media. Thus, it would be useful to investigate the effects of using different pressurizing media on the EOS to ascertain if there are conditions which might create discontinuities in the equation of state.

Errors in the volumes were calculated by propagating the errors in unit cell parameters that were calculated from the JADE program fits and are shown in Table I.

IV. SUMMARY

We have studied elemental thulium to 86 GPa, doubling the investigated pressure range of this material, and have seen the expected sequence of phase transitions as a function of pressure (hcp → Sm-type → dhcp → distorted fcc). Further studies will extend the pressure range of study and further investigate dynamics of the dhcp → distorted fcc transition[27] and will investigate the effect of using different pressurizing media on the equation of state.

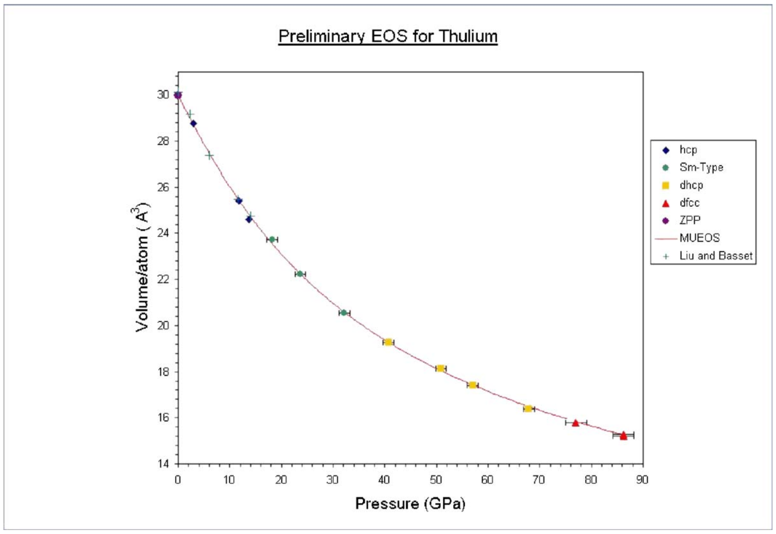

FIG. 3. (Color online) Measured volumes and fitted thulium equation of state. Included in the graph are data from Ref. 8 (crosses).

ACKNOWLEDGMENTS

We wish to thank our late colleague, Yongrong Shen, for suggesting the study of thulium. We would also like to thank David Hartnett and Walter J. Pravica (on sabbatical leave from Wilbur Wright College Spring 2005) for aid in the measurements and data processing. We also wish to thank the HPCAT staff for their technical assistance. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38. HPCAT is a collaboration among the University of Nevada Las Vegas, Lawrence Livermore National Laboratory, the Carnegie Institution of Washington, the University of Hawaii, and the Carnegie/DOE Alliance Center and is supported by DOE-BES, DOE-NNSA, NSF, DOD-TACOM, and the W. M. Keck Foundation. We gratefully acknowledge the support from the U.S. Department of Energy Cooperative Agreement No. DE-FC08-01NV14049 with the University of Nevada Las Vegas.

---

*Corresponding author. Email address: pravica@physics.unlv.edu

[1] S. D. Berrett and S. S. Dhesi, *The Structure of Rare Earth Metal Surfaces* (Imperial College Press, London, 2001), Chap. 1.

[2] W. B. Holzapfel, J. Alloys Compd. **223**, 170 (1995).

[3] N. Hamaya, Y. Sakamoto, H. Fujihisa, Y. Fujii, K. Takemura, T. Kikegawa, and O. Shimomura, J. Phys.: Condens. Matter **5**, L369 (1993).

[4] G. N. Chesnut and Y. K. Vohra, Phys. Rev. B **61**, R3768 (2000).

[5] U. Benedict, W. A. Grosshans, and W. B. Holzapfel, Physica B & C **144B**, 14 (1986).

[6] M. G. Pravica, E. Romano, and Z. Quine, Phys. Rev. B **72**, 214122 (2005).

[7] K. N. R Taylor and M. I. Darby, *Physics of Rare Earth Solids* (Chapman and Hall, London, 1972), Chap. 1.

[8] L-G. Liu and W. A. Bassett, Science **180**, 298 (1973).

[9] W. A. Grosshans and W. B. Holzapfel, Phys. Rev. B **45**, 5171 (1992). See also references contained therein.

[10] D. D. Jackson, V. Malba, S. T. Weir, P. A. Baker, and Y. K Vohra, Phys. Rev. B **71**, 184416 (2005).

[11] S. Heathman, T. Le Bihan, S. Darracq, C. Abraham, D. J. A. De Ridder, U. Benedict, K. Mattenberger, and O. Votgt, J. Alloys Compd. **230**, 89 (1995).

[12] C. M. Lim, C. Edwards, S. Dixon, and S. B. Palmer, J. Magn. Magn. Mater. **234**, 387 (2001).

[13] J. Dudas, A. Feher, and V. Kavecansky, J. Alloys Compd. **278**, 1 (1998).

[14] K-S. Lim, P. Babu, S-K Lee, V-T Pham, and D. S. Hamilton, J. Lumin. **102-103**, 737 (2003).

[15] K-S. Lim, P. Babu, C. K. Jayasankar, S-k. Lee, V-T. Pham, and H-J. Seo, J. Alloys Compd. **385**, 12 (2004).

[16] M. Breede, S. Hoffmann, J. Zimmermann, J. Struckmeier, M. Hofmann, T. Kleine-Ostmann, P. Knobloch, M. Koch, J. P. Meyn, M. Matus, S. W. Koch, and J. V. Moloney, Opt. Commun. **207**, 261 (2002).

[17] M. G. Pravica, Y. R. Shen, and M. F. Nicol, Appl. Phys. Lett. **84**, 5452 (2004).

[18] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[19] FIT2D was written by Andy Hammersley of ESRF, Grenoble, France (1987–2006).

[20] Materials Data, Inc., ver. 7.5.

[21] Th. Strässle, S. Jannssen, F. Juranyi, A. Furrer, O. Moze, A. O. Pecharsky, V. K. Pecharsky, and K. A. Gschneidner, Phys. Rev. B **68**, 134411 (2003).

[22] F. Porsch and W. B. Holzapfel, Phys. Rev. B **50**, 16212 (1994).

[23] P. Vinet, J. Ferrante, J. H. Rose, and J. R. Smith, J. Geophys. Res. **92**, 9319 (1987).

[24] S. K. Sikka, Phys. Rev. B **38**, 8463 (1988).

[25] G. N. Chesnut and Y. K Vohra, Phys. Rev. B **57**, 10221 (1998).

[26] H. Giefers and M. Nicol, J. Alloys Compd. (to be published).

[27] T. Krüger, B. Merkau, W. A. Grosshans, and W. B. Holzapfel, High Press. Res. **2**, 193 (1990).