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High-Pressure Polymorph of Thulium: An X-ray Diffraction Study

Abstract. An x-ray diffraction study of thulium at room temperature and high pressure by means of a diamond-anvil press has shown that thulium transforms from a hexagonal close-packed structure to the samarium type, as other rareearth elements (gadolinium, terbium, dysprosium, and holmium) do. Unlike the other rare-earth elements, thulium (hexagonal close-packed) has an axial ratio (c/a) that is independent of pressure within experimental error and the transition is reversible. The transition occurs with increasing pressure in the range of 60 to 116 kilobars. The lattice parameters of the samarium-type phase of thulium at about 116 kilobars are $a = 3.327 \pm 0.005$ angstroms and $c = 23.48 \pm 0.04$ angstroms, and the volume change at the transition is estimated to be -0.5percent of the volume of the hexagonal close-packed phase at the transition.

In a recent study of the correlation between the pressure-induced phase transformations and the periodicity of density for solid elements, one of us (L. L.) has proposed an empirical relation which serves as a better basis for predicting high-pressure polymorphism in solid elements than crystal

Table 1. X-ray data for thulium at about 116 kbar and room temperature. Values $I/I_{100^{-}}$ (obs), where I is intensity and I_{100} the intensity of the strongest line, were measured by a photoelectric densitometer for the stronger lines. The weak lines were estimated. The letter b denotes broad lines. Values of d(cal) for the hcp structure were computed from the assumed lattice parameters of a = 3.327 Å and c = 5.247 Å at 116 kbar (see Table 2). Values of d(cal) for the Sm-type structure were computed from a = 3.327 Å and c = 23.48 Å. The letter d denotes interplanar spacings, hkl are the indices of the crystal plane, and obs and cal stand for observed and calculated.

<i>I/I</i> ₁₀₀ (obs)	d(obs) (Å)	hcp s	structure	Sm-type structure		
		hkl	d(cal) (Å)	hkl	d(cal) (Å)	
		100	2.881			
77	2.853			101	2.860	
66b	2.793			012	2.798	
100	2.576	101	2.526	(009 (104	2.609 2.586	
73b	2.460			015	2.456	
5	2.203			107	2.186	
5	2.073			018	2.056	
		102	1.940			
3	1.828			10.10	1.820	
48	1.656	110	1.664	110	1.664	
5	1.530			10.13	1,530	
		103	1.495			
41	1.404	112	1.405	{ 119 024	1.403 1.399	
31b	1.385	201	1.389	205	1.377	
		202	1.262			

structure does (1). Liu predicted pressure-induced phase transformations at a few hundred kilobars for all the rareearth elements. With the exceptions of Pm, Er, Tm, and Lu, all the rare-earth elements have been found to have one or more high-pressure polymorphs (2-6). The presence of a high-pressure phase of Tm was reported by Liu (1). Identification of the crystal structure of the high-pressure phase of Tm is reported here.

The changes in volume and electrical resistance of Tm with pressure up to 40 and 100 kbar, respectively, were investigated by Bridgman (3). The latter figure should be reduced to about 76 kbar after the revision of the pressure scale by Kennedy and LaMori (7). No irregularities in Tm were reported by Bridgman. Drickamer (6), however, observed some minor deviations from normal behavior in the resistivity of Tm at 60 to 80 and 150 to 160 kbar. Until now, this was the only study that suggested the transition in Tm. Several rare-earth elements have been studied by shock experiments (8), but Tm was not studied.

The sample of Tm used in this study is from an ingot with a stated purity of 99+ percent (9). The ingot was filed and the powdered sample was then compressed between the diamond anvils and examined by x-ray diffraction. The diamond-anvil press technique used for the high-pressure x-ray diffraction study has been described elsewhere (10).

Thulium crystallizes in the hexagonal close-packed (hcp) structure at 1 atm and room temperature, as many of the other rare-earth elements do. The lattice parameters of the sample used in this study at 1 atm and room temperature are $a_0 = 3.534 \pm 0.005$ Å and $c_0 =$ 5.573 ± 0.008 Å, which compare well with the values of $a_0 = 3.530$ Å and $c_0 = 5.575$ Å reported by Klemm and Bommer (11). The x-ray diffraction powder patterns of hcp metals at high pressure are complicated by preferred orientation effects, as reported by Mc-Whan and Stevens (5). This effect is shown in Fig. 1b (run 3); the reflections with l greater than 1 are very weak or are not observable at high pressures.

To avoid interference in the diffraction patterns, no internal pressure calibrant was mixed with the sample. Hence, the pressure was estimated from the measured lattice parameters of Tm and the compression curve of Tm reported by Bridgman (3). Bridgman has reported the pressure-volume relation of Tm to about 40 kbar. We fitted his data to Birch's equation of state (12) and obtained values of 382 kbar for the isothermal bulk modulus and 5.7 for its pressure derivative. On this basis we are able to extrapolate Bridgman's measurements to higher pressures.

The hcp structure of Tm persists to a volume compression of at least $V/V_0 = 0.892$ which represents a pressure of approximately 60 kbar at room temperature. An x-ray diffraction film taken under these conditions was scanned by a photoelectric densitometer and the resulting trace is shown in Fig. 1b. When the pressure was further increased, new x-ray diffraction lines indicated the appearance of a new phase (Fig. 1a). The new lines can be indexed as the samarium-type structure (Table 1). The lattice parameters of the Smtype phase of Tm listed in Table 1 are $a=3.327\pm0.005\,$ Å and $c=23.48\pm$ 0.04 Å. Both the *hcp* and the Sm-type structures are close-packed structures, the only difference being the stacking order along the c-axis. In this respect, Tm behaves just like the other rare earths, Gd (4), Tb, Dy, and Ho (5), but the transition of Tm is reversible.

We have aligned the 110 reflection in the Sm-type pattern (Fig. 1a) with the 110 reflection in the hcp pattern (Fig. 1b). Since the two structures differ only in the stacking order, it seems reasonable to assume that the value of the spacing of the 110 layers is the same for both phases at the transition pressure. This assumption is supported by the sharpness of the 110 line in patterns produced by a mixture of the two phases. Although Fig. 1a shows the major changes that take place in the diffraction pattern during the phase transformation, it lacks the sensitivity and resolution to show all of the features in the original film. Measurements based on the original film are given in Table 1.

Lattice parameters and relative volumes calculated from the direct readings of the x-ray films are given in Table 2. In the first three of the patterns the c/a ratio of the hcp phase does not seem to change with pressure up to 60 kbar within experimental error. McWhan and Stevens (5) found that the c/a ratio in Gd, Tb, Dy, and Ho increases at the average rates of $7.1 \times$ 10^{-4} , 3.8×10^{-4} , 1.6×10^{-4} , and

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Table 2. The change in the lattice parameters and the crystal structure of Tm with compression; P, pressure.

Run No.	hcp structure				D	Sm-type structure			
	с (Å)	a (Å)	c/a	$V/V_{ m o}$	(kbar)	с Å	a Å	c/a	V/V_{0}
1	5.573	3.534	1.577	1.000	0				
2	5.483	3.475	1.578	0.951	23				
3	5.360	3.403	1.575	.892	60				
4	5.247*	3.327	1.577*	.834	116	23.48	3.327	7.057	0.830
5	5.206*	3.301	1.577*	.815	140	23.37	3.301	7.080	.813

* The value of the c/a ratio was assumed to be the same as that at zero pressure.

 1.2×10^{-4} per kilobar, respectively. If this represents a trend of decreasing pressure dependence of the c/a ratio with increasing atomic number, then a negligibly small rate for Tm is reasonable.

If on the basis of the foregoing argument it is assumed that the axial ratio of the hcp phase at the transition is the same as at 1 bar and the a-axis dimension does not change during the transformation, we may calculate the volume compression of the hcp phase in run 4 to be $V/V_0 = 0.834$ with a corresponding pressure of approximately



Fig. 1. (a) Trace of the densitometer scan of the x-ray diffraction photograph of the high-pressure phase of Tm at approximately 116 kbar. The densitometer lacks the sensitivity and resolution to show all the features in the original film. Hence, the detailed information for the highpressure phase based on the original film is given in Table 1. (b) Trace of the densitometer scan of the hcp phase of Tm at approximately 60 kbar. This photograph of the original strip charts is included to permit the most direct comparison. The angle of diffraction is 2θ .

116 kbar. The volume change associated with the transition is $\Delta V = -0.08$ $cm^3/mole$ or -0.5 percent. Thus, the phase transformation represents a very small change in volume and takes place at some pressure between 60 and 116 kbar. No further change in crystal structure was observed up to 140 kbar.

The small value of the volume change at the transition is consistent with the nature of the stacking rearrangement. This kind of phase transformation is difficult to detect by means of dilatometry and by shock methods, and so it is not surprising that the transition in Tm has escaped notice until now.

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