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Symmetry lowering under high pressure: Structural evidence for *f*-shell delocalization in heavy rare earth metal terbium

Nicholas C. Cunningham,[1] Wei Qiu,[1] Kevin M. Hope,[2] Hanns-Peter Liermann,[3] and Yogesh K. Vohra[1]
[1]*Department of Physics, University of Alabama at Birmingham (UAB), Birmingham, Alabama 35294-1170, USA*
[2]*Department of Biology, Chemistry and Mathematics, University of Montevallo, Montevallo, Alabama 35115, USA*
[3]*High Pressure Collaboration Access Team (HPCAT) and Geophysical Laboratory, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*
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Heavy rare earth metal terbium has been studied at synchrotron sources using both angular and energy dispersive x-ray diffraction to a maximum pressure of 155 GPa (volume fraction $V/V_0=0.39$). The complete regular trivalent rare earth structural sequence, hcp → α-Sm → double hcp → fcc → distorted fcc ($hR24$), is observed at low pressures except for the undistorted fcc. At 51±2 GPa, terbium undergoes a 5% volume collapse transitioning to $C2/m$ monoclinic. The open, low symmetry structure is reminiscent of the 4*f* delocalization phenomenon in the light rare earth metals, particularly the α'' phase of cerium.

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The nature of the 4*f* electrons in many rare earth metals and compounds may be broadly characterized as being either "localized" or "itinerant," and it is held responsible for a wide range of physical and chemical properties.[1–3] The localized state is marked by tightly bound shells or narrow bands of highly correlated electrons near the Fermi level, and it is observed at ambient conditions for all of the rare earth elements. The regular trivalent rare earth structural sequence,[4,5] observed at low pressures for La through Lu excepting Eu and Yb as a function of increasing pressure or decreasing atomic number, typifies this behavior. The structures are all close packed and of high symmetry, and the sequence hexagonal close packed (hcp) → α-Sm → double hexagonal close packed (dhcp) → face centered cubic (fcc) may be reproduced solely by transfer of *sp* electrons to the *d* band.[6,7] The same sequence is observed under pressure in 4*d* metal yttrium, which has no adjacent *f* states. Application of pressure directly increases the electron density, leading to a distortion of the fcc phase except in the case of cerium, which collapses isostructurally. At present, it is not clear whether this *d*-fcc phase is the same for all rare earth past Ce.[8–11] Under further compression, the 4*f* electrons become itinerant, fully participating in chemical bonding. This leads to open, low symmetry structures similar, and in some cases identical, to those observed in the light actinides. The transition is of first order and may be accompanied by a discontinuous drop in volume, a lowering of electrical resistivity, and a stiffening of the crystalline lattice.[12–15] This sudden formation of an additional conduction band is analogous to the Mott insulator-to-metal transition. Many features of the transition may also be explained by the Kondo volume collapse model,[16] and recent theoretical work[17] indicates that the models may be compatible. This change in *f*-electron behavior under pressure has a remarkable effect on the melting behavior, and a triple point or a broad minimum in melting curve is observed in rare earth metals.[18] In addition, *f*-electron delocalization induced insulator-metal transitions are expected in rare earth monochalcogenides,[19] and *f*-electron delocalization induces a considerable bond shortening in rare earth alloys.[20]

Perhaps the most studied and best-understood structural transitions in the rare earths are those of cerium, which, with only a single *f* electron per atom to drive them, are accessible at relatively low pressure. It has an isostructural fcc-fcc′ collapse at 0.7 GPa and room temperature, and attains a low symmetry structure more characteristic of *f*-electron participation in bonding at 5 GPa.[14] This delocalized phase may be either orthorhombic α-uranium (called α' phase) or monoclinic $C2/m$ (called α'' phase), depending on sample preparation and thermodynamic history, with the question of ultimate stability still not entirely settled.[21] Terbium, the first 4*f*-shell element past half-filling, occupies a homologous position to cerium in the heavy rare earths; the nominal filling of its *f* shell consists of seven *f* electrons forming a spherically symmetric half-shell and one additional electron with the opposite spin. Terbium is shown in this Brief Report to follow the same structural sequence under pressure as cerium, albeit without the isostructural collapse and at higher pressures with much broader regions of stability for each phase. The observation of the same monoclinic $C2/m$ in Tb after several other structural transformations and at a pressure well in excess of the expected influence of cold working in sample preparation argues that this should be the thermodynamically stable phase, though anisotropic strain may influence this result. It is also demonstrated that Tb lies at a local structural critical point, having a lower delocalization pressure than those of the neighboring elements. This is posited to represent either a minimum in the stability energy gained by localized correlation in the *f* shell or a maximum in the stability energy gained through delocalization and distortion into a low symmetry structure.

Two high-pressure diamond anvil cell powder diffraction experiments (I and II) were performed at ambient temperature on elemental terbium (99.9% stated purity foil purchased from Alfa Aesar) using stainless steel gaskets and no pressure medium. Samples sealed under argon atmosphere were opened under a microscope and were mechanically polished to remove any surface oxide layer and quickly loaded in the diamond anvil cell. The heavy rare earth metals are less reactive as compared to light rare earth metals (Ce and Pr), and x-ray diffraction of Tb loaded in the diamond anvil cell shows peak characteristic of a pure hcp phase and no contamination of an oxide phase was detected. Pressures were measured using a copper pressure marker.[22] Results are confirmed using both angular and energy dispersive x-ray diffractions (ADXD and EDXD). Experiment I used a matched pair of 300 μm culet anvils and was conducted at the National Synchrotron Light Source (NSLS) hutch X17-C using EDXD with a collimated beam cross section of approximately 10×10 μm^2. The EDXD spectra were collected to 54 GPa in experiment I and the sample was decompressed to ambient pressure. In experiment II, we employed a matched pair of beveled diamond anvils with a central flat of 100 μm, with a bevel angle of 7°, and a culet of 300 μm in diameter. Experiment II was conducted at the Advanced Photon Source (APS) beamlines BM-D (EDXD) and ID-B (ADXD) with a collimated spot size of approximately 5×5 μm^2. The highest static pressure of 155 GPa was achieved in experiment II, and x-ray diffraction data were both collected during compression and decompression. In EDXD experiments, product of energy (E) and interplanar spacing (d) was $Ed=50.836$ KeV Å. In ADXD experiments, the x-ray wavelength was $\lambda=0.3678$ Å and the sample-detector distance was 350 mm. Results from both techniques concur, indicating that the metal remains relatively "soft," and the choice to omit any pressure medium is valid; significant texturing would have led to a characteristic spottiness to the angular dispersive spectra and could have significantly altered or even obliterated the energy dispersive peak intensities. No long relaxation times were utilized between data points to ensure thermodynamic stability and possibly alleviate the observed polytypism, except for a delay of several months between compression and decompression of the highest-pressure sample. Further, heat annealing is contraindicated by the case of cerium, where the monoclinic α'' phase may be partially transformed to large grains of the orthorhombic α' phase by temperature cycling.[21] It remains possible that transition pressures were affected by shear stresses induced by anisotropic strain[23] though peak locations, intensity ratios, and widths do not vary unexpectedly for the fcc Cu pressure marker even to the highest pressure.

Terbium is the first of the heavy rare earths, those past half-filling of the f shell; the presence of only a single unpaired f electron may explain the observed similarities to cerium. It exhibits the complete regular trivalent rare earth structural sequence beginning with hcp, with the possible exception of fcc, which was not observed as a pure phase. This phase is also not observed in the two subsequent heavy rare earths, Dy (Ref. 24) and Ho (Ref. 10), and an argument is presented in Ref. 10 for its disappearance at some point in the rare earth series based on the fact that fcc symmetry can only exist at perfect close packing. The low-pressure phases of the rare earths are only approximately close packed; for instance, the c/a axial ratio observed in Tb at ambient pressure is only 1.58 rather than the ideal 1.63, with the degree of close packing being improved under pressure.

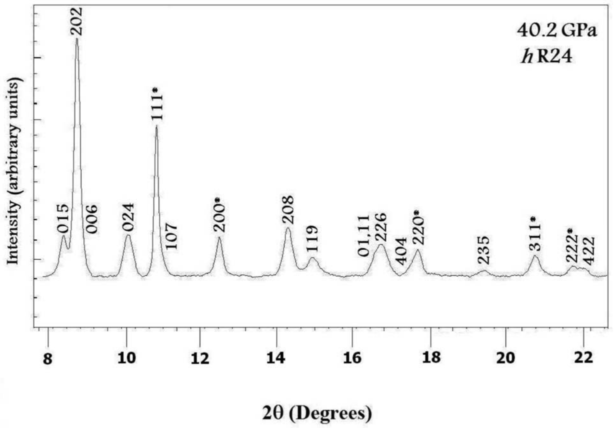

FIG. 1. Angle dispersive x-ray diffraction (ADXD) spectrum of terbium showing the $hR24$ distorted-fcc phase at 40.2 GPa. Sample peaks are labeled by their fitted hkl values, and reflections from the copper pressure marker are marked with an asterisk. This $hR24$ phase is similar to the one proposed by Hamaya *et al.* (1994) for light rare earth metal praseodymium, and is the first phase in terbium, which cannot be explained by pressure-induced occupation of the d band. The x-ray wavelength $\lambda=0.3678$ and sample-detector distance is 350 mm.

At 30±3 GPa, fcc peaks begin to be observed among the dhcp peaks. This is a first order transition with a region of coexistence between the phases, and the phase is initially represented only by a small portion of the sample. The weak superlattice peaks distinguishing the distorted-fcc phase from the pure fcc phase might have been present below the background limit in this region. After the disappearance of the dhcp phase, the spectra are clearly fit as the $hR24$ phase of Hamaya *et al.*,[8] which is also observed in neighboring elements Gd (Refs. 12 and 25) and Dy.[24] Figure 1 shows an angular dispersive diffraction spectrum of this phase at 40.2 GPa for the 24 h phase. Analysis was carried out using primarily the XRDA (Ref. 26) software. The measured lattice parameters are $a=6.006$ Å and $c=14.30$ Å with volume per atom of 18.61 Å^3/atom. Table I lists the refined atomic positions for the $hR24$ phase at 40.2 GPa.

At 51±2 GPa, Tb experiences a 5% collapse in volume per atom on compression and transforms to a low symmetry $C2/m$ monoclinic phase similar to the α'' phase of cerium [space group 12 with atoms at the 4(i) positions]. As explained in Ref. 21, the body centered monoclinic structure proposed for Gd (Ref. 12) and Dy (Ref. 24) is a special case of $C2/m$, and both are closely related to the fcc phase. The observation of additional peaks, not predicted by body centered monoclinic, precludes that additional symmetry, and the $C2/m$ phase is assigned in accordance with Ce and more recent results on Gd.[25] Figure 2 shows the ADXD pattern recorded at the highest pressure with diffraction peaks indexed to the $C2/m$ phase of terbium and a fcc phase indexed to the copper pressure marker. The measured lattice parameters for the $C2/m$ phase shown in Fig. 2 at 155 GPa are $a=4.519$ Å, $b=2.669$ Å, $c=4.296$ Å, and $\beta=105.4°$ with volume per atom of 12.48 Å^3/atom. Table I lists the refined atomic positions for the $C2/m$ phase at 155 GPa. Despite this sudden drop in volume, it is not clear that full delocalization of the f electrons occurs abruptly. Recent measurements on Gd (Ref. 27) show only a gradual loss of local magnetic ordering after the symmetry lowering transition, supporting the Kondo volume collapse model and screening of the correlated f-electron paramagnetic moments by the

TABLE I. Lattice parameters and atomic position parameters for the *hR*24 and *C*2/*m* high-pressure phases of terbium.

Pressure (GPa)	High-pressure phase	Lattice parameters	Atomic positions	Volume per atom (Å^3/atom)
40.2	*hR*24	a=6.006 Å, c=14.30 Å	Space group *R*-3*m* with atom positions 6*c*, x=y=0, z_1=0.272; 18*h*, x=0.508, y=−0.508, z_2=0.243	18.61
155	*C*2/*m*	a=4.519 Å, b=2.669 Å, c=4.296 Å, β=105.4°	Space group *C*2/*m* with atom positions 4*i* (0.280, 0, 0.252)	12.48

conduction electrons. Though the monoclinic *C*2/*m* phase is observed to be stable to at least 155 GPa, the presence of the tetragonal body-centered-tetragonal phase at extreme compressions in both cerium, which has one 4*f* electron, and thorium, which has one 5*f* electron, indicates the possibility of observing a similar phase in terbium at ultrahigh pressures. Figure 3 shows the measured equation of state of terbium to be 155 GPa at room temperature. The experimental data from both experiments have been included in Fig. 3 and a volume collapse of 5% at phase transformation to *C*2/*m* phase is obvious at 51 GPa. The decompression data indicated by filled symbols in Fig. 3 show good agreement with the compression data.

In conclusion, we performed several high-pressure experiments on heavy rare earth metal terbium, the first 4*f* element past half-filling, using both angular and energy dispersive x-ray diffractions. Two previously unknown transitions are observed, *hR*24 distorted fcc at 30±3 GPa, and *C*2/*m* monoclinic at 51±2 GPa. The latter phase is analogous to the α'' phase of cerium, providing evidence for *f*-electron delocalization in Tb and arguing for the thermodynamic stability of that phase in light rare earth metal Ce. The *C*2/*m* monoclinic phase was found to be stable to the highest pressure of 155 GPa or a volume compression V/V_0=0.39.

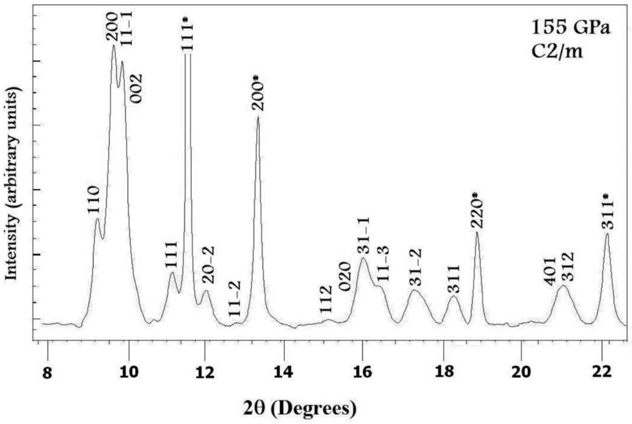

FIG. 2. ADXD spectrum of terbium at the highest pressure of 155 GPa in the *C*2/*m* phase. Sample peaks are labeled by their fitted *hkl* values, and reflections from the copper pressure marker are marked with an asterisk. The *C*2/*m* phase is similar to the α'' monoclinic phase observed in cerium and is taken as evidence in favor of delocalization of the *f*-shell electrons. The x-ray wavelength λ=0.3678 and sample-detector distance is 350 mm.

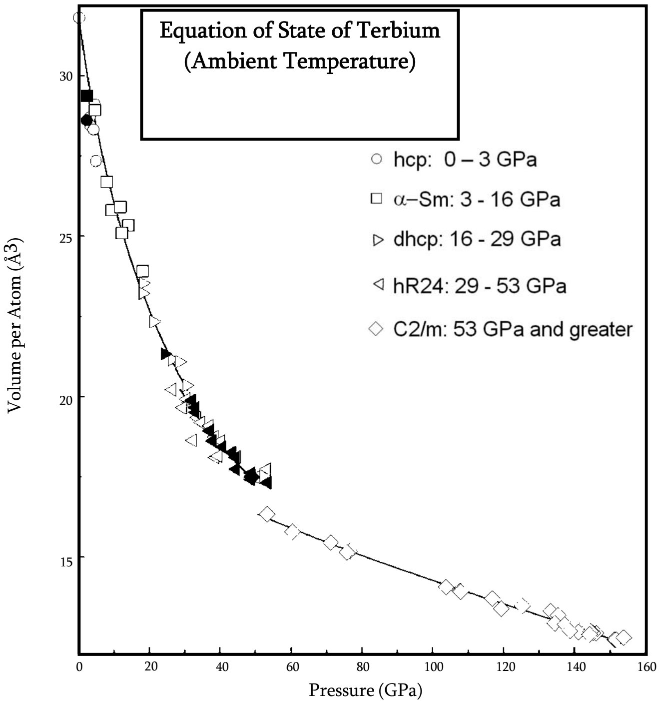

FIG. 3. Volume per atom as a function of pressure; filled symbols are decompression data points. The equation of state has been measured to 155 GPa at room temperature and includes data points from both experiments I and II. The complete regular trivalent rare earth structural sequence is observed with the exception of fcc, which was not observed as a pure phase. At 51±2 GPa, a 5% volume collapse is observed as the structure transitions to the open, low symmetry *C*2/*m* phase. Note the sharp decrease in compressibility for this phase, indicating a change in the character of the metallic bonds, which is argued to be the onset of *f*-electron participation in bonding.

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