

Unified High-Pressure Phase-Transition Sequence in the f -Electron Metals: $oF16 \rightarrow oF8$ Transition in Terbium

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(Received 18 March 2024; revised 15 October 2024; accepted 22 August 2025; published 24 September 2025)

The lanthanide elements have long been reported as having a common series of structural phase transitions on compression, but recent diffraction studies have revealed *two* series of transitions: one in the low- Z lanthanides (Nd and Sm) involving an 8-atom orthorhombic structure ($oF8$), also seen in some actinide elements, and another in the high- Z lanthanides (Gd, Tb, Dy, and Ho) involving an isosymmetric 16-atom structure ($oF16$), unique to the lanthanides. No element has yet been found to exhibit both structures. We have followed the structural evolution of Tb to 308 GPa and find that $oF16$ -Tb transforms to $oF8$ -Tb at 234 GPa, which is stable to at least 308 GPa. This transition is confirmed by theoretical results which show the $oF8$ phase becoming energetically favorable above 280 GPa. This observation of the $oF16 \rightarrow oF8$ transition unites the two phase-transition sequences and suggests that there is a common $oF16 \rightarrow oF8 \rightarrow oC4 \rightarrow tI2$ transition sequence in the lanthanide elements under pressure.

DOI: 10.1103/r3zx-k97x

Introduction—The lanthanide series of metals (La to Lu) are characterized by the monotonic increase in the number of their $4f$ electrons. As electron interactions are readily modified by changing interatomic distances, the study of the lanthanide elements under pressure has been critical in developing an understanding of f -electron behavior at high densities [1–6].

Compression of the predominantly trivalent lanthanides (La to Lu, excluding Ce, Eu, and Yb) results in an $s - d$ electron transfer, and the increased d -band occupancy gives rise to a common phase-transition sequence between structures comprising close-packed layers: hcp (space group $P6_3/mmc$ and $hP2$ in Pearson notation), Sm-type ($R\bar{3}m$ and $hR3$), double- hcp ($dhcp$, $P6_3/mmc$ and $hP4$), fcc ($Fm\bar{3}m$ and $cF4$), and distorted- fcc ($d - fcc$, $R\bar{3}m$ and $hR24$) ([5,6] and references therein).

At higher pressures, many of the lanthanides were long reported [6] to transform via a first-order transition into a monoclinic structure ($C2/m$ and $mC4$) first observed in Ce [7] and subsequently reported in Gd, Tb, Dy, Ho, Er, and Tm [6,8–11]. More recently, we have shown that the $mC4$ structure is *only* observed in Ce at high pressures: Nd and Sm [12,13] transform to an 8-atom orthorhombic structure ($Fddd$, $oF8$) first seen in Pu [14] and subsequently in Am, Cm, and Cf [15–18], while a transition to an isosymmetric 16-atom structure ($Fddd$, $oF16$) has been observed in the heavier lanthanides [19–23] and in Y [24,25].

In establishing the structural systematics of the lanthanides and the connection to the systematics seen in the actinides [2,4,5], the question arises as to what the $oF8$ and $oF16$ structures will transform to on further compression. $oF8$ -Nd has been reported to transform to the orthorhombic α -uranium ($oC4$) structure at 98 GPa, which is then stable to at least 302 GPa [13], and the same transition has been observed in Pr at 171 GPa [26]. In the actinides, the $oF8$ phases of Am, Cm, and Cf all transform to a phase which has a distorted- $oC4$ structure. However, there have been no reports to date of further transitions in the $oF16$ structure of any lanthanide.

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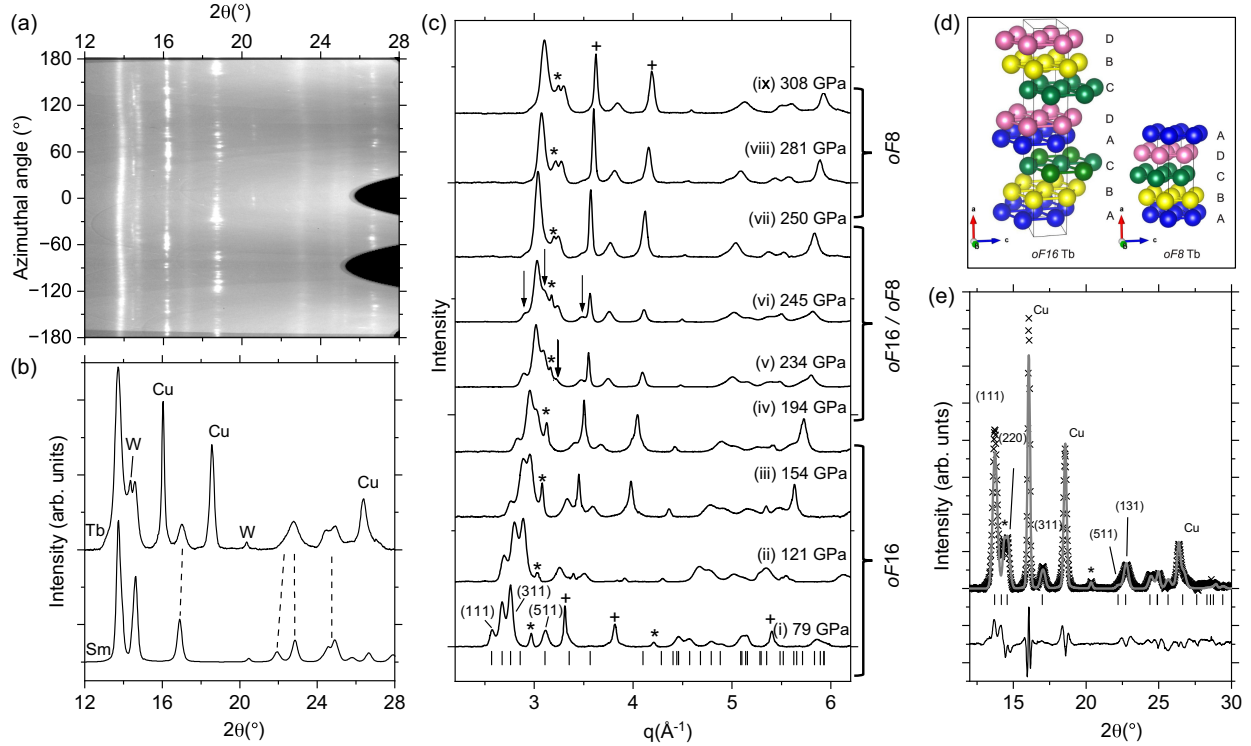


FIG. 1. (a) 2D “cake” plot of Debye-Scherrer diffraction pattern from Tb at 308 GPa. (b) Integrated and background-subtracted diffraction profile of Tb from (a), together with the analogous pattern from Sm-*oF8* [12], shifted in 2θ to facilitate comparison. (c) Waterfall plot of selected diffraction profiles collected from Tb on pressure increase, with *oF16*-Tb tick marks beneath profile (i) and peaks from W (asterisk) and Cu (plus) marked. The arrow in profile (v) marks the first appearance of a peak from the higher-pressure phase, while arrows in profile (vi) identify the (111), (311), and (511) peaks from *oF16*-Tb, which decrease in intensity at pressure above 234 GPa. (d) *oF16* and *oF8* structures, highlighting the different stackings of the layers. (e) *oF8* Rietveld fit to the diffraction profile at 302 GPa (crosses), with ticks at calculated reflection positions, asterisks marking peaks from W, and the difference profile shown below.

While the lanthanides and actinides clearly share a series of phase transitions, there is a missing link between the chain of transitions seen in the high-Z lanthanides,

$$hP2 \rightarrow hR3 \rightarrow hP4 \rightarrow hR24 \rightarrow oF16 \rightarrow ?,$$

and that observed in the low-Z lanthanides,

$$hP4 \rightarrow cF4 \rightarrow hR24 \rightarrow hP3 \rightarrow oF8 \rightarrow oC4 \rightarrow tI2,$$

and the actinides Am, Cm, and Cf,

$$hP4 \rightarrow cF4 \rightarrow mC4 \rightarrow oF8 \rightarrow \text{distorted-}oC4.$$

Terbium (Tb) transforms to the *oF16* structure at only 54 GPa, the lowest pressure of any of the trivalent lanthanides, and was therefore thought to transform to the post-*oF16* phase at the most accessible pressure. A transition had been previously noted by Finnegan [27], and an *oF8* structure was suggested, but mixed-phase patterns obtained up to 247 GPa prohibited any conclusive structure identification. We have now compressed Tb to

above 300 GPa and find that, on pressure increase from 226 to 234 GPa, *oF16*-Tb undergoes a structural transition to another phase that we conclusively show has the *oF8* structure.

Methods—High-purity distilled samples of Tb supplied by Ulrich Schwarz at the Max-Planck-Institut für Chemische Physik fester Stoffe in Dresden were loaded into three Boehler-Almax plate diamond-anvil cells (DACs) [28] in a dry argon atmosphere (< 0.1 ppm O_2 and < 0.1 ppm H_2O) to prevent oxidation. Tungsten (W) gaskets and copper (Cu) pressure markers were used in all DACs [29]. Electronic structure calculations and structure optimizations were performed with VASP [30], utilizing the Perdew-Burke-Ernzerhof functional [31]. Full experimental and computational details are provided in the End Matter.

Results—The 2D diffraction image, displayed as a so-called “cake” plot, and the integrated profile from Tb at the highest pressure reached in this Letter, 308 GPa, are shown in Figs. 1(a) and 1(b), respectively. Mild stress effects manifest as slightly “wavy” vertical lines, but these are not so wide as to significantly broaden the integrated diffraction peaks.

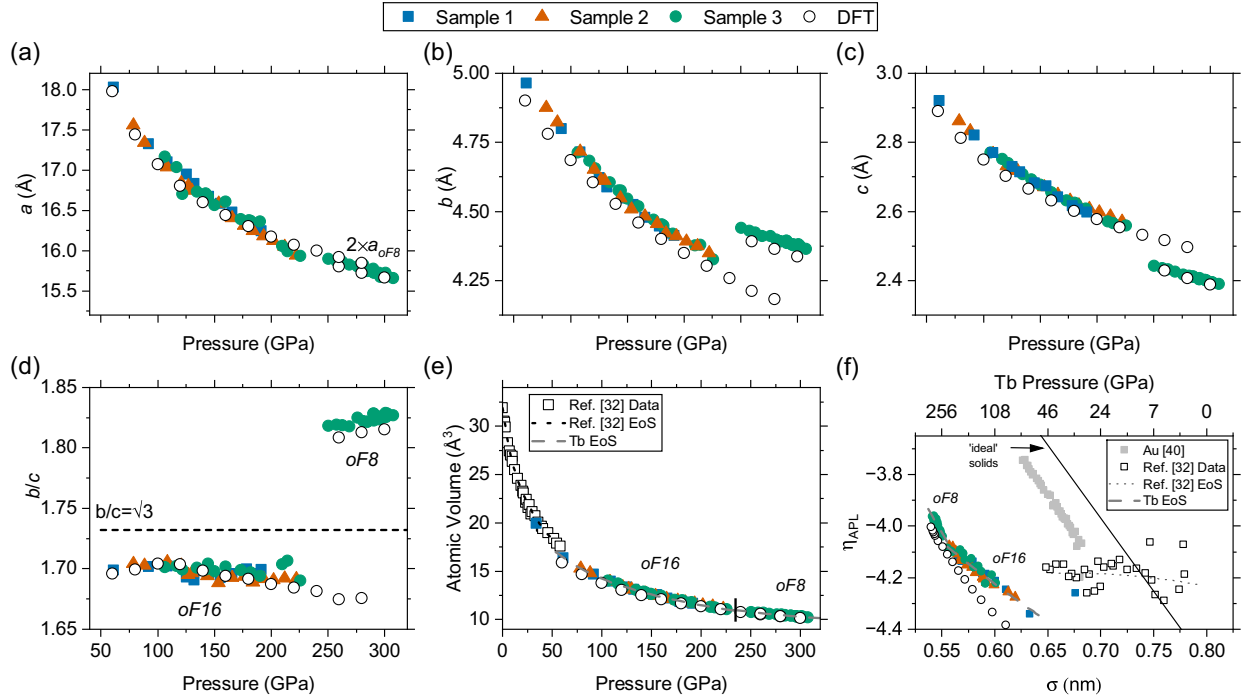


FIG. 2. (a)–(c) Pressure-dependence of a , b , and c lattice parameters, respectively, of the $oF16$ and $oF8$ structures across the phase transition, from our experimental (solid symbols) and theoretical (open symbols) results. (d) Hexagonality of the atomic layers in the $oF16$ and $oF8$ structures, as quantified by the b/c axial ratio. (e) Compressibility up to 308 GPa with fitted EoSs, with low-pressure data from Ref. [32]. (f) Linearization of the compressibility in $\eta_{APL}(\sigma)$ -space, with low-pressure data from Ref. [32]. In all panels the error bars are smaller than the symbols used to plot the data and have been omitted.

Single-phase $oF16$ profiles were observed at 79 GPa, and Fig. 1(c) shows a waterfall plot of selected diffraction profiles collected from Tb on further pressure increase from 79 to 308 GPa. As the data were collected from different samples during different synchrotron visits they are plotted as a function of wave-vector q to account for the different x-ray wavelengths used. No changes were seen until the pressure was increased to 234 GPa, where an additional diffraction peak began to appear on the high- q side of the W gasket (110) peak. This peak grew in intensity on further pressure increase [profiles (vi)–(ix)] while, simultaneously, the intensity of the (111), (113), and (115) peaks from the $oF16$ phase decreased. As a result, the (almost) single-phase diffraction profiles obtained above 250 GPa are simplified compared to those observed at lower pressures. At 308 GPa, the diffraction profile of Tb showed a clear resemblance to data obtained from the $oF8$ phases of Nd [13] and Sm [12] [Fig. 1(b)].

These similarities led us to perform a Rietveld fit to a diffraction profile from Tb at 302 GPa [chosen as it exhibits a weaker diffraction signal from the gasket than the 308 GPa profile shown in Figs. 1(a) and 1(c)]. The results are shown in Fig. 1(e), where preferred orientation in the (100) direction was accounted for. The fit is very good, with all observed diffraction peaks explained by the $oF8$ structure with atoms at Wyckoff positions $8a$, lattice

parameters $a = 7.827(5) \text{ \AA}$, $b = 4.365(1) \text{ \AA}$, and $c = 2.3893(6) \text{ \AA}$, resulting in $R_{\text{obs}} = 12.27\%$.

The $oF16$ and $oF8$ structures of Tb [Fig. 1(d)] both comprise stacking of quasi-close-packed layers, with an eight-layer ABCADCBD sequence in $oF16$ and a four-layer ABCD sequence in $oF8$. Despite the similarities of the structures, their high symmetry and the halving of the a axis at the transition mean that all but the (800) reflection of $oF16$ -Tb [which becomes the (400) of $oF8$ -Tb] disappear at the transition, replaced by new reflections from the $oF8$ phase. Thus, it was not possible to accurately determine the lattice parameters of the two phases from the mixed-phase profiles observed between 226 and 250 GPa.

The measured lattice parameters of the two phases across the phase transition are shown in Figs. 2(a)–2(c), together with the values obtained from our density functional theory (DFT) investigation. The experimental and theoretical results are in very good agreement, with only some systematic discrepancies in the b parameter, which is calculated to be 1.1(4)% smaller than observed.

In Fig. 2(a) we plot $2 \times a_{oF8}$ to allow for a direct comparison with a_{oF16} . Despite the similarities of these isosymmetric structures, discontinuities are observed in all three lattice parameters. In particular, there is a $\sim 0.15 \text{ \AA}$ increase in the b lattice parameter and a $\sim 0.1 \text{ \AA}$ decrease in the c lattice parameter at the transition. In each structure,

TABLE I. Fitted AP1 and AP2 parameters and cross-correlation terms of the *oF16* and *oF8* EoSs. V_0 was fixed to the ambient value [33] while fitting.

Phase EoS Form	<i>oF16</i> AP2	<i>oF8</i> AP1
V_0 (Å ³)	31.969	31.969
K_0 (GPa)	21.6(7)	7.74(2)
K'_0	4.52(6)	
$\sigma_{K_0}\sigma_{K'_0}$	-0.0378	
$w\text{-}\chi^2$	5.12	3.86

the distortion of the atomic layers from true hexagonal symmetry can be quantified by the deviation of the b/c axial ratio from the “ideal” orthohexagonal value of $\sqrt{3} = 1.732$, seen in the *hP3* phases of Nd and Sm [12,13]. Discontinuities observed in the b and c lattice parameters result in a sizable discontinuity in b/c [Fig. 2(d)] such that in the *oF16* structure the layers are elongated along c relative to hexagonal symmetry, while in the *oF8* structure they are elongated (relatively) along b . A comparison with the *oF16* and *oF8* structures reported previously [12,13,19–22,24,25] shows that in all cases the *oF16* structures have a b/c ratio of 1.70 while in the *oF8* structures the ratio is 1.79–1.81. The *oF8* structure has also been reported in the actinide elements Am [15], Cm [16], and Cf [17], where there is more variation in the b/c ratio, which ranges from 1.82 in Am to 1.94 in Cm.

The compressibility of Tb up to 308 GPa is shown in Fig. 2(e). Below 50 GPa, we show the compressibility data and best-fitting equation of state (EoS) of Grosshans and Holzapfel [32]. Extrapolating the fitted EoSs (Table I) to the phase-transition pressures, the volume changes ($\Delta V/V_0$) at the *hR24* $\rightarrow$ *oF16* and *oF16* $\rightarrow$ *oF8* transitions are 2.7% and 0.2%, respectively.

In recent studies [12,13,24,26,34–36], we utilized Holzapfel’s Adapted Polynomial of order L (APL) EoS [37,38] to analyze the compressibility. This has several advantages over other formalisms and enables the compressibility to be linearized straightforwardly, plotting it as $\eta_{\text{APL}}(x)$ where $x = (V/V_0)^{1/3}$. Nonlinear behavior can then be interpreted as a deviation from “regular” compressive behavior expected from a “normal” metal [39]. Here, we have substituted $x = \sigma/\sigma_0$, where σ_0 is the Thomas-Fermi radius $\sigma_0 = (3ZV_0/4\pi)^{1/3}$, to obtain $\eta_{\text{APL}}(\sigma)$, which facilitates comparison between different elements (details in the End Matter).

The linearized compression data of Tb obtained here, those of Grosshans and Holzapfel [32] below 50 GPa and those of “regular” Au for comparison [40], are shown in Fig. 2(f). The *oF16*-*oF8* transition is marked by a clear change in gradient, hardly perceptible on the P - V plot, which necessitated the fitting of two distinct EoSs to the two phases, with fitted parameters shown in Table I.

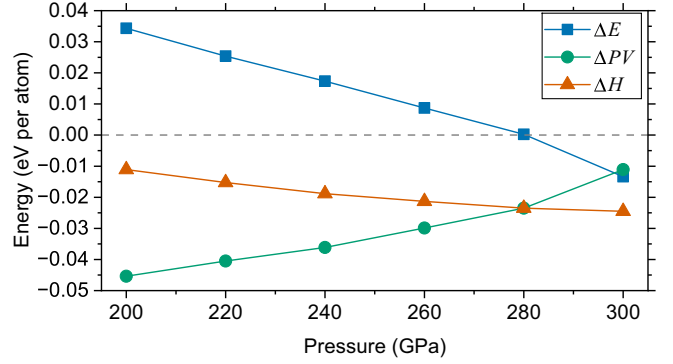


FIG. 3. Difference in total energy ($\Delta E = E_{oF8} - E_{oF16}$), PV [$\Delta(PV) = PV_{oF8} - PV_{oF16}$], and total enthalpy ($\Delta H = H_{oF8} - H_{oF16}$) between the *oF8* and *oF16* phases as a function of pressure between 200 and 300 GPa. The calculated transition pressure is 280 GPa. Here, $H = E + PV$, and hence, $\Delta H = \Delta E + \Delta(PV)$.

Notably, the *oF8* phase is well described by a simple, single-parameter (K_0) AP1 equation of state, with a slope close to the “ideal.” This contrasts with the nonideal or nonlinear behavior of the lower-pressure phases. In theory, this linear trend for *oF8*-Tb should persist to ultimate compression, mirroring the behavior of other lanthanides [12,13,26].

Electronic structure calculations—Comparing the total energy of the *oF16* and *oF8* phases as a function of pressure (Fig. 3), *oF16* is favorable up to 280 GPa, above which the *oF8* structure has the lowest energy. The calculated transition pressure at 0 K is thus ~ 45 GPa higher than the value of 234 GPa that we observe experimentally at room temperature. The optimized lattice parameters at each pressure and the b/c axial ratio are shown in Fig. 2. The agreement with the experimental results, including the discontinuity observed in the b/c ratio at the *oF16* $\rightarrow$ *oF8* transition, is excellent.

Recently, Sneed *et al.* [22] used beyond-DFT calculations, accounting for nonlocal interorbital interactions [41], to predict an *oF16* $\rightarrow$ *oF8* transition in Dy ($Z = 66$) at 275 GPa, almost the same pressure that we predict for neighboring Tb ($Z = 65$). The agreement between our DFT results and those of Sneed *et al.* stems, in our view, from the observation that, at such a high pressure, the minimization of the total enthalpy is driven by the minimization of the unit cell volume, while the difference in the electronic state is negligible between the two phases. In other words, at high pressure, the PV term is much larger than the internal energy term, although the electronic correlations ultimately determine the lowest-energy phase.

Since VASP’s pseudopotential formalism is designed to closely reproduce the all-electron results at ambient pressure, we have estimated the deviation of the pseudopotential results from those obtained by all-electron methods at the extreme pressures relevant in the present Letter.

The details of the calculations for *cF4*-Tb are given in Supplemental Material [42], and it appears that the pseudopotential results are precise up to ~ 150 GPa. At higher pressures, up to $P = 350$ GPa, VASP and all-electron results differ by a few dozen GPa, amounting to a difference of 32 GPa at $P = 280$ GPa. Taking this as an absolute uncertainty on the VASP pressure explains much of the ~ 46 GPa difference between the experimental and theoretical transition pressures.

Nonetheless, electronic correlation effects play a central role in the lower-pressure phase transitions in Tb. For instance, as reported in our earlier work [20], the *hR24* to *oF16* structural transition at 54 GPa exhibits a profoundly different magnetization behavior as a function of pressure, also seen experimentally [46], where the theoretical description of the unscreened magnetic moments is key to fully understanding the transition. Thus, at low pressure, electronic effects and nonlocal interactions dominate, and Tb can be seen as a network of weakly coupled unscreened magnetic moments [20]. Although local magnetic moments remain at higher pressure, the phase transition to the *oF8* phase is controlled by the interplay between volume and pressure and the stacking of the quasi-close-packed layers.

Discussion and conclusions—The observation of the *oF8* $\rightarrow$ *oF16* transition in Tb and our recent report of the *oC4* $\rightarrow$ *tI2* transition in Pr suggest that the full transition sequence in the lanthanides is as follows:

$$\begin{aligned} hP2(hcp) &\rightarrow hR3(\text{Sm-type}) \rightarrow hP4(dhcp) \rightarrow cF4(fcc) \\ &\rightarrow hR24(d-fcc) \rightarrow hP3 \rightarrow oF16 \\ &\rightarrow oF8 \rightarrow oC4 \rightarrow tI2, \end{aligned}$$

while that in the actinides is

$$hP4(dhcp) \rightarrow cF4(fcc) \rightarrow oF8 \rightarrow \text{distorted-}oC4/oC4.$$

However, there are a few additional points of note: (1) No lanthanide has yet been found to go through the entire transition sequence. Should Tb be compressed to significantly higher pressures in the future, then the remaining *oF8* $\rightarrow$ *oC4* and *oC4* $\rightarrow$ *tI2* transitions may be observed. (2) The *hP3* phase has been seen only in Nd and Sm at room temperature [47] and in the rare earth Yb [48]. (3) Some phases are “missing” in a number of the lanthanides: the *oF16* phase is not seen in La, Pr, Nd, or Sm, the lower-Z lanthanides, at 300 K. Similarly, the *cF4* phase has not been seen in any high-Z lanthanide beyond Gd. (4) The distorted-*fcc* phase has typically been reported as having the rhombohedral *hR24* structure [49], but in Dy [50], a different orthorhombic distorted-*fcc* structure has been reported. (5) No transition from the distorted-*oC4*/*oC4* phase to *tI2* has been observed in any actinide, though *tI2* is calculated to be the structure of the post-*oC4* phase in U above ~ 285 GPa [51] or 363 GPa [52].

While recent studies have illuminated the structural behavior of the lanthanide and actinide elements under pressure, a fully consistent picture has yet to emerge. Understanding the remaining differences will require experimental studies to higher pressures and perhaps non-ambient temperatures and computational studies calculating behavior at pressures currently inaccessible experimentally.

Note added—During the lengthy reviewing process for this manuscript, Li *et al.* published a study of Dy to 337 GPa and reported an *oF16* $\rightarrow$ *oF8* transition at 196 GPa [53]. The pressure dependence of the lattice parameters and *b/c* axial ratio across the transition in Dy are very similar to those shown in Fig. 2 for Tb.

Acknowledgments—This work was supported by Grants No. EP/R02927X/1 and No. EP/Z533671/1 from the UK Engineering and Physical Sciences Research Council (EPSRC). We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at PETRA III, and we would like to thank N. Giordano and H.-P. Liermann for their assistance in using beamline P02.2. Beamtime was allocated for Proposals No. I-20200606 EC and No. I-20220527. C.V.S., S.E.F., and J.D.M. are grateful to AWE for the award of CASE and iCASE studentships.

Data availability—The data that support the findings of this Letter are not publicly available. The data are available from the authors upon reasonable request.

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End Matter

Experimental methods—The plate DACs were equipped with tungsten (W) gaskets and diamonds [54] with 300 μm culets, beveled to diameters of 40 μm (Sample 1), 30 μm (Sample 3), and a toroidal 10 μm culet (Sample 2) milled using a focused ion beam according to the design of Jenei *et al.* [55]. The samples were loaded without any pressure transmitting medium to prevent contamination. All samples were loaded with a small (few μm diameter) Cu sphere to act as a pressure calibrant, using the recently published Cu equation of state (EoS) of Fratanduono *et al.* [29].

Diffraction data were collected in two experiments on the Extreme Conditions P02.2 beamline at the PETRA III synchrotron in Hamburg, Germany. Monochromatic x-ray beams of wavelength 0.4246 Å and 0.4839 Å were used,

focused down to a full-width at half-maximum (FWHM) of 850 nm $\times$ 850 nm [56], and the powder-diffraction data were recorded on a Perkin-Elmer area detector, placed 300–400 mm from the sample. A CeO₂ diffraction standard was used to calibrate the exact sample-detector distances and the detector tilts in each experiment. The highest pressure reached in each sample was 191 GPa using 40 μm -culet anvils and 222 GPa using toroidal anvils, while the 30 μm -culet anvils reached 308 GPa.

The two-dimensional (2D) diffraction images collected at each pressure were integrated azimuthally using Dioptas [57] to obtain standard one-dimensional diffraction profiles, which were then analyzed using Le Bail profile-fitting methods [58] or by fitting to the measured *d*-spacings of individual diffraction peaks [59].

The submicron beam available on beamline P02.2 enabled us to map the pressure distribution in each sample every ~ 25 GPa, with representative results at a central pressure of 270 GPa shown in Fig. S1 in Supplemental Material [42]. Notably, the FWHM of the x-ray beam is small in comparison to the pressure gradients present in the sample, negating their effect on the collected diffraction data.

Theoretical methods—The Monkhorst-Pack k -point mesh was chosen to ensure a k -point density of at least $0.02 \text{ \AA}^{-1}$ for both structures. A Gaussian smearing of 0.1 eV was used. During DFT structural optimization, a convergence on internal forces and stress tensor of $0.01 \text{ eV/\AA}$ was reached, and the plane-wave energy cutoff was set to 500 eV. Close to the transition pressure, where the energy differences between the structures are small, we verified our results using a higher energy cutoff of 800 eV.

The Tb pseudopotential was generated within the scalar relativistic Koelling-Harmon approximation [60], using the [Kr]4d¹⁰ core configuration and valence configurations of 4f⁸5s²5p⁶5d¹6s². For both phases, at all pressures, we performed spin-polarized calculations to treat the local magnetic moment but neglected spin-orbit coupling as we expected its contribution to the total energy to be negligible at extreme pressure.

APL EoS and linearization—The APL equation of state is of the form [37,38]

$$P(x) = 3K_0x^{-5}(1-x)e^{c_0(1-x)} \left[1 + x \sum_{k=2}^L c_k(1-x)^{k-1} \right], \quad (\text{C1})$$

where K_0 is the zero-pressure bulk modulus, K'_0 is its pressure derivative, $x = (V/V_0)^{1/3}$, $c_0 = -\ln(3K_0/P_{\text{FG0}})$, $c_2 = (3/2)(K'_0 - 3) - c_0$, c_k are independent fitting parameters for $k \in [3..L]$, $P_{\text{FG0}} = a_{\text{FG0}}(Z/V_0)^{(5/3)}$ is the Fermi-gas pressure, Z is the atomic number, and $a_{\text{FG0}} = 2337 \text{ GPa \AA}^5$ is a constant. Note that, in the lowest-order AP1 ($L = 1$) case, the summation term is zero and the only fitted parameters are the ambient pressure volume V_0 and bulk modulus K_0 .

To further investigate the compressive behavior, it is informative to display the data in a linearized space. The linearized form of an APL equation of state is

$$\eta_{\text{APL}}(x) = \ln \left[\frac{Px^5}{P_{\text{FG0}}(1-x)} \right],$$

with variables and constants as in Eq. (C1). In this space, a first-order AP1 equation of state is linear with the intercept at the origin. Finally, one can facilitate comparison between compression data from different materials by performing the substitution $x = \sigma/\sigma_0$, where σ_0 is the Thomas-Fermi radius $\sigma_0 = (3ZV_0/4\pi)^{1/3}$, to obtain a function $\eta_{\text{APL}}(\sigma)$.