

Crystal structures of ytterbium to 293 GPa

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Ytterbium (Yb) metal is unusual among the lanthanide elements in being divalent at ambient conditions, rather than trivalent, which gives it a distinct high-pressure phase transition sequence from that of other lanthanides. Here we describe an x-ray diffraction study of Yb up to 293 GPa to investigate the structure and compressibility of the *hP3* phase, which we find to be stable up to the highest pressure. We subsequently calculate a further phase transition to the orthorhombic *oF8* phase above ~ 330 GPa, in line with transitions seen in Nd and Sm. Our results underpin future studies of Yb compounds under pressure, in particular the synthesis of YbH_x polyhydrides, for which an accurate understanding of the structure and compressibility of elemental Yb is indispensable.

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I. INTRODUCTION

Unlike the other lanthanide elements, ytterbium (Yb) and europium (Eu) are divalent rather than trivalent at ambient conditions [1]. As a result, they have a significantly higher ambient atomic volume (Yb's volume is 40% larger than that of neighboring Lu) [1,2], and they have a behavior that is often compared to the divalent alkaline earth metals such as Sr and Ba [3] rather than the trivalent lanthanides. We have previously shown that Eu adopts complex incommensurate structures under compression unlike anything else seen in the other lanthanide elements, or indeed anywhere else in the periodic table [4,5]. Attempts prior to our work to unravel the complexities of Eu were hampered by the presence of contaminant phases [6], which were also clearly present (but not commented upon) in the most recent study [7].

The high-pressure phase transition sequence seen in Yb [*cF4*-I (fcc-I) $\rightarrow$ *cI2* (bcc) $\rightarrow$ *hP2* (hcp) $\rightarrow$ *cF4*-II (fcc-II) $\rightarrow$ *hP3*] (Fig. 1) [3] is very different to that in Eu [4,5], and is an intriguing hybrid between that of the alkaline metals and that of the trivalent lanthanides: the *cF4* $\rightarrow$ *cI2* $\rightarrow$ *hP2* phase transitions at 4 GPa and 26 GPa in Yb are seen in Sr and Ba [8,9], while the *cF4* and *hP3* phases seen in Yb above 53 GPa and 98 GPa, respectively, are found in Nd and Sm [10]. *hP3*-Yb is reported to be stable to 202 GPa, the highest pressure to which Yb has been studied [11,12]. However, in

both Nd and Sm, compression of the *hP3* phase results in a further transition to the orthorhombic *oF8* phase, found also in Pu [13,14].

This hybrid behavior in Yb arises from a continuous pressure-induced valence transition, where the valence increases from 2.0 at ambient pressure to 2.65 at 36 GPa [15,16]. As valence changes can lead to highly correlated electron effects, Yb's electrical resistivity and magnetic susceptibility have been studied to 179 GPa and revealed that Yb becomes a superconductor at 86 GPa with T_c increasing to 4.6 K at 179 GPa [17]. The same authors found that Yb remains mixed valent to at least 125 GPa, pointing to an active role of the *4f* electrons in the emergence of superconductivity. Comparison of the compressibility of Yb relative to that of the trivalent lanthanides shows the former to still be anomalously high at 200 GPa, as a result of valence fluctuations ($4f^{14} \rightarrow 4f^{13}$) and *s* – *d* electron transfer [11]. Indeed, at 200 GPa, Yb exhibits a V/V_0 of 0.26, while for neighboring Lu the compression ratio at the same pressure is 0.39 [12]. LDA + DMFT calculations by Ylvisaker *et al.* [18] attribute Yb's anomalous compressibility to a peak in the *4f* charge susceptibility near $n_f \approx 13.5$, a fluctuating-valence signature that single-particle methods cannot capture.

As such, while the high-pressure behavior of Yb is important for understanding both *f*-electron physics at high density and pressure-induced valence transitions, the discovery of superconducting lanthanide polyhydrides [19,20] has provided an additional stimulus to studying the high-pressure structural behavior of the lanthanide elements themselves. In particular, YbH_9 and YbH_{10} have both been predicted to form part of a “second island” of high- T_c superconductivity among the late-lanthanide polyhydrides as a result of their particular *f*-electron physics, with a predicted T_c as high as 80–100 K at 250 GPa [21]. While neither compound has yet been synthesized, great care must be taken in working with elements as chemically reactive as the lanthanides. As said, previous work on Eu [6,7] used contaminated samples, while

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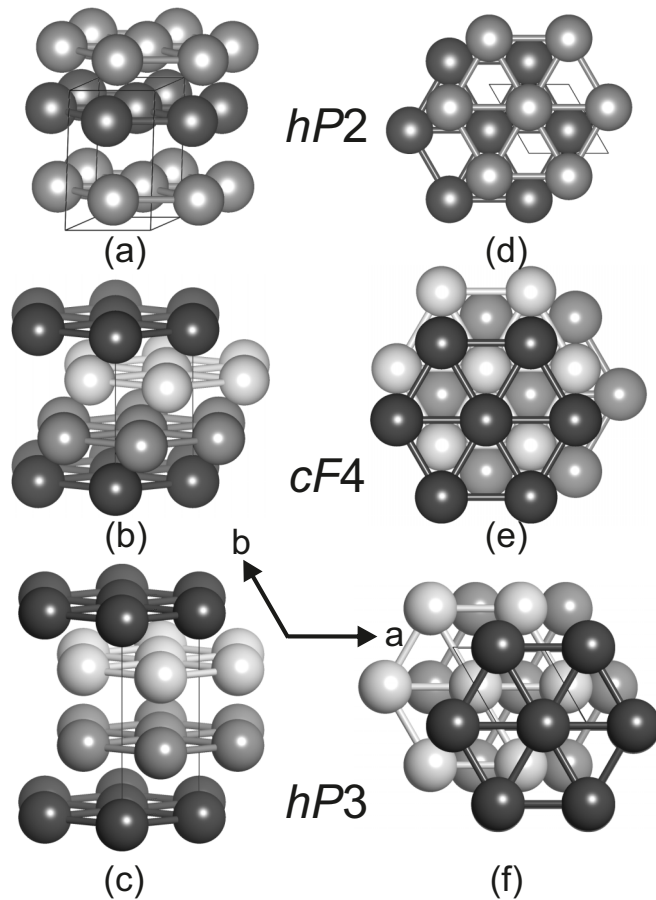


FIG. 1. The crystal structures of the hcp (*hP2*), fcc (*cF4*), and *hP3* phases of Yb, drawn so as to emphasize the packing of hcp-like layers in each structure. Note that while each atom in the hcp-like layers of *hP2* and *cF4* is equidistant from three atoms in each adjacent layer, giving 12-fold coordination, atoms in the hcp-like layers of *hP3* are equidistant from only two atoms in each of the adjacent layers, resulting in 10-fold coordination.

we have recently shown that 50% of the “lanthanum” used in previous work on synthesizing LaH_x [19,22] was actually a contaminant [23]. Accurate compression studies of pure Yb are thus required to underpin future synthesis research by providing the true crystal structure and the atomic volume at relevant pressures, from which the H stoichiometry can be determined accurately [23]. Here we describe a diffraction study of high-purity Yb to 293 GPa.

II. METHOD

High-purity distilled samples of Yb supplied by Ulrich Schwarz at the Max-Planck-Institut für Chemische Physik fester Stoffe in Dresden were loaded into two Boehler-Almax plate diamond-anvil cells (DACs) [24] in a dry argon atmosphere (<0.1 ppm O_2 and <0.1 ppm H_2O) to prevent oxidation. The plate DACs were equipped with tungsten (W) gaskets and diamonds [25] with 300 μm culets, beveled to diameters of 30 μm . The samples were loaded without any PTM to prevent contamination. All samples were loaded with

a small (few μm diameter) bismuth (Bi) grain to act as a pressure calibrant, using our recently published Bi equation of state [26].

Because this equation of state is only fitted for Bi-V, and because the peaks of *cI2*-Bi and *cI2*-Yb overlap too strongly to permit simultaneous measurement of both volumes below 11 GPa, no *P-V* data in this domain was included in the quantitative analysis.

Diffraction data were collected during experiments on the P02.2 beamline at DESY’s PETRA III synchrotron in Hamburg, Germany [27] (DAC1), and on the ID27 beamline at the ESRF-EBS synchrotron in Grenoble, France [28] (DAC1 continued and DAC2). At the ESRF-EBS, a monochromatic x-ray beam of wavelength 0.3738 Å was used, focused down to a full-width at half-maximum (FWHM) of 500 nm $\times$ 500 nm, and the powder-diffraction data were recorded on an EIGER2 X CdTe 9M photon counting area detector placed 190 mm from the sample. At PETRA III, a monochromatic x-ray beam of wavelength 0.4832 Å was used, focused down to a full-width at half-maximum (FWHM) of 850 nm $\times$ 850 nm, and the powder-diffraction data were recorded on a Perkin Elmer XRD 1621 photon counting area detector placed 342 mm from the sample. In both experiments, a CeO_2 diffraction standard was used to calibrate the exact sample-detector distance and the detector tilts.

The two-dimensional (2D) diffraction images collected at each pressure were integrated azimuthally using Dioptas [29] to obtain standard one-dimensional diffraction profiles, which were then analyzed using Le Bail or Rietveld profile-fitting methods in Jana2006 [30] or by fitting to the measured *d* spacings of individual diffraction peaks [31]. The 2D diffraction image and integrated profile from Yb at 293 GPa, the highest pressure reached in this study, are shown in Fig. 2. We saw no significant strain broadening or associated azimuth dependence of the *d* spacings (see Fig. S1 for an alternate “cake”-plot view of Fig. 2).

At each pressure, diffraction data were collected at two different locations within the sample chamber, one where diffraction peaks from the Bi pressure marker were clearly visible, and the second where the diffraction signal from the Yb was optimized, and peaks from the gasket and Bi were minimized. In addition, the submicron beam available on beamlines ID27 and P02.2 enabled us to map the pressure distribution in each sample every ~ 25 GPa, and we performed grid scans over either 8 $\times$ 8 μm^2 or 30 $\times$ 30 μm^2 areas. Representative results from a 30 $\times$ 30 μm^2 grid scan at a central pressure of ~ 185 GPa, are shown in Fig. S2 in the Supplemental Material [32]. 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, and enabling high-precision measurements of the compressibility.

The compressibility data presented later in Figs. 6 and 7 were obtained from those diffraction profiles where diffraction peaks from both the Yb and Bi were visible (see Fig. 2), such that the pressure could be precisely measured. But for the purposes of structure identification, the Bi-free profiles, such as those shown in Fig. 3, were analyzed, with the sample pressure being determined from the Yb equation of state derived from the Bi-containing profiles.

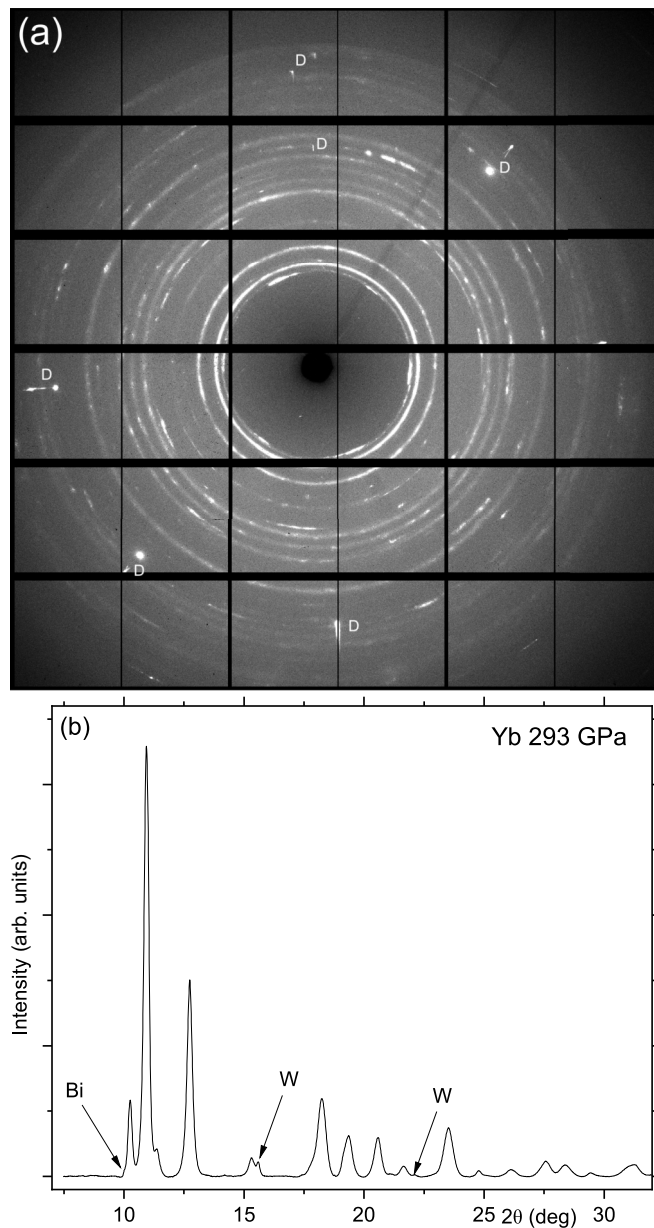


FIG. 2. (a) The 2D diffraction image collected from Yb at 293 GPa using the 500 nm $\times$ 500 nm FWHM x-ray beam at ID27 (ESRF-EBS). The intense diffraction spots from the diamond anvils are labeled “D” and were masked during integration. The nonactive areas between the detector tiles (shown as black) were also masked during integration. (b) The resulting background-subtracted integrated profile, with diffraction peaks from the Bi calibrant and W gasket labeled.

III. RESULTS

The aim of this study was to determine the structural behavior of Yb to 300 GPa, and so beveled diamond anvils with 30 μ m culets were used. This, and the fact that we ensured the DACs were fully sealed before extracting them from the glovebox, meant that no diffraction data were obtained from the *cF4-I* phase, stable below 4 GPa. We are then unable to confirm the predictions of Duan *et al.* of the stability of phases with $R\bar{3}m$ and $P3_121$ symmetry below 3 GPa [35].

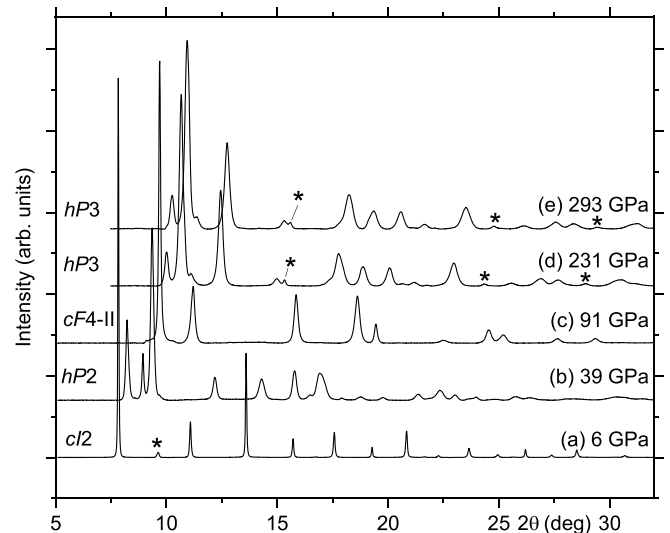


FIG. 3. Background-subtracted diffraction profiles obtained from the different high-pressure phases of Yb seen on compression. The profiles shown are from (a) the *cI2* phase at 6 GPa, (b) the *hP2* phase at 39 GPa, (c) the *cF4-II* phase at 91 GPa, and the *hP3* phase at (d) 231 GPa and at (e) 293 GPa. The asterisks in profiles (a), (d), and (e) identify weak diffraction peaks from the tungsten gasket, the positions of which suggest pressures [33] of 231 GPa and 291 GPa, respectively, for profiles (d) and (e), in excellent agreement with the pressures determined from the Bi calibrant. All profiles were collected at the ESRF. No spectra were recorded from the *cF4-I* phase which is only stable below 4 GPa.

A. Structure

Figure 3 shows selected diffraction profiles obtained on compression from 6 GPa to 293 GPa, illustrating the quality of the diffraction data obtained from the *cI2*, *hP2*, *cF4-II*, and *hP3* phases. The *cI2* $\rightarrow$ *hP2*, *hP2* $\rightarrow$ *cF4-II*, and *cF4-II* $\rightarrow$ *hP3* transitions were observed at 31, 64, and 93 GPa, respectively, in good agreement with the pressures reported in previous studies [11].

As shown in Fig. 4, the *hP3* phase was observed up to the highest pressure of 293 GPa reached in this study, where a Rietveld refinement, including a correction for preferred orientation, yielded best-fitting *hP3* lattice parameters of $a = 2.416(2)$ Å and $c = 5.667(12)$ Å, resulting in a volume of $9.55(3)$ Å³/atom. At this pressure, each atom has six nearest neighbors within the hcp-like layers at 2.416 Å, and a further four at a distance of 2.242 Å in the layers above and below (Fig. 1), giving 10-fold coordination.

In the lanthanide elements, the *hP3* structure is also found in trivalent Nd and Sm above 40 GPa [13,14,36], and both of these elements subsequently transform to the orthorhombic *oF8* phase on further compression. We see no evidence of a *hP3* $\rightarrow$ *oF8* transition in our experimental data from Yb up to 293 GPa, but such a transition might be seen in future higher-pressure diffraction studies.

To estimate where such a transition might occur, we have conducted computational studies of the relative stability of the *hP3* and *oF8* phases from 200 to 400 GPa, as well as additional candidate phases as described in the following section.

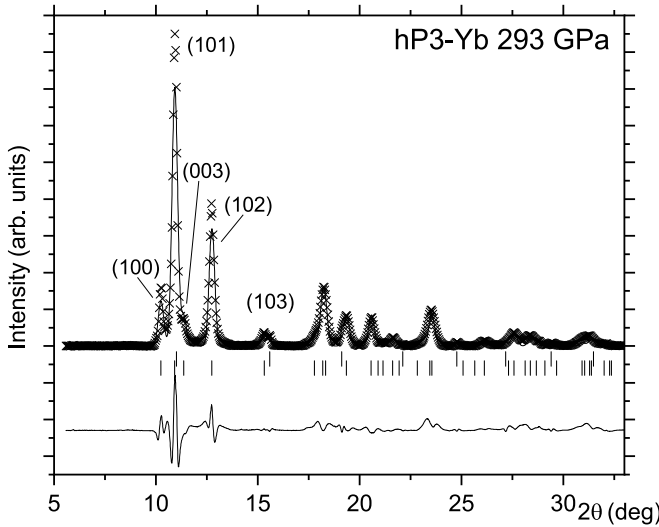


FIG. 4. Two-phase Rietveld refinement of the *hP3* structure and bcc-W to the background-subtracted diffraction profile from Yb at 293 GPa, showing the observed (crosses) and calculated (line) diffraction patterns, and the calculated reflection positions from the W (upper) and *hP3*-Yb (lower). The difference profile is shown beneath the calculated peak positions. The space group is $P6_222$ with Yb atoms on the $3c$ ($\frac{1}{2}, 0, 0$) Wyckoff site [34], with $a = 2.416(2)$ Å and $c = 5.667(12)$ Å. Indices are shown for the five lowest-angle *hP3* peaks.

B. Computational investigation

1. Method

To complement our experimental investigation, we performed a theoretical investigation to calculate the static transition pressure from the *hP3* phase to the *oF8*, *oF16*, *oC4*, and *tI2* phases, which are candidate phases which may become energetically favorable with increasing pressure following the known systematics in the lanthanide elements [34].

The continuous pressure-induced valence transition is well known to pose challenges for standard density-functional theory (DFT) treatments, with a complete description of the low-pressure phase sequence requiring explicit many-body methods such as LDA + DMFT [18]. Instead, we focus specifically on the post-*hP3* transition expected above 300 GPa, well past the pressure range over which the valence transition occurs [11,17]. In this regime, we believe that a PBE-based DFT + U approach is adequate for estimating the structural transition pressure.

Calculations were carried out using the Vienna *ab initio* simulation package (VASP), using a PBE PAW pseudopotential, with a Yb valence configuration of $4f^{14}5s^25p^66s^2$ [37,38]. We did not observe any stable spin-polarized magnetic moments, and a scan over fixed total spin yielded a significant energy penalty for the lowest nonzero moment state, consistent with the absence of magnetic ordering in elemental Yb reported to 179 GPa [17].

The Yb $4f$ electrons were treated with the Dudarev spherically averaged Hubbard U parameter [39], where we used Cococcioni's linear response method to estimate the value and volume dependence of U_{eff} [40] for both *hP3* and *oF8*, finding that U_{eff} was weakly phase dependent and

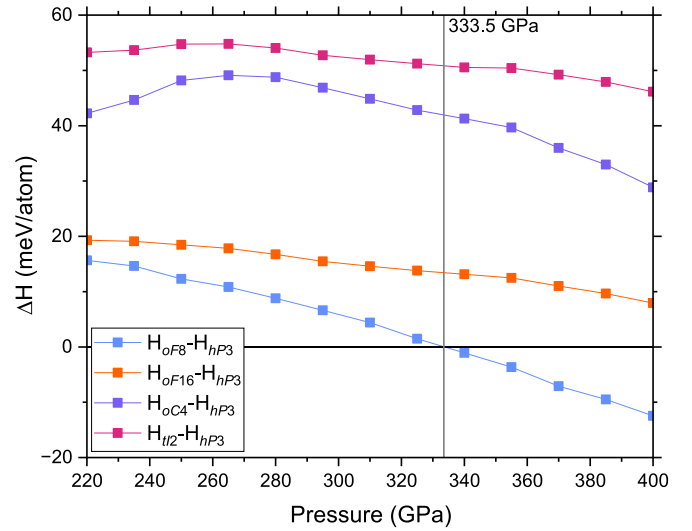


FIG. 5. Enthalpy differences ΔH between *hP3* and *oF8*, *oF16*, *oC4*, and *tI2* phases as functions of pressure. At 333.5 GPa, the *oF8* phase becomes favorable, though we estimate a 30 GPa standard error on this value.

varied linearly from 3.5–2.0 eV between 10.8–9.1 Å³/atom (~ 225 –400 GPa), with an uncertainty of ~ 0.2 eV. We obtained a best fit of

$$U_{\text{eff}}(V) = 0.85(3)V - 5.7(3) \quad (1)$$

(see Sec. C in the Supplemental Material for plotted fit [32]). Due to the weak phase dependence of U_{eff} , we did not calculate U_{eff} for the *oF16*, *oC4*, or *tI2* phases, but use $U_{\text{eff}}(V)$ fitted to the results from *hP3* and *oF8*.

Since U_{eff} affects the calculated equation of state, we varied the volume as the independent parameter and kept U_{eff} constant across phases at the same atomic volume, though this resulted in slightly different pressures for *hP3* and *oF8* data. For the enthalpy difference curve in Fig. 5, we therefore interpolated the enthalpies of both phases onto a common pressure grid.

We used a plane-wave cut off of 600 eV and a k -point density of $2\pi \times 0.02$ Å⁻¹ (Γ -centred grids of $21 \times 21 \times 8$ and $22 \times 22 \times 22$ for *hP3* and *oF8*, respectively), which yielded energy convergence to within 1 meV/atom. We used Gaussian smearing with width 0.1 eV. During relaxation, energies were converged to within 10^{-8} eV, and forces to within 0.01 eV/Å. Full spin-orbit coupling (SOC) calculations at 300 GPa and 400 GPa yielded phase-dependent SOC contributions of $\Delta E = 1.6$ meV/atom and 1.1 meV/atom, respectively. We therefore neglected SOC in the subsequent calculations, but account for this in the overall uncertainty on the transition pressure.

2. Results

We calculated the volume-dependent enthalpy $H = E + PV$ for each phase, letting internal coordinates and shape relax at each fixed volume. Here, the pressure $P = \text{Tr}(\sigma)/3$, where σ is the stress tensor calculated by VASP. This yielded a calculated *hP3* $\rightarrow$ *oF8* transition pressure of 333.5 GPa (Fig. 5).

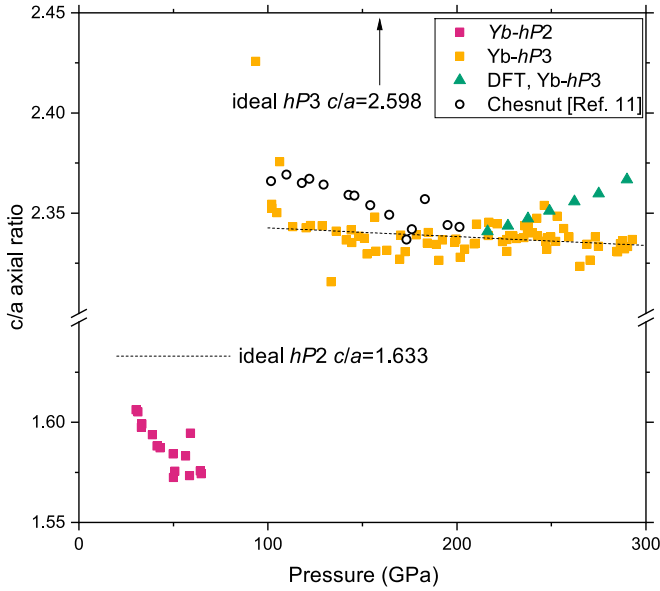


FIG. 6. The c/a axial ratios of hexagonal $hP2$ -Yb and $hP3$ -Yb with pressure. The ideal $hP2$ structure has a c/a ratio of $\sqrt{8/3} = 1.633$, as shown by the dashed line below 100 GPa. The ideal $hP3$ c/a ratio, where the atomic distances within and between the hcp-like layers are the same, is $3\sqrt{3}/2 = 2.598$, and lies well above the top of the graph. The dashed line through the $hP3$ data points shows the linear relationship $c/a = 2.347 - (4.37 \times 10^{-5})P$, as described in the text.

Near the predicted transition pressure, where the enthalpy differences between phases are small, we verified our results using a higher plane-wave cutoff (800 eV) and denser k -point grid $2\pi \times 0.01 \text{ \AA}^{-1}$, which shifted the calculated transition pressure by ~ 5 GPa, while alternative $+U$ treatments shift it by up to 30 GPa (see Fig. S4 [32]). From these and other methodological sensitivities, we estimate a ~ 30 GPa standard uncertainty on the reported transition pressure, and therefore find that the transition ought to occur between 300 and 340 GPa.

We see good agreement between the calculated and observed volumes, but note that the calculated compressibility appears to be slightly lower (i.e., stiffer), resulting in a steeper gradient on the linear plot.

Our DFT calculations extended to 400 GPa, and at this pressure the enthalpies of the $oF16$, $oC4$, and $tI2$ structures lay well above that of $oF8$. It is notable that the $oC4$ phase exhibits the steepest negative slope, supporting the expected transition sequence of $oF8 \rightarrow oC4$ at higher pressures.

C. c/a ratio and compressibility

The experimentally measured lattice parameters of Yb at each pressure were obtained either by peak fitting or profile refinement. The resulting c/a ratios for the hexagonal $hP2$ and $hP3$ phases are shown in Fig. 6, along with the calculated c/a ratio for the $hP3$ phase, and the previous data from $hP3$ -Yb by Chesnut and Vohra [11]. The c/a ratio for $hP2$ -Yb is smaller than the ideal value of $\sqrt{8/3} = 1.633$, and moves further away from this ideal value on compression. Our c/a ratio for $hP3$ -Yb is in good agreement with that of Chesnut *et al.*, and is

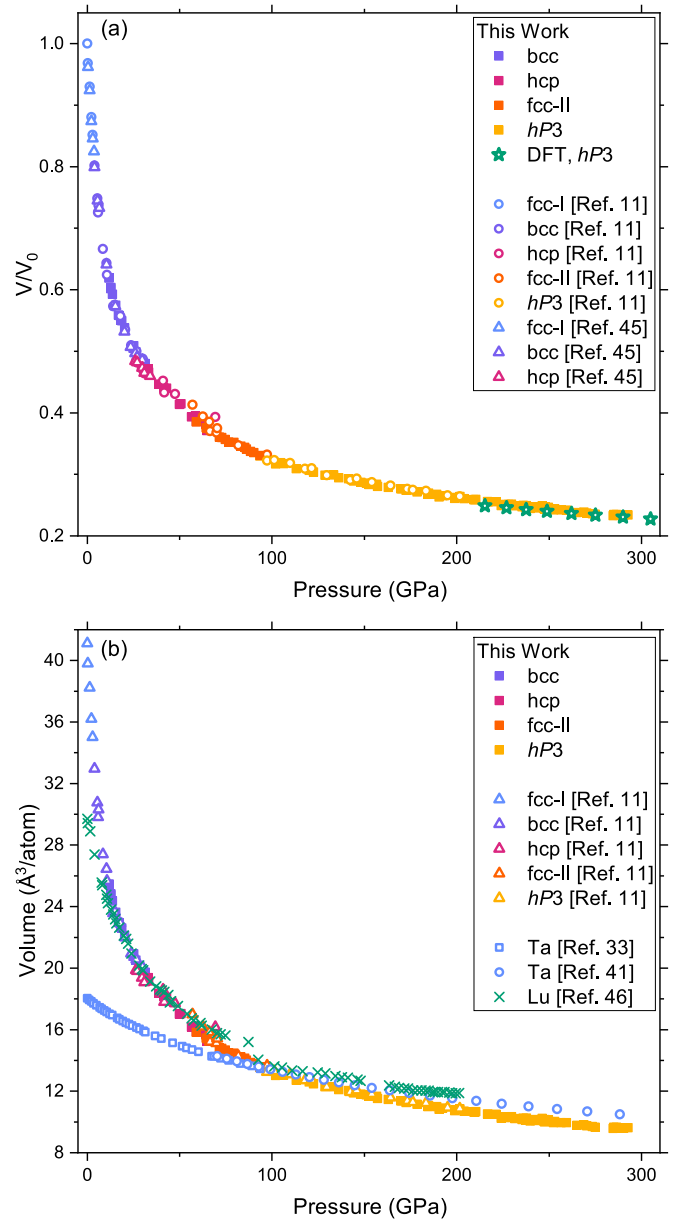


FIG. 7. (a) The reduced (V/V_0) compressibility of Yb from 11.7 to 293 GPa from this work's experiment (solid squares), theoretical $hP3$ results (open stars), along with earlier data of Takemura and Syassen to 30 GPa [45], and Chesnut and Vohra to 202 GPa [11] (open circles). (b) The volume compressibility of Yb ($Z = 70$) to 293 GPa from this work, compared to that of the neighboring trivalent lanthanide Lu ($Z = 71$) [46] and nonlanthanide Ta ($Z = 73$) [33,41].

very different to the ideal value of $3\sqrt{3}/2 = 2.598$, which lies well above the top of Fig. 6. The c/a ratio for $hP3$ -Yb also decreases slightly with pressure, with the linear relationship $c/a(P) = 2.347 - (4.37 \times 10^{-5})P$.

The V/V_0 compression curve obtained from our data is shown in Fig. 7(a), along with the previous data by Chesnut *et al.* [11] to 202 GPa, and the results from our DFT calculations. To aid future researchers utilizing our data, we provide these in full (see Data Availability). The volume

TABLE I. Fitted equation-of-state parameters for the observed high-pressure phases of Yb, using second-order Vinet, third-order Birch-Murnaghan (BM), and AP2 (APL) formulations. In every fit the zero-pressure volume was held fixed at the ambient value for $cF4$ -I, $V_0 = 41.281 \text{ \AA}^3/\text{atom}$ [2]. While different values of K_0 and K'_0 are obtained for different EoS forms, the calculated curves are almost indistinguishable.

Phase	EoS	K_0 (GPa)	K'_0	$\sigma_{K_0 K'}$ (GPa)
$cI2$	Vinet	7.2(2)	5.20(11)	-0.025
	BM	8.3(2)	4.28(7)	-0.016
	AP2	7.7(2)	4.86(7)	-0.013
$hP2$	Vinet	8.6(3)	4.71(9)	-0.028
	BM	10.2(2)	3.85(3)	-0.007
	AP2	9.3(2)	4.46(4)	-0.010
$cF4$	Vinet	6.5(6)	5.3(2)	-0.107
	BM	9.0(5)	4.00(7)	-0.031
	AP2	8.1(5)	4.64(9)	-0.048
$hP3$	Vinet	2.84(4)	7.05(3)	-0.001
	BM	6.14(8)	4.54(2)	-0.001
	AP2	5.08(8)	5.37(2)	-0.002

change ($\Delta V/V_0$) at the $cI2 \rightarrow hP2$ transition is 0.5(2)%, as determined from a mixed-phase profile at 30 GPa, while the volume changes at the $hP2 \rightarrow cF4$ -II and $cF4$ -II $\rightarrow hP3$ transitions were too small to determine. Our compression data are in very good agreement with that of Chesnut *et al.*, though our data exhibit considerably less scatter, particularly in the $hP2$ and $cF4$ -II phases.

The same compression data are shown as atomic volume versus P in Fig. 7(b), along with comparative compression data from the neighboring ($Z = 71$) trivalent lanthanide Lu [3] and nonlanthanide Ta ($Z = 73$) [33,41]. At low pressures, where Yb is divalent, both its atomic volume and compressibility are significantly larger than those of trivalent Lu. However, by 20 GPa, while Yb is in the $cI2$ phase, and its valence has increased to 2.65 [15], the atomic volume and compressibility of Yb and Lu are extremely similar. At higher pressures, above the first-order $hP4 - hR24$ transition in Lu at ~ 90 GPa [3], the compressibility and atomic volume of Lu undergo discontinuous changes and become almost identical to those of the group-5 element Ta. However, at the same pressure, Yb remains unusually compressible, behavior which Chesnut and Vohra have attributed to interconfiguration valence fluctuations ($4f^{14} \rightarrow 4f^{13}$) and $s - d$ electronic rearrangements in the compressed state [11].

Given the dramatic changes in the compressibility of Yb, it proved impossible to model the entire compression curve using a single equation of state. We have therefore fitted AP2 equations of state [42] to each of the $cI2$, $hP2$, $cF4$ -II, and $hP3$ phases, with parameters shown in Table I.

The APL equation of state is given by [43,44]

$$P(x) = 3K_0 x^{-5} (1-x) e^{c_0(1-x)} \left[1 + x \sum_{k=2}^L c_k (1-x)^{k-1} \right], \quad (2)$$

where K_0 is the zero-pressure bulk modulus, K'_0 is its pressure derivative, $x = (V/V_0)^{1/3}$, $c_0 = -\ln(3K_0/P_{FG0})$,

$c_2 = (3/2)(K'_0 - 3) - c_0$, c_k are independent fitting parameters for integer $k = 3, \dots, L$, $P_{FG0} = a_{FG0}(Z/V_0)^{(5/3)}$ is the Fermi-gas pressure, Z is the atomic number, and $a_{FG0} = 2337 \text{ GPa \AA}^5$ is a constant.

If the parameter V_0 is allowed to vary freely, interparameter correlations are so large that individual parameters have uncertainties greater than 10%. For this reason, we have fixed V_0 for each phase at the ambient value of $41.281 \text{ \AA}^3/\text{atom}$ ($a_0 = 5.4862 \text{ \AA}$ for $cF4$ -I) [2].

D. Linearization

Changes in the compressive behavior of Yb, and comparisons with that of Lu and Ta, are aided when the experimental data are displayed in a so-called $x - \eta_{\text{APL}}$ plot which provides a linearized space for the APL EoS formalism [42]. With $L = 1$, the linearization gives

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

In the APL formalism “ideal” and “simple” metals are well described by a first-order AP1 EoS and exhibit linear behavior with

$$\lim_{x \rightarrow 1} \eta_{\text{APL}}(x) = \ln \left(\frac{3K_0}{P_{FG0}} \right)$$

and

$$\lim_{x \rightarrow 0} \eta_{\text{APL}}(x) = 0.$$

Finally, one can facilitate comparison between the 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 $\eta_{\text{APL}}(\sigma)$ [42]. The linearized compressibility data from Yb, along with linearized data from the trivalent lanthanides Lu [46] and Nd [14], and the “regular” metal Ta [33,41], are displayed in a $\eta_{\text{APL}}(\sigma)$ plot in Fig. 8, which highlights the changes in compression of all four elements across extended pressure ranges over which they have all been studied. In such a plot, “regular” materials undergoing normal compression will show linear or quasilinear behavior with an average “ideal” gradient of $-0.567 \text{ \AA}^{-1}$ and with the correct theoretical limit of $\eta_{\text{APL}}(0) = 0$ [42]. The behavior of Ta exhibits this regular, albeit nonideal, form.

In marked contrast to the regular behavior of Ta, the data for Yb (and also for Lu and Nd) exhibit significant curvature, as noted previously by Grosshans and Holzapfel [47] for the trivalent lanthanides in general. The clear change in gradient within the bcc ($cI2$) phase of Yb at $\sigma = 7.7 \text{ \AA}$ (~ 9 GPa) marks a change in compression from being “irregular,” and larger than would be expected from the initial electron density, to more regular linear behavior which extrapolates toward the origin. We note that it is within the $cI2$ phase that the valence of Yb increases strongly from ~ 2 to ~ 3 [15]. Similar changes in gradient are visible in the data from Lu, and we have previously reported such changes in detail in the lanthanides La [23], Pr [48], Nd [14], Sm [13], and Tb [49], and also in the rare-earth Y [50]. The irregular, high-compressibility behavior of these metals at lower pressures arises as a result of $s - d$ electron transfer, with the gradient change at higher

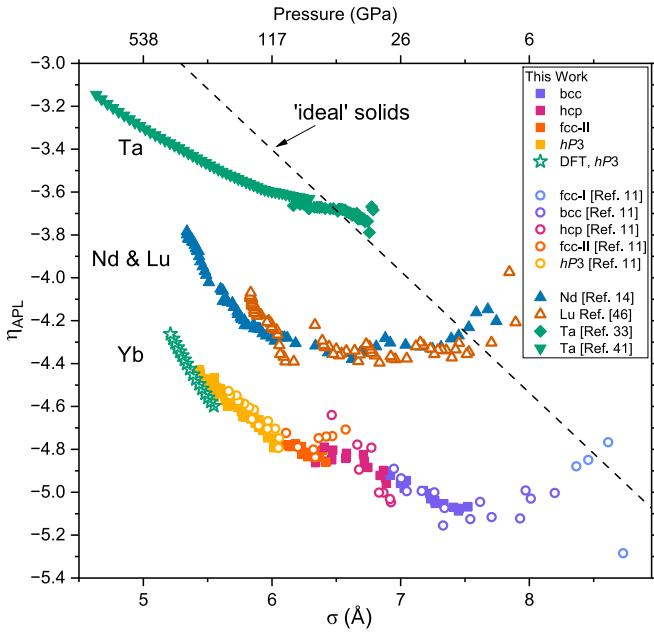


FIG. 8. The linearized observed and calculated compressibility of Yb in $\eta_{\text{APL}}-\sigma$ space, alongside that of the trivalent lanthanides Lu [46] and Nd [14], and Ta [33,41] as an example of a “regular” metal. The equivalent quasilogarithmic pressure scale for Yb is shown along the top axis. The dashed line labeled “ideal solids” has the gradient $\bar{\eta} = -0.567 \text{ \AA}^{-1}$, and is the average gradient expected for all elements with regular compression [42,44].

pressures likely corresponding to the completion of this electron rearrangement.

IV. DISCUSSION AND CONCLUSIONS

As reported previously [11], the high-pressure phase transition sequence in Yb is quite different to that seen in each of the other trivalent and divalent lanthanide elements, and also different to that seen in divalent Eu. At lower pressures, Yb has a significantly higher atomic volume and compressibility than neighboring trivalent Lu, and possesses the *cF4*, *cI2*, and *hP2* structures seen also in divalent alkaline earth metals such as Mg, Sr, and Ba [51], and in the second divalent lanthanide, Eu. While Yb has a significantly higher compressibility than Lu at lower pressures, above 20 GPa, while in the *cI2* phase where Yb’s valence increases strongly with pressure, its compressibility decreases, and becomes more like that expected from a regular metal.

hP3-Yb is stable from 93 GPa to at least 293 GPa, a stability range much larger than that seen for the same phase

in trivalent Nd (~ 40 GPa) and Sm (~ 50 GPa), in both of which there is a subsequent transition to the *oF8* structure. Our initial motivation for the present study was to find the same *hP3* $\rightarrow$ *oF8* transition in Yb, which would reinforce its behavior as that of a regular trivalent lanthanide series, and suggest that the further post-*hP3* transitions seen in the other trivalent lanthanides La, Pr, and Nd [14,23,48]

$$hP3 \rightarrow oF8 \rightarrow oC4 \rightarrow tI2$$

will also occur in Yb at sufficiently high pressures. Our calculations suggest that the *hP3* $\rightarrow$ *oF8* transition will occur between 300 and 340 GPa. Future studies using DACs equipped with two-stage [52] or toroidal [53,54] anvils will enable diffraction studies well above the ~ 300 GPa limit of the current study, thereby allowing these transitions to be located, guided by further computational studies to both predict the transition pressures and cast light on the further evolution of Yb’s electronic structure.

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C.V.S. prepared all samples and performed the diffraction data analysis. The project was jointly conceptualized, and the manuscript drafted by C.V.S. and M.I.M. Calculations were performed and results analyzed by C.V.S. All authors contributed equally to the experimental investigation and the final editing of the manuscript.

DATA AVAILABILITY

The data that support the findings of this article are openly available at [57].

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