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Structural Studies of the Trivalent Lanthanides at Ultra-High Pressures

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Abstract

The lanthanide and actinide metals have complex electronic and magnetic behaviour at high pressures and low temperatures, respectively, owing to the f electrons buried within the atoms participating in the bonding of those metals. As one traverses the lanthanide series with increasing Z at ambient conditions, each element adds one electron to the $4f$ shell, starting with cerium (Ce) and ending with a full $4f$ electron shell in lutetium (Lu). This thesis focuses on the trivalent lanthanides, which are considered to be all the lanthanides except Ce, europium (Eu) and ytterbium (Yb), and their structural systematics at high pressures. The trivalent lanthanides exhibit a common, pressure-induced, structural phase transition sequence: hexagonal close-packed (hcp) $\rightarrow$ Sm-type or α -Sm $\rightarrow$ double-hcp (dhcp) $\rightarrow$ face-centred cubic (fcc) $\rightarrow$ distorted-fcc (dfcc) $\rightarrow$ “volume-collapsed”. This sequence is thought to arise from the $5s \rightarrow 5d$ transfer of electrons, and, at ultra-high pressures, from the $4f$ electrons becoming delocalised and then participating in the bonding of these elements, leading to volume-collapsed phases with low-symmetry structures. However, there is still debate over the exact structures of the low-symmetry collapsed phases.

This thesis describes x-ray diffraction studies of the high-pressure structures of the collapsed phases of six trivalent lanthanide elements (neodymium (Nd), samarium (Sm), praseodymium (Pr), gadolinium (Gd), terbium (Tb) and dysprosium (Dy)), and also yttrium (Y) – a rare-earth element. Using diamond anvil cell (DAC) techniques and x-ray powder diffraction at the Diamond Light Source and PETRA-III synchrotrons, the structures of the collapsed phases of six of the seven elements are found to be face-centred orthorhombic, spacegroup $Fddd$, with either 8 atoms (Nd and Sm) or 16 atoms (Gd, Tb, Dy and Y) in the unit cell. The 8-atom structure ($oF8$) is the same as that seen previously in the actinides plutonium (Pu), americium (Am), curium (Cm) and californium (Cf), greatly strengthening the structural relationships between the $4f$ lanthanides and the $5f$

actinides. The 16-atom structure (*oF16*) found in Gd, Tb, Dy and Y is previously unknown in the elements, but, along with the *oF8* structure, and *hP3* structure seen in Nd and Sm at lower pressures, it is a member of a new structural family comprising different stackings of quasi-hcp layers.

This thesis also describes higher-pressure studies with the aim of determining the structural systematics of the post-*oF8/oF16* phases. Pr and Nd have been shown to exhibit the α -uranium (α -U) structure, *oC4*, in their collapsed phases. In Pr, a primitive orthorhombic structure was previously reported above 147 GPa, the post- α -U phase, a structure not seen in any other element. This thesis shows that the true structure is body-centred tetragonal, the same as the highest-pressure phase seen in the neighbouring lanthanide Ce, and also in the actinides thorium (Th) and uranium (U), suggesting that it is the “next” structure in the transition sequence of the trivalent lanthanides.

This work contained in this thesis completely rewrites the structural behaviour of the trivalent lanthanide elements at high-pressure and reveals that the high-pressure behaviour of the lanthanide and actinide metals is much more similar than previously believed.

Lay Summary

Science at extreme conditions incorporates the understanding of materials subjected to immense changes in pressure and temperature. Understanding the behaviour of matter at extreme pressures in the laboratory helps comprehend the exotic environments found on Earth and observed on other planets in the Universe. The study of materials at extreme conditions has led to the discovery and development of many life-altering instruments; from enabling space exploration to the creation of the atomic bomb, high pressure research has influenced many theatres of human advancement over the last century. Furthermore, studying materials affords us the opportunity to understand their behaviour in different atmospheric conditions. Be that in the Earth's crust, in its core or in other planets.

Studying the lanthanide elements, the series of the periodic table beginning with lanthanum and ending in lutetium, at high pressures helps to understand the properties and behaviours of some of the rarer, more complex, heavy elements. Correcting and extending the structural changes in the lanthanides will further the understanding of how electron movement alters the behaviour of heavy elements at ultra-high pressures.

At ambient conditions, many elements of the periodic table adopt high-symmetry structures. This means the atomic layers are in an ordered arrangement in three dimensions. Once pressure on these metals is increased, the high-symmetry structures transition to those of a considerable lower symmetry. In order to aptly study these changes in atomic structure, a number of instruments and techniques have been developed over the past sixty years. One such instrument is the diamond anvil cell, which is adopted in this thesis. The studies presented here provide solutions of structures of the lanthanides and yttrium (Y), a rare earth element, to 300 gigapascals (GPa), pressures close to that found at the centre of Earth.

X-ray diffraction is a technique that produces high qualitative and quantitative data of the atomic structure in a material. It is famously known by the method that produced ‘Photo 51’ – an image photographing the double helix structure of deoxyribonucleic acid (DNA) captured by Rosalind Franklin in 1960. This technique is used in this thesis to probe into the metal samples and provide visual representations of the structures existing at ambient conditions and high pressures.

Declaration

I declare that this thesis was composed by myself, that the work contained herein is my own except where explicitly stated otherwise in the text, and that this work has not been submitted for any other degree or professional qualification except as specified.

Parts of this work have been published in [1–4].

(Sarah Elizabeth Finnegan, September 2021)

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Chapter 1

Introduction

At ambient conditions, many elemental metals adopt simple structures of high symmetry. As pressure is applied, these elements generally transition to more complex, lower-symmetry structures. Highly complex structures have been observed in many elements throughout the periodic table [15, 29], for example in the alkali and alkaline earth metals many incommensurate host-guest structures are seen at high pressures and temperatures [30]. However, the only lanthanide known to exhibit such complex structures is Eu [31–33]. The lanthanide metals adopt hexagonal or cubic structures at ambient pressures and transition to, generally, increasingly less-symmetric structures at higher pressures.

The lanthanide, other rare-earth, and actinide metals have complex electronic and magnetic behaviour at high pressures. As one traverses the lanthanide series, each element adds one electron to the $4f$ shell, starting with Ce and ending with a full $4f$ electron shell in Lu. This thesis focuses primarily on all the lanthanides, except Ce, Eu and Yb, as all but these three are considered to have a valency of $3+$ at ambient conditions. The trivalent lanthanides, as they are better known, exhibit a common, pressure-induced, structural phase transition sequence: hcp $\rightarrow$ Sm-type or α -Sm $\rightarrow$ dhcp $\rightarrow$ fcc $\rightarrow$ distorted-fcc (dfcc) $\rightarrow$ “volume-collapsed”. This thesis will focus on determining the correct structural assignment of the volume-collapsed phase of the sequence and examining the evidence for two new structures. This work also reports on the volume-collapsed phase of Y, which has been previously assigned the same structure as that reported for the trivalent lanthanides. The common structural sequence is thought to arise from the $5s \rightarrow 5d$ -shell transfer of electrons, and that at ultra-high pressures, the $4f$ electrons

will become delocalised and then participate in the bonding of these elements. The literature has previously ascribed increasingly less-symmetrical, “volume-collapsed” structures to the trivalent lanthanides above the dfcc phase, however there is still debate over the identification of these low-symmetry, high-pressure structures.

To study these high-pressure structures, devices such as the diamond anvil cell (DAC) are required. The introduction of the bevelled diamond [34] has extended the frontier of pressures reached in static compression experiments to ~ 400 GPa [35]. Furthermore, this thesis will use novel techniques in order to reach unprecedented pressures in static compression of trivalent lanthanide samples inside DACs. Recent work by Dewaele [36] and Jenei [16] have utilised a focussed ion beam (FIB) to carve out a toroid shape around the diamond culet in an attempt to achieve pressures close to 1000 GPa in static compression experiments.

The samples used in this thesis were primarily loaded into DACs containing bevelled diamonds to achieve pressures of ~ 200 GPa with $300\text{ }\mu\text{m}$ culets bevelled to $100\text{ }\mu\text{m}$, and ~ 300 GPa with $300\text{ }\mu\text{m}$ culets bevelled to $30\text{ }\mu\text{m}$. A sample of Tb was loaded into a DAC containing diamonds with a toroidal-shaped cut culet in an attempt to achieve pressures exceeding 300 GPa. Previously, energy-dispersive x-ray powder diffraction (EDXD) techniques were employed to study these metals. This resulted in poor quality x-ray diffraction data as energy-dispersive techniques required a high x-ray flux which can produce inaccurate and indistinguishable Bragg peaks [37]. The introduction of third generation synchrotrons that generate more brilliant x-rays has been pivotal in producing high-quality diffraction data from small-sized samples [38]. The development of 2-dimensional (2D) area detectors provided significantly improved signal-to-noise ratios and improved powder averaging, giving angle-dispersive diffraction greater advantages over energy-dispersive methods [38, 39]. In fact, it is highly likely that the wrongly assigned, volume-collapsed structure observed in the high-pressure phases of the trivalent lanthanides and Y is a direct result of misinterpreted diffraction data. The data presented in this thesis were collected via angle-dispersive x-ray powder diffraction (ADXD), which allowed for the detection of distinguishable, high-angle, low-intensity peaks in the more complex, low-symmetry structures of Y and the trivalent lanthanides.

Previously, a monoclinic structure with 4 atoms in the unit cell was ascribed to the volume-collapsed phase of the trivalent lanthanides and Y. However, this assignment relied on poor EDXD data or used an “analysis by analogy”

approach, where the more recent ADXD data from higher pressure heavy trivalent lanthanides were interpreted using the data obtained at much lower pressures in the light trivalent lanthanides.

This thesis describes the electronic systematics and high-pressure structures of several trivalent lanthanide elements (praseodymium (Pr), neodymium (Nd), samarium (Sm), gadolinium (Gd), terbium (Tb) and dysprosium (Dy)) and yttrium (Y) – a rare-earth element. It rewrites the low-symmetry, structural phase transitions of the trivalent lanthanides at pressures between 50 and 300 GPa by use of DAC techniques and high-flux, sub-micron, x-ray powder diffraction.

As the trivalent lanthanides exhibit a common sequence it is intuitive that any newly determined phases observed in any one element may be observed in all of them, and most likely at higher pressures in higher- Z elements. Currently, the rewritten sequence proposed in this work cannot be verified experimentally for the heaviest lanthanides as a result of the extreme ultra-high pressures required to see a number of the transitions. Novel toroidal diamond anvil cell techniques may shed light on the identity of the structures at these unprecedented pressures. The implications of discovering the correct trivalent lanthanide phase transition sequence will provide vital input for computational studies exploring $4f$ electron behaviour and, by that design, studies into $5f$ electron behaviour in the actinides.

The electronic structure calculations presented in Chapters 4–8 were performed by Evgeny Plekhanov, Nicola Bonini and Cedric Weber (hereafter Plekhanov *et al.*) from King’s College London, and are included here for completeness.

Chapter 2

The Lanthanide, Actinide & Rare Earth Elements

2.1 Introduction

The lanthanides are a series of elements beginning with lanthanum (La) and ending with lutetium (Lu). The actinide series lies beneath the lanthanides, beginning with actinium (Ac) and ending with lawrencium (Lr). Both contain 15 elements and are characterised by the incremental filling of the $4f$ and $5f$ electron shells, respectively. The lanthanide and actinide metals make up some of the heaviest elements in the periodic table.

There have been extensive studies on the comparison of the high-pressure, low-symmetry structures of the lanthanide and actinide metals [40, 41], and a large number of reviews detailing the phases and structures of the lanthanides [10, 41, 42] and actinides [13, 43]. The theory behind f electron itinerant behaviour at extreme compression in both the lanthanide and actinide series is at the centre of these studies [14, 44, 45].

A number of publications, such as Young [15], Tonkov [29], Krüger *et al.* [42] and Samudrala & Vohra [10], have described the phase transitions and structural systematics of the lanthanide elements at high-pressure high-temperature, and presented the common structural phase transitions up to a “volume-collapsed” phase seen at ultra-high pressures in most of the lanthanides. However, this thesis has found inconsistencies with the diffraction data presented previously on the

lanthanides and the data collected in the studies presented in Chapters 4–8.

This chapter comprises a critical review of the lanthanides at high pressure, a detailed analysis of the structural systematics of the actinides and rare earth elements, and the analogous behaviour between these groups. It also reviews the electronic and magnetic behaviours of the lanthanide, actinide and rare earth elements, determined both experimentally through x-ray diffraction and theoretically using density functional theory (DFT).

2.2 The Lanthanide Elements

Predominantly, the lanthanides have an electronic valency of 3 at ambient conditions. Those with this valency are more commonly known as the trivalent lanthanides, and include all elements from La to Lu except cerium (Ce), europium (Eu) and ytterbium (Yb). However, the valency of Ce is disputed as its electronic behaviour is similar to the trivalent lanthanides at high pressure and exhibits a similar yet slightly different structural sequence to its trivalent neighbours [5].

This thesis focuses on the structural systematics of the trivalent lanthanides. However, a review of Ce, Eu and Yb, will first of all be given to compare and contrast these three elements with their lanthanide neighbours.

Ce adopts the fcc structure at ambient conditions [15] and transitions to a second fcc structure, coupled with a significant volume collapse, at 0.8 GPa [46]. It then transitions to a C-centred monoclinic structure, $mC4$ in Pearson notation and spacegroup $C2/m$, at ~ 4 GPa [5, 47] or to an orthorhombic structure, $oC4$ in Pearson notation and spacegroup $Cmcm$, depending on the type of Ce sample used in an experiment [5, 46]. Angle-dispersive x-ray powder diffraction (ADXRD) studies by McMahon & Nelmes on filed samples of Ce metal or foils of Ce found that the $mC4$ structure was observed between ~ 5 and ~ 12 GPa. However, when cut samples of Ce were used instead of foils or filings, only the $oC4$ (α -U) structure was observed between these pressures [5]. A more recent ADXRD study by Munro *et al.* on the high-pressure, high-temperature phase diagram of Ce only observed the α -U structure, however only cut samples of Ce were used in this case [46]. Interestingly, both these structures are assigned to high-pressure phases in the trivalent lanthanides which will be discussed in much greater depth later in this chapter. Ce is considered isostructural and isoelectronic with its

actinide neighbours thorium (Th) and uranium (U) as all three exhibit a body-centred tetragonal (bct) structure, above 14 GPa in Ce, at ambient and high pressures in Th [48, 49], and at ambient pressures and above 940 K in U [50]. This isostructural behaviour between Ce, Th and U is one of many analogous behaviours seen between other lanthanide and actinide elements and will be discussed later in this chapter.

Europium (Eu) is significantly different to Ce and the trivalent lanthanides where it is known to remain divalent to much higher pressures [51] and display more than one incommensurate structure [31, 33]. Around 20 GPa, the EOS of Eu resembles that of Gd, insinuating a mixed valence state but not purely trivalent [52]. The valency of Yb is different to both Ce and Eu and its structural sequence shares more structures with the trivalent lanthanides [53, 54].

Yb exhibits two fcc phases which is also seen in Ce [15], however it transforms to two different structures upon pressure increase before transitioning to its second fcc structure: fcc (I) $\rightarrow$ bcc $\rightarrow$ hcp $\rightarrow$ fcc (II) [53], where a transition from bcc to hcp occurs at 53 GPa, a phase transition that is also observed in Eu at 12 GPa [52]. Yb is divalent up to only 4 GPa where a structural transition to the bcc phase introduces a continuous transition to a valency of 3 [55].

As already mentioned, Ce, Eu and Yb all exhibit at least one structure seen in phases of the trivalent lanthanide at high pressures, however what sets the trivalent lanthanides apart is seen in their shared, pressure-induced, phase transition sequence [40].

2.3 The Trivalent Lanthanides

The high-pressure behaviour of the trivalent lanthanide metals is a subject of uncertainty. This is particularly true of the heavier members of the series (Gd to Lu), where the phase transitions occur at much higher pressures than the lighter members and, therefore, are much more difficult to observe in experiments. This has led to “analysis by analogy” where structure determination of the heavy trivalent lanthanides at high pressures depends on comparisons with the higher-quality data obtained from the lighter trivalent lanthanides at lower pressures, in particular from the monoclinic *mC4* structure first seen in Ce [56], and the rhombohedral *hR24* structure first observed in Pr [23].

Table 2.1 *Details of the common crystal structures observed in the trivalent lanthanides, in descending order of symmetry. The first column describes the structures in Pearson notation.*

Structure	Spacegroup	Wyckoff Positions	Atomic Positions
$cF4$	$Fm\bar{3}m$	$4a$	$(0,0,0)$
$hP2$	$P6_3/mmc$	$2c$	$(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$
$hP3$	$P6_222$	$3c$	$(0, \frac{1}{2}, \frac{2}{3})$
$hP4$	$P6_3/mmc$	$2a$ and $2c$	$(0,0,0)$ and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$
$hR9$	$R\bar{3}m$	$3a$ and $6c$	$(0,0,0)$ and $(0,0,\frac{2}{9})$
$hR24$	$R\bar{3}m$	$6c$ and $18h$	$(0,0,z_1)$ and (x,y,z_2)
$oI16$	$Ibam$	$8g$ and $8j$	$(0,y_1,\frac{1}{4})$ and $(x,-y_2,0)$
$mC4$	$C2/m$	$4i$	$(x,y,0)$
$oC4$	$Cmcm$	$4c$	$(0,y,\frac{1}{4})$

The trivalent lanthanides have long been known to exhibit the same structural sequence as they go through different pressure-induced phases: hcp ($hP2$ in Pearson notation, spacegroup $P6_3/mmc$) $\rightarrow$ Sm-type or α -Sm ($hR9$, $R\bar{3}m$) $\rightarrow$ dhcp ($hP4$, $P6_3/mmc$) $\rightarrow$ fcc ($cF4$, $Fm\bar{3}m$) $\rightarrow$ dfcc ($hR24$, $R\bar{3}m$) [15, 57]. Throughout this thesis, the structures will more often be referred to via their names in Pearson notation (first in parentheses inside the sequence above) or spacegroup (second in parentheses). These elements exhibit close-packed structures at atmospheric conditions, and display novel magnetic and electronic behaviours in low-temperature and high-pressure conditions, respectively.

Johansson & Rosengren were the first to recognise a pattern among the phase transition sequences of the trivalent lanthanides [40]. Prior to this, Gschneidner & Valetta had reported that the phase transitions of the trivalent lanthanides were a result of $4f$ electrons participating in the bonding [58]. However, Min *et al.* determined from electronic structure calculations that the $4f$ electrons are embedded deep within the atoms of the lanthanides and could not participate in bonding, and that, instead, increased occupancy of the d band from s band electron transfers could account for the changing structures [59].

The first five structures detailed in Table 2.1 are all close-packed. The five structures comprise different stacking of close-packed layers. All of the structures described in Table 2.1 differ only by the stacking in their layers. The $hR24$ and $oI16$ structures can be described as distortions of the fcc (or $cF4$) structure, and are often referred to as distorted-fcc (dfcc) or d- $cF4$ structures throughout this thesis.

All except *hR24*, *oI16*, *mC4* and *oC4* have been reported to occur at ambient conditions. The body-centred orthorhombic structure, *oI16*, has been assigned to the post-*hR24*, high-pressure phases of both Pr [23] and Nd [28]. The *C*-centred monoclinic structure, *mC4*, is reported as the post-dfcc structure of all the trivalent lanthanides and Ce [6, 9, 10, 18, 20, 56, 60–63]. The *C*-centred orthorhombic structure *oC4*, spacegroup *Cmcm*, is observed in Pr and Nd at high pressures [24, 64]. It is also observed in U in what is commonly known as the α -U phase [65]. It is expected that the *oC4* structure (or α -U structure) will be observed at extreme compression in all the trivalent lanthanides.

The fcc structure *cF4* is only observed in the high-pressure phases of the light trivalent lanthanides. It is considered to be mixed with the dfcc *hR24* structure in Gd for a very small pressure range [61], and has not been observed in any other heavy trivalent lanthanide. An argument has been made for the absence of the fcc structure in the high pressure phases [41]. In order to exhibit the fcc structure, a material must have perfect packing of layers, therefore, it may be thermodynamically impossible for this structure to be stable at high pressures in heavier, harder elements [41]. Indeed, data on low-temperature, high-pressure La show that the fcc $\rightarrow$ dfcc transition is seen at temperatures well above 0K [66], supporting the idea that the fcc structure may only be seen in high-temperature phases of the heavier lanthanides.

2.3.1 The dfcc Phases

At higher pressures, a phase transition occurs from the fcc phase to the dfcc phase in a number of the trivalent lanthanides. One of the dfcc structures, *hR24* in Pearson notation, was first discovered in a high-pressure phase of Pr [67], and has since been reported as the assigned structure to the dfcc phases in all other trivalent lanthanides [6, 9, 61, 62, 68–70]. The fcc $\rightarrow$ dfcc transition is characterised in x-ray diffraction patterns by the splitting of the fcc peaks and the appearance of superlattice reflections. There are a number of dfcc crystal structures reported in several publications on the trivalent lanthanides and are presented in Table 2.2.

Table 2.2 Details of the common dfcc crystal structures observed in the trivalent lanthanides, in descending order of symmetry. The first column describes the structures in Pearson notation.

Structure	Spacegroup	Wyckoff Positions	Atomic Positions
$hR24$	$R\bar{3}m$	6c and 18h	$(0,0,\frac{1}{4})$ and $(\frac{1}{2},-\frac{1}{2},\frac{1}{4})$
$oI16$	$Ibam$	8g and 8j	$(0,y_1,\frac{1}{4})$ and $(x,y_2,0)$
$oS8$	$Cmmm$	4g and 4j	$(x,0,0)$ and $(0,y,\frac{1}{2})$
$mI4$	$I2/m$	2a	$(0,0,0)$
$mC4$	$C2/m$	4i	$(x,y,0)$

Table 2.3 Structure candidates for the post-dfcc phases of the trivalent lanthanides.

Structure	Spacegroup	Wyckoff Positions	Atomic Positions
$hP3$	$P6_222$	3c	$(0,\frac{1}{2},\frac{2}{3})$
$mC4$	$C2/m$	4i	$(x,0,z)$
$oC4$	$Cmcm$	4c	$(0,y,\frac{1}{4})$
$oP4$	$Pnma$	4c	$(0,0,0)$
$oP4$	$P2_12_12_1$	4a	(x,y,z)
$tI2$	$I4/mmm$	2a/b	$(0,0,0)/(0,0,\frac{1}{2})$

2.3.2 Post-dfcc Phases

Despite the high-pressure behaviour of the trivalent lanthanides receiving a lot of attention, there is considerable debate regarding the structure of the post-dfcc phases. Further compression of the $hR24$ phase results in first-order phase transitions to the post-dfcc phases. Table 2.3 describes the structure candidates of the post-dfcc phases studied in this thesis.

The first pressure-induced, post- $hR24$ phase was assigned to the monoclinic $mC4$ structure in all the heavy trivalent lanthanides [6, 9, 61, 62, 68, 69], except Lu. Figure 2.1 displays the relationship between the cubic $cF4$ and monoclinic $mC4$ unit cells. This transition has been accompanied by a significant “collapse” in volume in all the lanthanides where it has been observed. It is expected that Lu will also transition from $hR24$ to $mC4$ at extreme compression but it has not yet been studied above 202 GPa, where the $hR24$ structure is still stable to that pressure [70]. Although refinements of the $mC4$ structure to diffraction patterns of the high-pressure phases in the heavy trivalent lanthanides were convincing, the misfitting peaks and absence of other peaks in the fits draw into question the validity of these findings.

The $mC4$ Structure

The $mC4$ structure was first assigned to a high pressure phase in Ce, labelled α'' , in 1974 by Ellinger & Zachariasen [47]. A more detailed study of this structure was published by Zachariasen four years later, describing the structure as a distortion of the fcc lattice [56]. Figure 2.1 shows the relationship between the $cF4$ and $mC4$ structures, where the large circles represent atomic coordinates of both the $cF4$ and $mC4$ structures.

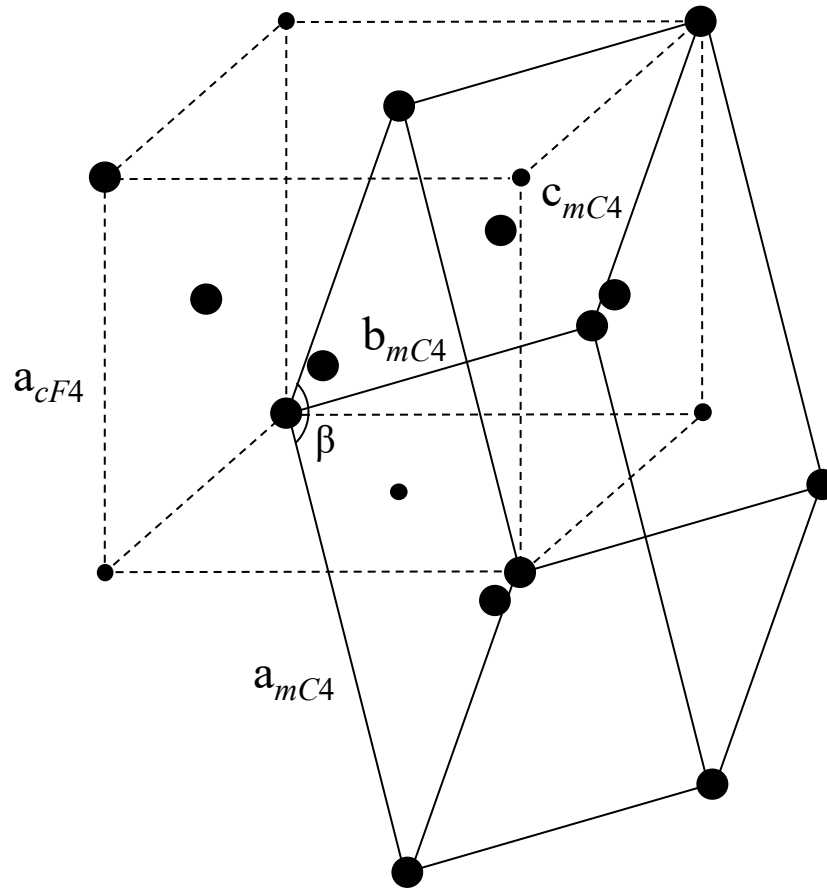


Figure 2.1 Relationship of the cubic $cF4$ (dashed line, with lattice parameter a_{cF4}), spacegroup $Fm\bar{3}m$, and monoclinic $mC4$ (solid line, with lattice parameters a_{mC4} , b_{mC4} , c_{mC4} and β), spacegroup $C2/m$, unit cells. The large circles are $mC4$ lattice points, and the small circles are additional lattice points of the $cF4$ unit cell. This figure is modified from Fig. 3 in Ref. [5].

The previously published literature on the high-pressure, post- $hR24$ phase of the heavy trivalent lanthanides provide decent refinements of the $mC4$ structure to diffraction patterns of the post- $hR24$. However, there is a peak not explained by the refined $mC4$ structure in any of the published data. This misfit was first noticed in the high-pressure diffraction data on Gd, Tb and Dy by Munro in his thesis [17]. The peak highlighted by the arrow in Figure 2.2 is striking as it is clearly separate from the $(\bar{3}12)$ peak to the left, and yet is not predicted by the $mC4$ structure, nor is it explained as a contaminant or arising from any pressure marker or PTM.

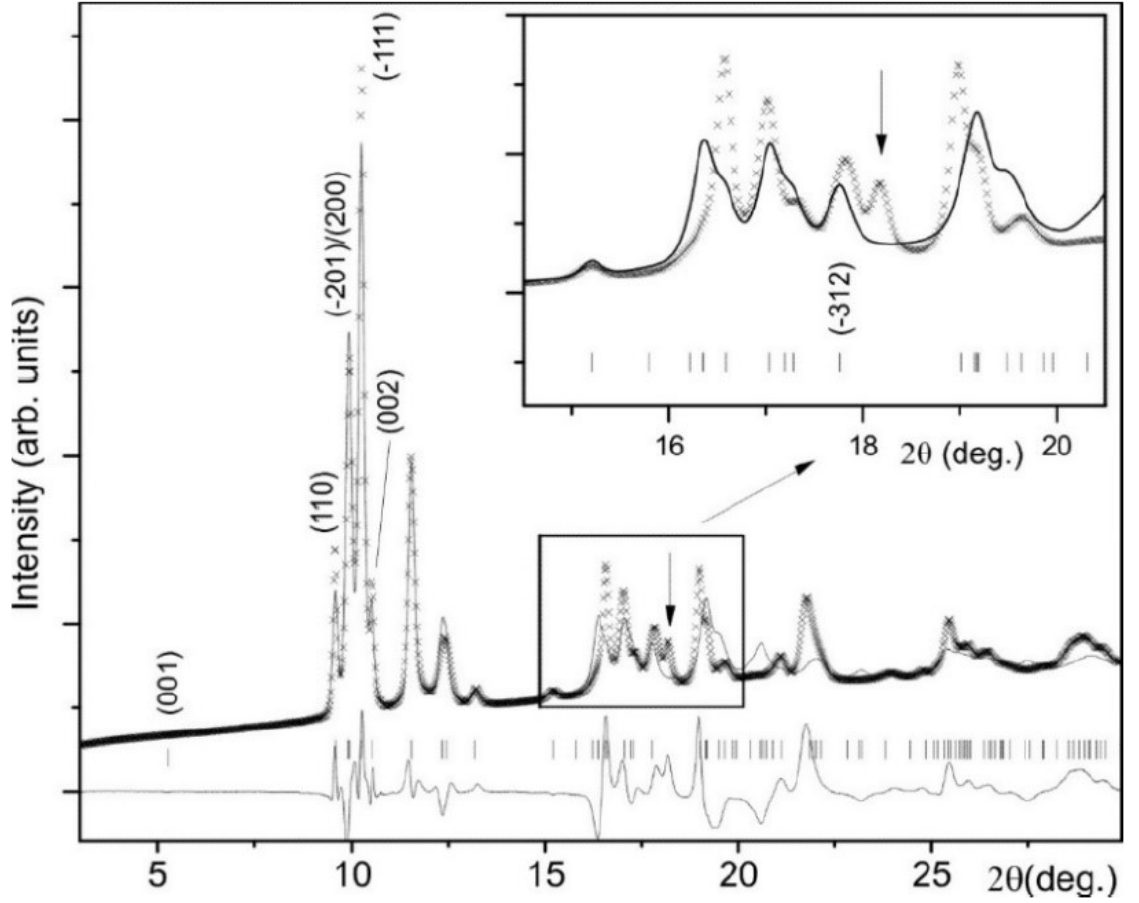


Figure 2.2 *Rietveld refinement of the $mC4$ structure to a diffraction pattern of Tb at 64 GPa. This pattern was collected by Keith Munro prior to the beginning of this thesis and taken from the Supplementary Material in Ref. [1].*

The arrows in Figure 2.3 highlight the same peak in diffraction profiles published on Tb (Figure 2.3, profile (a)) [6] and Ho (Figure 2.3, profile (b)) [7] that were fitted with the $mC4$ structure. In both profiles, the ‘bump’ next to the $(\bar{3}12)$ peak is once again unexplained.

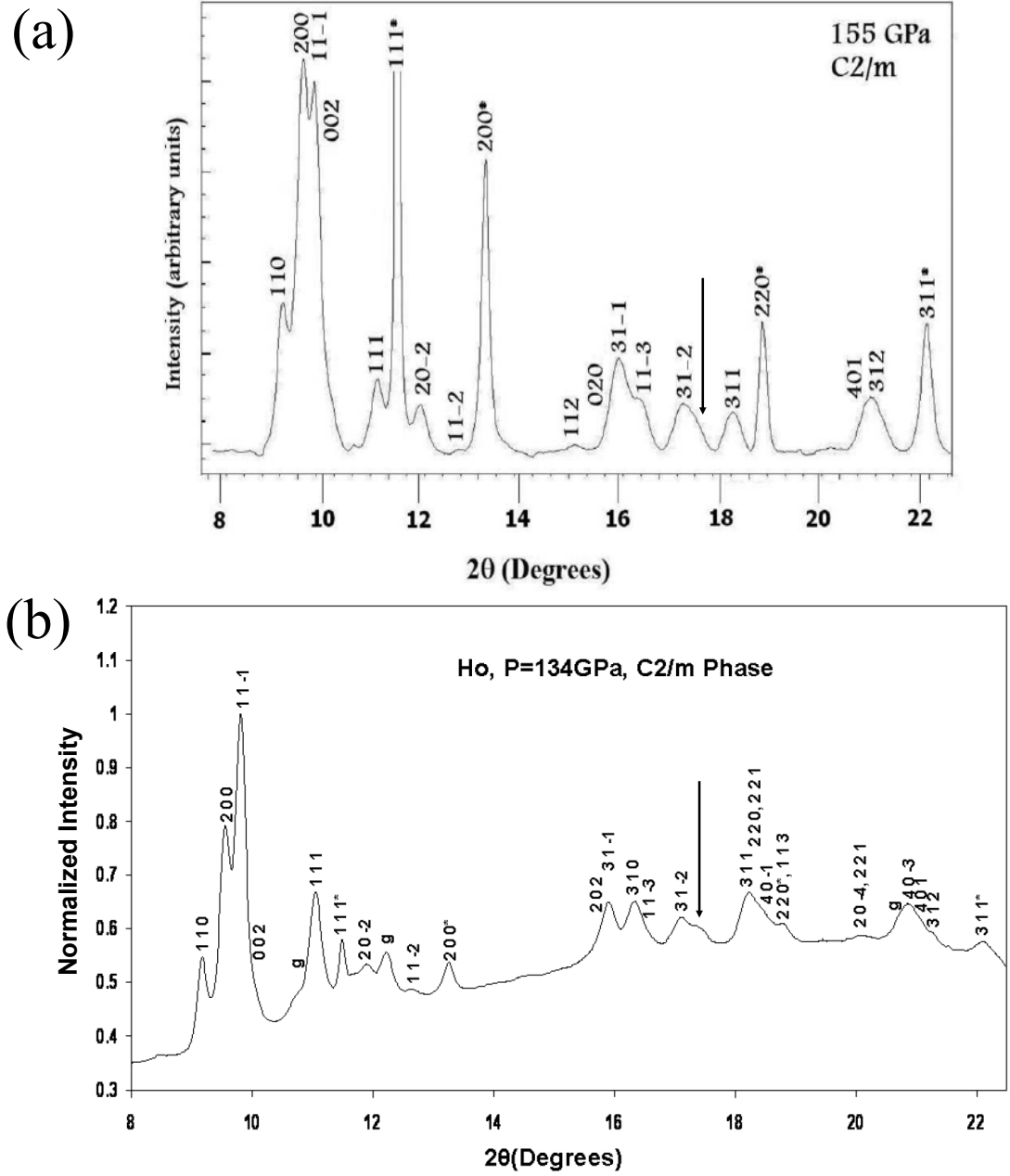


Figure 2.3 Rietveld refinements of the *mC4* structure to diffraction patterns of (a) Tb at 155 GPa (from Ref. [6]) and (b) Ho at 134 GPa (from Ref. [7]). The arrows in both profiles highlight a peak unexplained by the *mC4* fit.

Table 2.4 *Structural parameters for the $mC4$ structure observed in previously published literature on a number of lanthanides. The parameter values are taken from Ref. [10] and references therein.*

Lanthanide	Lattice Parameters ($\text{\AA}$)	β Angle
Ce	$a = 5.809, b = 3.178, c = 5.651$	112.8°
Nd	$a = 4.858, b = 2.712, c = 5.051$	118.6°
Sm	$a = 5.055, b = 2.604, c = 4.943$	112.8°
Gd	$a = 5.320, b = 2.802, c = 5.000$	112.0°
Tb	$a = 4.519, b = 2.669, c = 4.296$	105.4°
Dy	$a = 4.499, b = 2.627, c = 4.135$	106.1°
Ho	$a = 4.595, b = 2.696, c = 4.357$	105.8°
Er	$a = 4.540, b = 2.667, c = 4.355$	105.8°
Tm	$a = 4.325, b = 2.555, c = 4.314$	104.4°

Figure 2.4 displays two Rietveld refinements of the $mC4$ structure to diffraction profiles of (a) Dy and (b) Er, taken from publications by Samudrala *et al.* [8, 9]. The poor-fitting peaks are less obvious in Figures 2.2 and 2.3. However, the difference profile in (a) reveals a clear misfit. Furthermore, the tick mark in profile (b) that should indicate to the position of the $(\bar{3}12)$ or $(31\bar{2})$ peak lies significantly further left of the peak highlighted by the arrow.

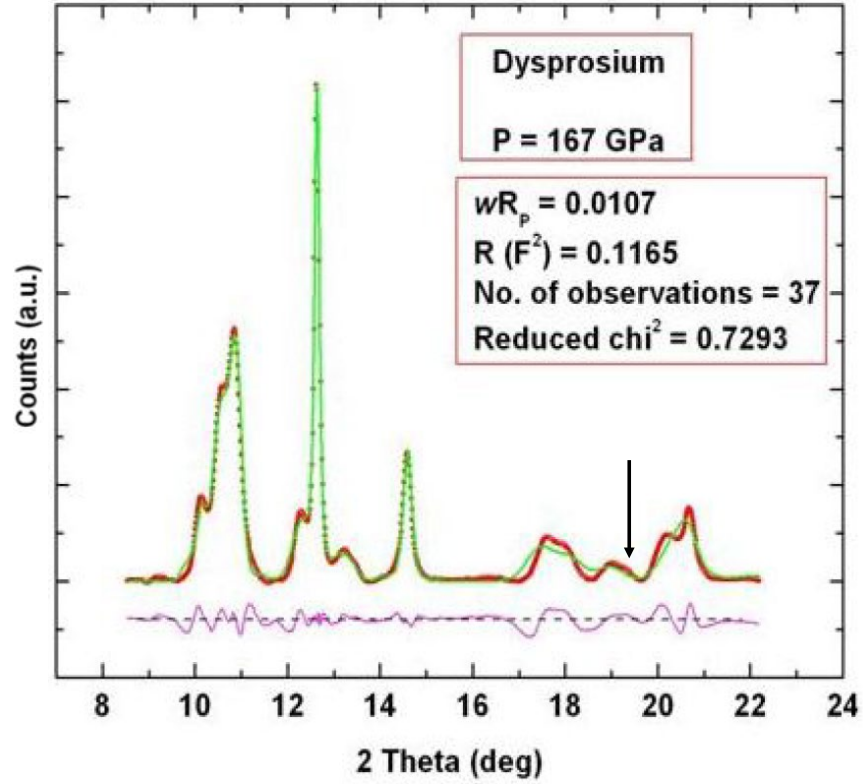
Unfortunately, no Rietveld refinements of Nd and Sm have been published. However, the structural parameters and, for the case of Nd, the (hkl) positions of the $mC4$ structures can be found in the literature [18, 20].

The structural parameters of the $mC4$ structure observed in the literature on the trivalent lanthanides are listed in Table 2.4. Although the lattice parameters, a , b and c , of the $mC4$ structure are all similar, the β angles of the $mC4$ structures of Tb – Tm are very different to those seen in Nd, Sm and Gd. Also, the β angles in $mC4$ -Tb – $mC4$ -Tm are markedly different to the β angle observed in $mC4$ -Ce. Finally, the β angle of the $mC4$ structure observed in Nd is significantly different to that of Sm, despite the similarities observed in the structural systematics of Nd and Sm (see Section 2.3.4).

2.3.3 Terbium, Gadolinium & Dysprosium

Tb ($Z = 65$) adds a lone electron to the half-filled $4f$ shell. At room temperature and pressure, Tb adopts the hcp structure, $hP2$ in Pearson notation, and transforms at ~ 3 GPa to $hR9$ – the Sm-type structure [15]. Upon further increase

(a)



(b)

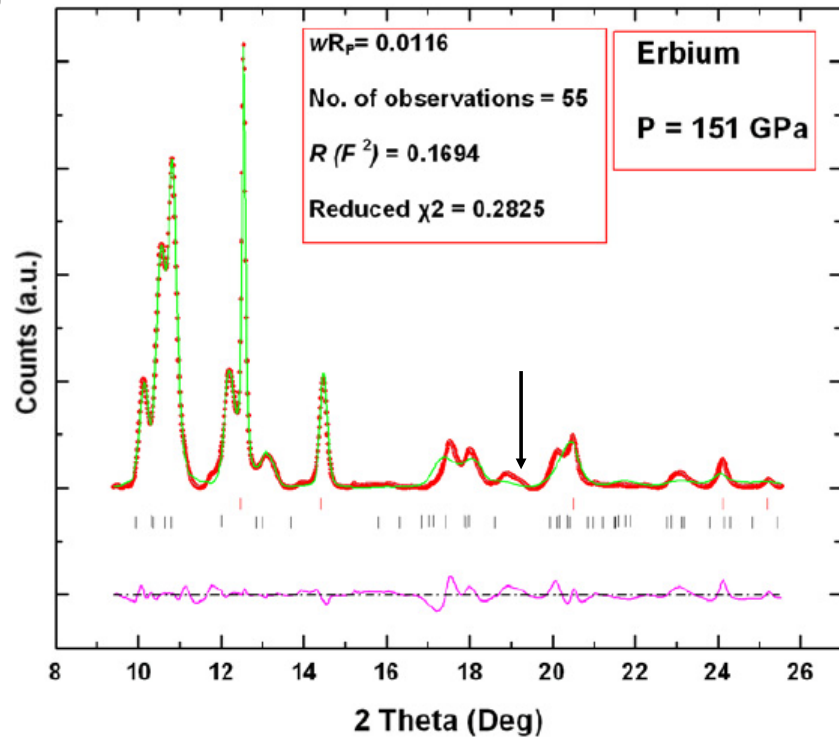


Figure 2.4 Rietveld refinements of the mC4 structure to diffraction patterns of (a) Dy at 167 GPa (from Ref. [8]) and (b) Er at 151 GPa (from Ref. [9]). The arrows in both profiles highlight a peak unexplained by the mC4 fit.

in pressure, Tb undergoes a transition to the dhcp phase between 14 GPa [67] and 16 GPa [10]. A phase exhibiting the fcc structure is believed to exist over a window of pressure between 30 and 40 GPa [6]. However, the $cF4$ peaks are seen in mixed-phase patterns with the $hP4$ structure, before reflections from the dfcc phase are observed after the remaining $hP4$ peaks from the dhcp phase disappear [6]. A sluggish phase transition to the dfcc phase occurs at 29 GPa, first marked by the appearance of weak fcc superlattice reflections, and whose structure has been assigned to $hR24$ – the same assignment first given to the post-fcc phase in Pr by Hamaya *et al.* [6, 67]. At pressures above 53 GPa, it is reported that the next phase exhibits the monoclinic $mC4$ structure and persists to the highest pressures studied [6].

Gd ($Z = 64$, a half-filled $4f$ shell) was the first lanthanide that was shown to exhibit the Sm-type structure on compression after it was first discovered in Sm at ambient conditions [57]. It is also the first lanthanide, as one traverses the elements from La to Lu, to exhibit the hcp structure at ambient conditions [15]. Therefore, this makes Gd the first lanthanide to exhibit the entire common structural phase transition sequence of the trivalent lanthanides.

Upon pressure increase, a transition to the Sm-type structure is reported to occur at ~ 2 GPa [57], and a further transition to the dhcp phase was observed at 10 GPa [41]. In studies on the heavy trivalent lanthanides, only Gd has been reported to exhibit the $cF4$ structure in single phase diffraction patterns in high-pressure conditions [61]. Although, in the study conducted by Errandonea *et al.* the diffraction profiles show strong peaks from the Ar pressure transmitting medium and, therefore, it cannot be ruled out that peaks from either the dhcp or dfcc phases may be present. The literature does not provide visual evidence of a clean, single phase fcc structure, and is only noted as mixed-phase with the dfcc structure in other works [71, 72]. Above 40 GPa, marked changes in the diffraction patterns have been reported to occur showing the transition to the dfcc phase. Errandonea *et al.* assigned the structure of this phase to $hR24$ [61]. Hua *et al.* reported a phase transition at 60 GPa to the post-dfcc phase in Gd, assigning a body-centred monoclinic structure to it [72]. However, Errandonea *et al.* claim that the structure is the same C -centred monoclinic structure, $mC4$, that is seen in the post-dfcc phase of Tb at high pressures [61]; yet, after examination of the data, the β angle of Gd is very different to that observed in this thesis.

Dy crystallises in the hcp structure at room temperature and pressure [15]. The subsequent transitions to the Sm-type, dhcp and dfcc phases were first

observed and resolved by Grosshans in his thesis at pressures of 8, 17 and 43 GPa, respectively [66]. Once again, no pure fcc phase has been observed in any reports from the literature, and instead a dhcp $\rightarrow$ dfcc transition [66, 68, 73, 74] occurs. Patterson *et al.* provided the first structural assignment of $hR24$ to the dfcc phase, marking it as the same structure as that assigned to the dfcc phase of Pr [67]. In contrast to the elemental neighbours of Dy, the dfcc phase has also been assigned by Shen *et al.* to an orthorhombic structure with 8 atoms in the unit cell, $oS8$ in Pearson notation, from the spacegroup $Cmmm$ [74].

Dy is similar to its trivalent lanthanide neighbours, Gd, Tb, Ho, Er and Tm, such that its post-dfcc structure has been assigned to the C-centred monoclinic $mC4$ structure [8]. It has also, however, been assigned to a body-centred monoclinic structure [68], iso-symmetrical with the structure assigned to the post-dfcc phase in Gd by Hua *et al.* [72].

The post- $hR24$ phases of Gd, Tb and Dy are all accessed at pressures under 100 GPa. Therefore, to study the structural systematics of the phases beyond post- $hR24$ of the heavy trivalent lanthanides, these three elements are the preferred candidates.

2.3.4 Samarium & Neodymium

There have been extensive x-ray diffraction studies on Sm and Nd as they both have a small number of $4f$ electrons that have caused researchers to query the participation of f electrons in the bonding [10].

At ambient conditions, Sm adopts the $hR9$, or Sm-type, structure [10]. At around 1 GPa, Sm undergoes a transition to a dhcp structure $hP4$, which then transitions again at 14 GPa to the fcc phase ($cF4$ structure) [10]. It undergoes a further transition to the dfcc phase ($hR24$ structure) at 20 GPa [75]. Above 42 GPa, Sm transitions to the $hP3$ phase [76], spacegroup $P3_121$, obtained via a volume collapse of 3.1% [75]. The next high pressure phase in Sm has also been indexed as the same monoclinic structure to that noted to exist in the post- $hR24$ phases of all the heavy trivalent lanthanides except Lu. Chesnut assigned this structure of the post- $hP3$ phase to $mC4$, spacegroup $C2/m$ [20]. Ten years previous to this, Vohra published work on the post- $hR24$ phase in Sm, assigning a body-centred tetragonal structure to this phase, first occurring at 91 GPa [49], noting that this structure had also been detected above 20 GPa in Ce by Endo and Olsen

previously [77, 78].

Nd crystallises in the dhcp structure at ambient pressure and temperature [15]. At 3.8 GPa, it undergoes a phase transition and adopts the fcc structure [79]. Nd then transforms to a dfcc phase at ~ 16 GPa [28]. This phase adopts the $hR24$ structure. This is the last structure in the commonly known structural phase transition sequence mentioned in Section 2.3.1 of this chapter and in Chapter 4. A second dfcc phase occurs at ~ 26 GPa with a structural assignment to a body-centred orthorhombic structure with sixteen atoms in the unit cell, $oI16$, with spacegroup $Ibam$ [28]. Pr is the only other known lanthanide to exhibit this structure [23]. This phase is stable until 40 GPa in Nd whence a transition to the $hP3$ phase occurs [76]. This then remains stable to ~ 75 GPa where the literature reports that it transforms to the $mC4$ phase [24].

The high-pressure structures of Sm and Nd are of interest to this work as previous publications have assigned the same $mC4$ structure to the post- $hP3$ phases as that assigned to the post-dfcc phases of the heavy trivalent lanthanides. Interestingly, comparisons of the diffraction patterns on the post-dfcc phases of the heavy trivalent lanthanides [6, 9, 10, 61–63] and the post- $hP3$ phases of Sm and Nd [18, 20] fitted with the $mC4$ structure highlight how remarkably different they are.

Previous studies of Sm have linked changes in its crystal structure and compressibility to changes in its electronic structure, particularly changes from d -bonding in the $hR24$ structure, to intermediate $4f$ -bonding in the $hP3$ structure, to itinerant $4f$ -bonding in the $mC4$ structure [76]. It is therefore intuitive that Nd would exhibit the same structural systematics resulting from similar electronic behaviour at high pressures.

2.3.5 Praseodymium

Pr adopts the dhcp structure, $hP4$ [15], at ambient conditions which persists until a transition to the fcc phase occurs at ~ 4 GPa [42, 80]. Hamaya *et al.* assigned a rhombohedral structure with 24 atoms in the unit cell to the next phase, which is described as a distortion of the fcc structure [67]. However, it also exhibits similar structural systematics to Ce such that the phase transition to α -U from the dfcc phase at 20 GPa is accompanied by a large volume collapse in Pr of ~ 9 –10% [64, 81]. Chesnut & Vohra reported a significantly larger volume

collapse of 16.7% from a monoclinic structure, $mC4$, to the α -U structure [60]. A study by Velisavljevic *et al.* reported a $\sim 10\%$ volume collapse on transition to the α -U phase, but does not indicate what structural assignment the previous phase adopted [22].

Pr is reported to transition at 147 GPa to another orthorhombic structure, spacegroup $P2_12_12_1$, and is described as a distortion of the α -U structure [22]. The same study reported a possible transition to a tetragonal phase above 260 GPa via anisotropic compression of the lattice parameters [22]. However, the data resulting from the energy-dispersive x-ray powder diffraction (EDXD) experiments were of poor quality.

2.3.6 Holmium to Lutetium

The last four trivalent lanthanides, holmium (Ho), erbium (Er), thulium (Tm) and Lu, have been studied to ~ 200 GPa in x-ray diffraction experiments. However, they are often overlooked as they require pressures much greater than their lighter lanthanide neighbours to enter the post-dfcc phases. Regardless, these elements are expected to exhibit the same structural sequence as the lighter trivalent lanthanides, as illustrated in Figure 2.5, and thus one can rely on the high-pressure structural results of the previous trivalent lanthanides.

The post-dfcc, volume-collapsed phases of Ho, Er and Tm have been assigned the $mC4$ structure [7, 9, 63]. They transition from the $hR24$ phase at 103, 118 and 124 GPa, respectively. It is expected that Lu will also transition to the volume-collapsed phase above 202 GPa, where it still remains in the $hR24$ phase [70].

2.3.7 Promethium

Along the lanthanide series, between Nd and Sm, sits promethium (Pm). It is considered a trivalent lanthanide and exhibits the common structural sequence with increasing pressure. However, it is a radioactive element and, therefore, is often left out of high-pressure x-ray diffraction study. Haire *et al.* studied Pm using EDXD, observing the dfcc phase from 18 GPa up to the maximum pressure of 60 GPa [82]. This study assigned a triple-hcp structure to the dfcc phase; however from more recent studies of the dfcc phases in the trivalent lanthanides,

it is probable that the correct structural assignment to this phase is the $hR24$ structure. One can expect Pm to exhibit the same post-dfcc structures observed in the trivalent lanthanides.

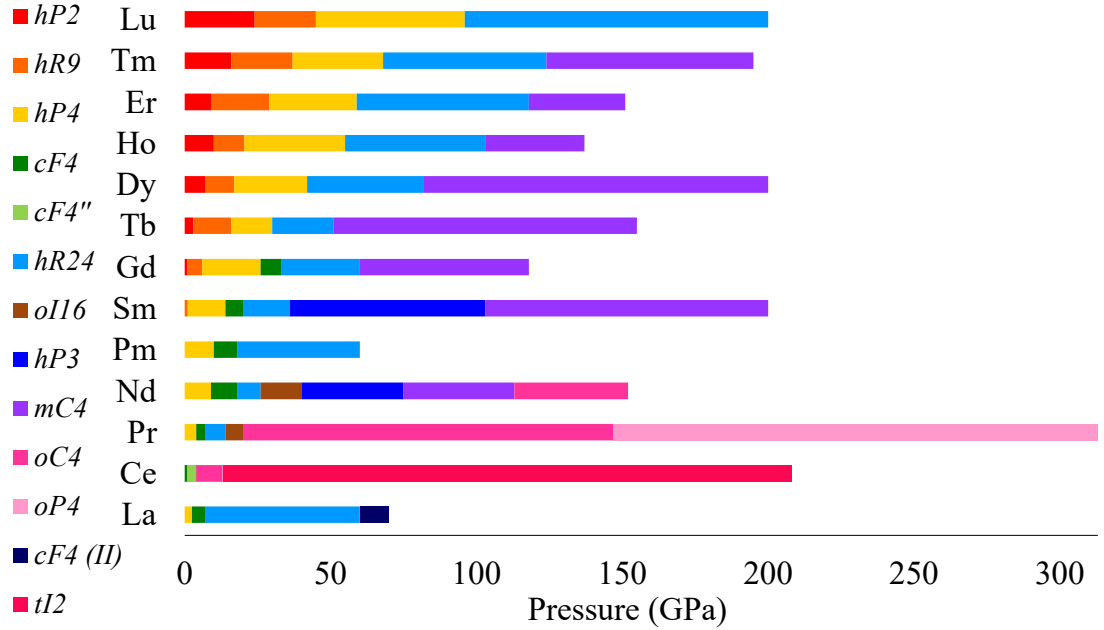


Figure 2.5 *The pressure-induced, structural phase transition sequences of the trivalent lanthanides and Ce to 313 GPa, taken from [10] and references therein. One can see that the $mC4$ structure is reported to exist at high pressures in most of the trivalent lanthanides.*

2.4 Analogous Behaviour of the Lanthanide & Actinide Elements

Despite the number of detailed reviews of the actinides and their electric and magnetic behaviour [14], little is understood publicly about them at high pressure. Their radioactivity means that studying them at synchrotron facilities is very expensive due to the health and safety precautions needed to carry out the experiments. As a result, they are generally only studied by a nation's nuclear research sector. The only one that is heavily researched outside of these sectors is U, yet more often in a compound, and only to 100 GPa in diffraction studies as its behaviour is classified above this pressure.

However, the behaviour of $5f$ electrons is of great interest to the high pressure community. Furthermore, many structures that exist at high pressures in

the lanthanides also exist at ambient conditions, high pressures and high temperatures in the actinides. For instance, Ce exhibits a body-centred tetragonal structure at high pressures [48, 83, 84] that is also seen in Th at ambient conditions [85, 86], and U above 940 K and at ambient pressures [50]. Another example is seen in high-pressure phases of Ce, Pr and Nd that exhibit the α -U structure – one that has been observed in U up to 100 GPa and room temperature [15]. A distortion of the α -U structure, with spacegroup $Pnma$ is observed in a high-pressure phases of americium (Am), curium (Cm) and Cf [19, 87, 88]. Furthermore, Am, Cm and Cf exhibit the dhcp and fcc structures [88–91], which are linked to $s \rightarrow d$ electron shell transfer.

Perhaps the most important note to take from the analogous behaviour of these two series of elements is that the f electrons in the actinides become itinerant and participate in the bonding at high pressures [91–93]. When this happens, the actinides exhibit particular structures. Therefore, if and when these structures are observed in the lanthanides at certain pressures, it can be expected that the $4f$ electrons would delocalise and participate in the bonding.

The heaviest actinide elements, einsteinium (Es) – lawrencium (Lr), have comparatively very short half lives to the lighter actinides and lanthanides. With a half-life of 472 days for Es to just 3.6 hours for Lr, the instability of these elements makes them almost impossible to study in most environments including large instruments such as synchrotrons.

2.5 The Rare Earth Elements

The four rare earth elements preceding the lanthanide and actinide series' are Y, scandium (Sc), La and Ac. Y has been studied extensively as its structural systematics are similar to the heavy trivalent lanthanides, and will be discussed in Section 2.5.1 and Chapter 8.

Sc exhibits the β -neptunium (β -Np) [94] and $hP3$ structures at high pressures [79], showing the analogous behaviour between itself, the actinides U [50] and Np, and the lanthanides Sm, Nd and Yb. Ac is radioactive and so, like many of the actinides, has not been studied as extensively on synchrotrons or at high pressures.

Although La is trivalent at ambient conditions [95], it does not contain any f

electrons and, perhaps because of this, it exhibits a slightly different pressure-induced, structural phase transition sequence: $hP4 \rightarrow cF4 \rightarrow hR24 \rightarrow cF4$ [15, 96]. La has not been studied much above 60 GPa, but as it is a member of the trivalent lanthanides it is expected to exhibit more of the common structures of the sequence at higher pressures. Indeed, theoretical studies suggest that La will have some $4f$ band occupancy above 1000 GPa [97].

2.5.1 Yttrium

Y is used as benchmark for comparison on electronic behaviour in rare earths. The common pressure-induced, structural phase transition sequence of the trivalent lanthanides was originally thought to arise from f electron band occupancy alone, but Y has no f electrons [45, 81].

The phase sequence of Y matches that, more specifically, of the heavy trivalent lanthanides, exhibiting the entire sequence beginning with a hcp structure, $hP2$, at ambient conditions [98]. Y transitions to the Sm-type structure $hR9$ at 13 GPa, which is complete by 16 GPa [98], and there is a transition to the $hP4$ structure begins at 25 GPa which is complete by ~ 34 GPa [11, 98]. Y undergoes sluggish transitions from $hP2 \rightarrow hR9 \rightarrow hP4$ and does not exhibit a single phase fcc pattern but rather a mixed dhcp-fcc phase, observed at 39 GPa and persisting to 50 GPa [11]. The sluggish transitions and large regions of mixed phases at lower pressures are thought to arise from the slight differences in stacking of the hexagonal layers [11]. There is debate over whether the dfcc phase adopts the $hR24$ structure [11] or a slight distortion thereof [99].

At ~ 100 GPa, a transition to the post-dfcc phase occurs. Samudrala *et al.* fitted the diffraction data of this phase with the $mC4$ structure [11]. Figure 2.6 displays a Rietveld refinement made by Samudrala *et al.* of the $mC4$ structure to a diffraction profile from Y at 120 GPa. The arrow in the diagram highlights the same misfitting peak as that highlighted in Figures 2.2, 2.3 and 2.4 from Section 2.3.2. The difference profile highlights the misfit, although the peak is not distinguishable from the more intense peak to the left.

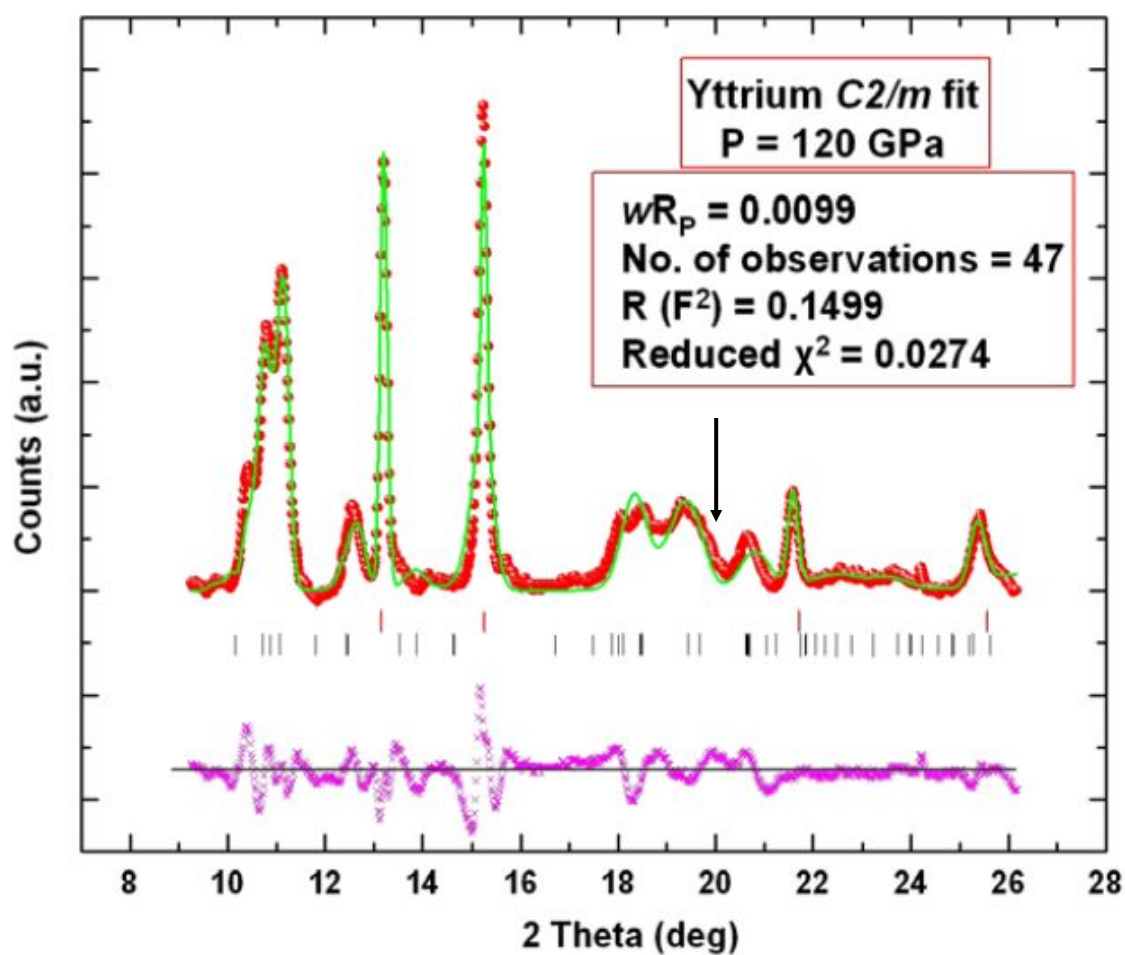


Figure 2.6 Rietveld refinement of the *mC4* structure to a diffraction patterns of Y at 120 GPa (from Ref. [11]). The arrow highlights a peak unexplained by the *mC4* fit.

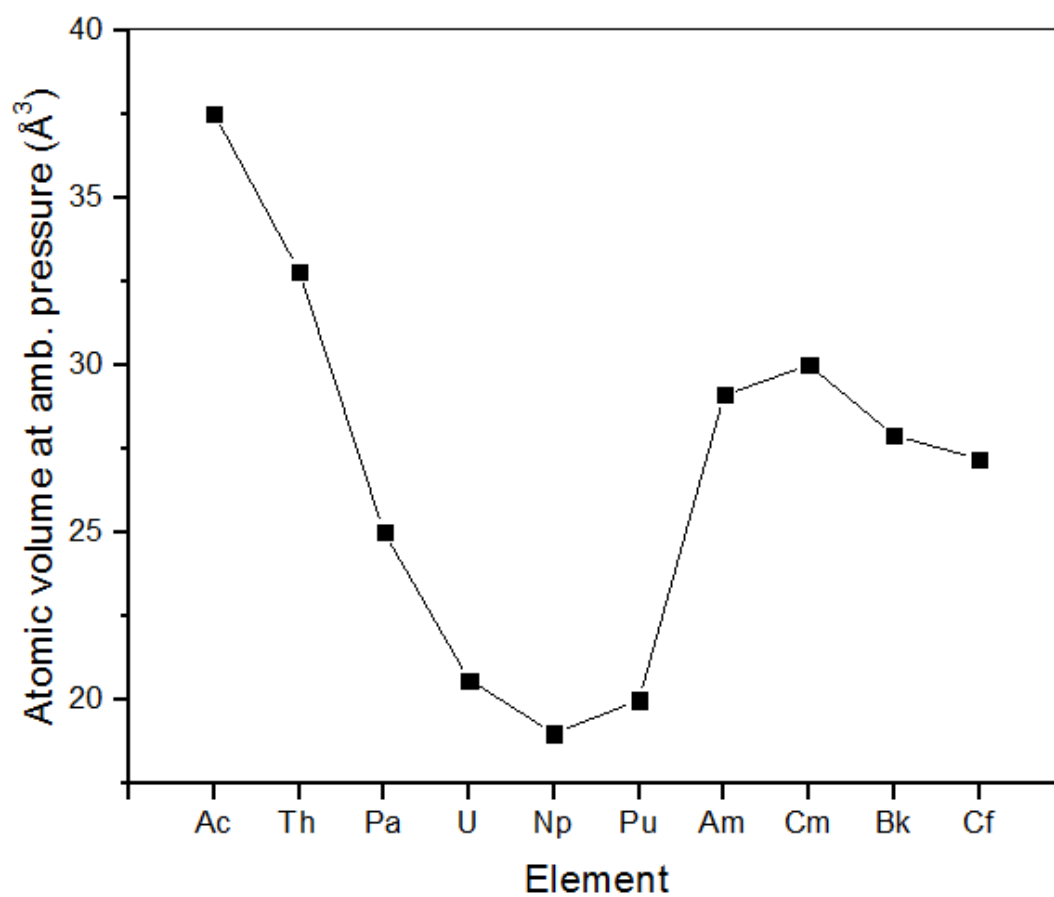


Figure 2.7 *Volume per atom of the actinides Ac – Cf at ambient conditions. This trend is referred to in many reviews on the actinides [12–14] and is modified from Fig. 15.7 in Ref. [15].*

2.6 Electrical & Magnetic Properties of the Rare Earth & Actinide Metals

As one traverses the lanthanides in increasing Z , a reverse structural sequence from dhcp $\rightarrow$ Sm-type $\rightarrow$ hcp is seen at ambient conditions. This was initially believed to arise as a result of the gradual increase of $4f$ shell occupation with increasing atomic number or pressure [58]. However, as mentioned in Section 2.5.1, Y challenges this theory due to an absence of any f electrons [45, 98].

It has been generally accepted that the f electrons only participate in the bonding at extreme compression, or when the f electrons become delocalised [100]. The common phase transitions exhibited by the trivalent lanthanides and Y at lower pressures support this understanding that no f electrons are participating in the bonding [101].

The $4f$ electron in Ce is believed to be itinerant at ambient pressure and participate in the bonding [102], making Ce the only lanthanide to behave as such. However, in the actinide series protactinium (Pa), U, Np and plutonium (Pu) all have delocalised $5f$ electrons that participate in the bonding. Figure 2.7 shows how the ambient volume of the actinides from actinium (Ac) to californium (Cf) changes with increasing Z . One can see the significant drop in atomic volume, reaching a minimum in Np to $<20 \text{ \AA}^3$ before rising sharply to $\sim 30 \text{ \AA}^3$ in Am. It is thought that the $5f$ electrons of Pa, U, Np and Pu are itinerant at ambient pressure because of their close proximity and orthogonality with the $4f$ electrons at such a small atomic volume, resulting in an increased spatial extension and, thus, become delocalised [15]. In Am, the stabilising of three $5f$ electron pairs overrides what stability is gained from delocalisation and, therefore, no longer participate in the bonding [59, 103]. However, the f electrons in Am become itinerant again at high pressures [104]. As mentioned in Section 2.4, this itinerant f electron behaviour is expected to occur at high pressures in the trivalent lanthanides as well, and produce a unified, pressure-induced, structural phase transition sequence for the lanthanide and actinide elements.

In Chapters 4–8, calculations have been performed by our collaborators Plekhanov *et al.* at King’s College London using DFT. Whereas DFT is not pivotal to this thesis, the results from their work bolster the findings presented in the following chapters. In the simplest understanding, examining the enthalpy of structurally different, pressure-induced phase transitions can help predict the

experimentally observed phase transitions. In short, the phase transition with the lowest predicted enthalpy will likely be the one observed in experiment. Theoretical studies by Schilling’s group have looked into the magnetic behaviour of several trivalent lanthanides at the $hR24 \rightarrow mC4$, or “volume-collapsed”, phase transition [105–108], revealing anomalous magnetic behaviours. Indeed, the theorised anomalous magnetic behaviours occur in the phases of interest in this thesis, and correctly interpreting these behaviours depend upon knowing the correct crystal structures assigned to these phases.

2.7 Conclusions

This critical review has brought forward a number of outstanding issues with the structural systematics of the trivalent lanthanides. The structure of the collapsed, post-dfcc phase of the heavy trivalent lanthanides is unclear and is likely incorrectly assigned to the $mC4$ structure as a result of a single peak not predicted by the $mC4$ structure. Furthermore, the significant differences in the β angles of the collapsed, post-dfcc phases of Nd and Sm indicate that the $mC4$ structure is also incorrectly assigned to those phases.

The post- $oC4$ phase of Pr and the post- $hR24$ phase of Y will also be studied. As mentioned in Section 2.3.5, the ultra-high pressure EDXD studies on the post- $oC4$ phases of Pr resulted in poor-quality diffraction profiles. These profiles have therefore drawn into question whether or not the phases have the correctly assigned structures. The $mC4$ structural assignment to the post- $hR24$ phase of Y is the same as that of the structural assignment to the post- $hR24$ phases of the heavy trivalent lanthanides. Furthermore, the published, high-pressure diffraction data has highlighted the same outstanding issue as that arose from the critical review of the heavy trivalent lanthanides.

The issues highlighted here will be explored in this thesis using state-of-the-art ADXD and high-pressure diamond anvil cell (DAC) techniques. These techniques will be described in detail in the following chapter, and the results from the experiments conducted will be discussed in Chapters 4–8.

Chapter 3

Experimental Techniques

3.1 Introduction

Many books and reviews on the understanding of high-pressure, high-temperature physics and chemistry within the Earth's interior have been published as interest in the behaviour of materials under changing conditions has always been an important topic [109–111]. These texts explore the different minerals and compounds that make up the Earth's crust, mantle and core. In order to study the conditions existing within the Earth, high-pressure, high-temperature experimental techniques are required. Many techniques, from anvil presses to utilising diamonds as anvils in metal cells, have developed significantly over the last 70 years, and reviews detailing current methods have been adopted here in this thesis [112]. These high-pressure, high-temperature experimental techniques are pivotal to this study.

This thesis describes results from many angle-dispersive, x-ray powder diffraction experiments performed on samples of lanthanide metals and Y. They were conducted to observe and study the structures and structural symmetry of the high-pressure phases of these elements. This chapter will describe the experimental techniques used throughout this work in detail. It is split into four main sections. Section 3.2 gives an overview of crystals and, in particular, the symmetry of periodic crystals. Section 3.3 provides an explanation of x-ray diffraction and its employment on synchrotron light sources. Section 3.4 details the DAC, which is the device used to achieve high-pressure in this thesis, and the

different types of DACs used throughout this work. Finally, Section 3.5 gives a brief overview of the methods used in data analysis.

3.2 Crystals

This section focuses on periodic crystals and their symmetry in Sections 3.2.1 and 3.2.2. A brief overview on Pearson notation is also given in Section 3.2.3.

3.2.1 Periodic Crystals

Any crystal where periodicity is consistent throughout a 3-dimensional lattice can be considered periodic. Conversely, any crystal where periodicity is absent in a 3-dimensional lattice can be considered aperiodic, although crystals with very little periodicity are also considered aperiodic by convention. A periodic crystal describes the opposite of an aperiodic crystal, and is the only type considered in this study. A periodic crystal is one where the lattice periodicity repeats often enough to produce sharp diffraction peaks of the reciprocal lattice.

The difference between aperiodic and periodic crystals is then determined via the intensities of such diffraction patterns. For a periodic crystal, the diffraction pattern will describe the spacegroup of a known crystal structure.

One can draw the identical points of a crystalline structure, the lattice points, in 3 dimensions. These lattice points can be defined by three translation vectors: $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ which make up the Bravais lattice, or direct lattice, of the structure and are related by translational symmetry using the following lattice vector Equation 3.1

$$\mathbf{R} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3 \quad (3.1)$$

where $\mathbf{R}$ is a lattice vector, $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are the translation or primitive lattice vectors and u , v and w are integers. The translation vectors form a parallelogram that defines the boundaries of the unit cell. This unit cell can then be translated through the entire crystal and fill all available space [113].

Within the unit cell, sit the atoms whose positions are determined by Equation

3.2

$$\mathbf{r} = x_1\mathbf{a} + x_2\mathbf{b} + x_3\mathbf{c} \quad (3.2)$$

where $\mathbf{r}$ is the position vector, and x_1 , x_2 and x_3 are fractional coordinates with respect to the basis vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$. The reciprocal lattice is the Fourier transform of the Bravais lattice and is defined by Equation 3.3, where h , k and l are integer numbers. These are the Miller indices and are specific to a crystal's unit cell.

$$\mathbf{G}_{hkl} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^* \quad (3.3)$$

The reciprocal lattice vectors, $\mathbf{G}_{hkl}$, are defined by the three translation vectors $\mathbf{a}_1^*$, $\mathbf{a}_2^*$, $\mathbf{a}_3^*$ described in Equation 3.4.

$$\begin{aligned} \mathbf{a}_1^* &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \\ \mathbf{a}_2^* &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \\ \mathbf{a}_3^* &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \end{aligned} \quad (3.4)$$

3.2.2 Symmetry of Periodic Crystals

For an object to have definite symmetry, there must be a distinguishable point, line or plane about which symmetry operations, such as reflection, inversion, rotation or translation, can apply. These operations must also be consistent with one another. When considering a molecule, the symmetry elements are required to pass through the centre of the molecule and are known as the molecule's point group. In contrast to this, the symmetry elements of a crystalline solid need not pass through one specific point, or indeed a centre of any one atom, but do pass through the unit cell of that solid. Those symmetry elements are then translated to all other unit cells [113].

In a perfect crystalline solid, the atoms are arranged in a regular way throughout its entire structure. This regular arrangement can be described via a crystal's symmetry operations. Some symmetry operations are forbidden in crystalline

solids due to a required combination of specific translational symmetry operations with those symmetry operations. Perfect crystalline solids can only have 1st, 2nd, 3rd, 4th and 6th orders of rotation. Rotation and reflection operations can be combined with translational operations to produce screw axes and glide planes as part of symmetry elements. Collectively, there are 230 arrangements of symmetry operations in the solid state and are known as the 230 spacegroups [114]. The information behind each spacegroup has been contained in the International Tables for Crystallography, Volume A [115]. The restriction imposed by the allowed orders of rotation means that only 32 point groups can be applied in the solid state, leading to only 7 different crystal systems. As mentioned previously, further restrictions are imposed on the unit cell parameters of a crystal. Combining these restrictions with that imposed by the orders of rotation gives a maximum of 14 distinctive lattices, otherwise known as the 14 Bravais lattices [116].

The symmetry elements can define atomic positions within the unit cell of a crystalline solid, known as Wyckoff positions. These can be split further into general (does not lie on a symmetry element) or special (lies on a symmetry element) positions. These positions will have a site multiplicity which describes the number of atoms generated by any one atom at that position. Therefore, a spacegroup will have a number of possible Wyckoff positions that are described in terms of the site multiplicity and a letter [114].

3.2.3 Pearson Notation

Throughout this thesis, the crystal structures described will most often be referred to using Pearson notation. This style describes the crystal structure using one lower case letter and one upper case letter, followed by a number.

The first letter, in lower case italics, indicates the crystal lattice, and in ascending order of symmetry are *a* = triclinic, *m* = monoclinic, *o* = orthorhombic, *t* = tetragonal, *h* = hexagonal and *c* = cubic. The second letter, in upper case italics, describes the lattice centring of the crystal or, in other words, the centring of the unit cell: *P* = primitive, *A*, *B*, *C* or *S* = centring on a specific face of the unit cell, *R* = rhombohedral (specific to hexagonal crystal lattices exhibiting rhombohedral centring), *F* = face-centred and *I* = body-centred. The number at the end of the notation indicates the number of atoms in the unit cell of the crystal. One such example is *hP2*, which is a primitive, hexagonal lattice with 2 atoms in the unit

cell. Another example is $oC4$, which is a C -centred, orthorhombic lattice with 4 atoms in the unit cell.

3.3 X-ray Diffraction

This section details X-ray diffraction. First of all it will explain the theory behind diffracted waves in a lattice of atoms in Section 3.3.1 by explaining the Bragg and Laue formalisms, the reciprocal lattice and the Ewald construction. Following on from this, the explicit study of x-ray powder diffraction will be detailed in Section 3.3.2 as this is the specific technique used in this work. Finally, Section 3.3.3 describes synchrotron x-ray diffraction.

3.3.1 Theory of X-ray Diffraction

The scattering of intense x-rays from matter was first described by Max von Laue, Lawrence Bragg and his father William Henry Bragg in 1912 [117]. In the Bragg description, one considers a plane of atoms from which incoming x-rays are scattered. In the Laue description, one considers an incoming wave that is scattered by points within a crystal. The Bragg and Laue formalisms are viewed as alternate descriptions of the same principle. Another way to view the two is to consider that the Laue formalism is a vector expression in reciprocal space, converse to Bragg formalism which is the scalar equivalent. Since then, the development of the Ewald construction by Paul Peter Ewald in the 1960s helped to visualise how both the conditions required by the Laue and Bragg formalisms could be mathematically allowed.

Bragg Formalism

The Bragg formalism gives the geometrical conditions in order to observe a diffracted beam of x-rays. It describes the periodic distribution of atoms in a solid as parallel planes that are defined by h , k and l – three integers, the Miller indices, that describe how the planes intersect the three lattice or basis vectors, $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$. When x-ray beams are diffracted from a crystal lattice planes a distance d apart, constructive interference occurs allowing us to observe the reciprocal lattice planes in a diffraction pattern. Figure 3.1 displays x-ray waves with an

incident wavevector $\mathbf{k}$ diffracting from planes of atoms separated by a distance d to produce x-ray waves with a wavevector $\mathbf{k}'$. The condition for constructive interference is described by Equation 3.5

$$n\lambda = 2d \sin \theta \quad (3.5)$$

where n is the order of reflection, d is the lattice plane spacing and θ is the angle between the incident wave and the lattice plane. In order for constructive interference to occur the path differences of these X-rays must be integer values so that the atomic structure can be observed in a diffraction pattern. When x-rays are incident on a plane of atoms in a crystal lattice they interact with the electrons in the electron clouds surrounding these atoms. This causes the clouds to move via the additional energy provided by the x-rays, which then re-radiate said x-rays with a frequency equal to the frequency of the moving electrons. This phenomenon is known as Rayleigh scattering [118].

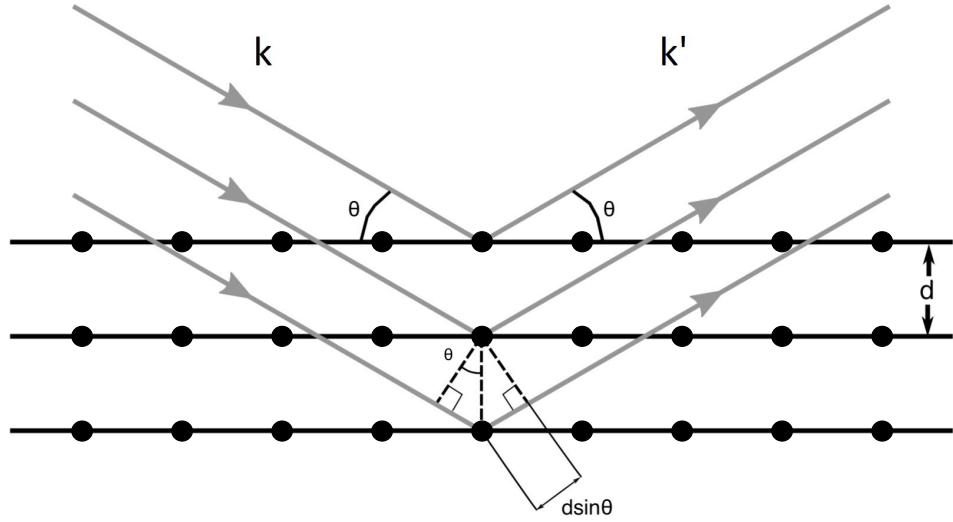


Figure 3.1 *Diffraction of incoming beams from lattice planes of atoms, separated by a distance d defined by the integer values of h , k and l of each plane. The angle between d and the dashed line normal to the incident and diffracted waves, or between each plane and the incident and diffracted waves, is θ .*

Laue Formalism

The Laue formalism considers the scattering of an incident wave from two points in a crystal. Consider an incident wave with wavevector $\mathbf{k} = 2\pi\hat{\mathbf{n}}/\lambda$ diffracting from two points in a crystal O and B, separated by a distance d , to give a diffracted wave with wavevector $\mathbf{k}' = 2\pi\hat{\mathbf{n}}'/\lambda$. Figure 3.2 displays an illustration of this, where the paths $\vec{AB} + \vec{BC} = d\cos\theta + d\cos\theta' = \mathbf{d} \cdot (\hat{\mathbf{n}} - \hat{\mathbf{n}}')$. Therefore, for constructive interference to occur, the condition $\mathbf{d} \cdot (\hat{\mathbf{n}}' - \hat{\mathbf{n}}) = m\lambda$ must be met. Finally, by multiplying both sides by $2\pi/\lambda$, and remembering that $\mathbf{k} = 2\pi\hat{\mathbf{n}}/\lambda$, one can obtain the condition for constructive interference in terms of the incident and diffracted wavevectors

$$\mathbf{d} \cdot (\mathbf{k}' - \mathbf{k}) = 2\pi m \quad (3.6)$$

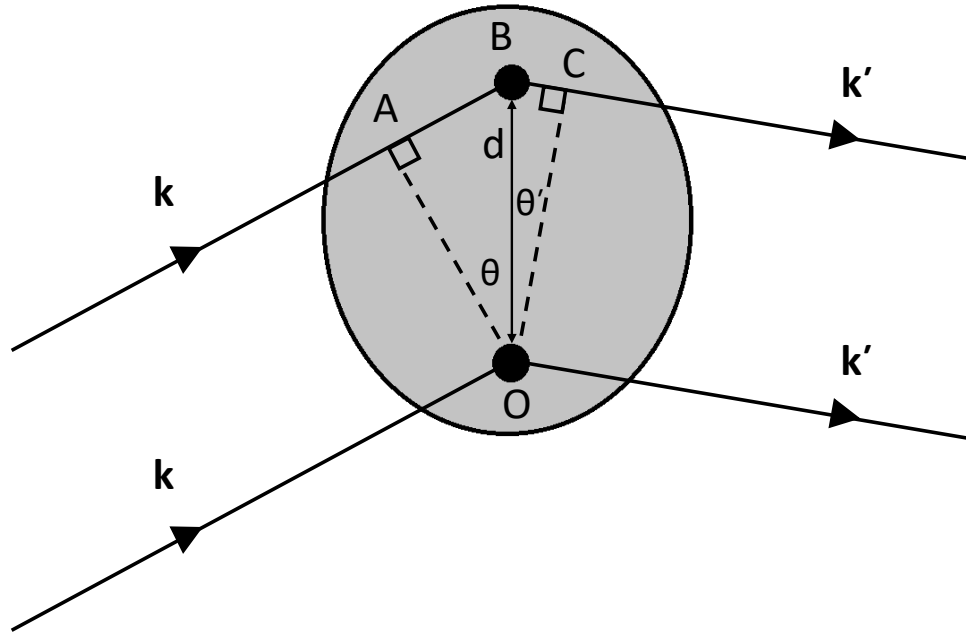


Figure 3.2 *Diffraction of incoming waves with wavevector $\mathbf{k}$ from two points in a crystal (grey ellipse), separated by a distance d , producing waves with wavevector $\mathbf{k}'$. The angle between d and $\vec{OA}$ (normal to the incident wave) is θ , and the angle between d and $\vec{OC}$ (normal to the diffracted wave) is θ' .*

where m is an integer and, in elastic scattering, $\mathbf{k}$ and $\mathbf{k}'$ must have the same wavelength and magnitude. When applying this to a Bravais lattice in a crystalline solid of points at position $\mathbf{R}$, and considering that the difference between the incident and diffracted x-ray beams, $\mathbf{K} = \mathbf{k}' - \mathbf{k}$, Equation 3.6 becomes

$$\mathbf{R} \cdot \mathbf{K} = 2\pi m \quad (3.7)$$

where $\mathbf{K}$ is the change in wavevector. Expanding Equation 3.7, one can then consider diffraction from an array of points within a Bravais lattice, giving three equations, known as the Laue Equations, to describe this array. Equations 3.8, 3.9 and 3.10 must be satisfied to allow for constructive interference to occur [119].

$$\mathbf{a} \cdot \mathbf{K} = 2\pi.h \quad (3.8)$$

$$\mathbf{b} \cdot \mathbf{K} = 2\pi.k \quad (3.9)$$

$$\mathbf{c} \cdot \mathbf{K} = 2\pi.l \quad (3.10)$$

The Laue Equations are satisfied if $\mathbf{K} = \mathbf{k}' - \mathbf{k}$ is equal to the reciprocal lattice vectors $\mathbf{G}_{hkl}$ from Equation 3.3. At a given scattering vector $\mathbf{K} = \mathbf{G}_{hkl}$, the scattering amplitude $A(\mathbf{G}_{hkl})$ can be written as the sum of scattering from all points, or atoms, in a lattice. The position of the n^{th} atom can be determined as $\mathbf{R}_n = (x_p + x_q)\mathbf{a} + (y_p + y_q)\mathbf{b} + (z_p + z_q)\mathbf{c}$, where (x_p, y_p, z_p) and (x_q, y_q, z_q) are the positions of the p^{th} lattice point and q^{th} atom in the unit cell, respectively [119].

$$A(\mathbf{G}_{hkl}) = \sum_{n=1} f_n \exp[i\mathbf{G} \cdot \mathbf{R}_n] \quad (3.11)$$

$$= \sum_{p=1} \exp[2\pi i(hx_p + ky_p + lz_p)] \sum_{q=1} f_q \exp[2\pi i(hx_q + ky_q + lz_q)] \quad (3.12)$$

$$= \sum_{p=1} \exp[2\pi i(hx_p + ky_p + lz_p)] F(\mathbf{G}_{hkl}) \quad (3.13)$$

where $F = \sum_{q=1} f_q \exp[2\pi i(hx_q + ky_q + lz_q)]$ and is called the structure factor. Intensities of Bragg reflections are proportional to the square of the net scattering amplitude $|A(\mathbf{G}_{hkl})|^2$. Furthermore, one can determine Bragg reflections with zero intensity, also known as systematic absences, from the exponent of Equation 3.11. The f_q term in Equation 3.12 is the atomic form factor and is the x-ray scatter from the electron cloud element integrated over the whole electron cloud [120].

$$f_q(\mathbf{K}) = -\frac{1}{e} \int_V \exp[2\pi i \mathbf{K} \cdot \mathbf{r}] \rho_j(\mathbf{r}) d\mathbf{r} \quad (3.14)$$

It is inversely proportional to θ , at a maximum when $\theta=0$ and is equal to the atomic number Z of the atom [119].

Ewald Construction

The Ewald construction can be visualised first of all in two dimensions, as demonstrated in Figure 3.3, and describes the Ewald sphere construction for a single crystal. Secondly, it is described in three dimensions, as illustrated in Figure 3.4, and describes the Ewald sphere construction for a powder. It describes the relationship between the wavevectors of the incident $\mathbf{k}$ and diffracted $\mathbf{k}'$ x-rays, the diffraction angle of a given reflection 2θ and the reciprocal lattice, where $\mathbf{K} = \mathbf{G}_{hkl}$, of the crystal.

For a wavevector incident on a reciprocal lattice point O , the origin (see Figures 3.3 & 3.4), the Ewald Sphere of radius $\mathbf{k}$ maps out every possible diffracted wavevector $\mathbf{k}'$ that lies on any other reciprocal lattice point P and, intuitively, $\mathbf{K}$. For any $\mathbf{K}$ that is connected to the sphere via the origin O , a Bragg reflection will occur.

3.3.2 X-ray Powder Diffraction

The mapping performed by $\mathbf{K}$ results in a cone of scattered radiation from a crystal powder. This radiated cone can be captured by detectors placed perpendicular to the incident beam of x-rays. Once captured, the cone forms a Debye-Scherrer ring. Any one powder diffraction sample will produce many Debye-Scherrer rings of varying intensities when probed with x-rays. These rings

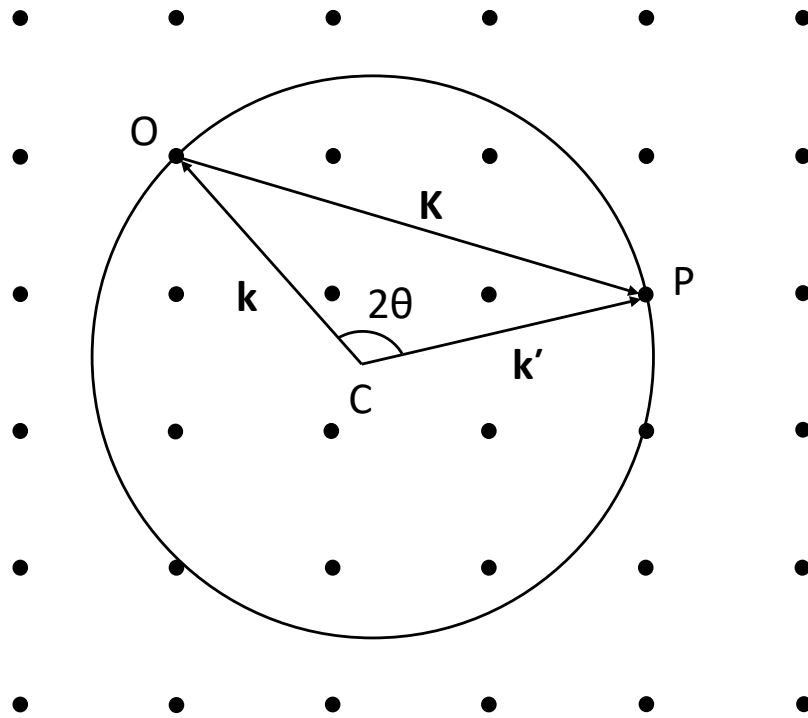


Figure 3.3 *The Ewald construction in 2D. The incident wavevector $\mathbf{k}$ is drawn from C to a reciprocal lattice point O , the origin of the circle. The Bragg condition is then satisfied for any reciprocal lattice point P that lies on the circle, when $\mathbf{K} = \mathbf{k}' - \mathbf{k} = \mathbf{G}_{hkl}$.*

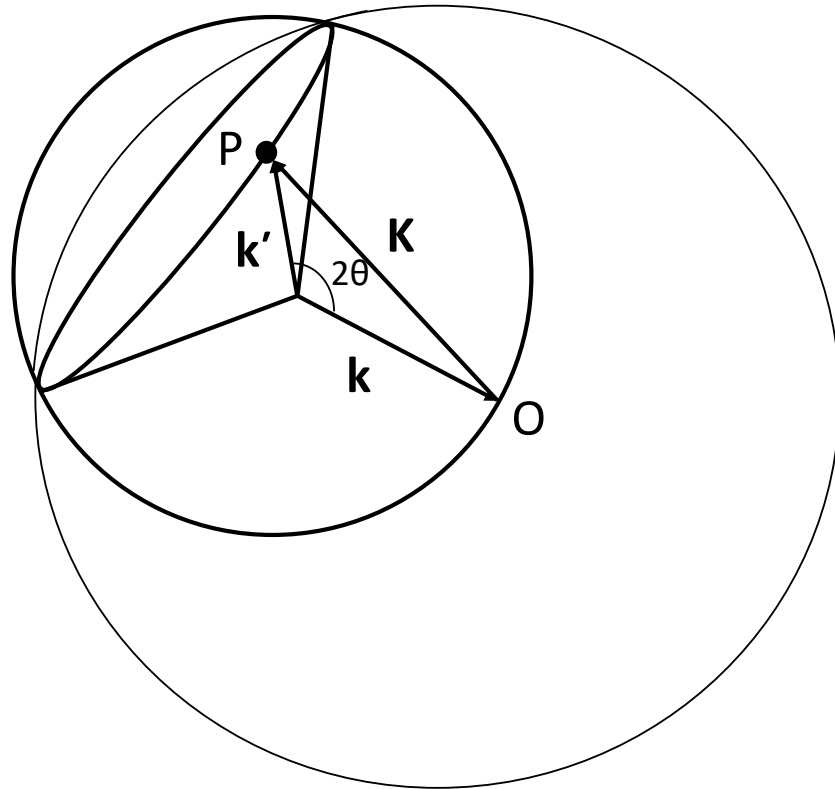


Figure 3.4 *The Ewald construction in 3D. The incident wavevector $\mathbf{k}$ is drawn from C to a reciprocal lattice point O , the origin of the sphere. The Bragg condition is then satisfied for any reciprocal lattice point P that lies on the sphere, when $\mathbf{K} = \mathbf{k}' - \mathbf{k} = \mathbf{G}_{hkl}$.*

can then be integrated azimuthally into a one-dimensional diffraction pattern displaying the intensities from each ring against the incremental increase of 2θ values.

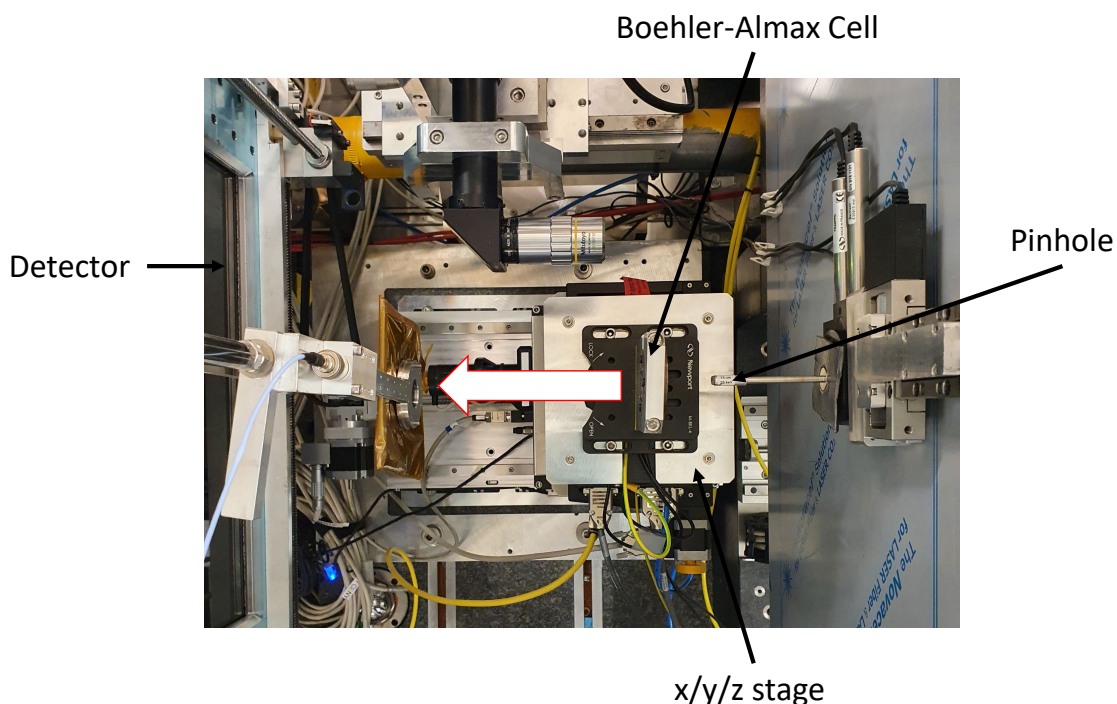


Figure 3.5 *A mounted experimental Boehler-Almax cell on the Extreme Conditions beamline at PETRA-III. The red-bordered white arrow shows the direction of the x-ray beam. The pinhole labelled collimates the x-ray beam to $\sim 10\ \mu\text{m}$ in diameter. The x/y/z stage is operated remotely to position the cell perpendicular to the path of the x-ray beam. The detector is positioned perpendicular to the direction of the beam to facilitate the collection of the diffracted x-ray data.*

3.3.3 Synchrotron X-ray Diffraction

The enhancement of third generation synchrotron light sources and improved experimental techniques has led to the achievement of extremely high-quality data of materials at unprecedented pressures. Synchrotrons are capable of accelerating electrons to relativistic velocities and, thus, generating high-energy x-rays. Diffraction data of the required quality in this thesis can only be obtained at a synchrotron.

Figure 3.5 displays an image of an experimental cell placed on the beamline at the PETRA-III synchrotron.

3.4 High-Pressure Techniques

This section will look at the techniques employed to study the lanthanide elements and Y at ultra-high pressures. Section 3.4.1 explores the history of the diamond anvil cell (DAC), how it is constructed, how it has developed technically, affords descriptions of the types of DACs used in this thesis and, finally, details the novel techniques used to achieve ultra-high pressures in static compression. Section 3.4.2 will describe the two methods used to calibrate the pressures during experiments, and will briefly explain non-hydrostatic effects caused by the DACs at ultra-high pressures.

3.4.1 Diamond Anvil Cells

The development of the DAC in 1959 by Weir *et al.* accelerated the evolution of static compression [121, 122]. This was made possible by the ingenious work leading to the invention of the Bridgman Press by Percy Williams Bridgman during the preceding decades of the 20th century [123–125], and the precursor to the DAC developed by Lawson in 1950 [126]. In 1965, van Valkenburg introduced the metal gasket in DAC operation, allowing the use of gases and liquids to surround samples generating hydrostatic or quasi-hydrostatic conditions for much larger pressure ranges. The introduction of bevelled diamonds allowed pressures of 172 GPa to be reached in DAC investigations as early as 1978 [127].

The introduction of the bevelled diamond has allowed the upper limit of achievable pressures within X-ray diffraction studies to increase to >400 GPa. Competing new ideas, such as the micro diamond anvil [128] and the toroidal diamond anvil [16, 36], are attempting to increase that limit to 1 terapascal (TPa); these pressures are only currently achievable in dynamic compression experiments [129].

To achieve the ultra-high pressures required to study the more complex crystal structures of the lanthanides and Y, samples of the metals were loaded into DACs. Figure 3.6 displays a sketch of a DAC, showing two opposing diamond culets

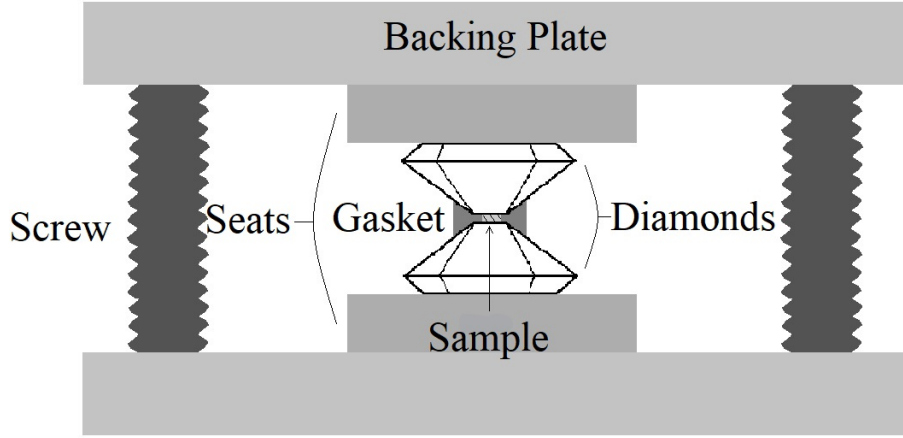


Figure 3.6 *Schematic of a DAC. The seats are generally made of tungsten carbide (WC). The gasket is made from a highly incompressible metal such as W or rhenium (Re). The diamonds are natural and chosen for their strength in the (001) direction. The screws and backing plates are made from work-hardened steel.*

centred on a gasket made of tungsten (W). The sample sits central in the gasket where the diamonds are then brought closer to one another by applying force, driving up the pressure exerted on the sample due to the relationship

$$P = \frac{F}{A} \quad (3.15)$$

where P = pressure in Pa, F = force applied in N and A = area in m^2 . To begin with, the diamond anvils must be aligned and glued to the backing seats shown in Figure 3.6, which contain holes at each centre to allow for x-ray beams to pass through. The backing seats are then attached to backing plates that, intuitively, also contain central holes to allow for the passage of x-rays. Once the diamonds are aligned in the cell, a gasket must be indented to a thickness of $\sim 3\text{--}15 \mu\text{m}$. This indentation is dependent on the culet size and, thus, the pressures required for the experiment. A hole is then drilled in the centre of the indent by either laser cutting or spark drilling with a W wire. After centring and fixing of the gasket on one of the diamond culets, the cell is ready to load with a sample and, if required, a pressure calibrant. The pressure calibrants used in this thesis are described in Section 3.4.2. The trivalent lanthanides and Y oxidise easily, thus samples of these metals must be loaded in a dry, argon (Ar)-filled glovebox.

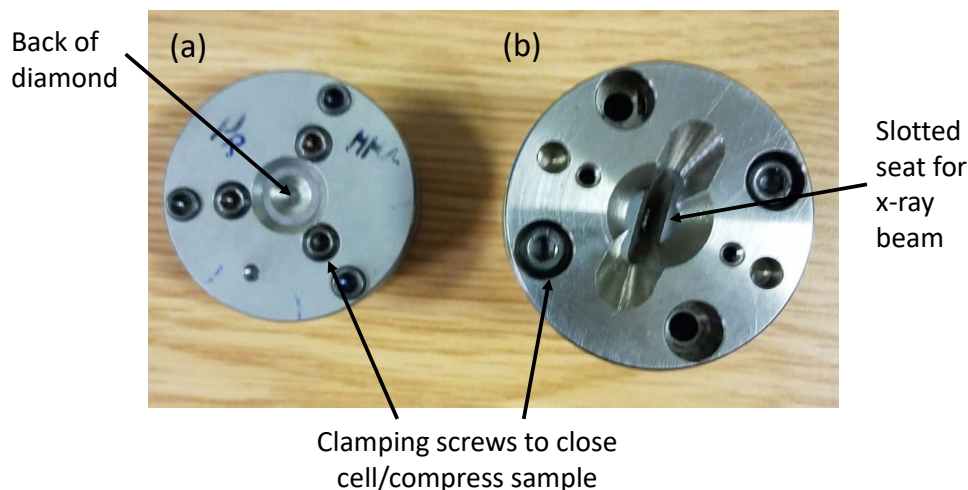


Figure 3.7 *Image of a top-down view of the (a) BA plate DAC and (b) LL piston cylinder DAC. The clamping screws drive the two parts of the cells closer together, inducing pressure on the diamonds and, therefore, samples. The back of one diamond from (a) and the style of backing seat in (b) are highlighted.*

Two types of DACs were used in this thesis: the Boehler-Almax (BA) plate DAC (see Figure 3.7, profile (a) and Figure 3.8), produced by Almax easyLab Group [130], and the Lawrence Livermore (LL) piston cylinder DAC (see Figure 3.7, profile (b) and Figure 3.9), produced by the Lawrence Livermore National Laboratory, USA [131]. Both cells use WC in the seats and backing plates so that the cells can be used at high temperatures.

The BA plate DACs are equipped with diamonds that have a conical shape cut into the sides furthest from the culets. This is so they sit flush with WC seats that also exhibit a conical shape where the hole meets the diamond. These were developed by Boehler & De Hantsetters [130] to improve stability and increase the aperture size. Furthermore, the diamond size is smaller than that of standard cut diamonds, making conical diamonds cheaper and reducing absorption of x-rays [130].

The LL piston cylinder DACs use standard cut diamonds that are glued onto standard cut WC seats. Normally, the seat placed on the bottom of the cell has a slot aperture. This is advantageous such that the maximum 2θ , thus minimum d-spacing, is larger than that of a standard seat. However, the disadvantages of a slotted seat are a reduced access to reciprocal space, which is a problem when studying single crystals, and only a small fraction of the Debye-Scherrer rings are captured.

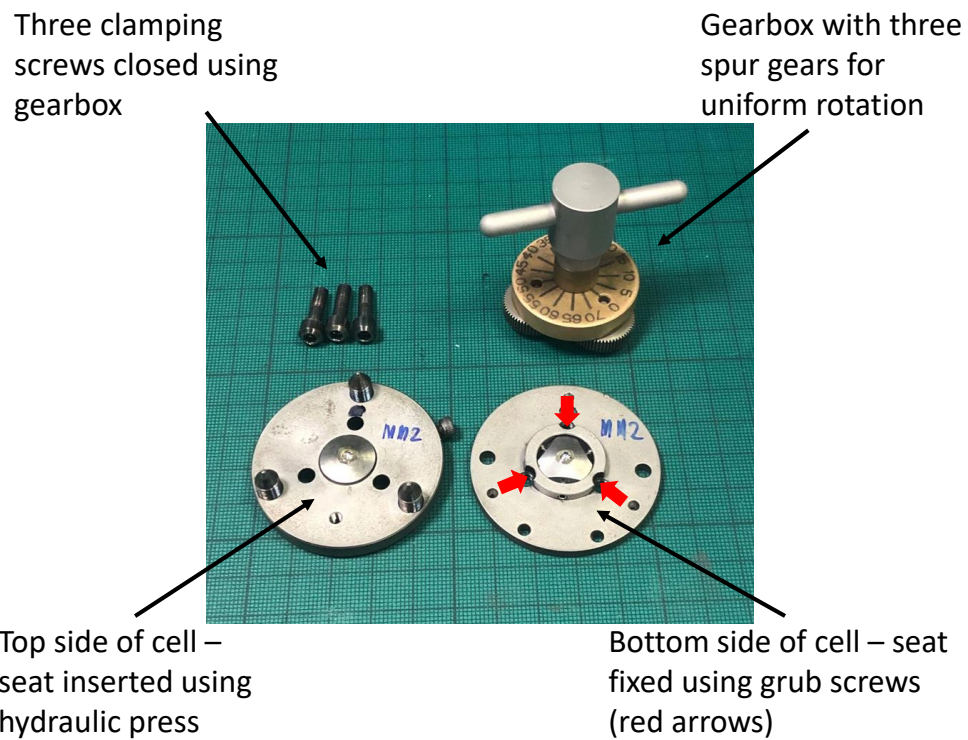


Figure 3.8 *Image of a BA plate DAC. The seats and backing plates (top and bottom sides of cell) are made of WC. The conical diamonds are natural, and are aligned and glued into each backing seat. The clamping screws are made of WC, and are inserted and uniformly tightened using the gearbox. One seat is placed into the top backing plate using a hydraulic press. The other seat is screwed into the bottom backing plate using grub screws tightened using Allen keys.*

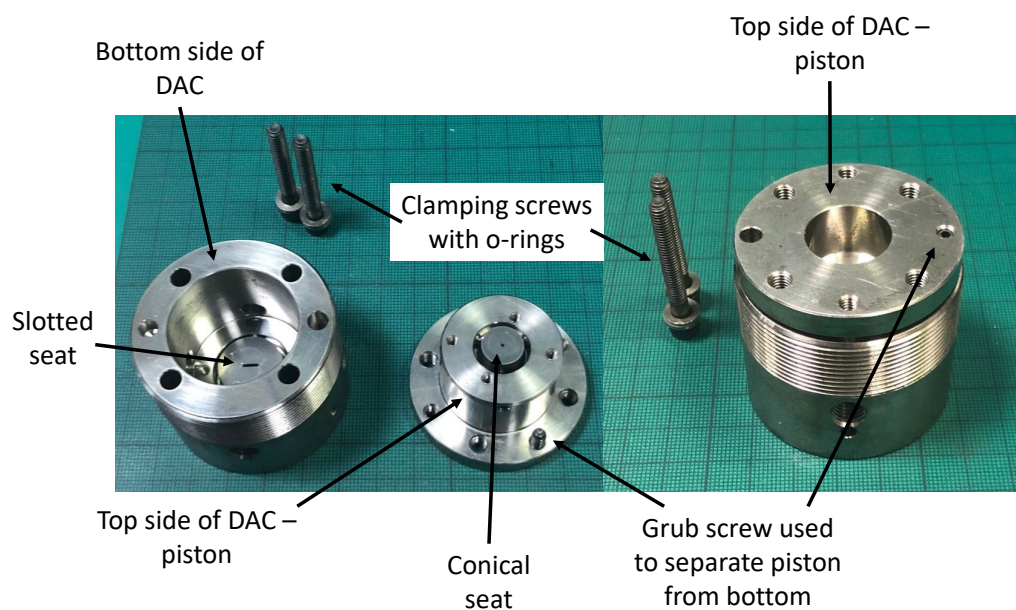


Figure 3.9 *Images of a LL piston cylinder DAC, (a) opened and (b) closed. The seats and backing plates (piston and bottom side) are made of WC. The standard cut diamonds (not shown) are natural. The clamping screws are made WC and are equipped with several o-rings to help reduce the speed at which a turn of each screw drives up the pressure in the sample. The diamonds are glued centrally on the slotted (bottom) and conical (piston) backing seats that are clamped into each side of the cell by grub screws. A grub screw is inserted as shown to ensure both sides of the cell remain separated during preparation.*

Toroidal Diamond Anvils

The toroid shape cut into a diamond is eroded via a FIB. This produces a very small culet diameter of $<10\text{ }\mu\text{m}$. In this thesis, bevelled diamonds with $\sim 30\text{ }\mu\text{m}$ diameter culets were modified using a FIB to $\sim 10\text{ }\mu\text{m}$.

Figure 3.10 shows the difference between a standard culet used in high-pressure experiments (dashed line) and a toroidal culet for extreme high-pressure experiments (solid line).

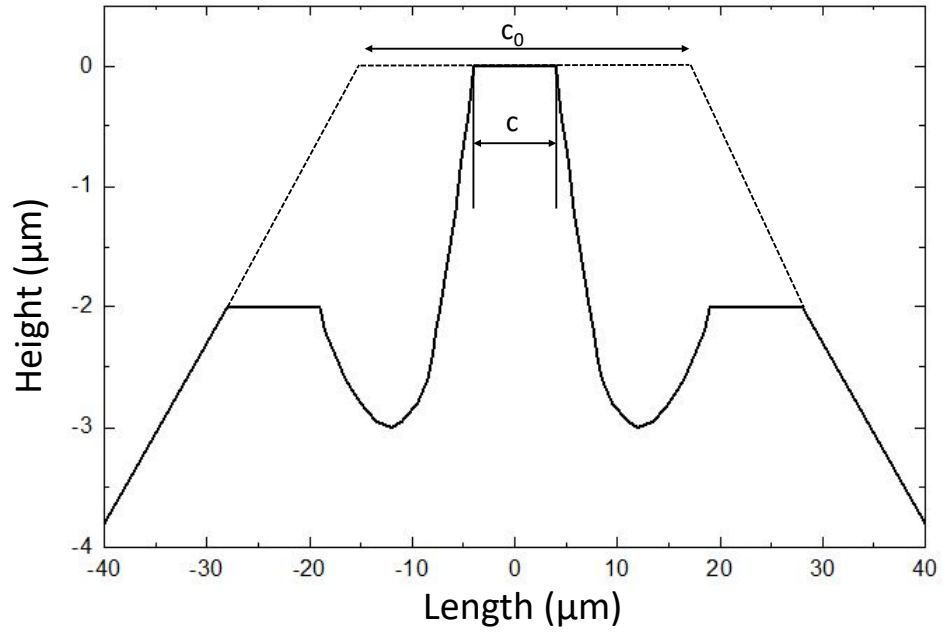


Figure 3.10 *A toroid-shaped cut (solid line) crafted using a FIB on a standard or bevelled diamond (dashed line), where c_0 is the original diameter of culet and c is the new diameter generated by the FIB. The scale difference between the x and y axes is chosen so that the tor shape can be clearly seen. This figure is modified from Fig. 1(a) in Ref. [16].*

3.4.2 Pressure Calibration

In order to verify pressures achieved in the experiments described in this thesis, most samples were loaded with Cu spheres or, in one case, the diamond phonon Raman mode was utilised when other calibrations were absent.

Copper as a Pressure Standard

In this thesis, the calibration of pressure for most of the data collected was determined using Cu as an internal pressure standard. The equation of state (EOS) of Cu is well known [21, 132]. An EOS in this case describes the pressure dependence of the atomic volume of a material. By accurately measuring the bulk modulus K_0 , its first derivative K' , the volume V_0 and the pressure P of a material, one can produce an EOS. The pressure-induced volume V of a material can be calculated from a diffraction pattern of a structure with a cubic unit cell

$$V = [d\sqrt{(h+k+l)}]^3 \quad (3.16)$$

where V is the volume in m^3 , and d is the d-spacing in $\text{\AA}$, of the (hkl) peak from the cubic structure. The pressure P of a material with the same cubic structural parameters and unit cell can then be determined using the EOS generated from the material's bulk modulus K_0 , its first derivative K' and other parameters that are described in the particular EOS used. This thesis uses the calculated EOS of Cu determined by Sokolova *et al.*, where the d-spacings of the (111) peak from the Cu were measured in the diffraction patterns containing the lanthanide and rare earth samples.

Diamond Raman Mode

In one case, the Cu pressure marker loaded with a sample of Nd was lost during the closing of a DAC. Therefore, another method of pressure calibration was used. The diamond Raman mode was employed using the calibrated least-squares method shown in Equation 3.17 [133]

$$P = A \frac{\Delta\omega}{\omega_0} \left[1 + \frac{1}{2}(B-1) \frac{\Delta\omega}{\omega_0} \right] \quad (3.17)$$

where $\frac{\Delta\omega}{\omega_0}$ is the relative Raman frequency change between the edge frequency at ambient pressure, ω_0 and the edge frequency at pressure P , ω , and A and B are fitting parameters that correspond to the bulk modulus K_0 and its pressure derivative K' .

Figure 3.13 displays the Raman spectra for a DAC containing a sample of Nd at

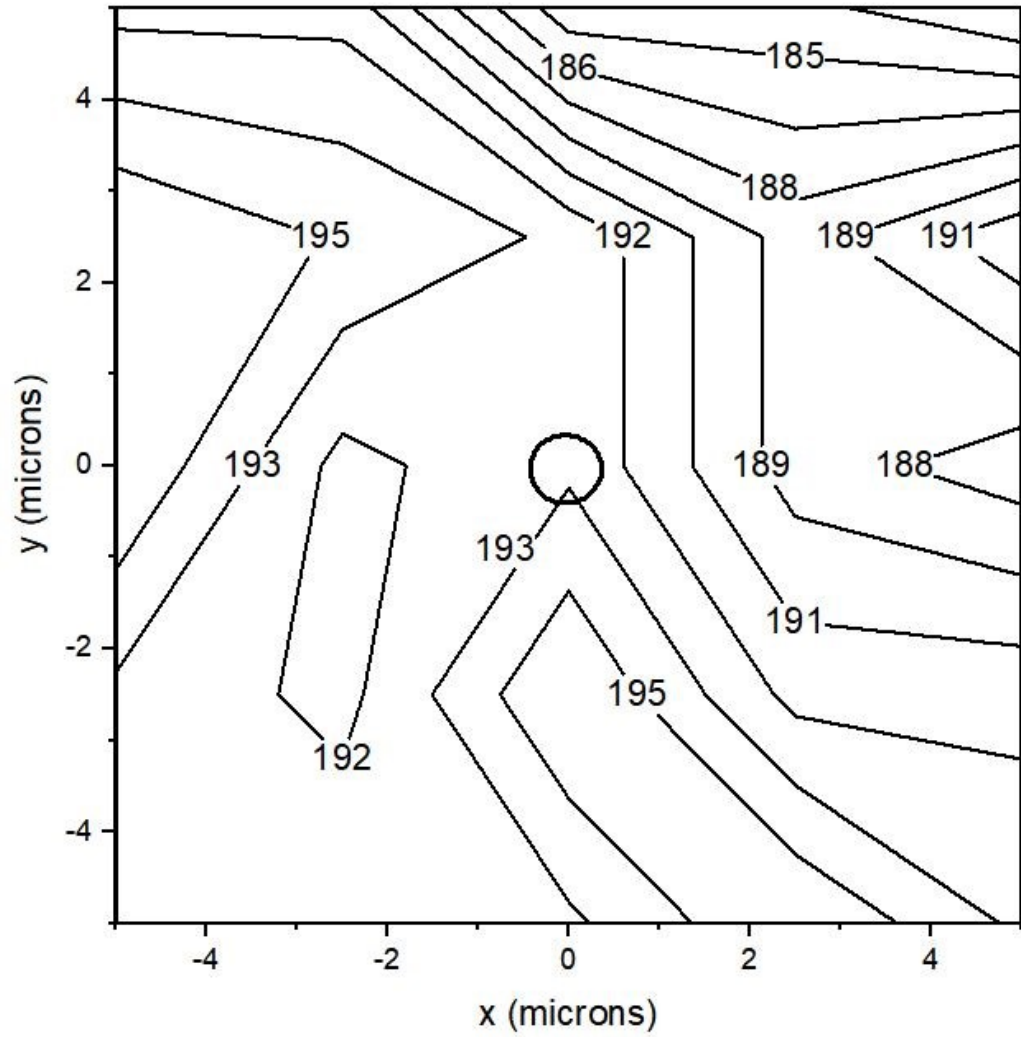


Figure 3.11 *The pressure distribution from a $\sim 30\ \mu\text{m}$ culet at 193 GPa over the central $10\ \mu\text{m} \times 10\ \mu\text{m}$ area of the sample. Also shown for comparison is the $0.85\ \mu\text{m}$ beam diameter used to obtain the diffraction data at PETRA-III.*

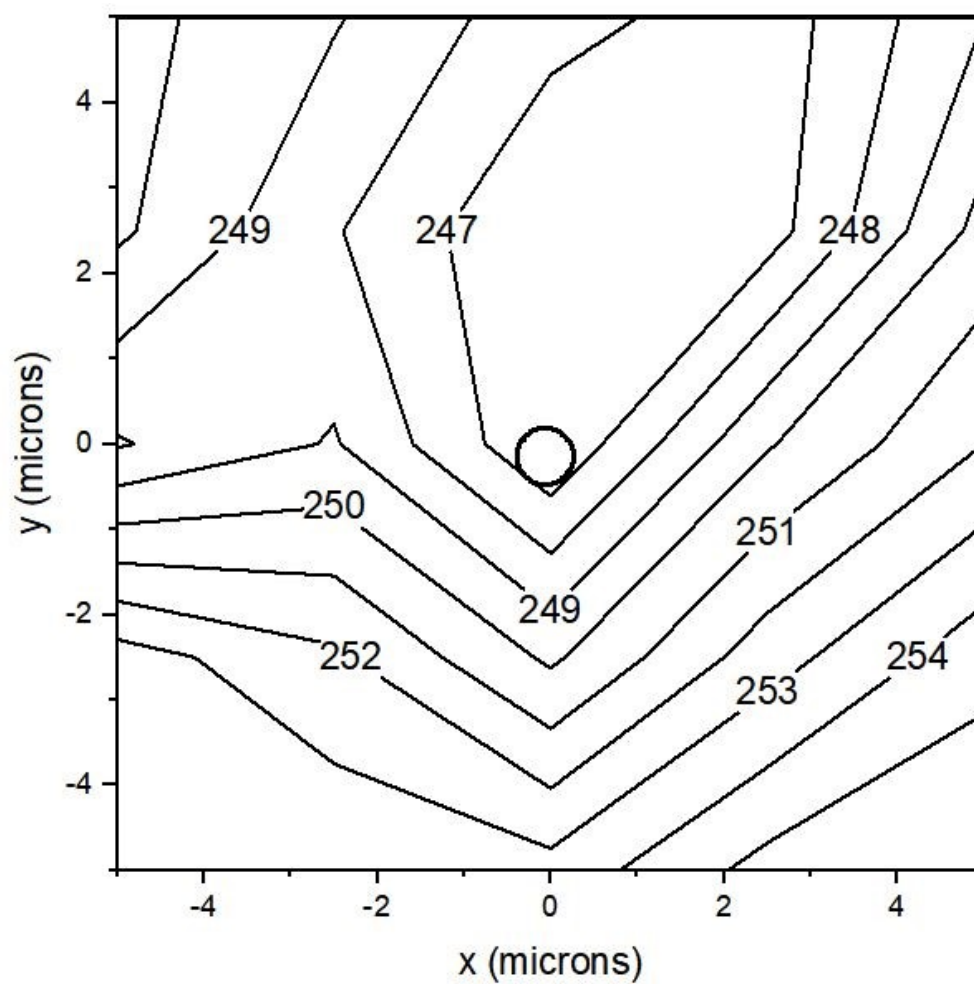


Figure 3.12 *The pressure distribution from a $\sim 10\ \mu\text{m}$ culet at 247 GPa over the central $10\ \mu\text{m} \times 10\ \mu\text{m}$ area of the sample. Also shown for comparison is the $0.85\ \mu\text{m}$ beam diameter used to obtain the diffraction data at PETRA-III.*

222 GPa. The (a) low-frequency and (b) high-frequency sides of the spectrum correspond to the back face and the culet of the diamond, respectively.

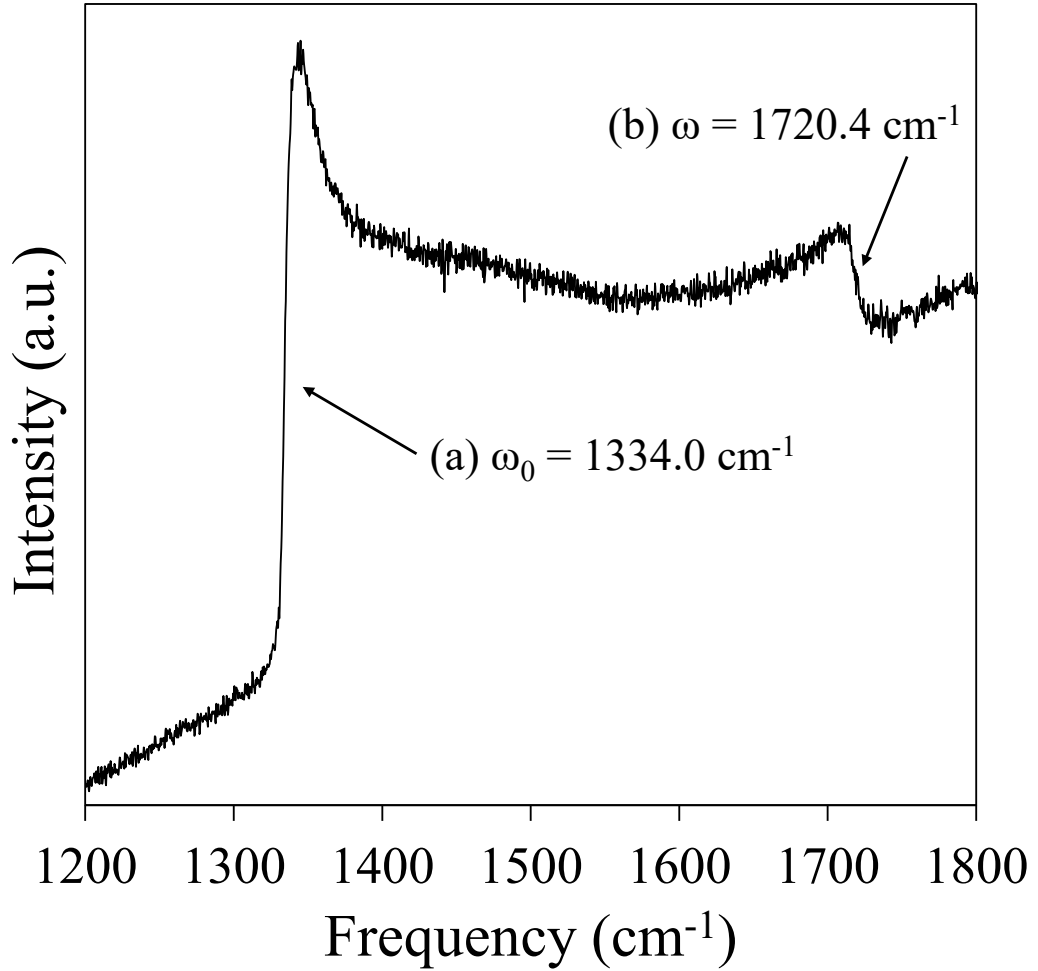


Figure 3.13 *Raman spectrum of the diamond anvil centre from a DAC containing a sample of Nd at 222 GPa. The edge frequency at ambient pressure is (a) $\omega_0 = 1334.0(10) \text{ cm}^{-1}$, and the edge frequency at 222 GPa is (b) $\omega = 1720.4(5) \text{ cm}^{-1}$.*

Non-Hydrostatic Effects

It is common for samples requiring high pressures to be immersed in a pressure transmitting medium (PTM), thus retaining their hydrostaticity in all directions. However, previous reports have shown that hydrostaticity is only maintained up to pressures of ~ 10 GPa, such as a 4:1 methanol-ethanol mixture [134].

No PTMs were used in any cells studied in this thesis as it was highly likely

that the diffraction peaks generated by a PTM would overlap with the diffraction peaks from the lanthanide samples. Furthermore, most common PTMs solidify below 20 GPa; for example, helium (He) solidifies at ~ 12 GPa, therefore most PTMs would only provide quasi-hydrostatic conditions at pressures much lower than that required to access the phases of interest in this work.

Figures 3.11 and 3.12 show the pressure gradients present in two cells containing samples of Pr at 193 GPa and Tb at 247 GPa, respectively. These pressure gradients induced by non-hydrostatic effects, or misaligned diamonds, are avoided by probing a very small area of a sample with a sub-micron (or sub- μm) beam. By analysis of Figure 3.12, it is intuitive that beams of diameters $>4\ \mu\text{m}$ would already introduce a pressure gradient of $>7\text{GPa}$ in a diffraction pattern.

3.5 Data Analysis

In this section, methods used to solve the crystal structures of the lanthanide metals and Y will be discussed. Section 3.5.1 will look at how one can determine the structure of a sample from x-ray powder diffraction patterns. Section 3.5.2 will describe the different methods of refining a structure to diffraction patterns collected in this thesis. Finally, Section 3.5.3 will explain the equations of state utilised in this work to describe the compression of the lanthanide and Y samples.

3.5.1 Indexing Periodic Structures

Over the years, many software applications have been developed to determine crystallographic structures from x-ray diffraction patterns. Throughout this thesis, the DIOPTAS [135] program was utilised to integrate the collected Debye-Scherrer ring patterns into 1-dimensional (1D) diffraction patterns. These 1D patterns, or profiles, were then inputted as x-y plots into CONOGRAPH [136] to determine possible structural solutions with estimated structural parameters. To visualise the different structures, VESTA [137] was used. Once these stages were complete, refinements to the diffraction patterns were performed using JANA2006 [138] to determine the precise spacegroups, structural parameters and preferred orientation of the lanthanide and Y samples.

3.5.2 Structural Refinements

Two methods of structural refinements were utilised in this thesis: the Le Bail [139] method and the Rietveld [140] method. A Le Bail refinement allows one to refine the lattice parameters (a , b , c , α , β and γ) of the crystal unit cell, peak shapes and background subtraction of the calculated diffraction pattern to the observed profile. A Rietveld refinement builds on a Le Bail refinement by refining the atomic positions within the unit cell. This refines the peak positions and intensities of the diffraction pattern, providing one with a full description of the crystal structure. Both methods are used to fit a theoretically determined diffraction pattern to an observed pattern.

The diffraction pattern generated via the theoretical model is used to constrain and refine the structural parameters by minimising a least-squares residual S_y until the model's diffraction pattern matches the experimentally determined diffraction profile.

$$S_y = \sum_i \omega_i |y_i - y_{ic}|^2 \quad (3.18)$$

where ω_i is the weight, y_i is the observed intensity at point i and y_{ic} is the calculated intensity at point i .

The next step is to determine the individual structure factors from the diffraction peaks by using the entire pattern to refine the intensity and position of each individual reflection. This means that overlapping peaks, which are very common in powder diffraction profiles, can be split into individual reflection contributions.

Another significant contribution to the refinement process is to determine the best peak shape, whether that be a Gaussian, Lorentzian or pseudo-Voigt peak shape. In this thesis, it was found that trial fitting of the three peak shapes yielded very similar refinements. The Gaussian (G) peak shape fitted appropriately to all diffraction profile refinements and was therefore used singularly for all refinements. Equation 3.19 presents the calculation for a Gaussian peak profile

$$G = \frac{(4 \ln 2)^2}{\sqrt{\pi} H} \exp -4 \ln 2 \frac{2\Delta\theta^2}{H} \quad (3.19)$$

where H is the full width half maximum (FWHM) and found by Equation 3.20

and $\Delta\theta$ is the difference between the measured θ and the Bragg angle [65].

$$H = (U \tan^2 \theta + V \tan \theta + W)^{\frac{1}{2}} \quad (3.20)$$

where U , V and W are the variables in the Gaussian peak shape refinement.

Another step that can be refined for in a sample is possible preferred orientation of the grains within a powder. In ultra-high pressure experiments, it is generally accepted that the sample grains will orientate to a preferred direction. This thesis found that high-pressure diffraction patterns exhibited preferred orientation that could be refined via a March-Dollase correction of the preferred orientation functions, P_k [141]

$$P_k = (p^2 \cos^2 \phi + \frac{\sin^2 \phi}{p})^{-\frac{3}{2}} \quad (3.21)$$

where p is a refinable parameter and ϕ is the angle between a plane with indices (hkl) and the preferred orientation vector.

To display diffraction profiles collected using different wavelengths on the same graph, the diffraction angles were converted into Q wavevectors using Equation 3.22.

$$Q = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d} \quad (3.22)$$

Systematic Absences & Reflection Conditions

In crystals, it is possible for a reflection of a plane to have zero intensity due to destructive interference of x-rays in a diffraction pattern. This is due to either systematic absences or the reflection conditions of a particular spacegroup.

Systematic absences occur when the structure factor of a reflection is zero. The centring of the lattice or glide and screw axes symmetry elements are at the cause of this. A systematic absence is converse to reflection conditions, therefore when the structure factor is not zero, the absence of a peak in a diffraction pattern may be explained via the reflection conditions of a spacegroup. These reflection conditions apply to all Wyckoff positions of a spacegroup.

3.5.3 Equations of State

Obtaining such a large volume of high quality diffraction data in incremental pressure steps allows one to fit an appropriate equation of state (EOS) to the data set. The compressive behaviours of Sm, Nd, Pr and Y were analysed using the Adapted Polynomial of the Order L EOS determined by Holzapfel [142–144].

Anomalies in the EOS data for the individual phases of Sm, Nd, Pr and Y can be most readily visualised by using a simple “linearisation” procedure whereby the anomalies related to electron transfer can be distinguished from the “regular” compressive behaviour of simple metals [76]. Materials undergoing regular compression will show linear or quasi-linear behaviour.

Adapted Polynomial of the order L

Comparisons of the various EOSs were made by Holzapfel in a number of publications [142, 143, 145]. The studies showed which EOSs suitably described the compressive behaviour of metals in varying conditions. In the regime of static compression and room temperature, Holzapfel determined that the Adapted Polynomial of the Order L (APL) EOS best described the compressive behaviour of metals. Furthermore, Holzapfel found that the APL form correctly determined the values for the limits $x \rightarrow 0$ and $x \rightarrow \infty$. In other words, the APL EOS describes the compressibility of a material to that of a Fermi gas. For a neutral Fermi gas, the Thomas-Fermi model describes an equation to satisfy its behaviour:

$$P_{FG} = (3\pi^2)^{\frac{2}{3}} \frac{\hbar^2}{5m_e} \left(\frac{N}{V}\right)^{\frac{5}{3}} \quad (3.23)$$

which can be written as

$$P_{FG} = a_{FG}(Z/V_0)^{5/3} \quad (3.24)$$

where P_{FG} is the pressure of a Fermi gas. If one fits the compression data using the second order (AP2) form of the APL EOS [142, 143]:

$$P = 3K_0 \frac{(1-x)}{x^5} \exp(c_0(1-x)) \left(1 + x \sum_{k=2}^L c_k (1-x)^{k-1}\right) \quad (3.25)$$

where K_0 is the zero pressure bulk modulus, K' is its pressure derivative, $x = (V/V_0)^{1/3}$, $c_0 = -\ln(3K_0/p_{\text{FG}})$, $c_2 = (3/2)(K' - 3) - c_0$, Z is the atomic number, and $a_{\text{FG}} = [(3\pi^2)/5](\hbar^2/m_e) = 0.02337 \text{ GPa nm}^5$ is a constant, then the compression data can be linearised in a so-called $\eta_{\text{APL}} - x$ plot:

$$\eta_{\text{APL}}(x) = \ln\left(\frac{px^5}{p_{\text{FG}}}\right) - \ln(1 - x) \quad (3.26)$$

where $x = (V/V_0)^{1/3}$, the Fermi-gas pressure $p_{\text{FG}} = a_{\text{FG}}(Z/V_0)^{5/3}$, and $a_{\text{FG}} = 0.02337 \text{ GPa nm}^5$, with the correct theoretical limit of $\eta(0) = 0$ at $x = 0$. The “regularity” of a metal will determine the order of which the summation term will extend to [143]. For “ideal” metals, such as aluminium (Al), the summation term will reduce to zero, and the EOS reduces to the AP1 form:

$$P = 3K_0 \frac{(1 - x)}{x^5} \exp(c_0(1 - x)) \quad (3.27)$$

For the case of gold (Au), an AP1 EOS does describe the behaviour very well, but the resulting linearisation is non-ideal [143] (see Figure 5.15 for an example). More “irregular” metals require higher order APL EOS’s to describe their behaviour. The linearisations in Chapters 5–8 illustrate irregularities in the compressibilities of Sm, Nd and Pr [27].

An APL linearisation with respect to the radius ratio R_{WS}/R_I [40], as opposed to x , can be used, where R_{WS} is the pressure dependent Wigner–Seitz radius and R_I is a pressure independent individual value for the ionic radius of each element [143]. The pressure dependent values of R_{WS} were determined from the measured atomic volumes, while R_I were taken to be the R_{5p} radii [42], as reported by Waber and Cromer [25].

Chapter 4

The Heavy Trivalent Lanthanides

4.1 Introduction

Despite the high-pressure behaviour of the lanthanides receiving decades of study since the pioneering work of Bridgman [123], there is thus considerable debate regarding the structure of the more complex, high-pressure phases. As described in Chapter 2, the literature has provided extensive studies confirming that the trivalent lanthanides exhibit a common, pressure-induced, structural sequence as one moves through the different, pressure-induced phases: $hP2 \rightarrow hR9 \rightarrow hP4 \rightarrow cF4 \rightarrow hR24$ [10, 15]. The last common structure, $hR24$, is a distortion of the $cF4$ structure and has been assigned to high pressures post- $hP4$ (Gd) or post- $cF4$ (Tb to Lu) phases in all of the heavy trivalent lanthanides [6, 9, 61, 62, 68–70].

The first pressure-induced, post- $hR24$ phase was assigned to a monoclinic $mC4$ structure in all the heavy trivalent lanthanides [6, 9, 61, 62, 68, 69], except Yb and Lu. This transition has been accompanied by a significant “collapse” in volume in all the lanthanides where it has been observed. As noted in Chapter 2, Yb has divalent tendency at ambient conditions and trivalent above ~ 30 GPa and, therefore, exhibits a different pressure-induced structural sequence [53–55]. It was expected that Lu would also transition from $hR24$ to $mC4$ at extreme compression but has not been studied above 202 GPa, where the $hR24$ structure is still stable to that pressure [70]. Although refinements of the $mC4$ structure to diffraction patterns of the high-pressure phases in the heavy trivalent lanthanides were convincing, the misfitting peaks, with low R-factors and Goodness of Fit

(GoF), and absence of other peaks in the fits (see Figures 2.2, 2.3 and 2.4) draw into question the validity of these findings. To study this, x-ray powder diffraction experiments were performed on Tb to 260 GPa in order to solve for the correct structure assignment to these high-pressure lanthanide phases. Previous diffraction data on the same high-pressure phases of Gd [17] and Dy collected by Keith Munro were analysed prior to collection of the new data, then analysed in retrospect by this author.

The first element discussed will be Tb. Although Gd is the first of the heavy trivalent lanthanides, the high-pressure, post-dfcc phase of greatest interest to this project is accessed at lower pressures in Tb. This makes Tb the easiest material to obtain and observe the post-dfcc phase. The results of previous high-pressure high-temperatures studies on Gd and high-pressure studies on Dy will then be discussed.

4.2 Terbium

Tb exhibits the entire pressure-induced phase transition sequence of the trivalent lanthanides [40] and has been studied up to 155 GPa [6]. A transition to the post-dfcc phase occurs at 51 GPa, and has been assigned to the $mC4$ structure. However, as said, the misfits of the refined $mC4$ structure to the diffraction patterns in the literature draws into question what the correct structural assignment to the post-dfcc phase is.

To resolve the correct structural assignment of the high-pressure, “volume-collapsed” phase with the $mC4$ structural assignment, ADXD experiments were performed on Tb samples. The findings have been published in Physical Review B [1] and contain data collected by Keith Munro prior to this work. The data described here were collected during this project.

4.2.1 Experimental Details

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 one DAC in a dry argon atmosphere (<1 ppm O_2 and <1 ppm H_2O) to prevent oxidation. The DAC was equipped with a W gasket. The sample was loaded

without a pressure medium in order to avoid having any peaks from an additional material overlapping with those from either the sample or pressure marker, and were loaded with a small piece of Cu foil to act as a pressure calibrant, using the published Cu equation of state of Sokolova *et al.* [132].

Diffraction data were collected in an experiment on the Extreme Conditions P02.2 beamline at the PETRA-III synchrotron in Hamburg, Germany. A monochromatic x-ray beam of wavelength $0.4834\text{\AA}$ focussed down to $0.85\text{ }\mu\text{m} \times 0.85\text{ }\mu\text{m}$, was used, and the powder-diffraction data were recorded on a Perkin-Elmer area detector, placed $\sim 400\text{ mm}$ from the sample. A CeO_2 diffraction standard was used to calibrate the exact sample-detector distance and the detector tilt in the experiment. The 2D diffraction images collected at each pressure were integrated azimuthally using DIOPTAS [135] to obtain standard 1D diffraction profiles, which were then analysed using Rietveld [138] and Le Bail profile-fitting methods or by fitting to the d -spacings of individual diffraction peaks [146].

4.2.2 Experimental Results

Diffraction patterns were collected from 12 to 247 GPa in incremental pressure steps on the Tb sample. The DAC used in this experiment contained toroidal diamond anvils (described in Chapter 3) that have culets of $\sim 10\text{ }\mu\text{m}$ in diameter. This makes loading significantly more difficult with not only smaller sample sizes, but also greater opportunities for errors and unwanted material in the sample area. Due to the relatively small sample size compared with the Cu foil, a large number of the diffraction patterns had Cu peaks that are significantly more intense than the peaks from the Tb metal. Furthermore, despite the sub-micron diameter x-ray beam utilised, intense peaks from W were also observed in many diffraction patterns. It is possible these arose from either the gasket or pieces from the needle used in loading the DAC. In order to reduce the intensities of the undesired peaks, masking of the 2D images was employed in the initial stages of analysis. Furthermore, larger pressure gradients of $\sim 5\text{ GPa}$ over $2\text{ }\mu\text{m}$ were found in the toroidal cell. However, as the x-ray beam diameter was $< 1\text{ }\mu\text{m}$, the error in pressure for each data collection was still relatively small. Figure 3.12 shows the pressure gradients of the cell containing the Tb sample, and illustrates the diameter of the beam for comparison.

Initially, the compression increments were small so that the pressure did not

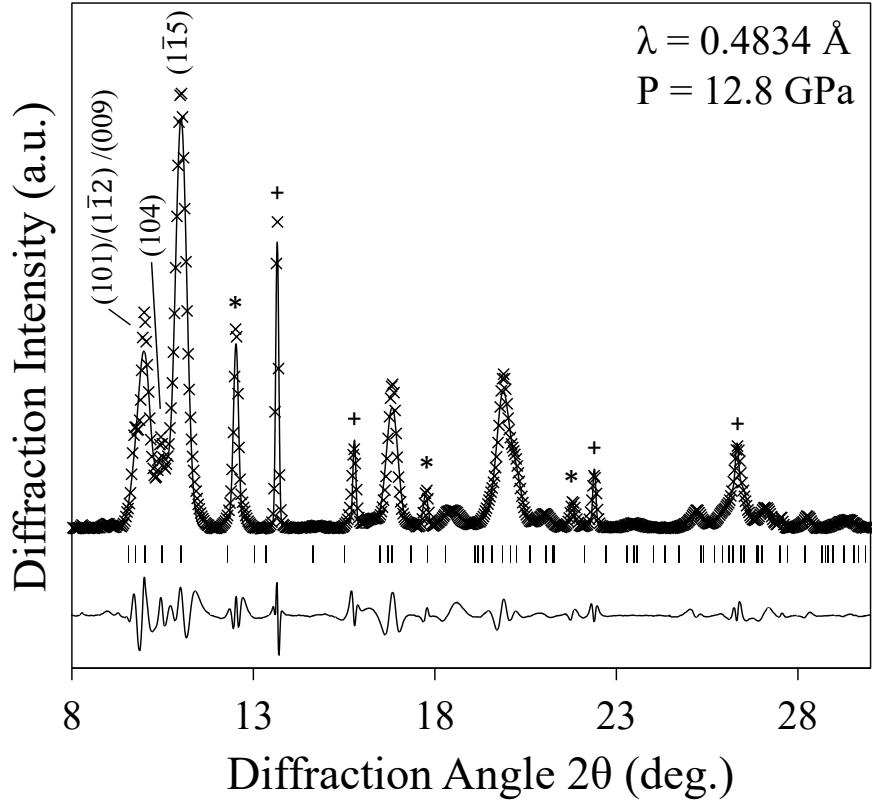


Figure 4.1 *Le Bail refinement of the hR9 structure to a diffraction profile from Tb at 12.8(5) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first five peaks of the hR9 phase are labelled with their Miller indices. The asterisks identify peaks from the W gasket. The + sign identifies peaks from the Cu pressure calibrant.*

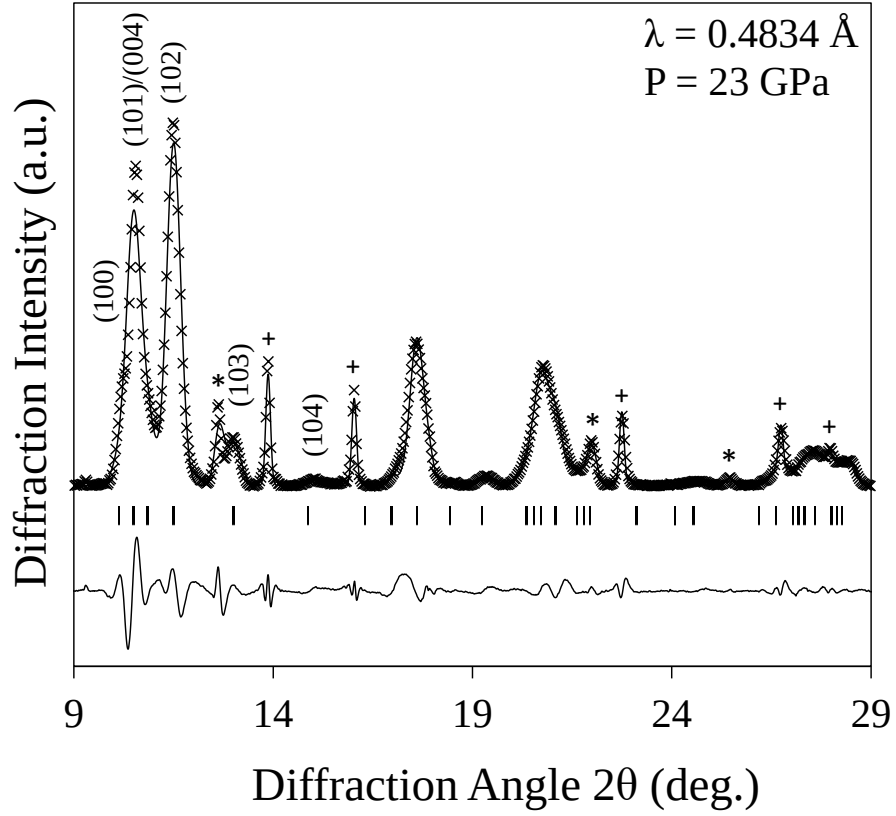


Figure 4.2 *Le Bail refinement of the hP4 structure to a diffraction profile from Tb at 23(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first six peaks of the hP4 phase are labelled with their Miller indices. The asterisks identify peaks from the W gasket. The + sign identifies peaks from the Cu pressure calibrant.*

increase dramatically. This allowed for collection of a small number of profiles of the low-pressure phases of Tb. The initial integrated diffraction patterns showed single phase profiles of the Sm-type phase with the $hR9$ structure. Figure 4.1 displays a Le Bail refinement of the $hR9$ structure, spacegroup $R\bar{3}m$, to a single phase pattern of Tb at 12.8(5) GPa. A transition to the $hP4$ phase was observed in the diffraction patterns at 14.2(5) GPa, and was stable up to 23(2) GPa. A Le Bail refinement of the $hP4$ structure, spacegroup $P6_3/mmc$, to a diffraction pattern of Tb at 23(2) GPa is shown in Figure 4.2. The diffraction patterns of the $hR9$ and $hP4$ phases are strikingly similar. The most notable changes that distinguish the two phases are seen at 13 and ~ 21 degrees. The (103) peak from the $hP4$ structure appears at 13 degrees in Figure 4.2, and an increased number of more intense reflections from the $hP4$ structure broaden the ‘peak’ at ~ 21 degrees. Upon further compression, reflections from the $hR24$ structure were observed in the diffraction patterns. Figure 4.3 displays a mixed phase diffraction pattern of Tb at 34(2) GPa. The pattern has been fitted with both the $hR24$ and $hP4$ structures. A single phase pattern of the $hR24$ structure was not seen in the data collection as the pressure increments taken whilst in the $hR24$ phase were larger than initial pressure increments. The sluggish transitions and large regions of mixed phases are well-known to occur in the lanthanides and are thought to arise from the slight differences in stacking of the hexagonal layers.

As described previously, the literature has reported that a monoclinic structure, $mC4$, spacegroup $C2/m$, fits diffraction patterns of Tb above 50 GPa [6]. However, the current study described in this chapter has found significant misfits of this structure to Tb diffraction profiles above this pressure. Figure 4.4 shows a Rietveld refinement of the $mC4$ structure to a diffraction pattern collected on Tb at 122 GPa, with preferred orientation in the (002) direction. The refined lattice parameters are $a = 4.334(5)$ Å, $b = 2.7358(8)$ Å, $c = 4.6711(15)$ Å, and $\beta = 105.74(5)^\circ$, $V/V_0 = 0.42(2)$ Å³, with atoms on the $4i$ site at (0.26(3), 0, 0.308(7)). The inset to Figure 4.4 shows peaks highlighted by arrows which were also evident in previously published profiles that cannot be fit by the $mC4$ structure. This misfit around 20 to 23 degrees is what triggered the study into finding the correct structural assignment.

In order to resolve the correct structural solution for this high pressure phase, the CONOGRAPH software [136] was employed to determine a few structure candidates, all with the same Patterson symmetry – $Fmmm$. The CONOGRAPH software determined these orthorhombic structures to be the next most likely

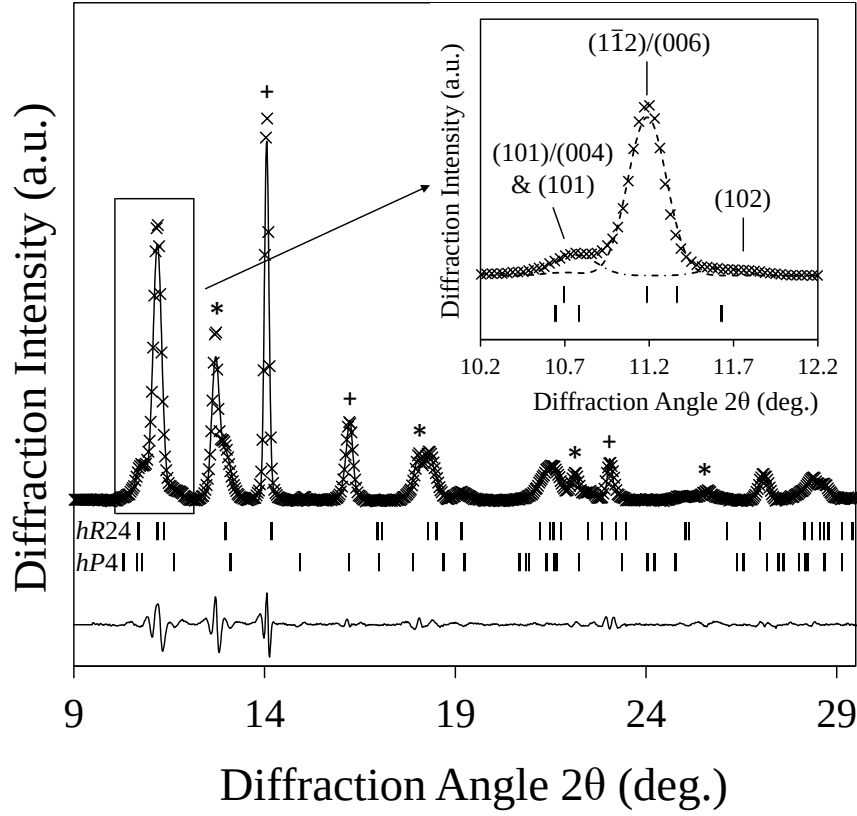


Figure 4.3 *Le Bail refinement of the hP4 and hR24 structures to a mixed-phase diffraction profile from Tb at 34(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions of the hP4 (below) and hR24 (above) phases, and the difference profile. The (101), (112) and (006) peaks of the hR24 phase (dash) and the (101), (004) and (102) of the hP4 phase (dot-dash) are labelled in the inset. The asterisks identify peaks from the W gasket and the + signs identify peaks from the Cu pressure marker.*

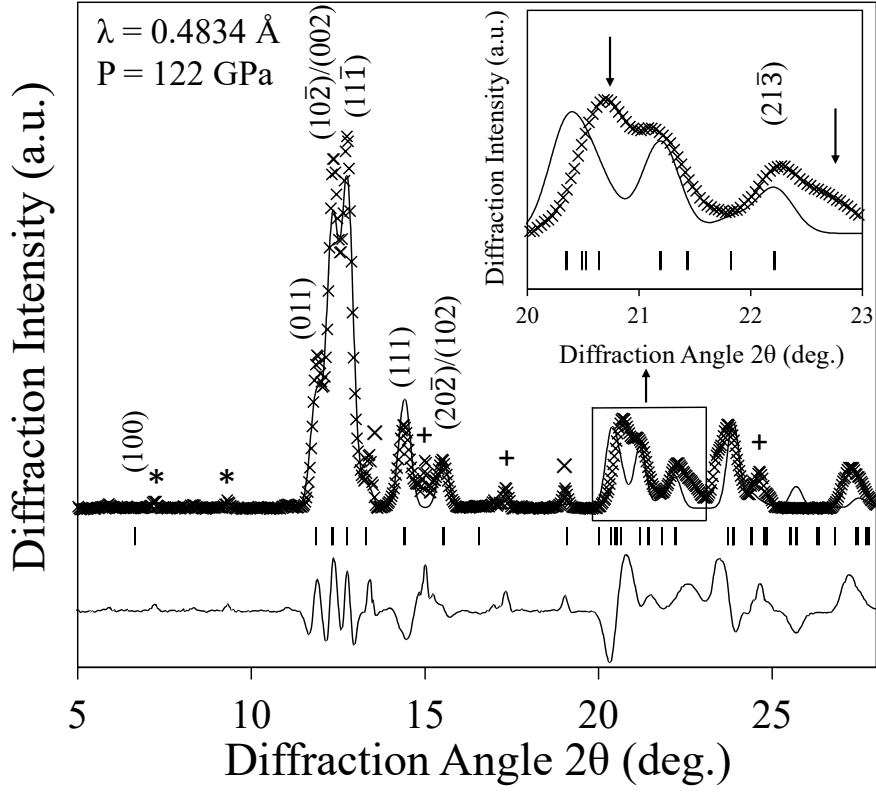


Figure 4.4 Rietveld refinement of the *mC4* structure to a diffraction profile from Tb at 122(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first eight peaks of the *mC4* phase are labelled with their Miller indices. The $\times$ identifies first the (101) peak from the W gasket and the $(\bar{1}11)$ peak from the Tb, and second the (002) from W and the (112) from Tb. The + signs identify peaks from the Cu pressure calibrant. The asterisks identify weak contaminant peaks.

Table 4.1 *Structural data for four different pressure-induced phases of Tb observed at room temperature, including spacegroups, lattice parameters and pressures with their uncertainties.*

Structure	Lattice Parameters (Å)	Pressure (GPa)
<i>hR9</i>	$a = 3.3712(3), c = 24.943(3)$	12.8(5)
<i>hP4</i>	$a = 3.1587(2), c = 10.230(3)$	23(2)
<i>hR24</i>	$a = 3.0425(2), c = 14.644(4)$	34(2)
<i>oF16</i>	$a = 16.749(5), b = 4.6614(4), c = 2.7352(5)$	122(2)

structural candidates after those from the best-fitting triclinic and monoclinic candidates. The $C2/m$ spacegroup is sub-group related to a number of spacegroups with the $Fmmm$ Patterson symmetry. It was then a process of elimination by comparison of which reflections from each candidate accounted for all the peaks present in the diffraction pattern, and, more importantly, whether any extinction rules accounted for peaks of zero intensity.

The second point was the deciding factor when determining the correct solution. In Figures 4.4 and 4.5, the first indexed peaks are the (100) and (400), respectively. By the rules founded in the reflection conditions, these peaks have some intensity (Figure 4.4) and zero intensity (Figure 4.5). It can be seen in the diffraction pattern from Tb at 122 GPa in both figures, that this peak has little or no intensity. The arrows shown in the inset to Figure 4.4 highlight a poorly misfitting peak (left-hand arrow) and the last peak which is not predicted by the $mC4$ structure (right-hand arrow). The inset in Figure 4.5 shows that the refinement of the orthorhombic $Fddd$ structure fits the first peak and predicts the (602) reflection underneath the last peak.

It was then necessary to determine the correct Wyckoff site which would give clues as to where the atoms would sit in the unit cell of the orthorhombic structure. By analysing the reflection conditions of the $Fddd$ structure, the 16e Wyckoff site was resolved.

Figure 4.5 displays a Rietveld refinement of an orthorhombic structure with 16 atoms in the unit cell, *oF16* in Pearson notation, spacegroup $Fddd$, to a diffraction pattern from Tb at 122(2) GPa, with preferred orientation in the (001) direction. The fit is excellent, with all peaks accounted for. The refined lattice parameters are $a = 16.749(5)$ Å, $b = 4.6614(4)$ Å, and $c = 2.7352(5)$ Å, where $V/V_0 = 0.417(7)$ Å³ and atoms on the 16e site at $(\frac{3}{16}, 0, 0)$. The fit is excellent, with all peaks accounted for. When $x = \frac{3}{16}$, the intensity of the (400) peak is exactly zero

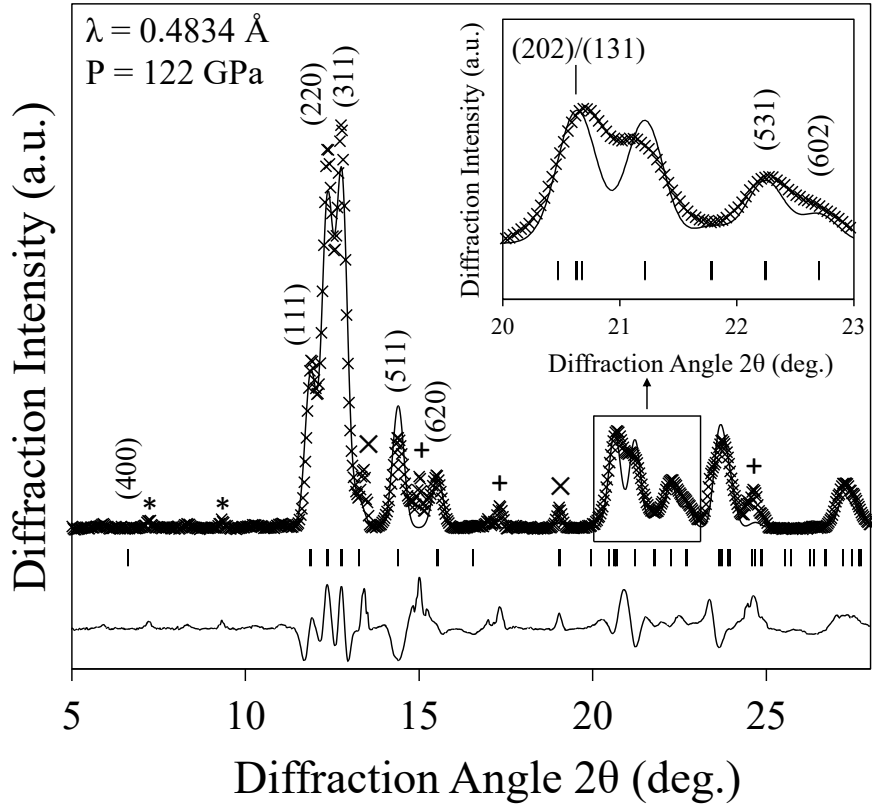


Figure 4.5 Rietveld refinement of the oF16 structure to a diffraction profile from Tb at 122(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first six peaks of the oF16 phase are labelled with their Miller indices. The inset shows an excellent fit to the same section of peaks poorly fitted to the mC4 structure in Figure 4.4. The $\times$ identifies first the (101) peak from the W gasket and the (008) peak from the Tb, and second the (002) from W and the (0012) from Tb. The + signs identify peaks from the Cu pressure calibrant. The asterisks identify weak contaminant peaks.

These findings then prompted studies into the post-dfcc phases of Gd and Dy, of which data had already been collected prior to this study.

4.3 Gadolinium

The post-dfcc phase of Gd has also been assigned to the $mC4$ structure [61]. However, the presence of Ar peaks in the diffraction patterns means that one cannot be sure whether or not the refinement of the $mC4$ structure is correct, and, in particular, whether the peak not predicted in the $mC4$ refinement to the post-dfcc phase in Tb exists in the $mC4$ refinement in Gd. Furthermore, the published β angle for this phase in Gd is very different to those published for the same phases in the other trivalent lanthanides (see Table 2.4).

To investigate the structural systematics of Gd in the post-dfcc phase, data collected during previous high-pressure, high-temperature, x-ray diffraction experiments have been analysed.

4.3.1 Experimental Details

The set of data were collected by Keith Munro prior to the beginning of this project. High-purity distilled samples of Gd supplied by Ulrich Schwarz at the Max-Planck-Institut für Chemische Physik fester Stoffe in Dresden were loaded into one DAC in a dry argon atmosphere (<1 ppm O_2 and <1 ppm H_2O) to prevent oxidation. The DAC was equipped with tungsten (W) gaskets. The sample was loaded without a pressure medium in order to avoid having any peaks from an additional material overlapping with those from either the sample or pressure marker, but were loaded with a small piece of tantalum (Ta) foil to act as a pressure calibrant, using the published Ta equation of state of Sokolova *et al.* [132].

Diffraction data were collected in an experiment on the high-pressure I15 beamline at the Diamond Light Source (DLS) synchrotron, United Kingdom. A monochromatic x-ray beam of wavelength $0.4245\text{\AA}$ focussed down to $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ was used, and the powder-diffraction data were recorded on a Mar345 area detector, placed ~ 350 mm from the sample. LaB_6 and Si diffraction standards were used to calibrate the exact sample-detector distances and the detector tilts

in each experiment. The 2D diffraction images collected at each pressure were integrated azimuthally using DIOPTAS [135] to obtain standard 1D diffraction profiles, which were then analysed using Rietveld [138] and Le Bail profile-fitting methods or by fitting to the d -spacings of individual diffraction peaks [146].

4.3.2 Experimental Results

Refinements of the diffraction patterns displaying the high-pressure, high-temperature phases of Gd from the $hP2$ phase to the $hR24$ phase are presented in Munro’s thesis [17] and, therefore, will not be refined again here. The highest pressure diffraction patterns were fitted with the $mC4$ structure but similar misfits that were found in Tb were also reported in these profiles. Figure 4.6 displays a poor-fitting Rietveld refinement of the $mC4$ structure to a diffraction profile from Gd at 81(2) GPa and 473 K with preferred orientation in the (001) direction. The refined lattice parameters are $a = 4.695(3)$ Å, $b = 2.8756(4)$ Å, $c = 4.8844(7)$ Å, and $\beta = 105.43(2)^\circ$, $V/V_0 = 0.481(13)$ Å³, with atoms on the $4i$ site at (0.2537(6), 0, 0.3098(8)). The refined β angle determined in this study reflects that determined for Tb, and is significantly different to that determined by Errandonea [61]. The left-hand arrow in the inset of Figure 4.6 shows a peak that cannot be fit by the $mC4$ structure. The arrow to the right in the inset highlights a peak not predicted by the $mC4$ structural refinement, which, as previously mentioned, is the same peak not predicted in the $mC4$ refinement of the post-dfcc phase in Tb. As a result of the findings from the analysis of high-pressure diffraction patterns from Tb samples, the data collected above 60 GPa can now be accurately resolved.

As the heavy trivalent lanthanides are known to exhibit the exact same structures from ambient conditions to ultra-high pressures at room temperature, the newly assigned structure to the high-pressure, post-dfcc phase discovered in Tb was the immediate candidate for the same high-pressure phase in Gd. Figure 4.7 displays a Rietveld refinement of the 16-atom orthorhombic $oF16$ structure to a diffraction pattern from Gd at 81(2) GPa and 473 K. The refined lattice parameters are $a = 18.0319(4)$ Å, $b = 4.8841(3)$ Å, and $c = 2.8786(2)$ Å, where $V/V_0 = 0.480(6)$ Å³ and atoms on the $16e$ site at ($\frac{3}{16}$, 0, 0). The fit is excellent with all peaks accounted for, including evidence of the zero-intensity peak discussed in Section 4.2.2, with Miller indices (400), at 5.3 degrees. The high-temperature data was favoured over room temperature data due to a large number of contaminant

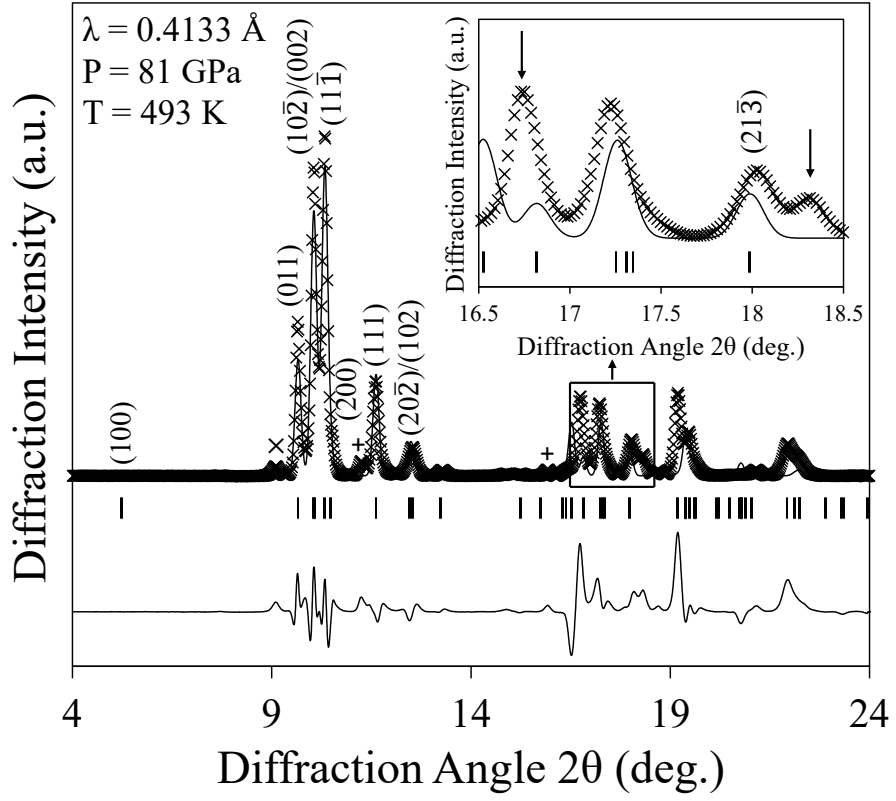


Figure 4.6 Rietveld refinement of the *mC4* structure to a diffraction profile from Gd at 81(2) GPa and 473 K, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first nine peaks of the *mC4* phase are labelled with their Miller indices. The $\times$ identifies a contaminant peak from an fcc structure of unknown origin [17]. The asterisks identify peaks from the Ta pressure calibrant.

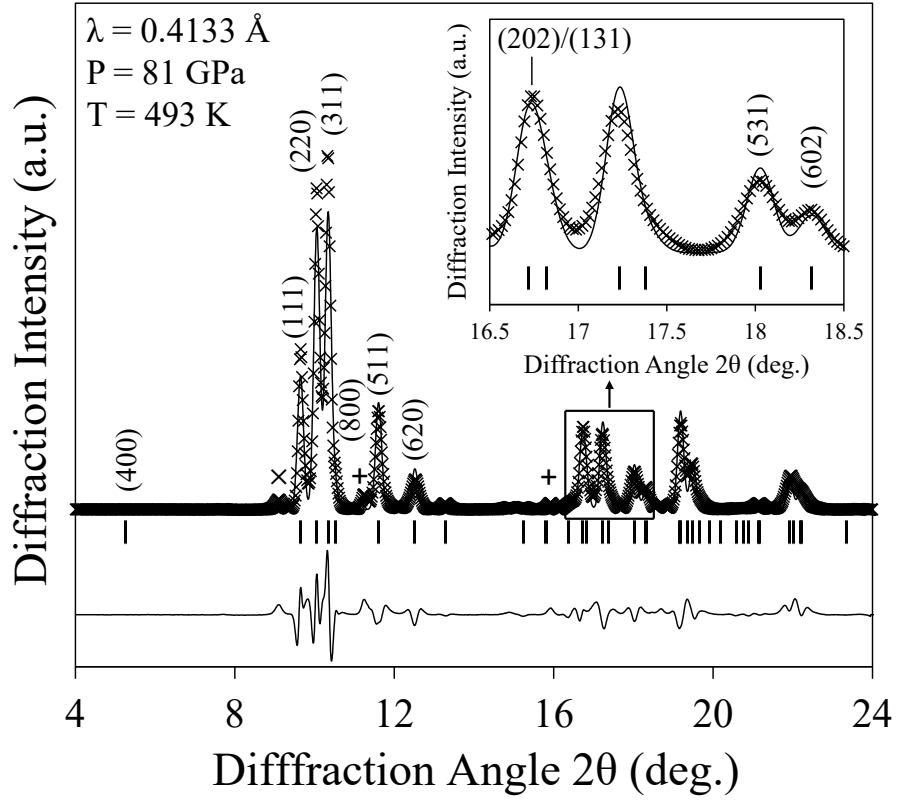


Figure 4.7 Rietveld refinement of the oF16 structure to a diffraction profile from Gd at 81(2) GPa and 473 K, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first seven peaks of the oF16 phase are labelled with their Miller indices. The inset shows an excellent fit to the same section of peaks poorly fitted to the mC4 structure in Figure 4.6. The $\times$ identifies a contaminant peak from an fcc structure of unknown origin [17]. The asterisks identify peaks from the Ta pressure calibrant.

peaks present in the patterns. One can see that the peaks in Figure 4.7 are much sharper than those in Figure 4.5. This is likely to have arisen from the heating of the sample which has been known to improve the quality of diffraction patterns collected from powder samples. Furthermore, the pattern was collected at a lower pressure than that seen in Figure 4.5 on the post-dfcc phase of Tb and the Gd was loaded into a DAC with a relatively large-diameter culet.

4.4 Dysprosium

The post-dfcc structure of Dy has been assigned to the C-centred monoclinic structure [8], just like its heavy trivalent lanthanide neighbours Gd, Tb, Er, Ho and Tm. It has also, however, been assigned to a body-centred monoclinic structure [68], iso-symmetrical with the structure assigned to the post-dfcc phase in Gd by Hua *et al.*.

High-pressure diffraction profiles collected prior to the beginning of this work have been analysed to correctly assign structure of the post-dfcc phase of Dy and, therefore, determine whether or not the findings contradict that which is reported in the literature.

4.4.1 Experimental Details

The data set presented here were collected by Keith Munro prior to the beginning of this project. High-purity distilled samples of Dy supplied by Ulrich Schwarz at the Max-Planck-Institut für Chemische Physik fester Stoffe in Dresden were loaded into two DACs in a dry argon atmosphere (<1 ppm O_2 and <1 ppm H_2O) to prevent oxidation. The DACs were equipped with tungsten (W) gaskets. The first sample was loaded without a pressure medium in order to avoid having any peaks from an additional material overlapping with those from either the sample or pressure marker, and loaded with a small piece of tantalum (Ta) foil to act as a pressure calibrant, using the published Ta equation of state of Sokolova *et al.* [132]. The second sample was loaded with a helium (He) pressure medium and without a pressure calibrant. The detected pressures from the second sample were determined using the Ta EOS calculated from the first sample.

Diffraction data were collected in an experiment on the high-pressure I15 beamline

at the Diamond Light Source (DLS) synchrotron, United Kingdom, and in another experiment on the High Pressure ID09 beamline at the European Synchrotron Radiation Facility (ESRF) synchrotron in Grenoble, France. Both sets of data were collected prior to the beginning of this project by Munro. Monochromatic x-ray beams of wavelength 0.4245 Å (DLS) and 0.4118 Å (ESRF), focussed down to $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ (DLS) and $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ (ESRF) were used, and the powder-diffraction data were recorded on Mar345 (DLS) and Mar555 (ESRF) area detectors, placed $\sim 350\text{ mm}$ from the sample. LaB_6 and Si diffraction standards were used to calibrate the exact sample-detector distances and the detector tilts in each experiment. The 2D diffraction images collected at each pressure were integrated azimuthally using DIOPTAS [135] to obtain standard 1D diffraction profiles, which were then analysed using Rietveld [138] and Le Bail profile-fitting methods or by fitting to the d -spacings of individual diffraction peaks [146].

4.4.2 Experimental Results

The data presented here on Dy were collected by Munro prior to the beginning of this project. As answers can now be provided as to the systematics of the ultra-high pressure phases, refinements of lower pressure phases have been provided as they were not resolved before by Munro.

Initial diffraction patterns of Dy were collected in the dhcp phase. Figure 4.8 displays a Le Bail refinement of the $hP4$ structure, spacegroup $P6_3/mmc$, to a diffraction pattern of Dy at 21(2) GPa.

Weak reflections from the dfcc phase were found in diffraction profiles from 38(2) GPa. This transition occurs at a pressure $\sim 5\text{ GPa}$ lower than what is reported in the literature [66, 68, 74]. Refinements of the $hR24$ structure were done to diffraction patterns collected between 38 and 67 GPa. Figure 4.9 displays a Le Bail refinement of the $hR24$ structure, spacegroup $R\bar{3}m$, to a diffraction profile from Dy at 58(2) GPa. This phase was stable up to 70 GPa, where a transition to the post-dfcc phase occurred.

Figure 4.10 displays a Rietveld refinement of the $mC4$ structure to a diffraction profile from Dy at 86(2) GPa with preferred orientation in the (001) direction. The refined lattice parameters are $a = 4.456(3)\text{ }\text{\AA}$, $b = 2.8007(6)\text{ }\text{\AA}$, $c = 4.7525(9)\text{ }\text{\AA}$, and $\beta = 105.63(3)^\circ$, $V/V_0 = 0.452(14)\text{ }\text{\AA}^3$, with atoms on the $4i$ site at

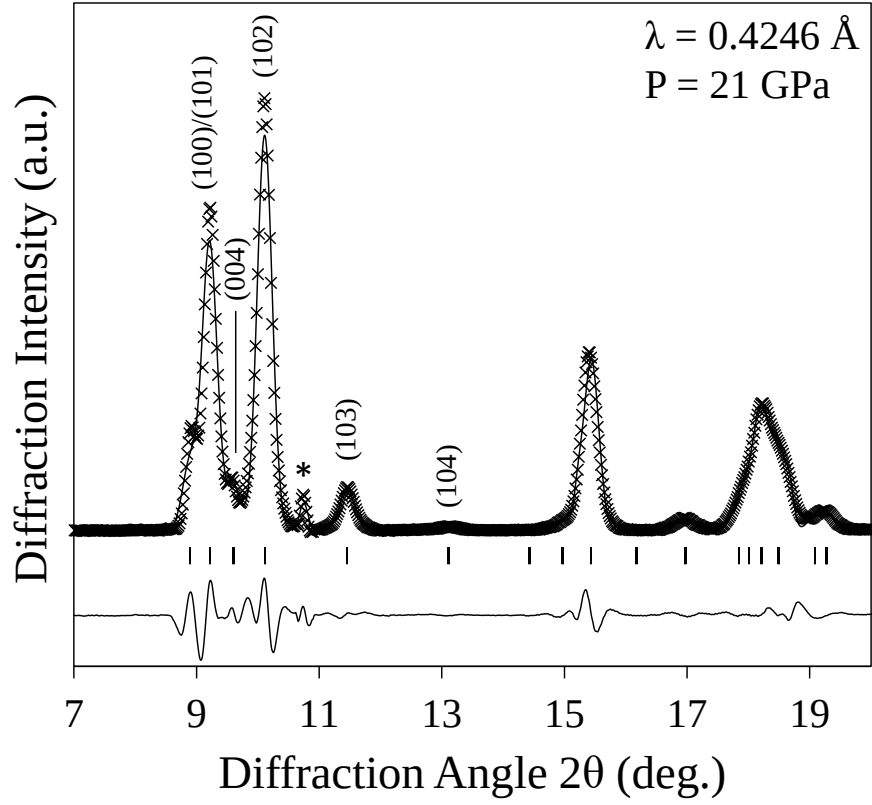


Figure 4.8 *Le Bail refinement of the hP4 structure to a diffraction profile from Dy at 21(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first six peaks of the hP4 phase are labelled with their Miller indices. The asterisk identifies the (101) peak from the Ta pressure marker.*

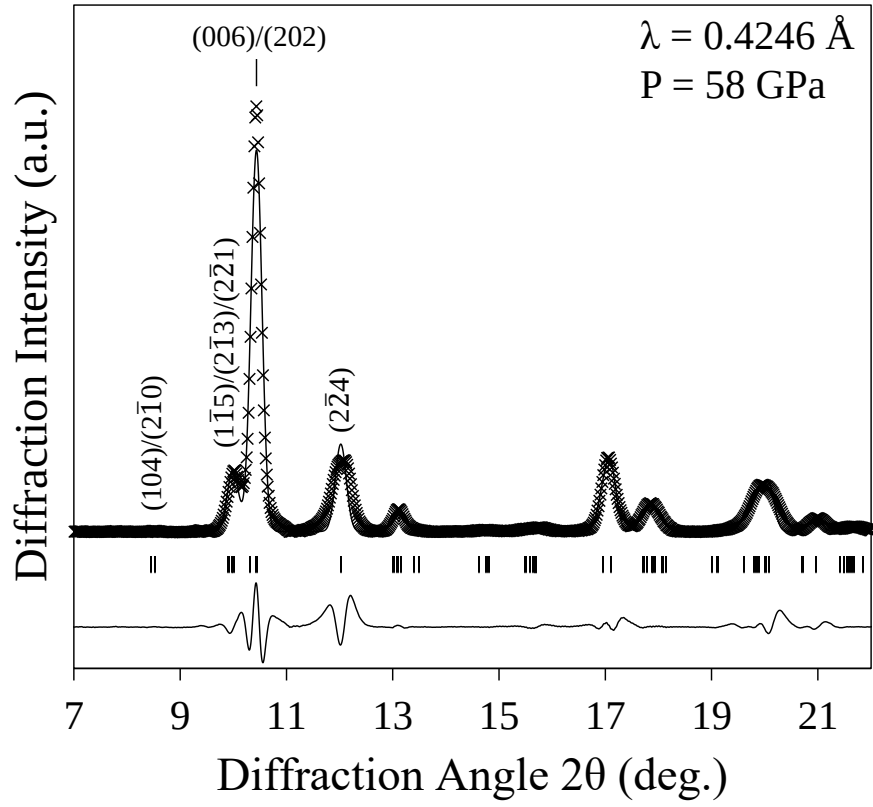


Figure 4.9 *Le Bail refinement of the hR24 structure to a diffraction profile from Dy at 58(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first eight peaks of the hR24 phase are labelled with their Miller indices.*

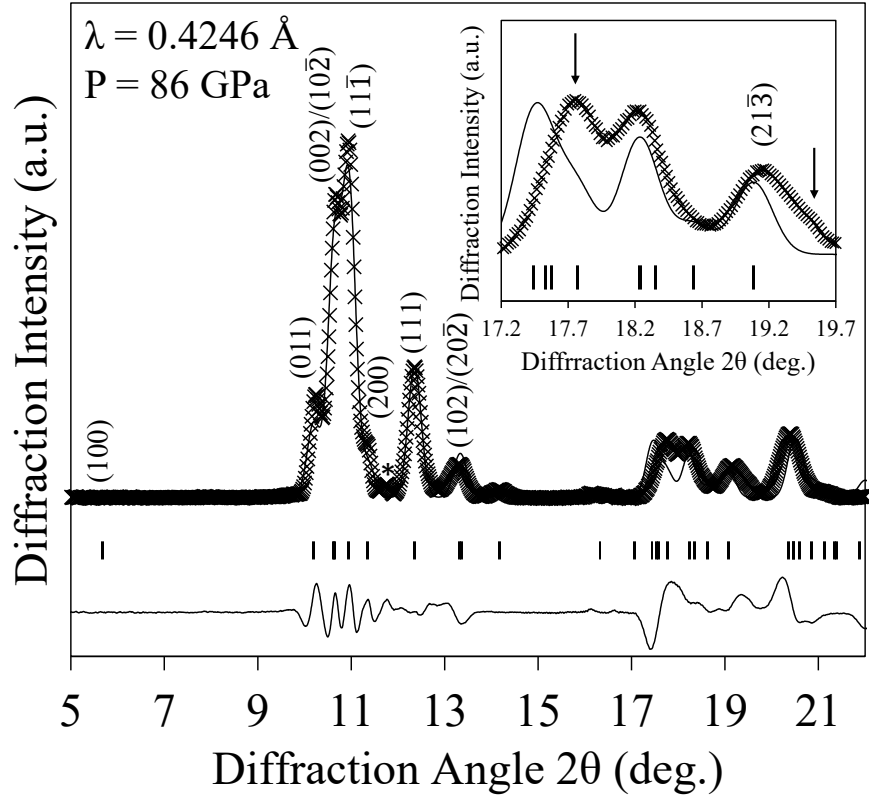


Figure 4.10 Rietveld refinement of the *mC4* structure to a diffraction profile from *Dy* at 86(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first nine peaks of the *mC4* phase are labelled with their Miller indices. The asterisk identifies the (101) peak from the Ta pressure marker.

Table 4.2 *Structural data for three different pressure-induced phases of Dy observed at room temperature, including lattice parameters and pressures with their uncertainties.*

Structure	Lattice Parameters (Å)	Pressure (GPa)
<i>hP4</i>	$a = 3.16154(14), c = 10.145(2)$	21(2)
<i>hR24</i>	$a = 5.7090(3), c = 14.170(4)$	58(2)
<i>oF16</i>	$a = 17.239(5), b = 4.7436(5), c = 2.7963(3)$	86(2)

(0.248(3), 0.303(6)). In general, the fit is good, however the peaks highlighted in the inset to Figure 4.10 are poorly fitted by the *mC4* structure. In fact, the right-hand arrow highlights the same peak that is not predicted by the *mC4* structural refinement in both Tb and Gd. As a result of the findings from the analysis of high-pressure diffraction patterns from Tb samples, the data collected above 60 GPa can now be accurately resolved.

At this stage, the “analysis by analogy” approach was taken with the structural determination of the post-dfcc phase of Dy. Therefore, just as in Gd, the immediate candidate was the *oF16* structure. Figure 4.11 displays a Rietveld refinement of this orthorhombic structure to a diffraction pattern of Dy at 86(2) GPa. This is an excellent fit, with all peaks accounted for, including evidence of the zero-intensity peak discussed in Section 4.2.2, with Miller indices (400), at 5.6 degrees. The refined lattice parameters are $a = 17.239(5)$ Å, $b = 4.7436(5)$ Å, and $c = 2.7963(3)$ Å, where $V/V_0 = 0.453(8)$ Å³ and atoms on the 16*e* site at ($\frac{3}{16}, 0, 0$). Once again, by determining x to equal $\frac{3}{16}$, the (400) peak is predicted to have zero intensity, which can be clearly seen in the difference profile in Figure 4.11. This phase remained stable up to 102 GPa – the maximum pressure obtained in this study.

4.5 Comparisons Between Orthorhombic & Monoclinic Crystal Structures

In the heavy trivalent lanthanides, the first low-symmetry, “volume-collapsed” phase has been described as having a structure of monoclinic symmetry with 4 atoms in the unit cell, *mC4* in Pearson notation, and all describing the spacegroup *C2/m*. The structure is also assigned to high-pressure phases in Ce, Pr, Nd and Sm. However, as noted in Section 2.3.2, the β angles for the *mC4* structures in

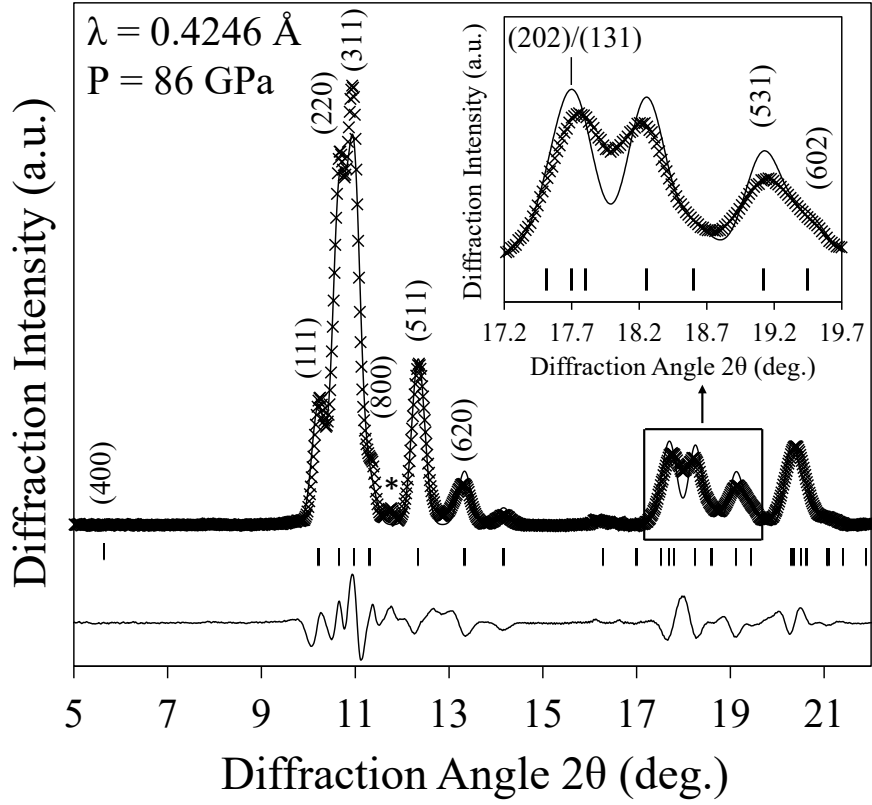


Figure 4.11 Rietveld refinement of the oF16 structure to a diffraction profile from Dy at 86(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first seven peaks of the oF16 phase are labelled with their Miller indices. The inset shows an excellent fit to the same section of peaks poorly fitted to the mC4 structure in Figure 4.10. The asterisk identifies the (101) peak from the Ta pressure marker.

the heavy and light trivalent lanthanides, and Ce, are significantly different from each other.

In this chapter, the $mC4$ structure of the post-dfcc phase in Tb, Gd and Dy has been reassigned to the $oF16$ structure. Therefore, it is interesting to show how the two structures are related and, furthermore, describe comparisons to the structures described in similar phases in the light trivalent lanthanide and actinide elements.

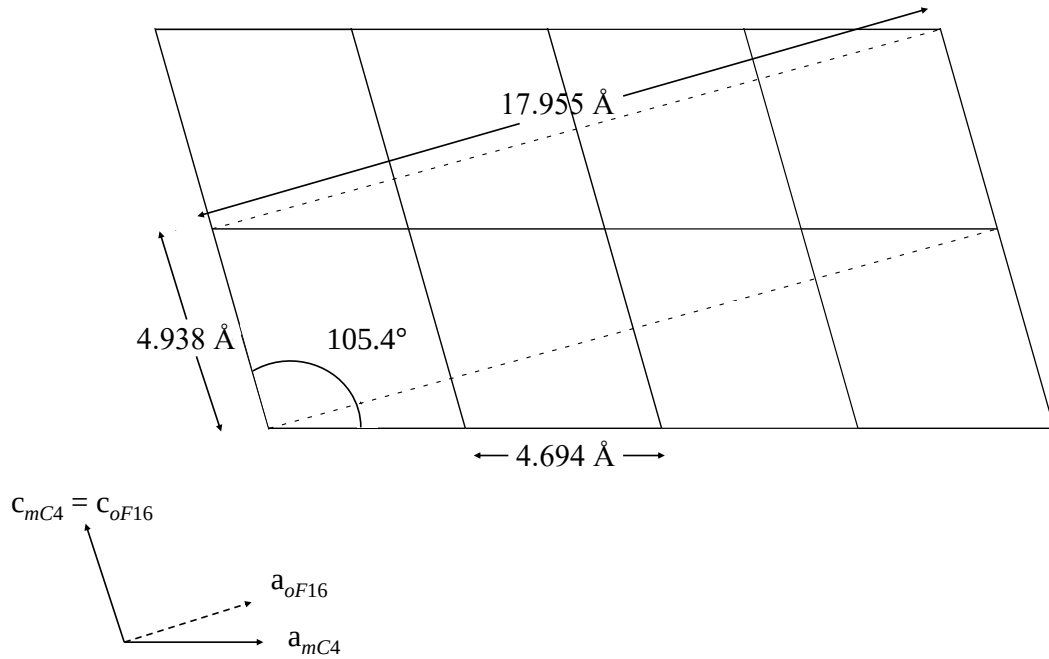


Figure 4.12 The 2-dimensional construct displays the relationship between the unit cells of the $mC4$ and $oF16$ structures in Tb at ~ 60 GPa.

As seen in Figure 4.4, the $mC4$ structure still fits the diffraction pattern from Tb reasonably well. However, Figure 4.5 shows that the $oF16$ structure fits the peaks between 20 and 23 degrees which are poorly fit by the the $mC4$ structure. Figure 4.12 displays the relationship between the unit cells of the $mC4$ and $oF16$ structures, showing that when equating the c -axis of both unit cells the $oF16$ unit cell neatly fits across 8 of the $mC4$ unit cells. Indeed, the $mC4$ structure can be described as pseudo-orthorhombic (see Supplemental Material of [1]). Figure 4.13 shows the stacking of quasi-hexagonal layers in both the $mC4$ and $oF16$ structures.

The $oF16$ structure in Tb, Gd and Dy comprises 8 quasi-close-packed layers, where, stacked along the a -axis, the ratio $b/c \sim \sqrt{3}$ is converse to stacking in the

cubic and hexagonal structures seen at lower pressures in the three elements. The atoms in each layer are centred above the midpoint of 2 atoms in the previous layer, resulting in 10-fold (6+2+2) coordination. The stacking sequence is ABCADCBD. This is different to the 6+3+3 coordination, where each atom in a layer is centred above the midpoint of 3 atoms in the layer below, of the hcp and fcc structures.

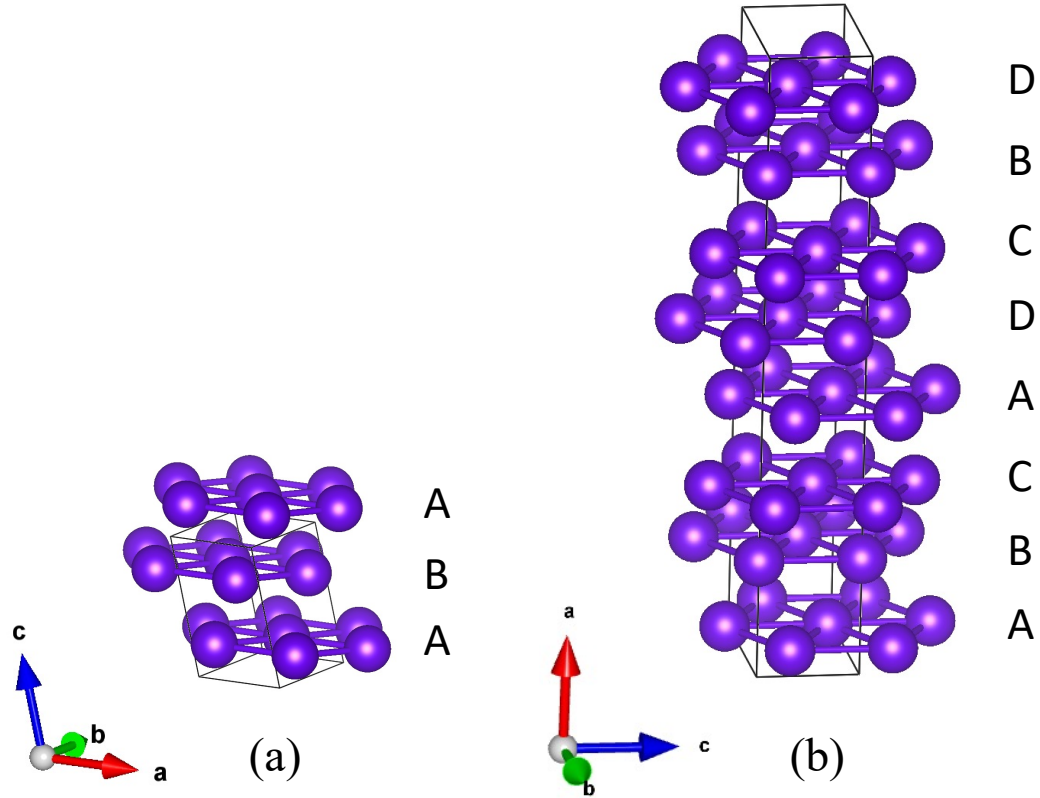


Figure 4.13 *The crystal structures of (a) mC4-Tb and (b) oF16-Tb at 122 GPa. The structure in (a) is the $C2/m$ spacegroup, while the structure in (b) is the $Fddd$ spacegroup. Both differ in the stacking of their flat, quasi-hexagonal atomic layers. The stacking sequence in mC4 it is AB and in oF16 it is ABCADCBD.*

The same monoclinic structure assigned to the post-dfcc heavy trivalent lanthanide phases has also been assigned to the post-dfcc (Pr) and post-*hP3* phases (Nd and Sm) in the light trivalent lanthanides. However, when one sees the diffraction patterns collected from these elements, one cannot help but notice significant differences in the number of peaks and differing intensities (see profile (b) of Figure 4.14), nor ignore the significant differences in their β angles. Only one monoclinic structure has currently been ascribed to a high pressure, room temperature phase in the actinide metals. The third high pressure phase in

Cm is known to exhibit a $C2/c$ spacegroup structure [87]. Interestingly, upon transition to the next phase in Cm , the monoclinic $C2/c$ structure transforms to an orthorhombic structure with 8 atoms in the unit cell, $oF8$ in Pearson notation [87]. In addition, high-pressure phases in the trans-U actinides, Pu, Am and Cf, also exhibit an orthorhombic structure with 8 atoms in the unit cell [15, 19, 88], of which the diffraction profiles bear striking resemblance to those of high-pressure phases in Nd and Sm. Figure 4.14 shows x-ray diffraction patterns collected on (a) Tb, (b) Nd [18] and (c) Am [19] at high pressures. One can see the significant differences between the Tb diffraction pattern in profile (a) and those in profiles (b) and (c). Furthermore, it is clear that the patterns shown in profiles (b) and (c) are strikingly similar and yet these high-pressure phases of Nd and Am have been assigned to very different structures.

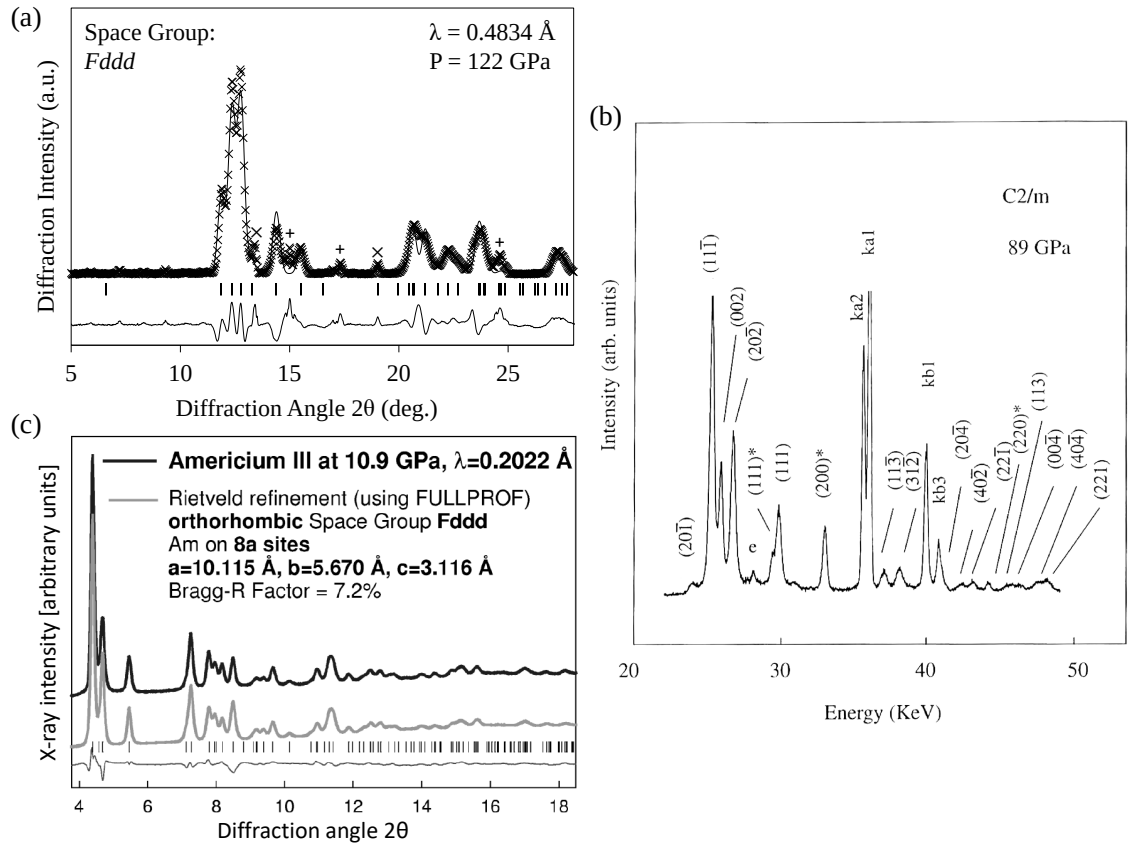


Figure 4.14 Diffraction profiles from (a) Tb at 122 GPa, (b) Nd at 89 GPa and (c) Am at 10.9 GPa. The ADXD pattern of Tb in profile (a) is the same as that shown in Figure 4.5. The EDXD pattern of Nd in profile (b) shows a fit made by Akella of the $C2/m$ structure [18]. The ADXD pattern of Am in profile (c) displays a Rietveld refinement made by Heathman of the $Fddd$ structure [19].

From observation of the published diffraction data from the $mC4$ phases of Er

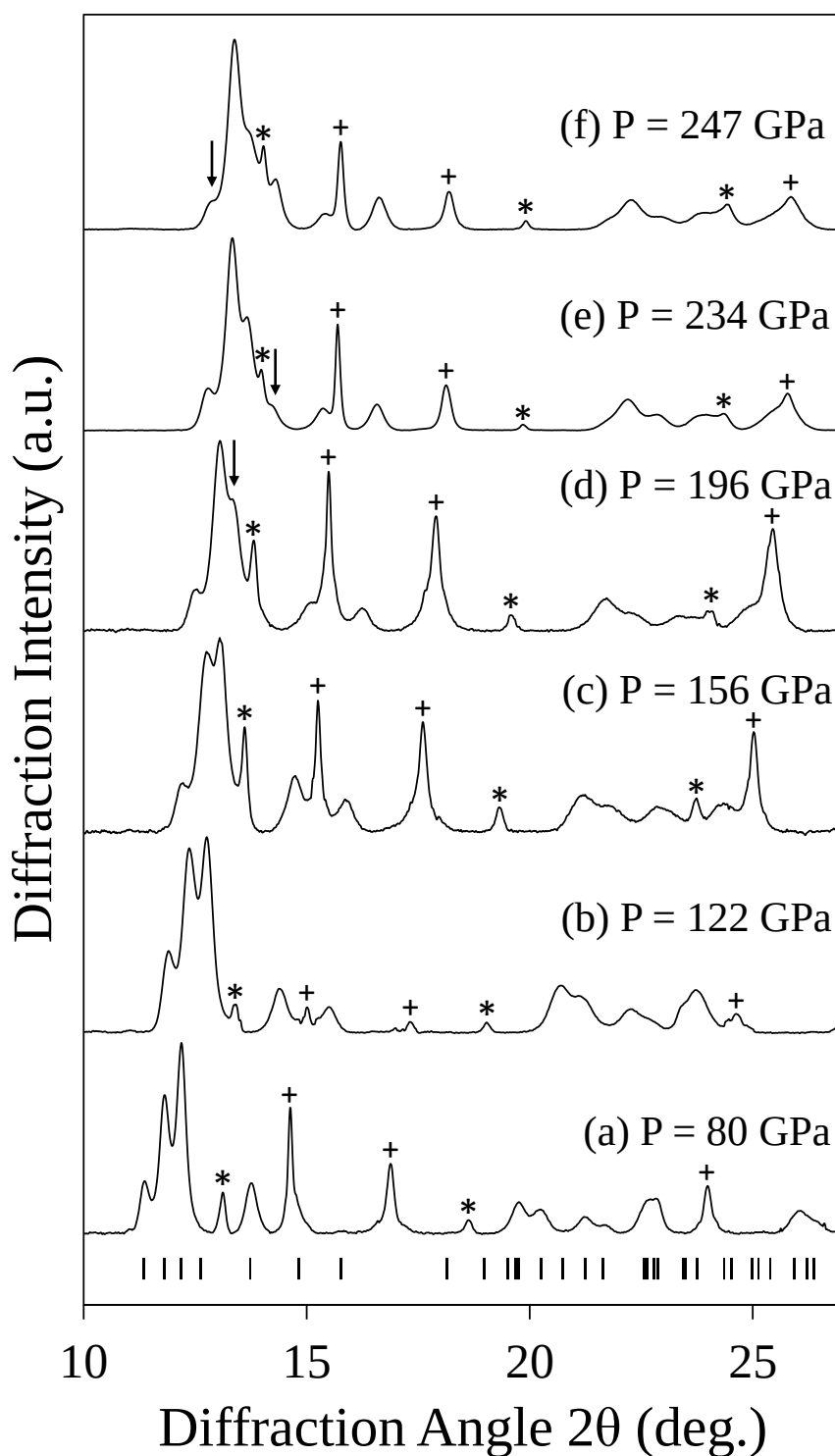


Figure 4.15 *Diffraction profiles collected from Tb on pressure increase. Tick marks beneath profile (a) mark calculated peak positions from the oF16 phase. The peaks marked with asterisks are from the W gasket, and the peaks marked with + signs are from the Cu foil pressure calibrant. The arrows in profiles (d) and (f) mark significant reductions in intensity of the main peak, with Miller indices (311) (profile (d)), and the (111) peak (profile (f)) from the oF16 phase. The arrow in profile (e) indicates a new peak growing.*

[9] and Tm [63], one can see the stark similarities between them and newly-published diffraction data of the other heavy trivalent lanthanides, thus allowing one to conclude that both Er and Tm also exhibit the *oF16* structure and not the *mC4* structure.

4.6 Transition to the Post-*oF16* Phase in Tb

At pressures between 150 and 247 GPa, marked changes occur in the diffraction patterns from Tb. However, the structure of this new phase is yet to be confirmed as all the patterns collected are phase-mixed with the *oF16* structure. Further complicating refinement of this new phase are the presence of intense peaks from the W gasket and Cu foil pressure marker.

Figure 4.15 displays diffraction profiles from Tb on pressure increase. Profile (c) shows the highest-pressure diffraction profile collected of *oF16* phase. The onset of the new phase was marked by changes in the diffraction profiles collected above 160 GPa. The arrow in profile (d) highlights the reduction in intensity of the (311) peak from the *oF16* phase. Profile (e) shows an arrow at ~ 14 degrees indicating the growth of a new peak. It is highly likely that this peak exists in lower-pressure diffraction patterns, but the intense reflection from the (101) peak of the W gasket has masked the region where this peak would be observed. Finally, the arrow in profile (f) shows the continuing reduction in the (111) peak from the residual *oF16* phase.

This study has found that these mixed-phase profiles last for more than 80 GPa upon compression to 247 GPa, the highest pressure reached in this study. This large pressure range of mixed-phase Tb indicates that the unit cells of both the *oF16* structure and new structure may share similarities in the stacking of their quasi-close-packed layers. It is often reported that the low-pressure phase transitions of the trivalent lanthanides exhibit sluggish transitions from $hP2 \rightarrow hR9 \rightarrow hP4 \rightarrow cF4$ [15, 17, 28, 147]. These low-pressure structures share similarities in the stacking of their close-packed layers where each atom in the unit cell sits above the centre point of 3 atoms in the layer below. It could then be inferred that structures of the high-pressure phase seen above 160 GPa in this study shares the same coordination, whereby each atom in the unit cell sits above the mid-point of 2 atoms in the previous layer, as that of the structure in the *oF16* phase.

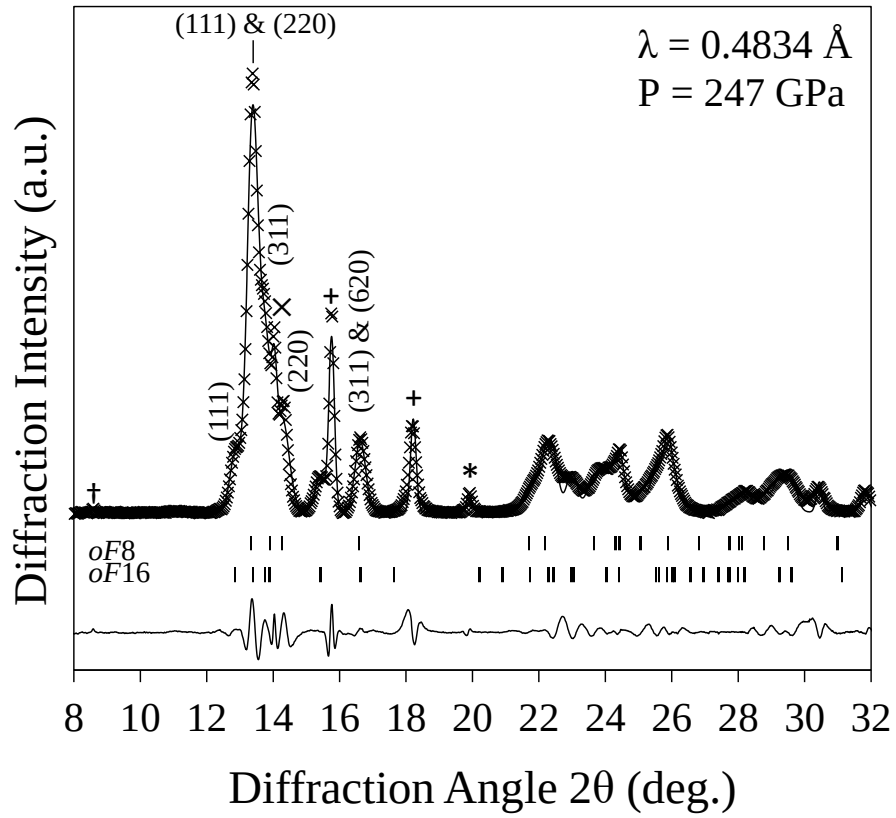


Figure 4.16 *Le Bail refinement of the oF16 and oF8 structures to a mixed-phase diffraction profile from Tb at 247(4) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions of the oF16 (below) and oF8 (above) phases, and the difference profile. In the instances where doublets are labelled, the first set of Miller indices identifies a peak from oF8-Tb, and the second from oF16-Tb. The labelled singlets identify the (111) and (311) peaks from oF16-Tb, and the (220) peak from oF8-Tb. The dagger identifies a weak contaminant peak. The × identifies the (101) peak from the W gasket, the (800) peak from oF16-Tb and the (400) peak from oF8-Tb. The asterisk identifies a peak from the W gasket and the + signs identify peaks from the Cu pressure marker. Finally, the dagger highlights a contaminant peak.*

Although the diffraction patterns collected above 200 GPa were still heavily phase-mixed, the CONOGRAPH software was utilised to try and determine structure candidates between 204 and 247 GPa. The best-fitting structure determined by the software was orthorhombic with 8 atoms in the unit cell, *oF8* in Pearson notation, from the spacegroup *Fddd*. Figure 4.16 displays a Le Bail refinement of both the *oF16* and *oF8* structures to a mixed-phase diffraction profile from Tb at 247(4) GPa. The fit is good, with all peaks accounted for. The refined lattice parameters for the *oF8* phase are $a = 7.983(3)$ Å, $b = 4.4566(8)$ Å, and $c = 2.4674(6)$ Å, where $V/V_0 = 0.343(9)$ Å³; the refined lattice parameters of the *oF16* phase at the same pressure are $a = 15.9884(3)$ Å, $b = 4.2940(8)$ Å, and $c = 2.5316(6)$ Å, where $V/V_0 = 0.343(9)$ Å³. This provides evidence of another structure candidate (the *oF8* structure) for the common structural phase transition sequence of the trivalent lanthanides at high pressures.

Trial fits of the other structural candidates of the post-*hR24* were made. These included the *oC4* structure, seen in high-pressure phases of Ce [5], Pr [64, 81] and Nd [18]. A trial fit of the *oP4* structure, seen in the high-pressure phases of Am [19], Cm [87] and Cf [88], was also made. However, neither the *oC4* nor the *oP4* structures provided good fits.

4.6.1 Electronic Structure Calculations

Zero-temperature DFT calculations performed by our collaborators at King's College London (KCL) examined the enthalpy change in the *oF16* and *oC4* phases at high pressures [148]. The *oC4* structure is seen in U at ambient pressures and up to 100 GPa [15], and has also been observed in the high-pressure phases of Ce [5], Pr [64, 81] and Nd [18]. It is understood that all the trivalent lanthanides will exhibit the *oC4* structure at high pressures. The results revealed that the *oC4* phase had lower enthalpy above 300 GPa.

4.7 Conclusions

The previously reported transition sequence $hP2 \rightarrow hR9 \rightarrow hP4 \rightarrow cF4 \rightarrow hR24$ has been observed in Tb (*hR9* and above), Gd (*hP2* and above) and Dy (*hP4* and above) upon increasing pressure at ambient temperatures up to 54, 60 and 67 GPa, respectively. Upon transition to the next phase, all three adopt the same

orthorhombic structure with 16 atoms in the unit cell, $oF16$, spacegroup $Fddd$, rather than the monoclinic $mC4$ structure previously described in the literature.

Comparisons of the $mC4$ and $oF16$ structures in Tb provide understanding of the unit cell relationships between both, and further comparisons of the x-ray diffraction patterns from $oF16$ -Tb, $mC4$ -Nd and $oF8$ -Am have been made. These comparisons have brought to light contradictions in the literature.

Further compression of Tb above 160 GPa has shown a transition to another phase. Initial analysis has determined that the structure in this phase is an 8-atom orthorhombic structure, $oF8$. However, no single-phase pattern of the new phase was observed up to 247 GPa, the highest pressure reached in this study. Furthermore, DFT calculations performed by Plekhanov *et al.* have determined that Tb may transition to the α -U phase above 300 GPa. Therefore, x-ray diffraction experiments to pressures of at least 300 GPa would be required to determine accurately the structure of the post- $oF16$ phase.

Chapter 5

The Post- $hP3$ Structure of Samarium

5.1 Introduction

After determining the identity of the low symmetry structure of the post-dfcc, “volume-collapsed” phase of the heavy trivalent lanthanides (Gd to Lu, except Yb), it seems prudent to then look at the post-dfcc phase in the light trivalent lanthanides (La to Sm, except Ce). Accessed at lower pressures, the structure of the post-dfcc phase in Nd and Sm has also been assigned to the monoclinic $mC4$ structure. However, once again, analysis of the data collected for this thesis has found inconsistencies with that published in previous literature. Moreover, Sm and Nd access this low-symmetry phase via a different phase, not the $hR24$ phase, but one with a 3-atom hexagonal structure assigned to it ($hP3$ in Pearson notation). This chapter describes the study of x-ray powder diffraction data on Sm up to 222 GPa. It includes the refinement of the $hP3$ and post- $hP3$ phases. Furthermore, it will discuss the fitting of APL equations of state to the compression data. By doing so, we are thus able to observe the effects of Sm’s electronic behaviour on the phase transitions with increasing pressure.

In order to investigate the post- $hP3$, low-symmetry phase and the different pressure-induced route to which it is accessed via the $hP3$ phase, angle dispersive x-ray powder diffraction studies have been performed on Sm metal to 222 GPa.

First of all, it is reported here that the $hP3$ phase that provides the different route

to which the next phase is accessed has a slightly higher hexagonal symmetry (see Ref. [30] in Ref. [1]) than what was published by Husband *et al.* [75].

In the previous chapter, it was shown that the long-reported $mC4$ structure is incorrect in Tb, Gd, Dy, Ho, Er and Tm, and that the true structure of these collapsed phases is orthorhombic, spacegroup $Fddd$, with 16 atoms per unit cell [1]. We can confirm that Sm does not exhibit the $oF16$ structure but does share the same spacegroup $Fddd$. In fact, the structure of the “volume-collapsed” phase in Sm is found to be iso-structural with the γ -Pu phase that exhibits the $oF8$ structure – an orthorhombic structure, spacegroup $Fddd$ with 8 atoms in the unit cell. The data that describes this finding, and the evidence for a higher symmetry $hP3$ phase, will be discussed later in this chapter and have been published in Physical Review B [2].

5.2 Experimental Details

High-purity distilled samples of Sm supplied by Ulrich Schwarz at the Max-Planck-Institut für Chemische Physik fester Stoffe in Dresden were loaded into three diamond-anvil cells in a dry argon atmosphere (<1 ppm O_2 and <1 ppm H_2O) to prevent oxidation. The cells were equipped with bevelled diamonds with $100\mu m$ culets and W gaskets. The samples were loaded without any pressure medium in order to avoid having any peaks from an additional material overlapping with those from either the sample or pressure marker, but were loaded with a small copper (Cu) sphere to act as a pressure calibrant using the published Cu equation of state of Sokolova *et al.* [132].

Diffraction data were collected in three experiments on the Extreme Conditions P02.2 beamline at the PETRA-III synchrotron in Hamburg, Germany, and in a fourth experiment on the high-pressure I15 beamline at the Diamond Light Source (DLS) in the United Kingdom. Low-pressure data were obtained on beamline ID09 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France prior to the beginning of this project by Rachel Husband and is also published in [147]. Monochromatic x-ray beams of wavelength $0.2895\text{\AA}$ $0.4808\text{\AA}$ $0.2898\text{\AA}$ (PETRA-III), $0.4248\text{\AA}$ (DLS) and $0.4135\text{\AA}$ (ESRF), focused down to $10\text{ }\mu m \times 10\text{ }\mu m$, $3\text{ }\mu m \times 6\text{ }\mu m$ and $0.85\text{ }\mu m \times 0.85\text{ }\mu m$ (PETRA-III), $20\text{ }\mu m \times 20\text{ }\mu m$ (DLS) and $15\text{ }\mu m \times 15\text{ }\mu m$ (ESRF) were used, and the powder-diffraction data were recorded on Perkin-Elmer (PETRA-III), Mar345 (DLS) and Mar555 (ESRF)

area detectors, placed 300-400 mm from the sample. In the third experiment conducted at PETRA-III, the area detector was moved from ~ 400 mm to ~ 600 mm from the sample in order to improve the low-angle peak resolution. CeO_2 , LaB_6 and Si diffraction standards were used to calibrate the exact sample-detector distance and the detector tilts. The 2D diffraction patterns collected at each pressure were integrated azimuthally using DIOPTAS [135] (this work) and Fit2D [149] (Husband) to obtain standard 1D diffraction profiles, which were then analysed using Rietveld [138] and Le Bail methods or by least-squares fitting to individual diffraction peak positions [146].

5.3 Experimental Results

Angle-dispersive x-ray powder diffraction experiments were performed on samarium metal up to 222 GPa. Up to 50 GPa we observed the $hR9 \rightarrow hP4 \rightarrow cF4 \rightarrow hR24 \rightarrow hP3$ pressure-induced transition sequence of Sm, discussed in Chapter 2.

The need to focus on high pressure data collection, and already having low pressure data collected by Rachel Husband prior to the beginning of this project [147], allowed us to take relatively large pressure steps up to 50 GPa. As a result, the first diffraction pattern observed was of the $hP4$ phase at 10 GPa. As can be seen from Figure 5.1, remnant peaks from the $hR9$ phase are still present in the diffraction profile, most notable are the ‘shoulder’ to the left of the main $hP4$ -(102) peak and the relatively sharp $(\bar{1}\bar{1}8)$ peak at ~ 7.5 degrees. The transition to $hP4$ will have occurred at ~ 1 GPa according to previous literature [10]. However, this is not wholly unexpected as the transition has been reported as ‘sluggish’, thus a significant pressure range of phase-mixing is expected. The relatively low-intensity, broad-fitting peaks from the refinement to the $hR9$ structure displayed in the inset of Figure 5.1 illustrates that although the structure is still persisting at this pressure, it is indeed disappearing.

A diffraction profile collected at 15.0(5) GPa did not show any signs of a transition to the $cF4$ phase. However, a mixed $cF4/hP4$ phase was observed at 17.0(5) GPa. The inset in Figure 5.2 displays shoulders on either side of the $cF4$ -(111) peak. The data presented in Figure 5.2 agrees with previous work, illustrating that only mixed diffraction patterns of the $cF4$ structure have been observed for Sm, which has also been noted in this thesis to occur in Tb, Gd and Dy.

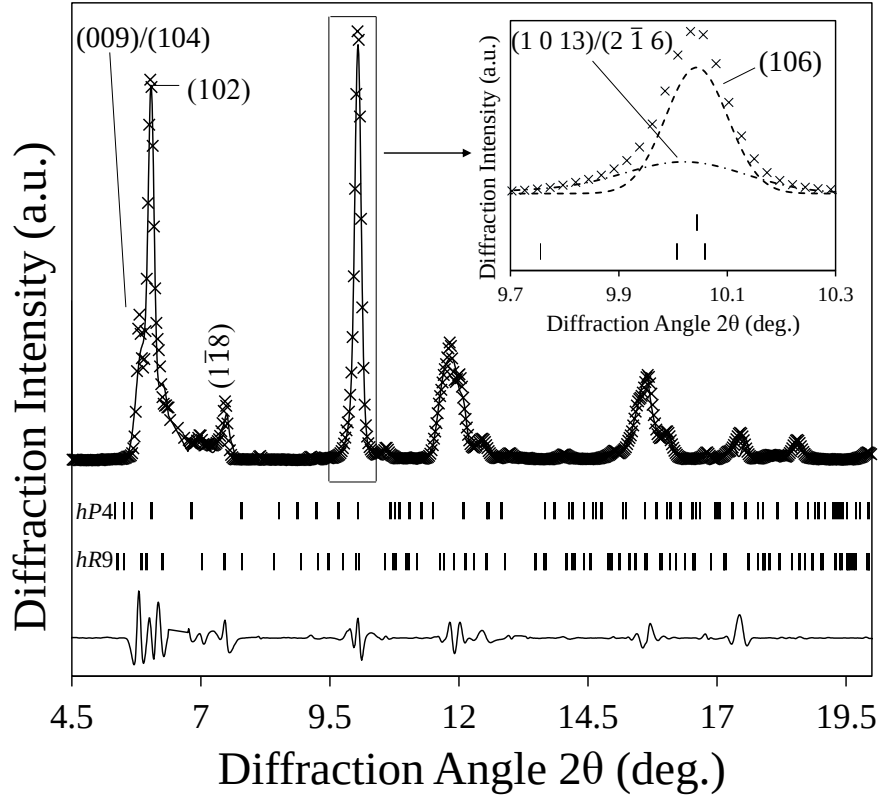


Figure 5.1 *Le Bail refinement of the hR9 and hP4 structures to a mixed phase diffraction profile from Sm at 11.4(5) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions of the hR9 (below) and hP4 (above) phases, and the difference profile. The first two main peaks of the hP4 phase, and the first two peaks of the remainder hR9 phase are labelled with their Miller indices. The inset labels the fit of the hR9 (dot-dash line) and the hP4 (dash line) structures at ~ 10 degrees.*

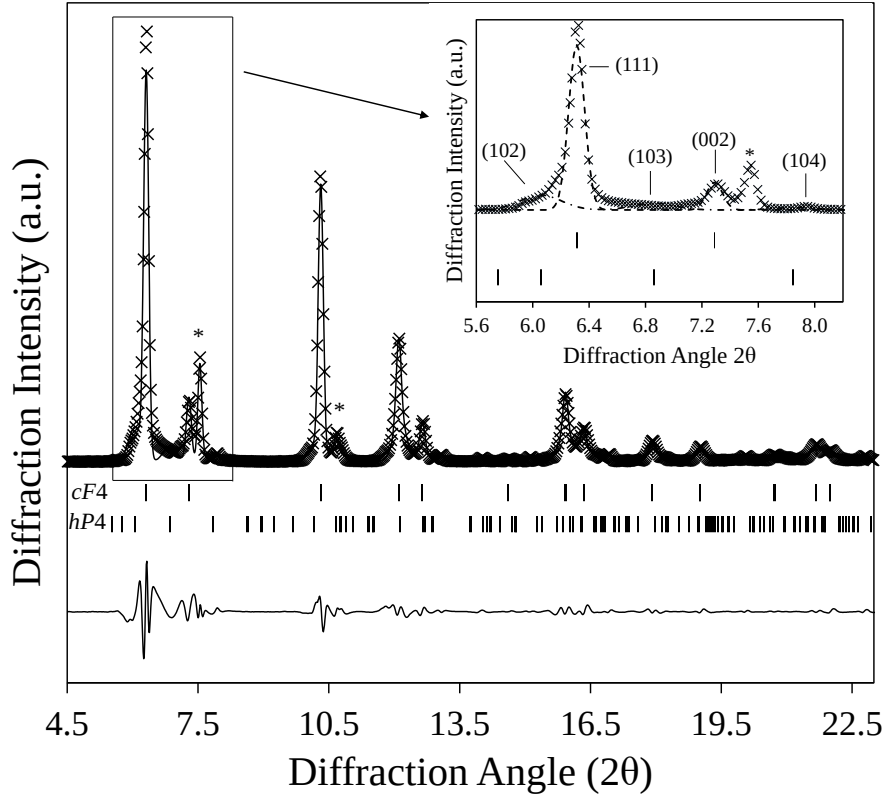


Figure 5.2 *Le Bail refinement of the hP4 and cF4 structures to a mixed phase diffraction profile from Sm at 17.0(5) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions of the hP4 (below) and cF4 (above) phases, and the difference profile. The (111) and (002) peaks of the cF4 phase (dash) and the (102), (103) and (104) of the hP4 phase (dot-dash) are labelled in the inset, and the asterisk identifies the (110) peak from the W gasket.*

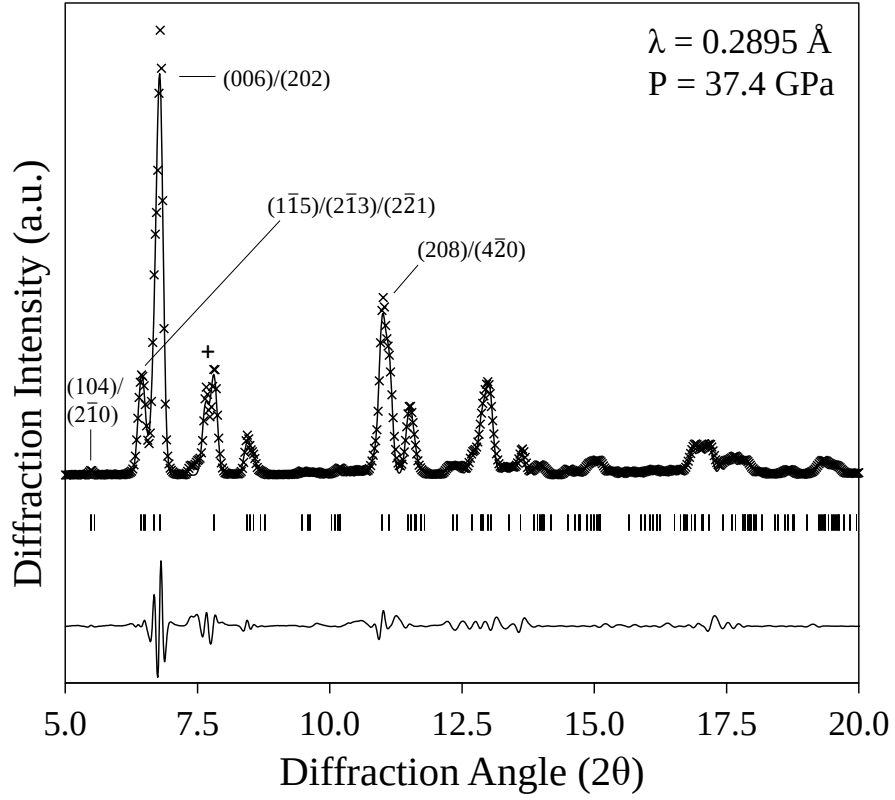


Figure 5.3 *Le Bail refinement of a single phase profile of hR24 to a diffraction profile from Sm at 37(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The nine most ‘intense’ peaks are labelled. The + sign identifies the (110) peak from the W gasket (left) and the (224) peak from the hR24-Sm (right).*

The next diffraction pattern collected in this study was at a pressure of 21.5(2) GPa where the transition to $hR24$ was observed. As mentioned previously, larger pressure steps were taken; however, these data remain consistent with those of previous studies. Figure 5.3 shows an excellent fit of the $hR24$ phase, spacegroup $R\bar{3}m$, to a diffraction profile at 37.4 GPa – the highest pressure $hR24$ -Sm diffraction profile collected. The large pressure regions of mixed-phase $hR9/hP4$, $hP4/cF4$ and $cF4/hR24$ diffraction patterns observed are thought to arise from the slight differences in stacking of the hexagonal layers in the four different structures.

5.3.1 Higher Symmetry $hP3$

Diffraction patterns were initially collected from 10 GPa to below 50 GPa, to compare results with those collected previously by Husband *et al.* [75]. The transition to the $hP3$ phase was observed at 42(5) GPa, showing consistent results with previous studies [75]. Analysis of the $hP3$ patterns confirmed that the systematic absences were consistent with spacegroup $P6_222$ rather than $P3_121$. This resulted from assuming the atomic positions of the $P3_121$ structure $(0, 0.513(5), \frac{1}{3})$ to instead be the ideal values of $(0, \frac{1}{2}, \frac{1}{3})$. Chen *et al.* noted that if $x = \frac{1}{2}$, the spacegroup of the $hP3$ structure would instead be $P6_222$ [150]. After performing Rietvelds of both structures to the same integrated diffraction pattern of Sm at 78 GPa shown in Figure 5.4 this was proven to be correct. Furthermore, Figure 5.4, profile (b) clearly shows that the peak intensities of the $P6_222$ Rietveld refinement are an excellent match to the diffraction profile of the $P3_121$ refinement in Figure 5.4, profile (a). One can clearly see the absence of the $(1\bar{1}1)$ and $(1\bar{1}2)$ peaks in the Rietveld refinement of profile (b), as the reflection conditions of the higher symmetry $P6_222$ spacegroup dictate.

5.3.2 Lower Symmetry Structures

On compression above 50 GPa, a sluggish transition to the post- $hP3$ phase is observed at 93(4) GPa. This is illustrated in Figure 5.5, profile (c). On further compression, the peaks from the post- $hP3$ phase increased in intensity (see Figure 5.5, profiles (d)–(f)), and single-phase profiles were not obtained until pressures above 157 GPa were reached (see Figure 5.5, profile (g)). Figure 5.5 displays diffraction patterns over a pressure range of 93 – 157 GPa, where peaks from

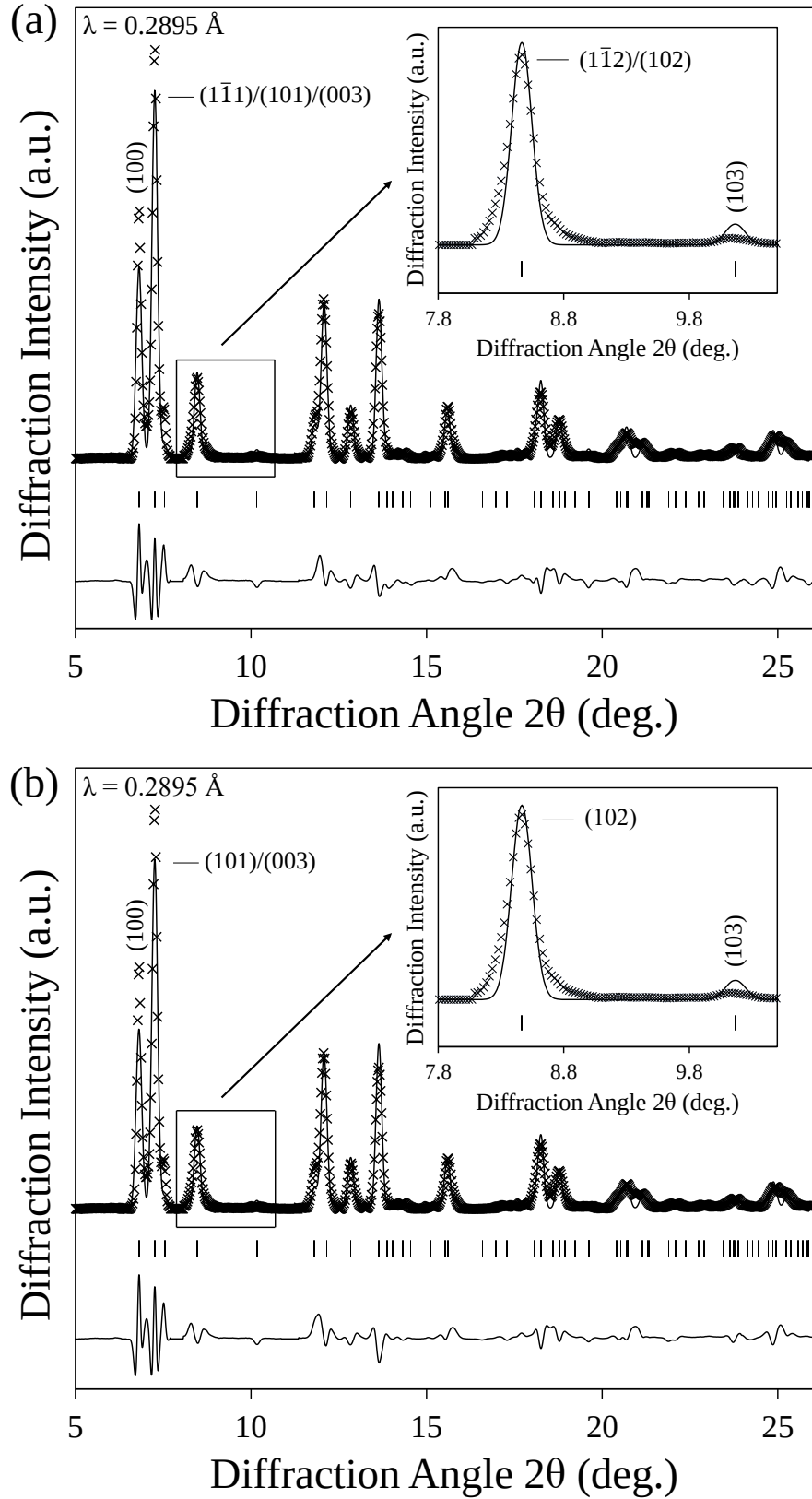


Figure 5.4 Rietveld refinements of the (a) $P3_121$ and (b) $P6_222$ structures to the same diffraction profile from Sm at 78(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profiles. The first (a) seven and (b) five peaks of the hP3 phase are labelled with their Miller indices. The inset in profile (b) highlights the absent $(1\bar{1}2)$ peak seen in the inset of profile (a).

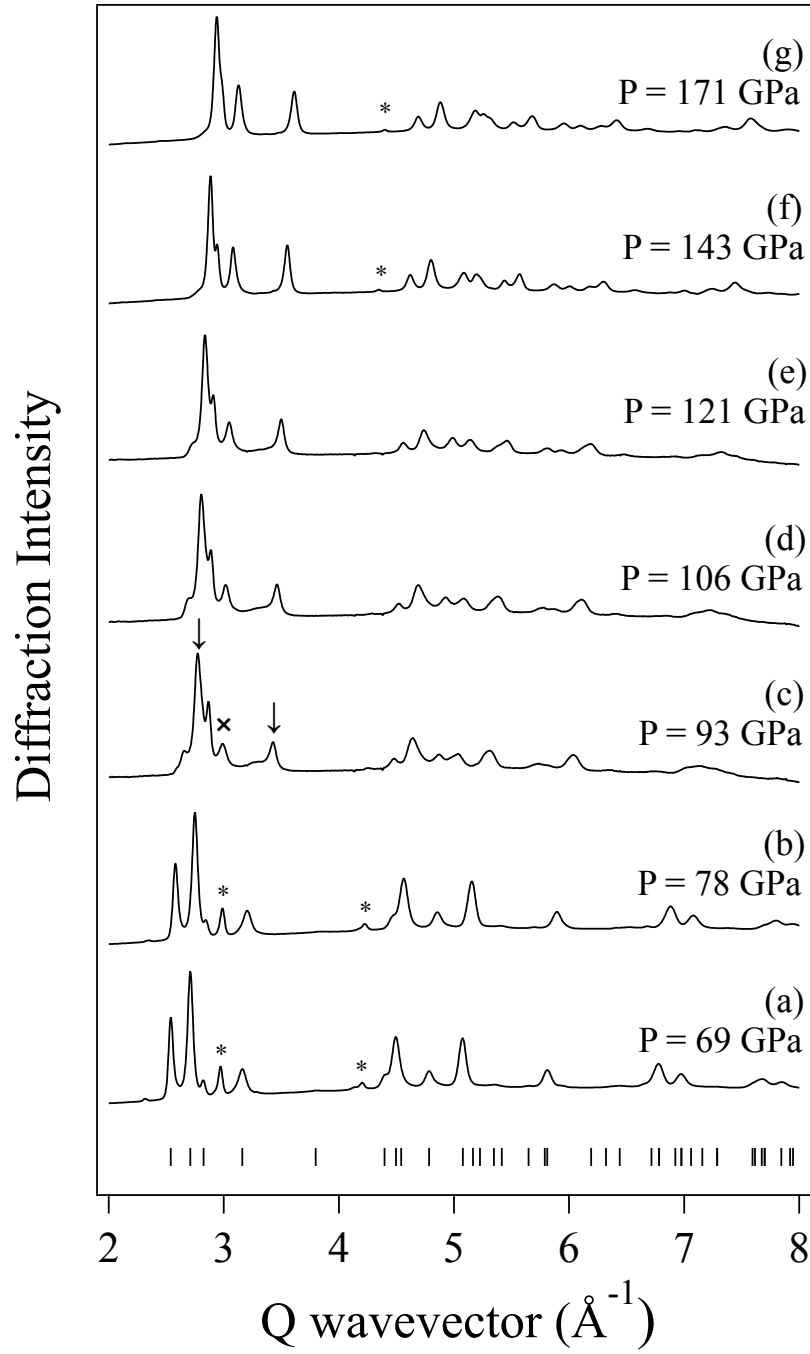


Figure 5.5 *Diffraction profiles collected from Sm on pressure increase. The data were collected from the same sample during two different synchrotron visits, and so are plotted as a function of wavevector (Q) in order to take account of the two different x-ray wavelengths used. Tick marks beneath profile (a) mark calculated peak positions from the hP3 phase. The peaks marked with asterisks are from the W gasket. The arrows in profile (c) marks the first appearance of peaks from the new phase. The reflections labelled with a $\times$ in profile (c) indicate a doublet including the (101) peak from the W gasket and a peak from the post-hP3 phase. Single phase patterns are seen in profiles (f) and (g).*

both phases can be seen in the diffraction profiles. The post-*hP3* phase remained stable up to 222(2) GPa, the highest pressure reached in this study.

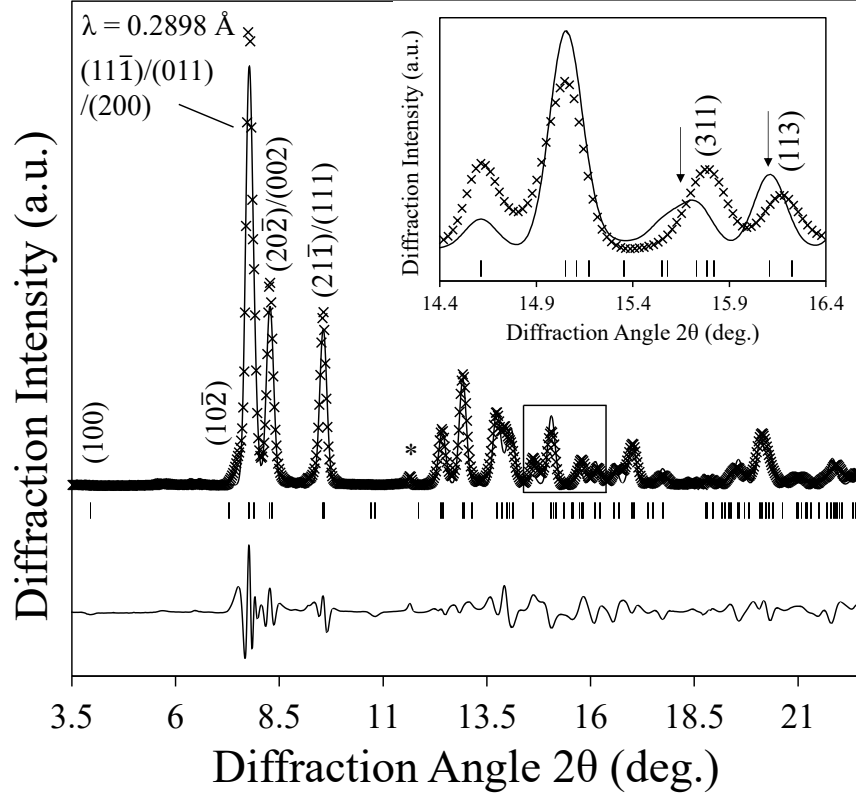


Figure 5.6 *Rietveld refinement of the $mC4$ structure to a diffraction profile from Sm at 173(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first nine peaks of the $mC4$ phase are labelled with their Miller indices. The (100) and (302)/(102) doublet from the Rietveld fit all have intensity. The inset shows a significant misfit to a section of peaks from the profile, especially at ~ 15.7 and ~ 16.1 degrees. The asterisk identifies the (200) peak from the W gasket (the (110) peak from the gasket is overlapped by the (202)/(002) reflections from the Sm).*

The literature has reported that a monoclinic $mC4$ structure, spacegroup $C2/m$, fits diffraction profiles of Sm above 100 GPa [20]. However, the study reported here has found significant misfits of this monoclinic structure to Sm diffraction profiles above this pressure. Figure 5.6 shows a Rietveld fit of the $mC4$ monoclinic structure to a diffraction pattern collected from Sm at 173(2) GPa, with preferred orientation in the (206) direction. The refined lattice parameters are $a = 4.8057(9)$ Å, $b = 2.5311(3)$ Å, $c = 4.5576(11)$ Å, and $\beta = 118.799(19)^\circ$, $V/V_0 = 0.366(12)$, with atoms on the $4i$ site at (0.256(16),0,0.267(4)). The

reflection peaks labelled in the fit of the main graph in Figure 5.6 are all expected to have some intensity and yet none have observed intensity in the raw pattern; this can be seen via the ‘bumps’ in the difference profile. The inset shows a clear misfit, similar, yet distinctly different, to a misfit observed in the post-dfcc phase of Tb, fitted with the $mC4$ structure, in Figure 4.5.

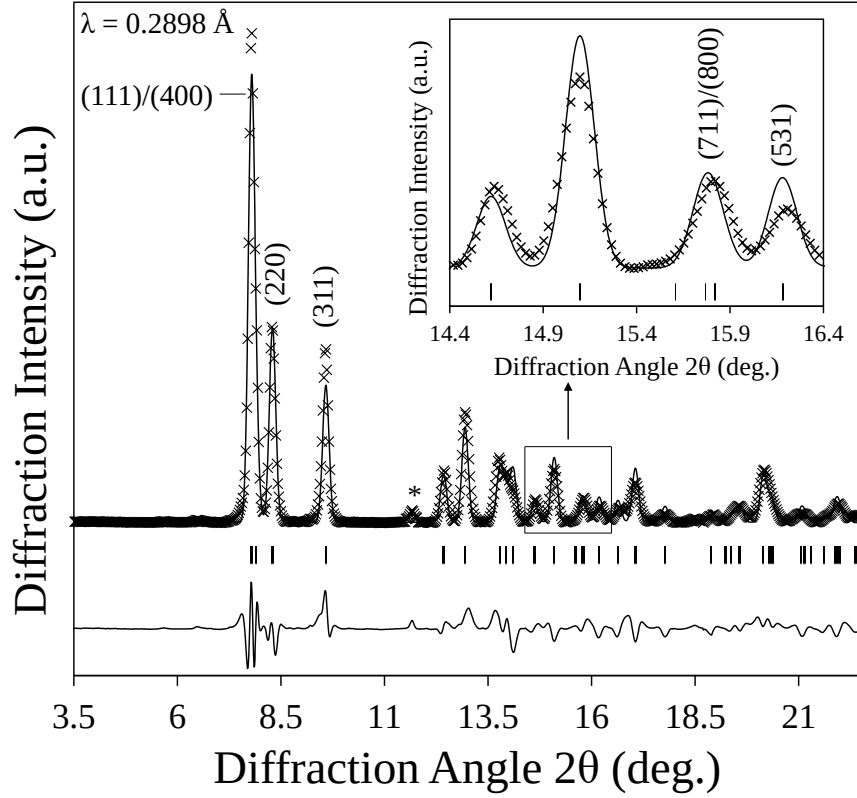


Figure 5.7 Rietveld refinement of the oF8 structure to a diffraction profile from Sm at 173(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first four peaks of the oF8 phase are labelled with their Miller indices. The inset shows a good fit to the same section of peaks highlighted in the inset from Figure 5.6. The asterisk identifies the (200) peak from the W gasket (the (110) peak from the gasket is overlapped by the (220) reflection from the Sm).

The CONOGRAPH software was employed to resolve for an accurate structural assignment to the post- $hP3$ phase of Sm by peak selection of the diffraction patterns from the samples. The top structural results were once again those from the $Fmmm$ Patterson symmetry group, just as what resulted from CONOGRAPH analysis of diffraction patterns from the post-dfcc phase of Tb. Furthermore, the top result from this Patterson symmetry group was from the $Fddd$ spacegroup. However, the length of the c -axis was predicted to be

Table 5.1 *Structural data for six different pressure-induced phases of Sm observed at room temperature, including spacegroups, lattice parameters and pressures with their uncertainties.*

Structure	Lattice Parameters (Å)	Pressure (GPa)
<i>hR9</i>	$a = 3.5830(7), c = 25.536(5)$	11.4(5)
<i>hP4</i>	$a = 3.6080(2), c = 11.6946(3)$	11.4(5)
<i>cF4</i>	$a = 4.5493(2)$	17.0(5)
<i>hR24</i>	$a = 5.9749(2), c = 14.899(2)$	37(2)
<i>hP3</i>	$a = 2.8130(3), c = 6.622(2)$	78(2)
<i>oF8</i>	$a = 8.4228(15), b = 4.5548(5), c = 2.5216(2)$	173(2)

approximately half the length of the c -axis measured in the post-dfcc phases of the heavy trivalent lanthanides. Structural refinement of the $Fddd$ spacegroup to diffraction patterns from the post- $hP3$ phase of Sm provided excellent fits. One can see from Figure 5.7, and in particular from the peaks highlighted by arrows in the inset, that this orthorhombic structure fits the diffraction patterns from the post- $hP3$ phase of Sm. The fit is clearly more accurate and has significantly fewer tick marks. In fact, this diffraction pattern resembles profiles from Am, Cm and Cf above 10, 56 and 38 GPa, respectively [19, 87, 88]. Figure 4.14 in Chapter 4 illustrates the differences between diffraction profiles of Tb and Nd at 64 and 89 GPa, and the similarities between Nd and Am at 89 and 10 GPa, respectively.

Figure 5.7 displays an excellent Rietveld fit, with all observed peaks accounted for, to a diffraction pattern from Sm at 173(2) GPa of an orthorhombic phase with 8 atoms in the unit cell, $oF8$ in Pearson notation, spacegroup $Fddd$, with preferred orientation in the (350) direction. The refined lattice parameters are $a = 8.4228(15)$ Å, $b = 4.5548(5)$ Å, and $c = 2.5216(2)$ Å, $V/V_0 = 0.364(3)$, with atoms on the $8a$ site at (0,0,0).

The $oF8$ structure of Sm at 175 GPa is shown in Figure 5.10 alongside the $hP3$ structure of Nd at 58 GPa and the $oF16$ structure of Tb at 64 GPa. The flat, quasi-close-packed layers of $oF8$ -Sm and $oF16$ -Tb are wrested from hexagonal symmetry via deviation from the ideal ortho-hexagonal value of $\sqrt{3}=1.732$ due to the distortion of the b/c axial ratio. This pressure dependent behaviour is shown in Figure 5.9 alongside the ideal ratio value of $\sqrt{3}=1.732$ from the previous phase in Sm that exhibits the same $hP3$ structure seen in Nd between 46 and 71 GPa. The discontinuity in hexagonal symmetry at the $hP3 \rightarrow oF8$ transition is clearly seen via an abrupt growth in the b/c ratio from 1.732 to 1.775(13) (see Figure 5.9). This discontinuity continues to grow to a maximum of 1.818(5) at 222 GPa.

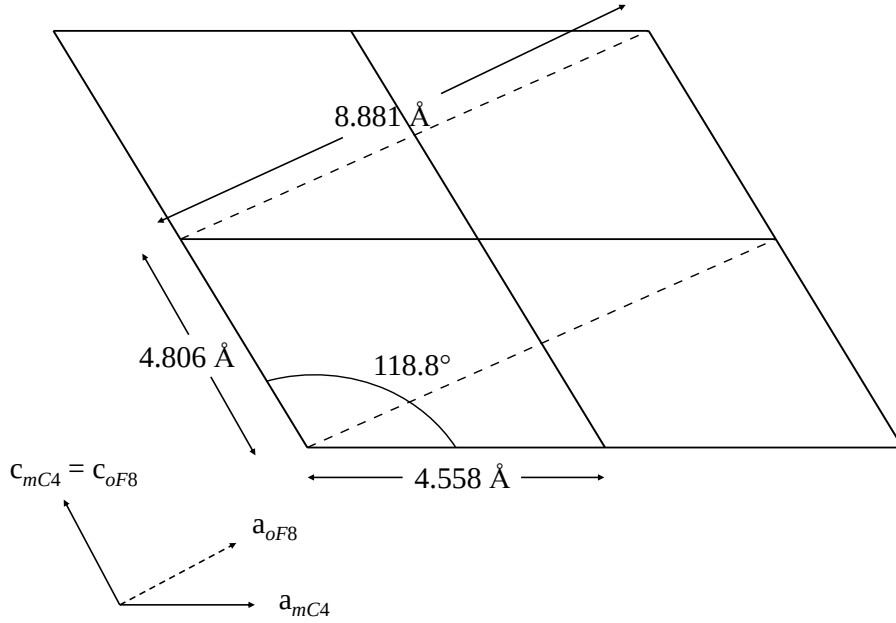


Figure 5.8 *This geometrical construct displays the relationship between the unit cells of the $mC4$ and $oF8$ structures.*

The nature of the stacking in the structures of the $hP3$, $oF8$ and $oF16$ phases of Nd, Sm and Tb, respectively, is the same. The atoms within each layer are centred above the midpoint of two atoms in the layer beneath. This results in all three structures having a liganacy of 10 (6+2+2). This stacking is shown in Figure 5.10.

The diffraction patterns previously reported from Sm above 100 GPa [20] are very different to those found in the the data presented in this thesis. Figure 5.11 illustrates a diffraction pattern from Sm at 106 GPa displaying a mixed phase of $hP3$ and $oF8$. Comparison of this and a diffraction profile from Sm at 109 GPa reported by Chesnut [20] shows strong similarity. Therefore, it is fair to conclude that the analysis in Chesnut's thesis was incorrect and caused by this phase mixing.

5.3.3 APL Equation of State

The compressibility of Sm up to the $hR24 \rightarrow hP3$ phase transition was fitted using an AP2 EOS [142]. This gave an excellent fit with $K_0 = 31.6(5)$ GPa and $K' = 3.23(3)$. However, beyond this transition, the AP2 fit becomes increasingly

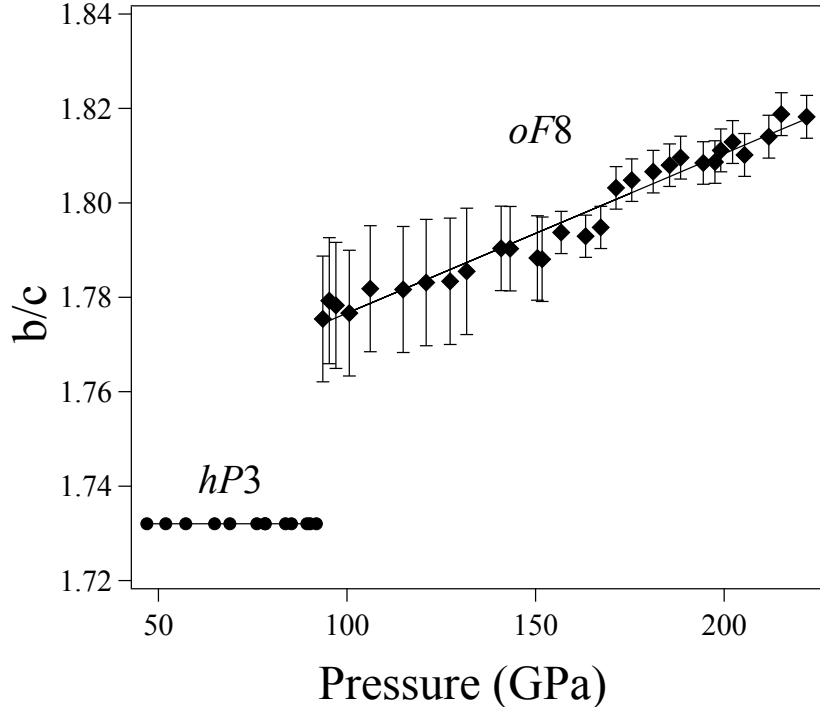


Figure 5.9 *The pressure dependence of ‘hexagonality’ of the atomic layers in the oF8 phase of Sm. The distortion can be quantified by the deviation of the b/c ratio from the ideal ortho-hexagonal value of $\sqrt{3}$ (1.732). The atomic layers in the hP3 phase have perfect hexagonal symmetry, and hence have the ideal ortho-hexagonal value. The discontinuity in the geometry of the layers at the hP3 $\rightarrow$ oF8 transition at 93 GPa is very clear and suggests that the transition is not continuous.*

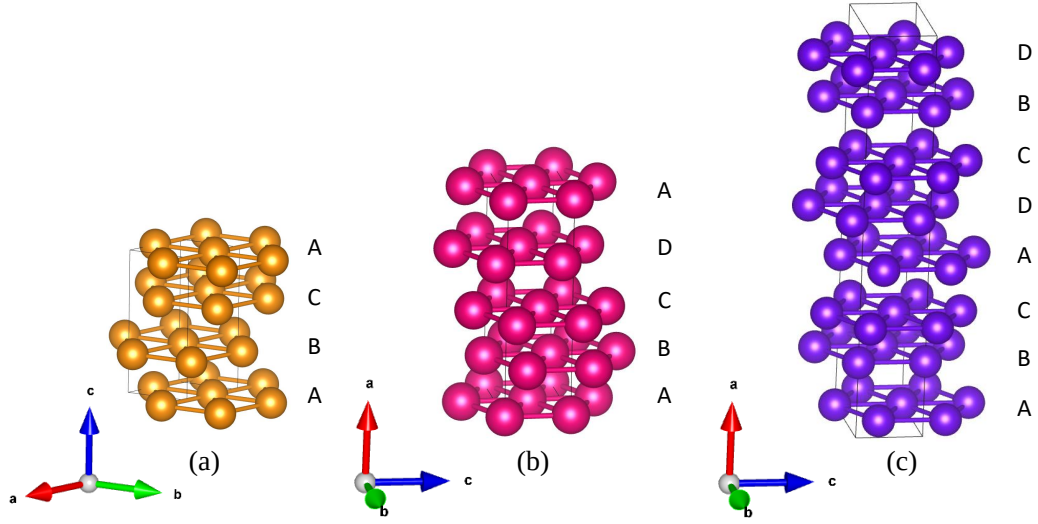


Figure 5.10 *The crystal structures of (a) $hP3$ -Nd at 58 GPa, (b) $oF8$ -Sm at 175 GPa and (c) $oF16$ -Tb at 64 GPa. The structure in (a) is iso-symmetric with the $P6_222$ spacegroup, while the structures in (b) and (c) are iso-symmetric with the $Fddd$ spacegroup. All three differ in the stacking of their flat, quasi-hexagonal atomic layers, yet all three have tenfold coordination. The stacking sequence in $hP3$ it is ABC, in $oF8$ it is ABCD and in $oF16$ it is ABCADCBD.*

poor. Figure 5.13 shows the quality of the AP2 fit declining with compression above 43 GPa. The compressibilities of the $hP3$ and $oF8$ phases are clearly smaller than those predicted by extrapolating the AP2 fit. Previous studies by Zhao [76] and Chesnut [20] have noted issues with fitting 2^{nd} order EOSs to the compressibility of Sm. These studies both found that 3^{rd} order EOSs yielded better fits to their data.

The P-V diagram shown in Figure 5.14 displays an AP3 fit to the compressibility of Sm to 222 GPa. This was fitted to the full compression curve with $K_0=40.6(11)$ GPa, $K'=1.57(6)$ and $K''=-0.0524(3)$. A 3.1% volume “collapse” occurs at the $hP3 \rightarrow oF8$ transition, allowing one to stipulate that the transition is 1^{st} order.

Figures 5.13 and 5.14 clearly illustrate that the AP3 form fits the full compression curve significantly better than the AP2 form. However, the K_0 value of 40.6(11) GPa is larger than the value of 31.6 GPa obtained by fitting the data up to the $hR24 \rightarrow hP3$ transition, and the value of 33 GPa reported previously [76]. This larger value is a result of the volume discontinuity mentioned above, causing a slight overestimation in the compressibility of the phases up to 43 GPa. The inset in Figure 5.14 illustrates the volume collapse.

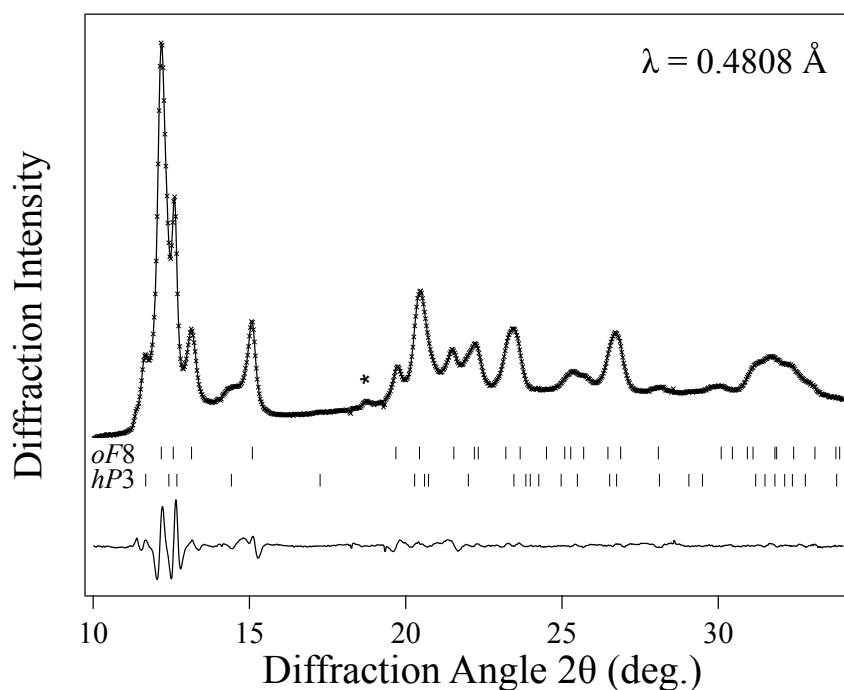


Figure 5.11 *Diffraction profile from a Sm sample at 106 GPa showing a mixed-phase pattern of $P6_222$ (hP3) and $Fddd$ (oF8). This is the same profile as that shown in Figure 5.5(d). The asterisk identifies the (200) peak from the W gasket. The residuals lie beneath the experimental data, and the tick marks mark the calculated peak positions of the two phases. This profile bears a striking resemblance to that reported by Chesnut at 109 GPa (Figure 5.12) which was fitted with the monoclinic $mC4$ structure [20].*

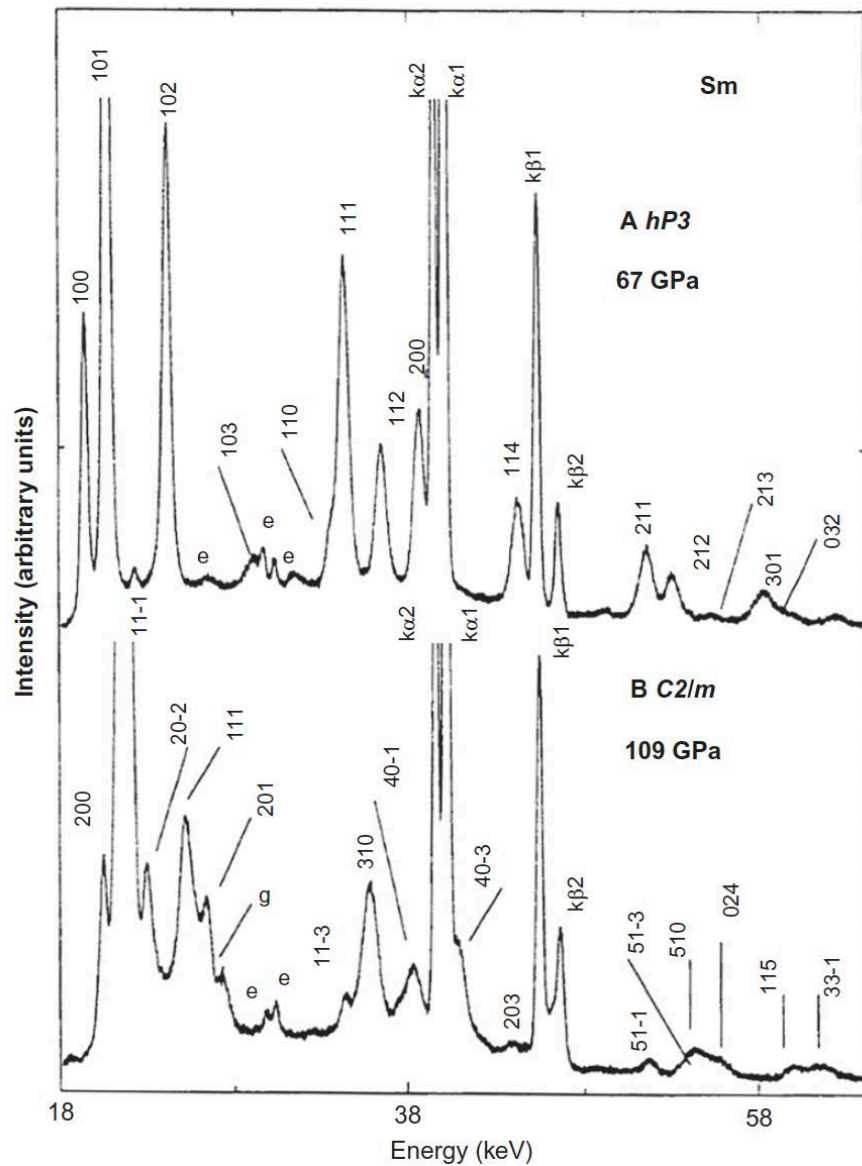


Figure 5.12 *Diffraction profiles from a Sm sample at (A) 67 and (B) 109 GPa showing patterns of the (A) hP3 and (B) C2/m structures. These profiles were collected in an EDXD experiment by Gary N. Chesnut and published in his thesis [20]. The ‘e’ identifies escape peaks resulting from photoelectrons in the detector material. The ‘g’ identifies a peak from the W gasket in (B). The profile in (A) greatly resembles profiles (a) and (b) in Figure 5.4. The profile in (B) bares a striking resemblance to the mixed phase pattern in Figure 5.11.*

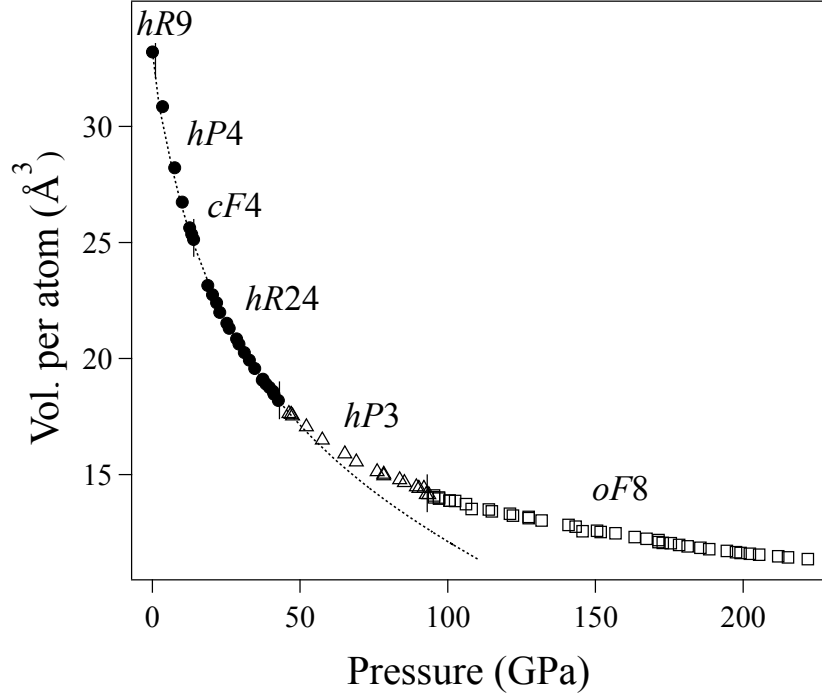


Figure 5.13 *The compressibility of Sm up to 222 GPa. The dotted line shows the AP2 equation of state obtained from fitting the data to 43 GPa. The misfit beyond 43 GPa can be clearly observed.*

As discussed in Chapter 3, elemental metals with more complicated structures and anomalous behaviour under pressure can begin to behave like “regular” metals at certain pressures. Figure 5.15 shows the APL linearised compression data for Sm in the form of a $\eta_{APL} - x$ plot

$$\eta_{APL}(x) = \ln(px^5/p_{FG}) - \ln(1 - x) \quad (5.1)$$

where $x = (V/V_0)^{1/3}$, $p_{FG} = a_{FG} \cdot (Z/V_0)^{5/3}$ and $a_{FG} = 0.02337 \text{ GPa nm}^5$

along with linearised data for the “regular” metals Au and Pt [21]. The data trend for Sm begins almost perpendicular to the direction expected by “regular” metals and curves with increasing pressure (decreasing volume and, therefore, x) to exhibit the same linear trend as that of Au and Pt. Around the $hR24 \rightarrow hP3$ transition, the gradient sharply changes to show this “regular” behaviour such that the data can be extrapolated to the ideal value $\eta(0) \sim 0$. This “regular” compressive behaviour was previously noted by Grosshans and Holzapfel for the trivalent lanthanides [71], and, more specifically, by Zhao *et al.* [76] for Sm.

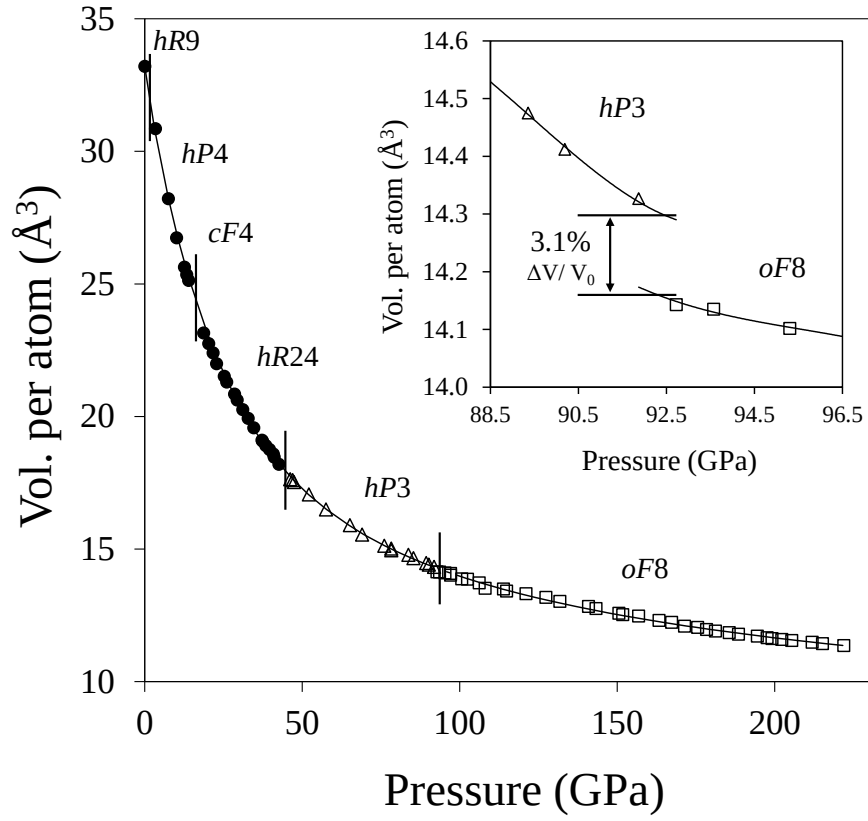


Figure 5.14 *The compressibility of Sm up to 222 GPa. The solid line shows the best fitting third-order AP3 EOS to the full compression curve.*

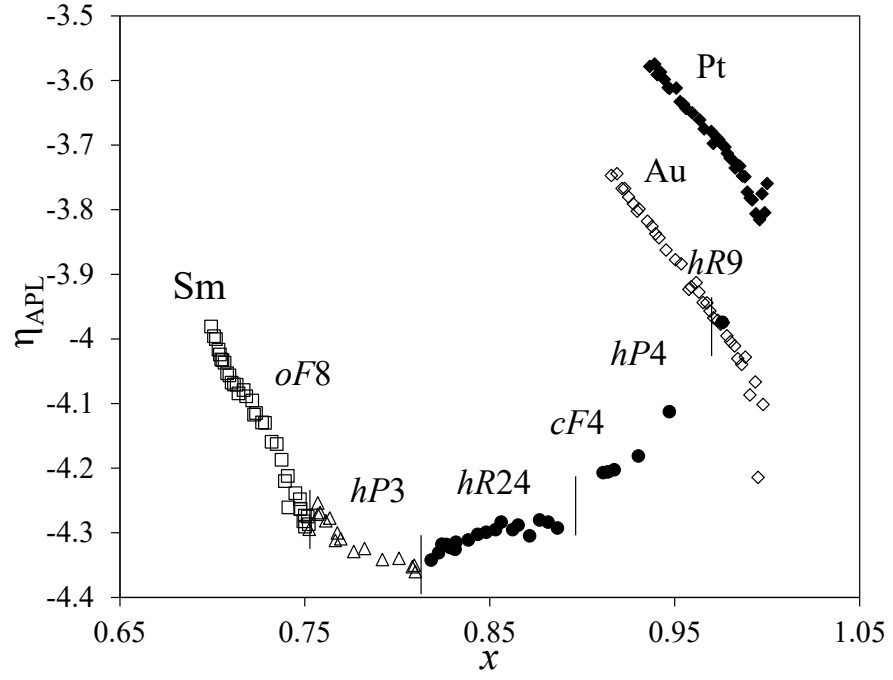


Figure 5.15 *Linearisation of the compression of Sm shown in the form of an η_{APL} - x plot, where $x = (V/V_0)^{1/3}$. The data from the different phases of Sm are plotted using different symbols, and the “regular” compressibilities of Au and Pt, as calculated from the compression data of Dewaele et al. [21], are shown for comparison.*

5.3.4 Magnetic Studies

The transition sequence $hR9 \rightarrow hP4 \rightarrow cF4 \rightarrow hR24$ has been observed in low-temperature high-pressure magnetic studies in Sm up to 50 GPa [151]. In more recent studies, the magnetic ordering temperature T_0 of Sm metal has been measured to pressures of 150 GPa, whereby Deng and Schilling observed an increase in T_0 between ~ 60 K and ~ 140 K at pressures above 85 GPa [108]. This study, conducted at 300 K, found that the $hP3 \rightarrow oF8$ transition occurs at a pressure close to this in Sm, which infers that the $oF8$ phase of Sm has a highly-correlated electron state.

Predicting the Next Phase Transition

DFT calculations, performed by our collaborators at King’s College London (KCL), of the $oF8$ and $oC4$ phases of Sm, reveal that both phases are very close in volume and energy at all pressures. Plekhanov *et al.* found that while the magnetisation of both phases reduces with further compression, it does not reach zero in either phase up to 240 GPa [4]. Furthermore, the results show that the $oC4$ phase has a lower calculated enthalpy between 185 and 225 GPa. Therefore, considering this small stability range, coupled with a small enthalpy gain per atom, it accounts for no transition witnessed to the $oC4$ phase in the experimental data of Sm up to 222 GPa [4].

5.4 Conclusions

Studies on Sm metal up to ~ 50 GPa are shown to agree with previous work. However, the $hP3$ phase is shown to have a similar yet more highly-symmetric structure, $P6_222$ than that previously published in the literature. This structure is only slightly different to the $P3_121$ previously reported and accounts for the additional systematic absences observed in the diffraction profiles from this phase.

The “volume-collapsed”, high-pressure structure observed in the post-dfcc phase above 93 GPa, previously reported as having a monoclinic $mC4$ structure with spacegroup $C2/m$, is found to be orthorhombic, spacegroup $Fddd$, with 8 atoms per unit cell. This structure, $oF8$ in Pearson notation, is iso-symmetrical with that of γ -plutonium at atmospheric pressure, and in the high-pressure phases of

Am, Cm and Cf. It is different to the $oF16$ structure observed in Tb, Gd, Dy, Ho, Er and Tm, yet similar when considering that they share the same spacegroup $Fddd$ and share similar stacking in their quasi-hexagonal layers of atoms.

Analysis of Sm’s EOS reveals marked changes in compressibility on entering the $hP3$ and $oF8$ phases, with that of the $oF8$ phase being that of a “regular” metal. Low-temperature magnetic studies have shown that the $oF8$ phase of Sm is likely to have a highly-correlated electron state. Electronic structure calculations are now required to determine why the high-pressure, orthorhombic phase of Sm is similar yet different to the same phase in Tb and the other heavy trivalent lanthanides.

Comparison calculations performed by Plekhanov *et al.* on the $oF8$ and $oC4$ phases of Sm, in which the $oC4$ phase has not been seen experimentally at pressures up to 222 GPa at 300 K, predict that $oC4$ -Sm is the more stable of the two over only a small pressure range of 185 – 225 GPa at 0 K. The calculations predict no loss of magnetism in $oC4$ -Sm to at least 240 GPa, meaning that the stability range of the $oF8$ phase would be greatly extended.

Chapter 6

Low Symmetry Structures in Neodymium

6.1 Introduction

The high-pressure phases of the heavy trivalent lanthanides (Gd–Lu, except Yb) are accessed at lower pressures in lower-Z members (La–Sm, except Ce). It is therefore intuitive to study these elements to not only observe transitions to the lower-symmetry phase discussed in the previous two chapters, but also to witness transitions from this phase to the next high-pressure phases not currently seen in any previous high-pressure studies of the higher-Z lanthanides. Previous literature has noted the transition from the monoclinic phase to a C-centred orthorhombic phase with four atoms in the unit cell under 100 GPa in Nd [24]. This phase is commonly known as α -U as it was first seen as the ambient phase in U [15].

Akella *et al.* assigned the post-*hP3* phase of Nd to the monoclinic *mC4* structure [18]. However, significant misfits of Bragg peaks from the *mC4* structure to diffraction patterns of Nd above 100 GPa raises the question as to whether or not this high-pressure phase in Nd has the correct structural assignment. Furthermore, after reassigning the structure of the post-*hP3* phase of Sm from the *mC4* structure to the *oF8* structure [2], it will be interesting to see whether or not Nd follows the same structural systematics.

After conducting x-ray powder diffraction experiments on Nd to 302 GPa, this

thesis reports different structural systematics of Nd above 75 GPa to those published in the literature. The data describing this study, and the assignment of a higher symmetry *hP3* phase, will be discussed later in this chapter and have been published in Physical Review B [4].

6.2 Experimental Details

High-purity distilled samples of Nd supplied by Ulrich Schwarz at the Max-Planck-Institut für Chemische Physik fester Stoffe in Dresden were loaded into two DACs in a dry argon atmosphere (<1 ppm O_2 and <1 ppm H_2O) to prevent oxidation. The DACs were equipped with bevelled diamonds, one with 100 μm diameter culets and the other with 50 μm diameter culets, and W gaskets. The samples were loaded without any pressure medium in order to avoid having any peaks from an additional material overlapping with those from either the sample or pressure marker. Both samples were loaded with a small (few μm) copper (Cu) sphere to act as a pressure calibrant, using the published Cu equation of state of Sokolova *et al.* [132]. However, in one cell the Cu sphere was lost on closing the DAC, and the sample pressure was subsequently determined using the diamond Raman mode method [133].

Diffraction data were collected in two experiments on the high-pressure I15 beamline at the Diamond Light Source (DLS) synchrotron, United Kingdom, and in a further two experiments on the Extreme Conditions P02.2 beamline at the PETRA-III synchrotron in Hamburg, Germany. Low-pressure data were obtained on beamline 9.5 at the Synchrotron Radiation Source (SRS) at Daresbury Laboratory in the UK prior to the beginning of this project by Shaun Evans and is also published in [28]. Monochromatic x-ray beams of wavelength 0.4246 Å (DLS), 0.2898 Å and 0.4830 Å (PETRA-III) and 0.4438 Å (SRS), focused down to $20\ \mu\text{m} \times 20\ \mu\text{m}$ (DLS), $3\ \mu\text{m} \times 6\ \mu\text{m}$ and $0.85\ \mu\text{m} \times 0.85\ \mu\text{m}$ (PETRA-III) and $50\ \mu\text{m} \times 50\ \mu\text{m}$ (SRS) were used, and the powder-diffraction data were recorded on Mar345 (DLS and SRS) and Perkin-Elmer (PETRA-III) area detectors, placed 300–400 mm from the sample. LaB_6 and CeO_2 diffraction standards were used to calibrate the exact sample-detector distances and the detector tilts in each experiment. The 2D diffraction images collected at each pressure were integrated azimuthally using DIOPTAS [135] (this work) and FIT2D [149] (Evans) to obtain standard 1D diffraction profiles, which were then analysed using Rietveld [138] and Le Bail profile-fitting methods or by fitting to the *d*-spacings of individual

diffraction peak positions [146].

6.3 Experimental Results

Diffraction patterns were collected at DLS and, at a later stage, at PETRA-III from 4 to 166 GPa in incremental pressures steps on one sample. The second sample was compressed to 193 GPa on closing the DAC which resulted in a ~ 27 GPa gap in data. Those data are further complicated as a result of the necessity to use another form of pressure calibration, the diamond Raman mode method, which was discussed in the Experimental Details above.

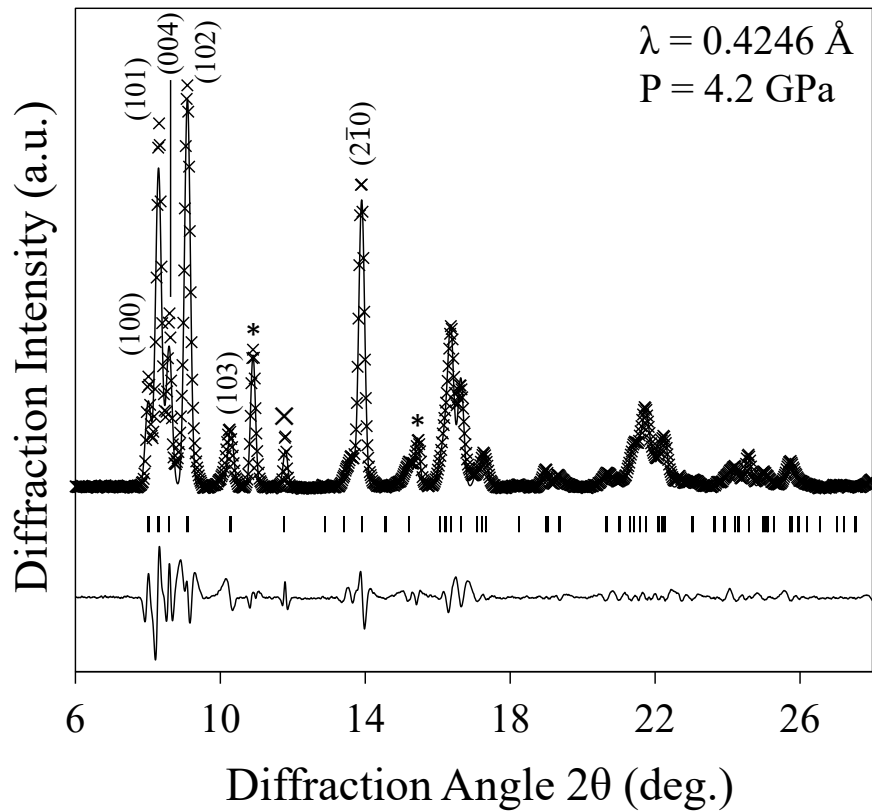


Figure 6.1 *Le Bail refinement of the hP4 structure to a diffraction profile from Nd at 4.2(1) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. Six peaks from the hP4 structure are labelled with their Miller indices. The asterisks identify peaks from the W gasket. The $\times$ identifies a closely-spaced doublet of the (104) peak from the Nd and the (111) peak from the Cu pressure calibrant.*

The initial integrated diffraction data showed single phase dhcp patterns. Figure

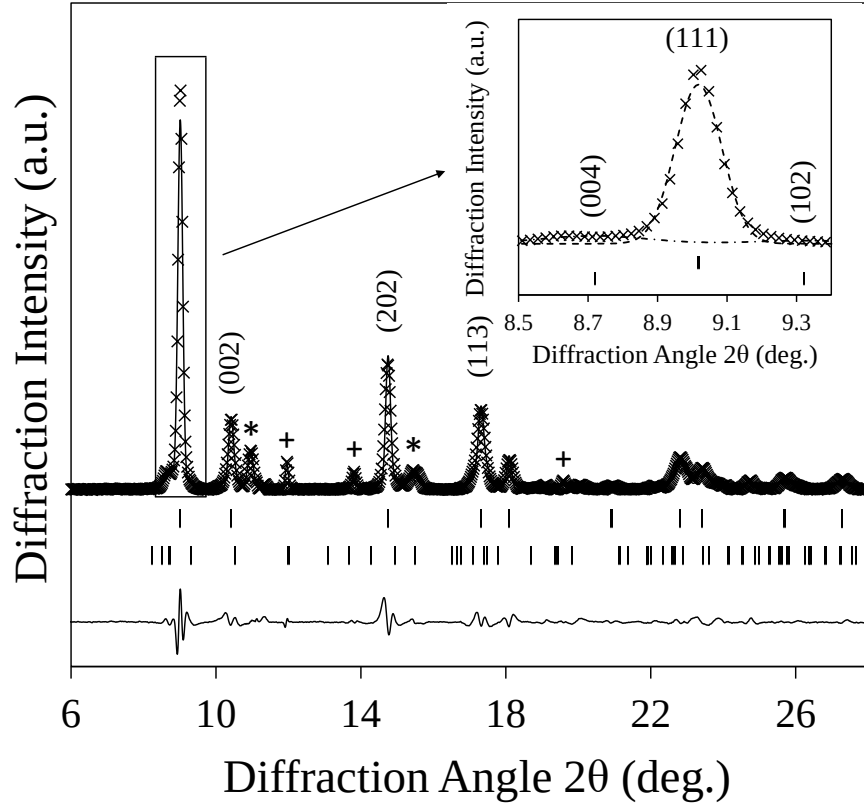


Figure 6.2 *Le Bail refinement of the hP4 and cF4 structures to a mixed-phase diffraction profile from Nd at 11.8(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first four peaks from the cF4 structure are labelled with their Miller indices. The asterisks identify peaks from the W gasket, and the + signs identify peaks from the Cu pressure calibrant. The inset labels the fit of the hP4 (dot-dash line) and the cF4 (dash line) structures at ~ 9 degrees.*

6.1 displays a Le Bail refinement of the $hP4$ structure to a diffraction pattern at 4.2(1) GPa. Only one diffraction profile was collected in the fcc phase, however weak reflections from the dhcp phase are still seen in the refined diffraction pattern at 11.8(2) GPa as illustrated in Figure 6.2. The inset to Figure 6.2 identifies the ‘shoulders’ from the (004) and (102) reflections of the $hP4$ phase to the left and right of the main $cF4$ -(111) peak at ~ 9 degrees. The sluggish phase transition from $hP4 \rightarrow cF4$ arise from the slight differences in stacking of the hexagonal layers.

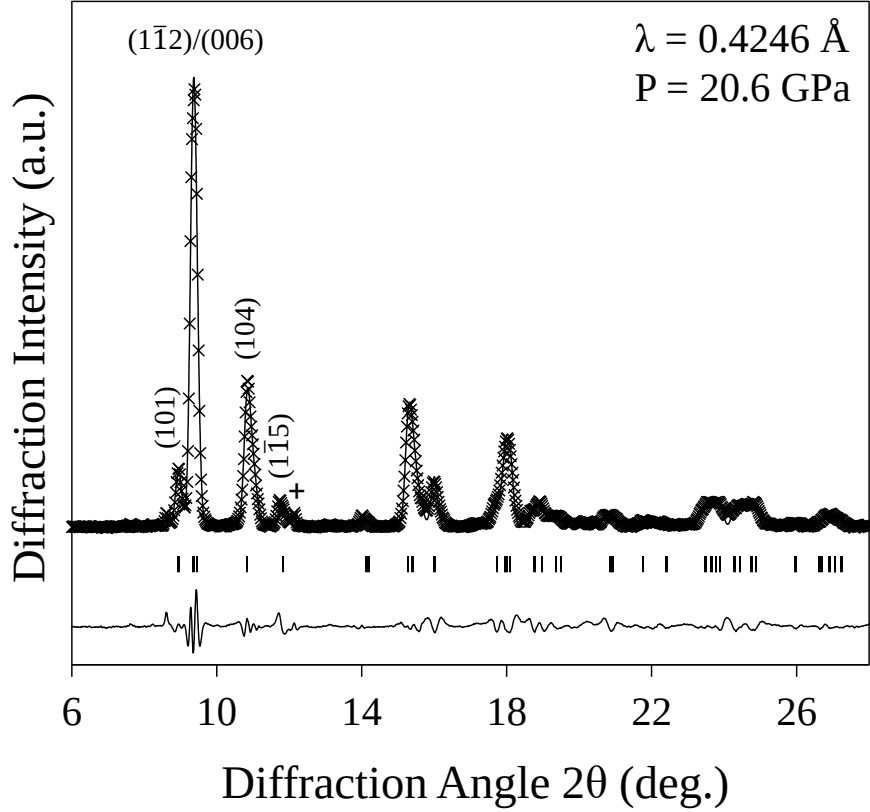


Figure 6.3 *Le Bail refinement of the $hR24$ structure to a diffraction profile from Nd at 20.6(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first five peaks from the $hR24$ structure are labelled with their Miller indices. The + sign identifies a peak from the Cu pressure calibrant.*

At 15.1(3) GPa, a transition to the rhombohedral dfcc phase, $hR24$, was observed in agreement with previous studies. Unlike in Sm, this phase is stable for only ~ 10 GPa before a transition to a second dfcc phase, $oI16$, previously observed between the $hR24$ and $hP3$ phases, occurred at 25.6(3) GPa [28]. Figure 6.3 shows a Le Bail refinement of the $hR24$ structure (spacegroup $R\bar{3}m$) at 20.6(2)

GPa. The *oI16* phase was stable to ~ 40 GPa, where a transition to the *hP3* phase was observed by Evans [28]. These results agree with the data collected in this project. The data collected by Evans between 1.7 and 40 GPa were used in this thesis for the production of a compression curve fitted with an appropriate EOS that is shown in Figure 6.12 as only a small number of patterns were collected up to 45 GPa. The current project was interested in phases seen at pressures above 70 GPa and, therefore, made relatively large pressure increments up to the *hP3* phase.

6.3.1 Higher Symmetry *hP3*

On compression above 40 GPa, the *hP3* phase was found to be stable to 70 GPa. In Chapter 5, it was shown that the structure of the *hP3* phase has higher symmetry than that previously described in the literature. As the systematics of Nd are considered to be the same as those of Sm, the more symmetrical *P6₂22* structure was fitted to the diffraction pattern of Nd at 69(1) GPa shown in Figure 6.4. The refined lattice parameters are $a = 2.8504(3)$ Å, $c = 6.861(4)$ Å, $V/V_0 = 0.471(9)$. Figure 6.5 displays a waterfall plot where a transition from the *hP3* to the post-*hP3* phase is observed at 74 GPa (see profile (c) of Figure 6.5). Above this pressure, the diffraction peaks from the *hP3* phase decreased in intensity while those from the post-*hP3* phase became more intense.

6.3.2 Lower Symmetry Structures

The arrows in Figure 6.5 profile (d) point to peaks from the new phase. Single-phase profiles of this higher-pressure phase were seen above 90 GPa in profiles (e) and (f) of Figure 6.5, and these are strikingly similar to those obtained from Sm at pressures above 157 GPa [2]. Therefore, this evidence was deemed enough to fit the *oF8* structure, spacegroup *Fddd*, to diffraction patterns of Nd above 70 GPa, without trialling a fit of the *mC4* structure first.

Figure 6.6 shows a Rietveld fit of the *oF8* structure to the diffraction profile from Nd at 97 GPa, where the refined lattice parameters are $a = 2.6806(2)$ Å, $b = 4.7810(5)$ Å, and $c = 8.7832(10)$ Å, $V/V_0 = 0.413(2)$, with atoms on the $8a$ site at (0,0,0). The fit is excellent, with all of the observed diffraction peaks accounted for.

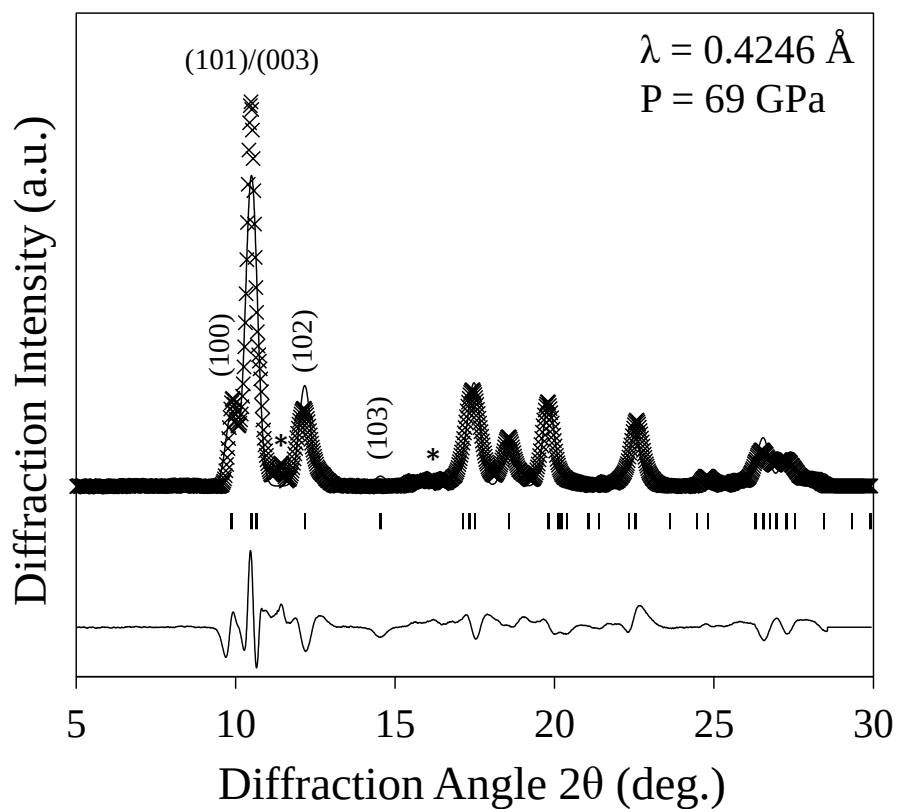


Figure 6.4 *Rietveld refinement of the hP3 structure to a diffraction profile from Nd at 69(1) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. Five peaks from the hP3 structure are labelled with their Miller indices. The asterisks identify peaks from the W gasket.*

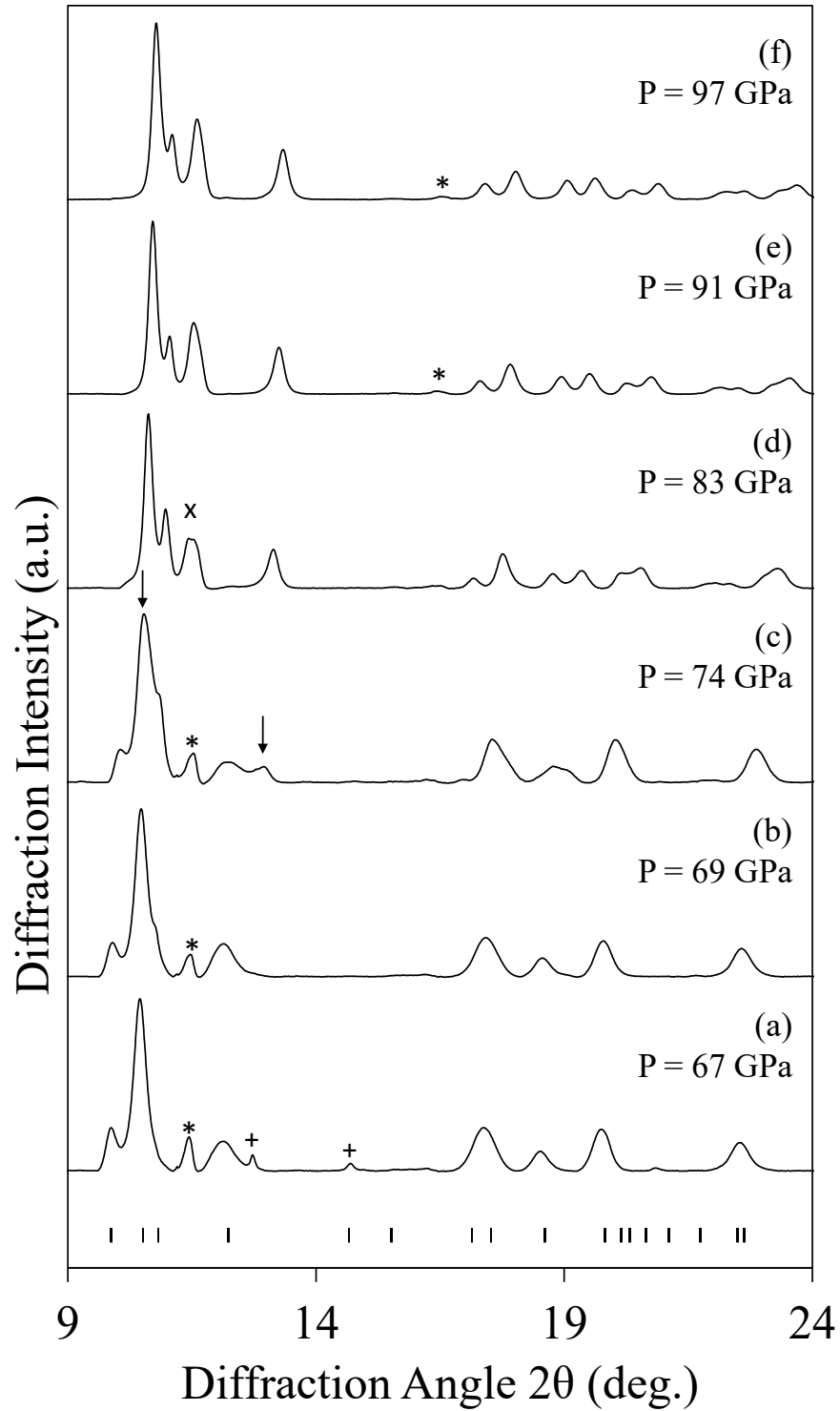


Figure 6.5 *Diffraction profiles collected from Nd on pressure increase. The data were collected from the same sample at DLS using a wavelength $\lambda = 0.4246 \text{ \AA}$. Tick marks beneath profile (a) mark the calculated peak positions in the hP3 phase. The peaks marked with asterisks are from the W gasket, and the peaks marked with a + are from the Cu calibrant. The arrows in profile (c) mark the disappearance of the most intense peak from the hP3 phase and the first appearance of a peak from the post-hP3 phase, respectively. The reflections labelled with a $\times$ in profile (d) highlights a closely-spaced doublet which included the (110) peak from the W gasket and a peak from the new phase. Single phase patterns from the post-hP3 phase are seen in profiles (e) and (f).*

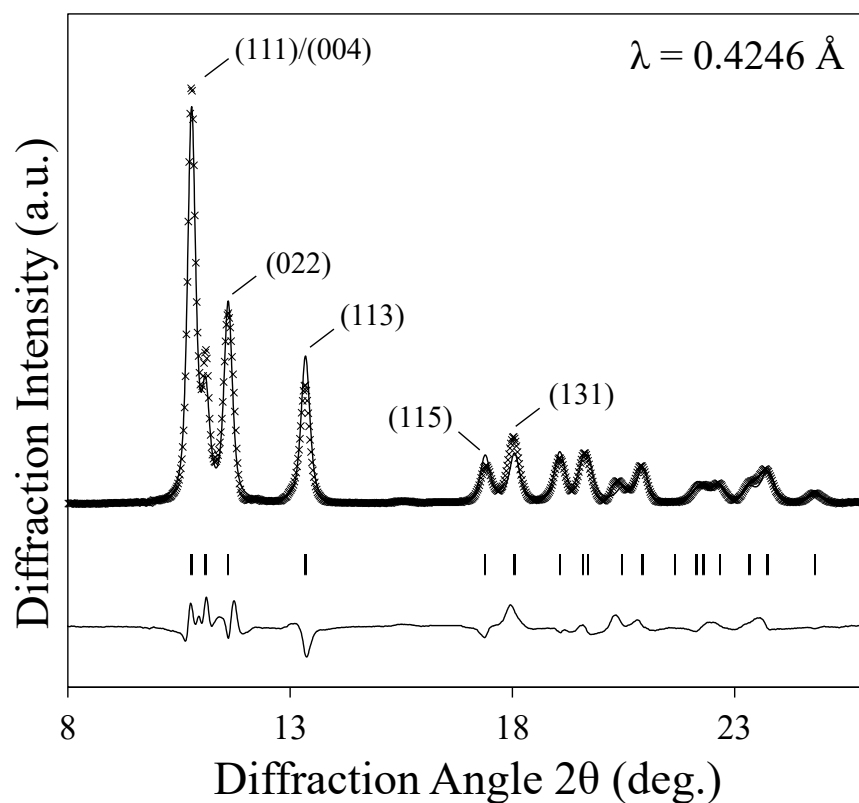


Figure 6.6 *Rietveld refinement of the oF8 structure to a diffraction profile from Nd at 97 GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first six peaks of the oF8 phase are labelled with their Miller indices, and the asterisk identifies the (200) peak from the W gasket (the (110) peak from the gasket is overlapped by the (022) reflection from the Nd).*

Table 6.1 *Structural data for seven different pressure-induced phases of Nd observed at room temperature, including spacegroups, lattice parameters and pressures with their uncertainties. The data for the oI16 structure were taken from Ref. [28].*

Structure	Lattice Parameters (Å)	Pressure (GPa)
<i>hP4</i>	$a = 3.50827(12), c = 11.3397(12)$	4.2(2)
<i>cF4</i>	$a = 4.67762(10)$	11.8(2)
<i>hR24</i>	$a = 3.19335(11), c = 15.4612(11)$	20.6(2)
<i>oI16</i>	$a = 8.751(3), b = 6.2325(9), c = 6.1036(11)$	26.6(2)
<i>hP3</i>	$a = 2.8504(3), c = 6.861(4)$	69(1)
<i>oF8</i>	$a = 8.7832(9), b = 4.7810(4), c = 2.6806(6)$	97(2)
<i>oC4</i>	$a = 2.2803(2), b = 4.5151(8), c = 4.129(2)$	302(2)

Further sample compression showed that the *oF8* phase was stable to 97 GPa, where the appearance of new diffraction peaks signalled a transition to the post-*oF8* phase. This transition was sluggish, and single-phase profiles, which were very similar to those reported previously by Chesnut *et al.* [24], were obtained only above 170 GPa.

6.3.3 The α -Uranium Phase

New peaks from the post-*oF8* phase are seen in Figure 6.7, profile (b). In profile (c), the arrow points to one peak of a few remaining from the *oF8* phase. Single phase patterns of the new phase are seen in profiles (d)–(f).

Figure 6.8 shows a Rietveld fit of the *oC4* structure, spacegroup *Cmcm*, to the background-subtracted diffraction profile from Nd at 302(2) GPa, the highest pressure reached in this study. The refined lattice parameters at this pressure are $a = 2.2803(2)$ Å, $b = 4.5151(8)$ Å, and $c = 4.129(2)$ Å, $V/V_0 = 0.312(6)$, with atoms on the $4c$ site at (0,0.114(6),0.25). The fit is again excellent, with all of the observed diffraction peaks being accounted for. This structure is isosymmetric with the α -U structure seen at ambient conditions in U [15].

Nd is the only lanthanide in which the *oF8* $\rightarrow$ *oC4* transition has been observed to date. However, the similarity of the phase transition sequences in Nd and Sm at lower pressures suggests that the latter will also transform to the *oC4* structure, but at a higher pressure than it has been studied to date [2]. It is therefore of interest to determine whether the structural data obtained from the present study might enable us to determine at which point *oF8*-Sm will become

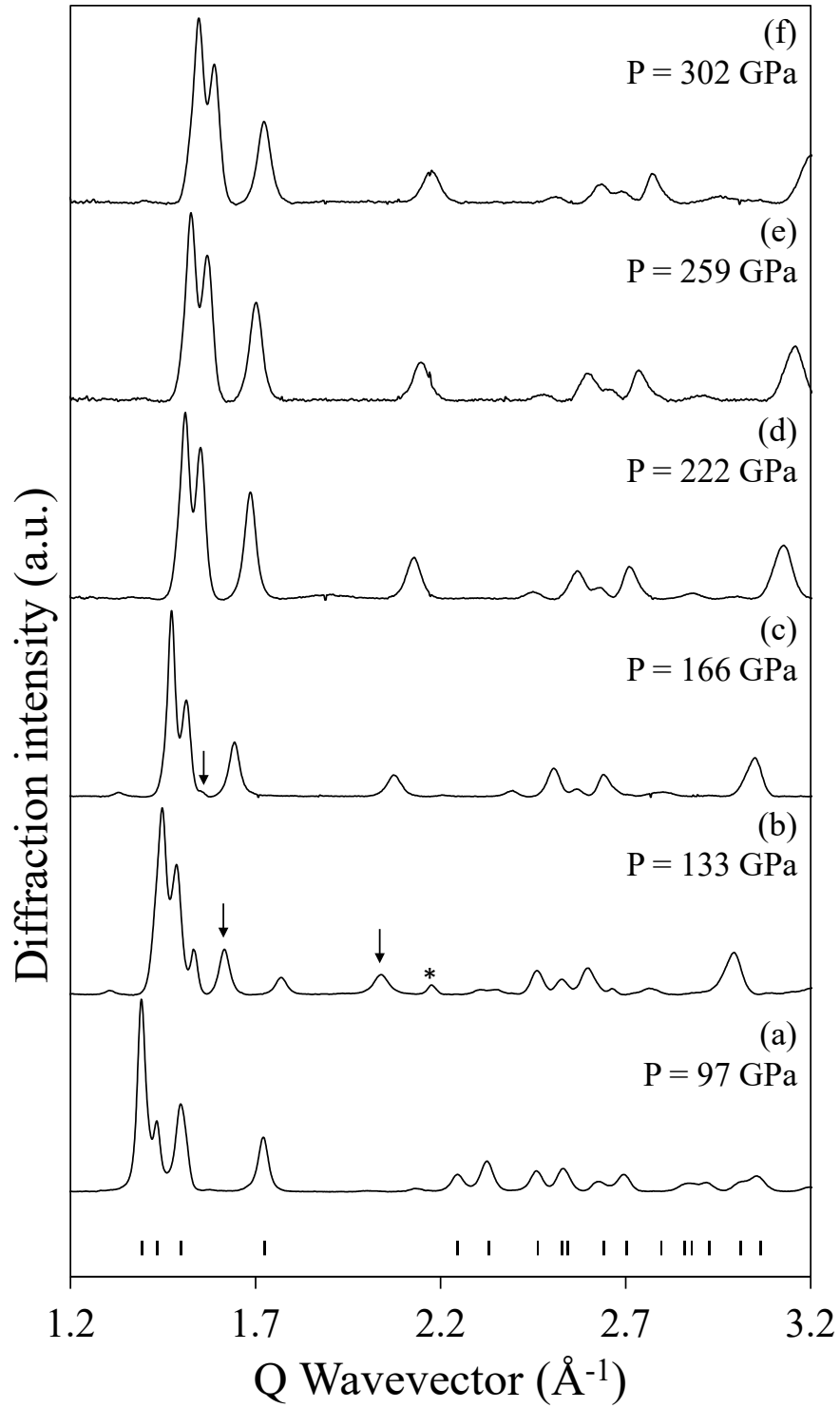


Figure 6.7 *Diffraction profiles collected from Nd on pressure increase. The data were collected from two samples at DLS and Petra III using wavelengths $\lambda = 0.4246 \text{ \AA}$ (DLS) and $\lambda = 0.483 \text{ \AA}$ (Petra III) and so are plotted as a function of wave vector Q to take into account the two different wavelengths. Tick marks beneath profile (a) mark calculated peak positions from the oF8 phase. The peak marked with the asterisk is from the W gasket. The arrows in profile (b) mark the appearance of peaks from the oC4 phase, and the arrow in profile (c) marks the disappearance of a peak from the remainder of the oF8 phase. Single phase patterns are seen in profiles (d), (e) and (f).*

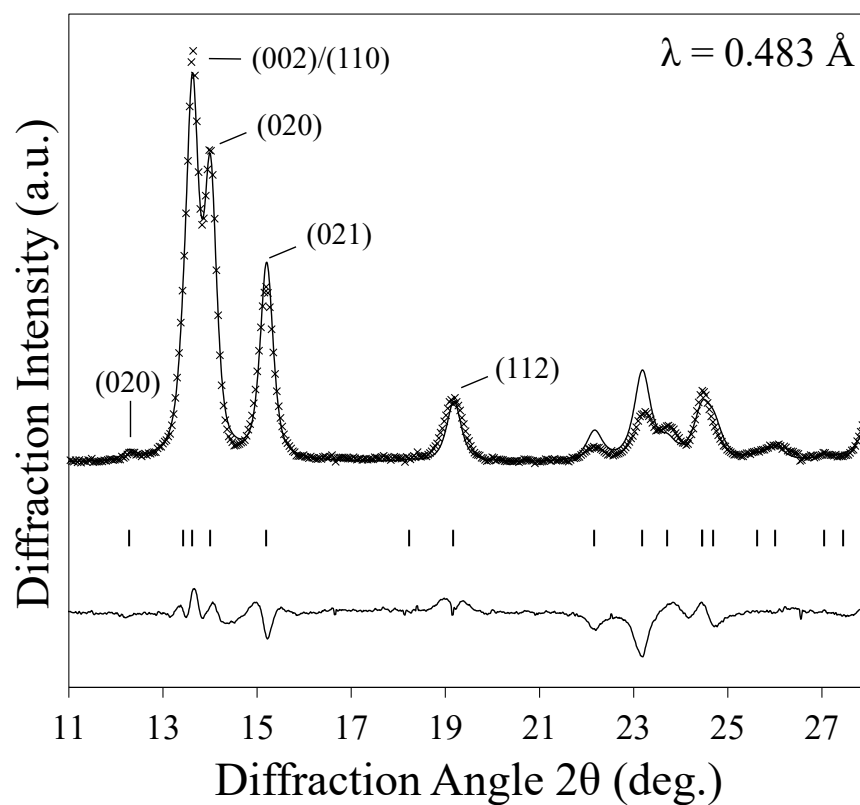


Figure 6.8 *Rietveld refinement of the oC4 structure to a diffraction profile from Nd at 302(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first six peaks of the oC4 phase are labelled with their Miller indices.*

unstable against a transition to the *oC4* structure. As was explained further in the discussion of theoretical work in Section 5.3.4, one can say this is unlikely to occur up to pressures of 240 GPa.

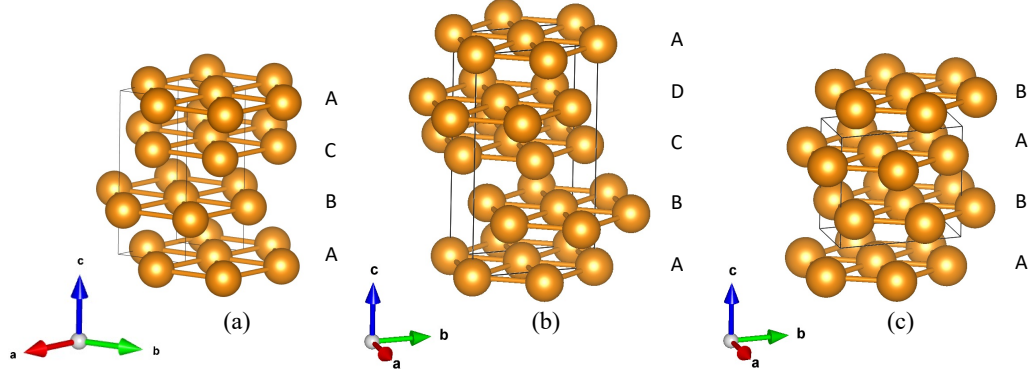


Figure 6.9 *The crystal structures of Nd: (a) *hP3* at 58 GPa, (b) *oF8* at 92 GPa and (c) *oC4* at 302 GPa. All three structures comprise stackings of flat, distorted-hcp atomic layers: the 3-layer stacking sequence has a ABC repeat, the 4-layer stacking sequence in *oF8* is ABCD, while *oC4* has a 2-layer AB repeat. The distortion of the layers from hexagonal symmetry can be quantified by the deviation of the b/a axial ratio in *oF8* and *oC4*, from the ‘ideal’ ortho-hexagonal value of $\sqrt{3}=1.732$.*

The *oF8* structure comprises a 4-layer ABCD stacking of flat, quasi-close packed layers, the distortion of which from hexagonal symmetry can be quantified by the deviation of the b/a axial ratio from the ideal ortho-hexagonal value of $\sqrt{3}=1.732$. The *hP3* structure comprises a 3-layer ABC stacking of the same layers, which are exactly hexagonal in this structure. The *oC4* structure can also be described as a 2-layer stacking of heavily-distorted hcp layers with their distortion being quantified by deviations of the b/a ratio in the *oC4* structure from the ideal ortho-hexagonal value of 1.732. The structures of *hP3* at 58 GPa, *oF8* at 92 GPa and *oC4* at 302 GPa are shown in Figure 6.9, drawn so as to highlight the arrangement of the quasi-hexagonal layers in each.

The pressure dependence of the b/a ratio in *oF8*-Nd is shown in Figure 6.10, along with the ideal value of $\sqrt{3}$ in the *hP3* phase, and the b/a ratio in the *oC4* structure. As was seen previously in Sm [2], there is a clear discontinuity in the “hexagonality” of the atomic layers from 1.732 to ~ 1.78 at the *hP3* $\rightarrow$ *oF8* transition. However, in contrast to Sm, where the b/a ratio of *oF8*-Sm increases monotonically with pressure (see Figure 5.9), reaching a value of 1.82 at 222 GPa

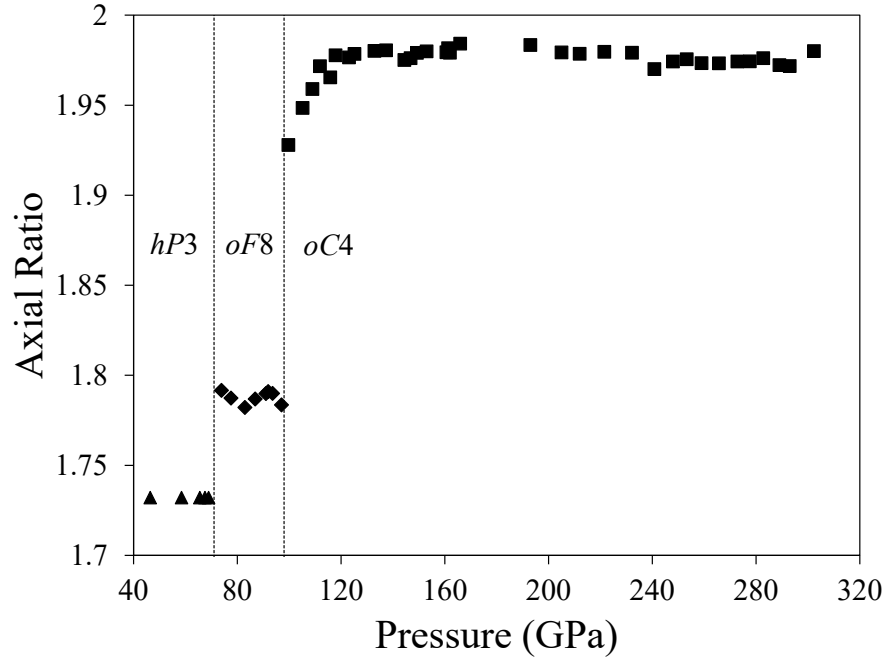


Figure 6.10 *The pressure dependence of the hexagonality of the atomic layers in the hP3, oF8 and oC4 structures of Nd, as quantified by the b/a axial ratios – see Figure 6.9. As a result of the extended y-scale, the error bars on the axial ratios are smaller than the symbols used to plot the points, and have therefore been omitted.*

[2], the b/a ratio of $oF8$ -Nd remains constant with pressure at ~ 1.79 up to 100 GPa. The transition to the $oC4$ structure results in a further sharp increase in the axial ratio to ~ 1.98 , with only minor changes above and below this value as pressure increases to 302 GPa. As the b/a ratio of $oF8$ -Sm surpasses the value of 1.79 at ~ 140 GPa without undergoing a transition to the $oC4$ structure, the hexagonality of the atomic layers in the $oF8$ structure would appear to offer no insight into either the $oF8 \rightarrow oC4$ transition pressure or the mechanism by which the transition occurs.

6.3.4 APL Equation of State

The compressibility of Nd up to 302 GPa is shown in Figure 6.12, and it is almost continuous; there are small volume changes of 2.5% and 1.4% at the transition to the $hP3$ and $oF8$ phases, but the $oF8 \rightarrow oC4$ transition is continuous, in agreement with the results of Chesnut *et al.* [24]. The full compression curve can therefore be fitted with a single EOS.

In our recent studies of Sm [2], Holzapfel’s Adapted Polynomial of order L (APL) EOS formalism was utilised to analyse the compressibility of Sm. This EOS has several advantages over other formalisms, and enables the compressibility to be linearised in a straightforward manner. Non-linear behaviour can then be interpreted as arising from deviations from “regular” compressive behaviour expected from a “regular” metal, perhaps arising from changes in the electronic structure [152].

The compression data can be fitted using the second order (AP2) form of the APL EOS [142, 143] described in detail in Chapters 3 and 5.

To highlight the similarities and differences in compression data of different lanthanides with respect to “ideal” behaviour, and to also highlight the systematics in phase transition pressures, an APL linearisation with respect to the radius ratio R_{WS}/R_I [40] was used, where R_{WS} is the pressure dependent Wigner–Seitz radius and R_I is a pressure independent individual value for the ionic radius of each element [143], instead of with respect to x . The pressure dependent values of R_{WS} were determined from the measured atomic volumes, while R_I were taken to be the R_{5p} radii [42], as reported by Waber and Cromer [25].

Figure 6.11 shows the APL linearised compression data for Nd in the form of

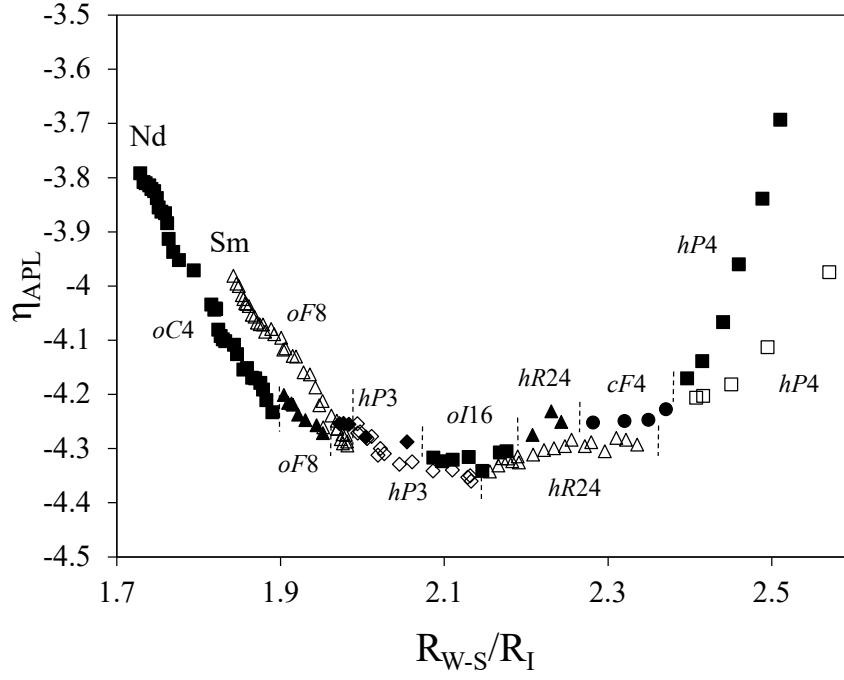


Figure 6.11 *Linearisation of the compression of Nd shown in the form of an η_{APL} - R_{WS}/R_I plot, where R_{WS} is the Wigner-Seitz radius in angstroms and R_I is the . The data from the different phases of Nd are plotted using different symbols. The compressibilities of Au and Pt, calculated from compression data of Dewaele et al., are shown for comparison.*

a $\eta_{APL} - R_{WS}/R_I$ plot, along with the recently-published data for Sm to 222 GPa. In such a plot, materials undergoing regular compression will show linear or quasi-linear behaviour, with the correct theoretical limit of $\eta(0)=0$. This is not the case for Nd, the data for which exhibit significant curvature, very similar to that of Sm [2]. As in Sm, there is a striking change in behaviour within the $hP3$ -Nd phase, such that both $oF8$ -Nd and $oC4$ -Nd display the linear behaviour expected of a “regular” metal, and with a gradient very similar to that exhibited by Sm [152].

It was previously reported by Kruger *et al.* that the three transitions between the $hP2$, $hR9$, $hP4$ and $cF4$ structures of the regular trivalent lanthanides exhibit constant critical radii ratios R_{WS}/R_{5p} [42]. This report suggests that these transitions arise from changes in the d -band occupancy without any essential contributions from $4f$ electron bonding. The evidence suggested that the transitions to the low-symmetry structures at higher pressures, that is $hR24$, $oF8$, $oF16$ and $oC4$, did not occur at similarly critical radii, therefore suggesting that itinerant $4f$ electrons played a role in these transitions [42].

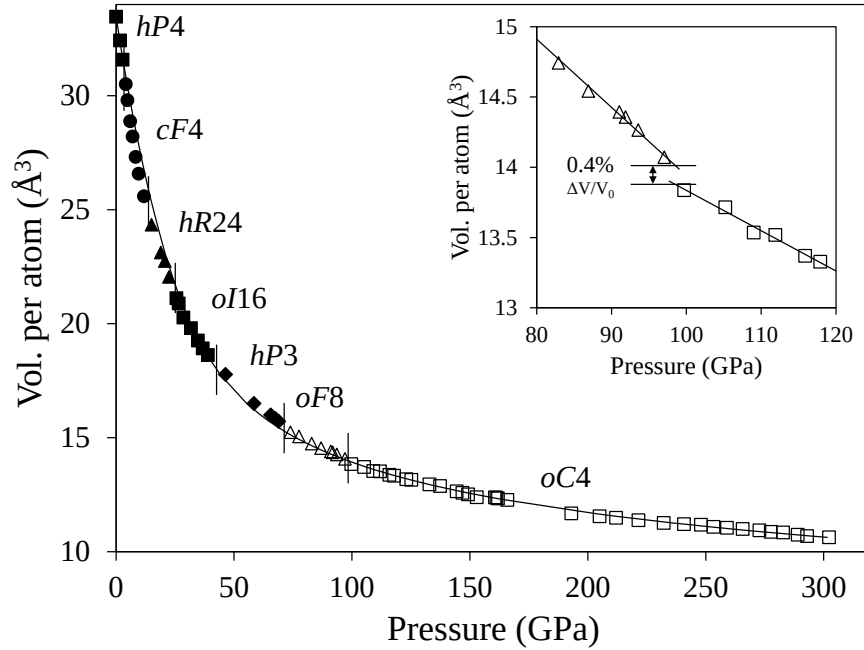


Figure 6.12 The compressibility of Nd up to 302 GPa. The solid line shows the best fitting third-order APL EOS to the full compression curve.

Figure 6.11 shows the locations of all the known phase transitions in Nd and Sm. The phase boundaries in Nd are displaced systematically to lower values of R_{WS}/R_{5p} compared to those in Sm, with a displacement of 0.1 or less. However, it

is intuitive to note the extended stability range of *oF8*-Sm, which extends down to $R_{WS}/R_{5p}=1.84$, whereas Nd transforms into the *oC4* structure at $R_{WS}/R_{5p}=1.90$. This suggests that *oF8*-Sm would transition to *oC4*-Sm at only 145 GPa when one accounts for the offset in R_{WS}/R_{5p} between the transitions in Nd and Sm.

The non-linear behaviour of Nd illustrated in Figure 6.11 means that its compressibility cannot be fitted by a single second-order AP2 EOS. However, as was the case with Sm [2], the compression curve of Nd can be fitted with the third-order AP3 EOS, as illustrated in Figure 6.12, which shows both the compression curve to 302 GPa, and the AP3 fit. The best-fitting parameters are $K_0 = 37.2(2)$ GPa, $K' = 1.57(2)$ and $K'' = -0.051(2)$ [142]. It can be seen from the curve that the AP3 fit slightly underestimates the compressibility of the *hP4*, *cF4* and *hR24* phases in order to more accurately fit the higher-pressure data.

6.3.5 Magnetism

From DFT analysis, it has been found that the magnetic behaviour of Nd is significantly different to that of Sm, despite the similarity in structural behaviour. From 180 to 120 K and between 70 and 110 GPa, the magnetic ordering temperature T_0 sharply decreases, where it adopts the *oF8* structure at RT, before decreasing again to 0K at ~ 150 GPa [105].

Zero-temperature DFT calculations performed by our collaborators at KCL examined the enthalpy change in the *hP3*, *oF8* and *oC4* phases at high pressures [4]. The results by Plekhanov *et al.* revealed that the *hP3* phase had the lowest enthalpy to 66 GPa, the *oF8* phase had the lowest to 88 GPa, after which the *oC4* exhibited the lowest enthalpy above 88 GPa. Therefore, these results largely agree with the experimental ones, where the *hP3* $\rightarrow$ *oF8* transition occurs at 71(2) GPa, with the *oF8* $\rightarrow$ *oC4* transition occurring at 98(1) GPa.

Furthermore, the DFT calculations performed by Plekhanov *et al.* suggest that the *oC4* phase observed in the experiment has no net magnetisation. This agrees with low temperature resistivity measurements performed by Song *et al.* [105]. The drop in T_0 at 100 GPa is much less sharp than that of the drop witnessed between 70 and 110 GPa. This can be explained by the sluggish transition from *oF8* $\rightarrow$ *oC4* as the sample is mixed-phase until 170 GPa (see Figure 6.7). Velisavljevic *et al.* debated the same point to explain the gradual decrease in resistivity they observed in Nd above 100 GPa [153].

The DFT studies predict a 0.9% volume collapse at the true $oF8 \rightarrow oC4$ transition [4]. As illustrated in the inset of Figure 6.12, experimental results of the $oF8 \rightarrow oC4$ transition show a 0.4% volume collapse solved from patterns collected at 97 and 100 GPa. However, the DFT calculations still further corroborate the experimental analysis and provide further insight to why this transition occurs. The volume collapse is accompanied by a reduction in compressibility in Nd, suggesting the sample is in a higher-density, non-magnetic state and that the transition to the $oC4$ phase takes place below 100 GPa [4]. Furthermore, Plekhanov *et al.* found that the sluggish transition and mixed-phase patterns up to ~ 170 GPa suggest that single phase patterns of $oC4$ -Nd may also exist for a large pressure range on decompression to far below 100 GPa.

These studies explain the significant difference in stability ranges of the $oF8$ phases in Nd and Sm. This loss in magnetisation in the $oC4$ phase of Nd accounts for the drop in enthalpy relative to the preceding $oF8$ phase, and, therefore, explains why $oF8$ -Nd is stable over a much smaller pressure range than in $oF8$ -Sm.

6.4 Conclusions

The structure of Nd metal above 69(1) GPa is found to be face-centred orthorhombic ($oF8$) rather than monoclinic as reported previously. The same structure is observed at high temperatures in Pu, and at high pressures in Am, Cm and Cf at high pressure, and also in Sm [2]. However, this structure is different to the isosymmetric $oF16$ structure observed in the heavy trivalent lanthanides Gd–Tm (except Yb) [1] and also in Y [3, 154]. The $oF8$ phase of Nd is stable to 98(1) GPa, where it transforms to the $oC4$ phase, which is itself stable to 302 GPa, the highest pressure reached in this study. High-precision measurements of the compressibility of Nd reveal that it becomes less compressible after the transition to the $hP3$ phase at 43 GPa and that in the $oF8$ and $oC4$ phases its compressibility is that of a ‘regular’ metal.

Electronic structure calculations performed by Plekhanov *et al.* of the $hP3$, $oF8$ and $oC4$ phases of Nd predict that the $hP3 \rightarrow oF8$ and $oF8 \rightarrow oC4$ transitions take place at 66 and 88 GPa, respectively, and that the latter transition results from the loss of magnetism in $oC4$ -Nd which reduces both its volume and enthalpy.

Chapter 7

The Post- α -Uranium Structure of Praseodymium

7.1 Introduction

Beyond the high-pressure dfcc phases of the trivalent lanthanides, complicated, low-symmetry, “volume-collapsed” phases are seen. In Chapters 4, 5 and 6, the post-dfcc phases seen in Nd, Sm, Gd, Tb and Dy at pressures between ~ 50 and ~ 300 GPa have been studied.

In Nd and Sm, the $hP3$ phase has been assigned to a more highly-symmetric structure, spacegroup $P6_222$ [2, 4]. The post- $hP3$ phase has been assigned to an face-centred orthorhombic structure with the same symmetry, spacegroup $Fddd$, as the structure assigned to the post-dfcc phases of Gd, Tb and Dy discussed in Chapter 4, but with 8 atoms [2, 4] as opposed to 16 atoms in the unit cell [1]. Diffraction studies on Nd above 100 GPa confirmed a transition from the face-centred orthorhombic structure to a C-centred orthorhombic structure with 4 atoms in the unit cell, $oC4$ in Pearson notation [4]. This structure is more commonly known as the α -U structure as it is seen at ambient conditions in U [15]. It is assumed that, at very high pressures, all the trivalent lanthanides will transition from the $oF8$ or $oF16$ phases to the α -U phase and adopt the $oC4$ structure.

Previously, the post- $hP3$, face-centred orthorhombic structure had been assigned to a monoclinic structure, $mC4$, in Nd and Sm [18, 20]. This structure has

also been ascribed to the post-dfcc phases of all the other trivalent lanthanides except Lu [6, 9, 60–62, 68, 69]; however, it was expected that Lu would transition to the $mC4$ phase at ultra-high pressures. This monoclinic structure was first assigned to the post-fcc phase, or α' phase [15] as it is commonly known, in Ce [47]. However, the post-fcc phase has more recently been assigned to the α -U structure [5, 46]. The α -U phase remains stable in Ce to ~ 13 GPa, where a transition occurs to a body-centred tetragonal (bct) structure [48, 83, 84]. U adopts the bct structure at ambient pressure and temperatures above 940 K [50]. It is also found in a high-pressure phase in Th and is thought to arise as a result in the participation of $5f$ electrons in the bonding [85, 86].

Next to Ce sits Pr, which is known to exhibit the common structural phase transition sequence of the trivalent lanthanides [15]. At ambient conditions, Pr adopts the dhcp structure, $hP4$ [15], which persists until a transition to the fcc phase occurs at ~ 4 GPa [42, 80]. Hamaya *et al.* assigned a rhombohedral structure with 24 atoms in the unit cell to the next phase, which is described as a distortion of the fcc structure [67]. However, it also exhibits similar structural systematics to Ce such that the phase transition to α -U from the dfcc phase at 20 GPa is accompanied by a large volume collapse in Pr of ~ 9 – 10% [64, 81]. Chesnut & Vohra reported a significantly larger volume collapse of 16.7% from a monoclinic structure, $mC4$, to the α -U structure [60]. A study by Velisavljevic *et al.* reported a $\sim 10\%$ volume collapse on transition to the α -U phase, but does not indicate what structural assignment the previous phase adopted [22]. As the transition to the α -U phase in Pr occurs at relatively very low pressures in Pr, its higher pressure behaviour is indicative of how the higher-Z lanthanides behave above the post-dfcc phases.

Pr is reported to transition at 147 GPa to another orthorhombic structure, spacegroup $P2_12_12_1$, and is described as a distortion of the α -U structure [22]. The same study reported a possible transition to a tetragonal phase above 260 GPa via anisotropic compression of the lattice parameters [22]. However, these data, obtained in an EDXD study, are of relatively poor quality.

In order to assess the structure of the post- α -U phase, ADXD studies were conducted on Pr between 65 and 205 GPa. One cannot rule out that the post- α -U phase of Pr has the distorted- α -U structure, spacegroup $Pnma$, that is seen in the actinide elements at high pressures [19] or the bct structure, $tI2$, seen in the high-pressure phases of Ce and Th [83–86].

7.2 Experimental Details

High-purity distilled samples of Pr supplied by Ulrich Schwarz at the Max-Planck-Institut für Chemische Physik fester Stoffe in Dresden were loaded into two DACs in a dry argon atmosphere (<1 ppm O_2 and <1 ppm H_2O) to prevent oxidation. The DACs were equipped with bevelled diamonds, one with $100\text{ }\mu\text{m}$ diameter culets and the other with $50\text{ }\mu\text{m}$ diameter culets, and W gaskets. Sample 1 and sample 2 were loaded without any pressure medium. Both samples were loaded with a small (few μm) copper (Cu) sphere to act as a pressure calibrant, using the published Cu equation of state of Sokolova *et al.* [132].

Diffraction data were collected in one experiment on the two samples on the Extreme Conditions P02.2 beamline at the PETRA-III synchrotron in Hamburg, Germany. Low-pressure data were obtained on beamline 9.5 at the Synchrotron Radiation Source (SRS) at Daresbury Laboratory in the UK prior to the beginning of this project by Shaun Evans and is also published in [28]. Monochromatic x-ray beams of wavelength 0.4834Å (PETRA-III) and 0.4438Å (SRS), focussed down to $0.85\text{ }\mu\text{m} \times 0.85\text{ }\mu\text{m}$ (PETRA-III) and $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ (SRS) were used, and the powder-diffraction data were recorded on Perkin-Elmer (PETRA-III) and Mar345 (SRS) area detectors, placed 300–400 mm from the sample. A CeO_2 diffraction standard was used to calibrate the exact sample-detector distance and the detector tilts in each experiment. The 2D diffraction images collected at each pressure were integrated azimuthally using DIOPTAS [135] (this work) and FIT2D [149] (Evans) to obtain standard 1D diffraction profiles, which were then analysed using Rietveld [138] and Le Bail profile-fitting methods or by fitting to the d -spacings of individual diffraction peak positions [146].

7.3 Experimental Results

The low-pressure phases of Pr have been well studied, and considering the phase of interest was known to exist above 150 GPa, no effort was made to collect low-pressure data. Fortunately, diffraction patterns from sample 1 were collected up to 191 GPa, meaning that there is only a ~ 2 GPa gap between the data collected from it and that from sample 2.

7.3.1 The α -Uranium Phase

Profile-fitting of diffraction data collected from 65 to 165 GPa showed that the α -U structure is stable for ~ 150 GPa in Pr, as the transition to the α -U phase occurs at 20 GPa [64]. Figure 7.1 shows a Rietveld refinement of the $oC4$ (α -U) structure to the diffraction profile from Pr at 165(3) GPa, where the refined lattice parameters are $a = 2.4199(4)$ Å, $b = 4.7817(5)$ Å, and $c = 4.3799(7)$ Å, $V/V_0=0.367(5)$, with atoms on the $4c$ site at $(0,0.115(17),0.25)$. The fit is excellent, with all of the observed diffraction peaks accounted for.

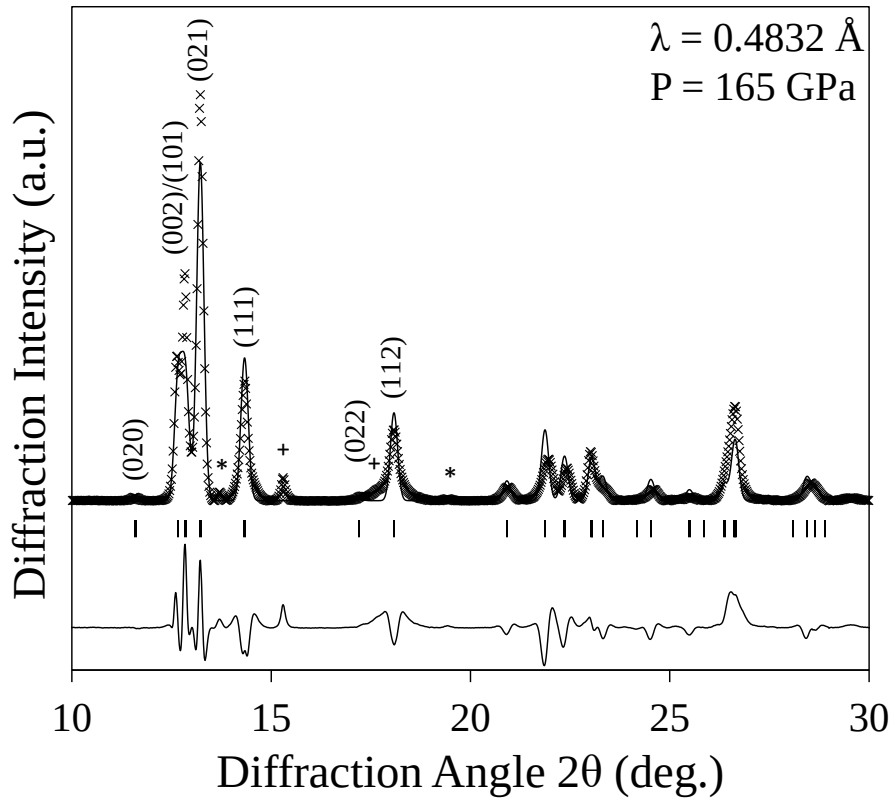


Figure 7.1 *Rietveld refinement of the $oC4$ structure to a diffraction profile from Pr at 165(3) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first seven peaks of the $oC4$ phase are labelled with their Miller indices.*

7.3.2 Indexing the Post- α -Uranium Structure

The diffraction data collected on compression of Pr above 170 GPa showed abrupt changes in the diffraction peaks. These changes indicated a phase transition to

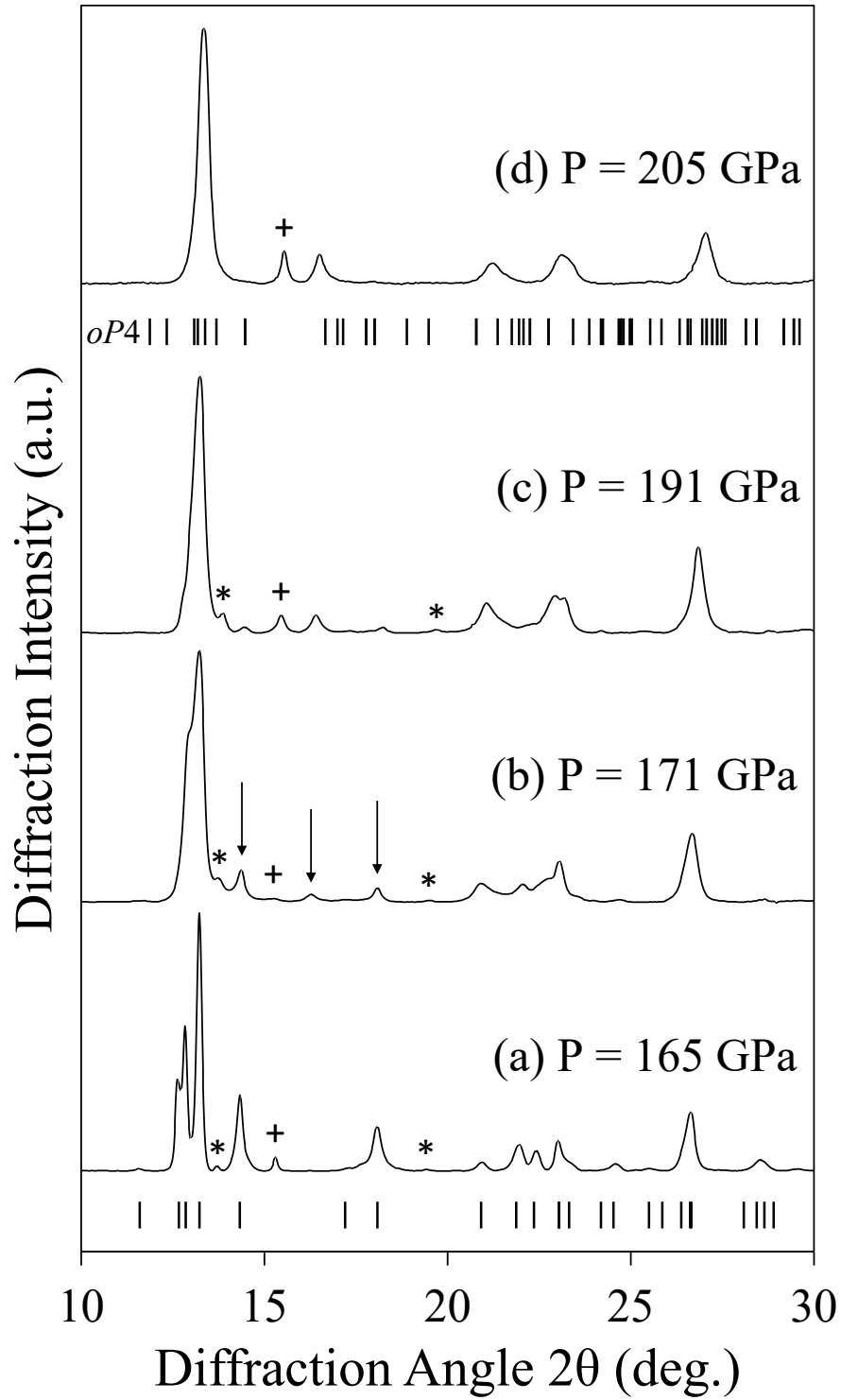


Figure 7.2 Diffraction profiles collected from *Pr* on pressure increase. The data were collected from two samples at PETRA III using wavelength $\lambda = 0.4832 \text{ \AA}$. Tick marks beneath profile (a) mark calculated peak positions from the oC4 phase, and tick marks beneath profile (d) mark calculated peak positions from the published oP4 phase [22]. The peaks marked with asterisks are from the *W* gasket, and the + signs mark peaks from the Cu pressure marker. Profiles (a), (b) and (c) are patterns collected from sample 1, and profile (d) shows a pattern collected from sample 2. A single phase pattern is seen in profile (d).

the post-*oC4* phase. Figure 7.2 displays a waterfall plot where a transition from the *oC4* to the post-*oC4* phase is observed between 165 and 205 GPa. Profile (a) in Figure 7.2 shows the highest pressure diffraction pattern collected from the *oC4* phase. Above this pressure, the diffraction peaks from the *oC4* phase decrease in intensity while those from the post-*oC4* phase become more intense. The left hand and right hand arrows in profile (b) mark peaks from the *oC4* phase that significantly reduce in intensity upon further pressure increase. The centre arrow in profile (b) marks the appearance of a peak from the post-*oC4* phase. Profile (d) shows a single-phase pattern from the post-*oC4* phase.

Velisavljevic & Vohra previously reported a transition in the *oC4* phase at 147(5) GPa [22], characterised by the appearance of a new diffraction peak between the (021) and the (111) peaks of the *oC4* phase which moved to longer d-spacings with increased pressure. However, comparison of Figure 1 in Reference [22] with Figure 7.2 shows that no new peak is seen at that location.

The tick marks beneath Figure 7.2(d) show the expected peak positions of the $P2_12_12_1$ structure, *oP4* in Pearson notation, as determined from the lattice parameters at this pressure, which were estimated from Figure 3 in Reference [22]. Although a number of the tick marks align with observed peaks in the diffraction profile, many of the peaks predicted by the $P2_12_12_1$ structure are not observed in this study. In particular, the peak at 13.69° , which indexes as the (012) in the $P2_12_12_1$ structure and the appearance of which was a key indicator of the transition to the post-*oC4* phase in the study of Velisavljevic & Vohra, is not observed.

The onset of the new phase was characterised by a dramatic ‘simplification’ of the diffraction pattern, whereby the number of intense peaks were significantly reduced. Published diffraction data on Ce has shown a similar reduction in the number of intense peaks from the α -U phase [5] to the tetragonal phase [84]. Therefore, a trial refinement was made of the same bct structure, *tI2*, as that published by Vohra *et al.* [84] to the diffraction patterns of the post-*oC4* phase in Pr. The *tI2* structure was an excellent fit to the diffraction patterns from Pr above 170(2) GPa. Figure 7.3 shows a Rietveld fit of the *tI2* structure, spacegroup $I4/mmm$, to a diffraction profile from Pr at 205(3) GPa, where the refined lattice parameters are $a = 2.3812(4)$ Å and $c = 4.1685(4)$ Å, $V/V_0 = 0.342(6)$, with atoms on the $2a$ site at (0,0,0). The fit is excellent, with all of the observed diffraction peaks accounted for. Any remaining intensity observed in the diffraction profile is explained by the appearance of peaks from the Cu pressure calibrant.

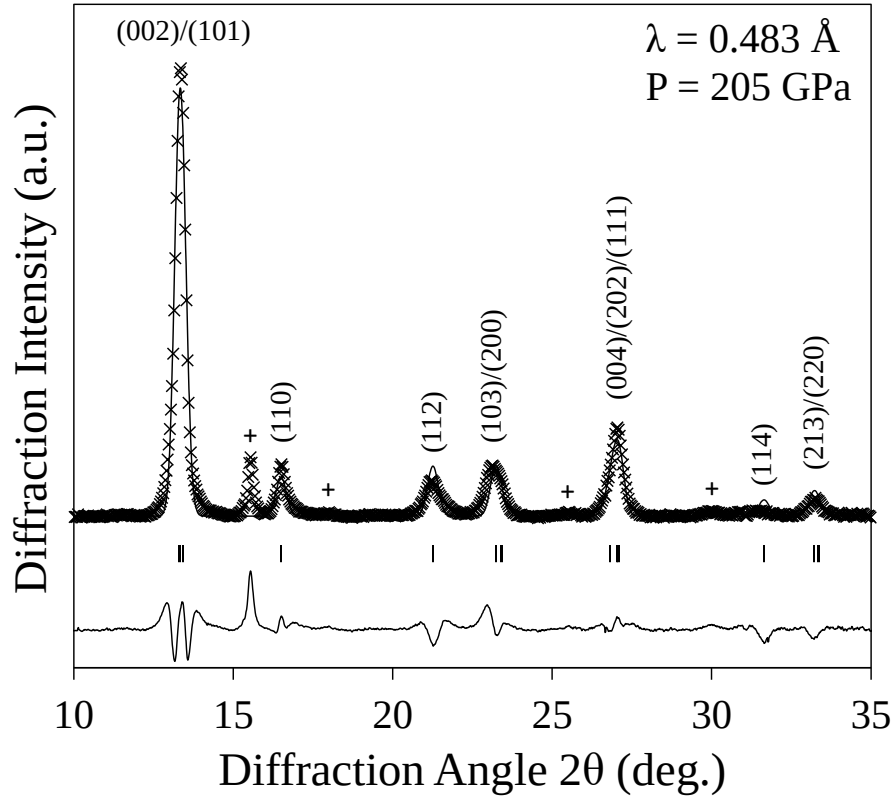


Figure 7.3 *Rietveld refinement of the $tI2$ structure to a diffraction profile from Pr at 205 GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. All of the peaks from the $tI2$ phase are labelled with their Miller indices.*

Table 7.1 *Structural data for two different pressure-induced phases of Pr observed at room temperature, including spacegroups, lattice parameters and pressures with their uncertainties.*

Structure	Lattice Parameters (Å)	Pressure (GPa)
$oC4$	$a = 2.4199(4)$, $b = 4.7817(5)$, $c = 4.3799(7)$	165(3)
$tI2$	$a = 2.3812(4)$, $c = 4.1685(4)$	205(3)

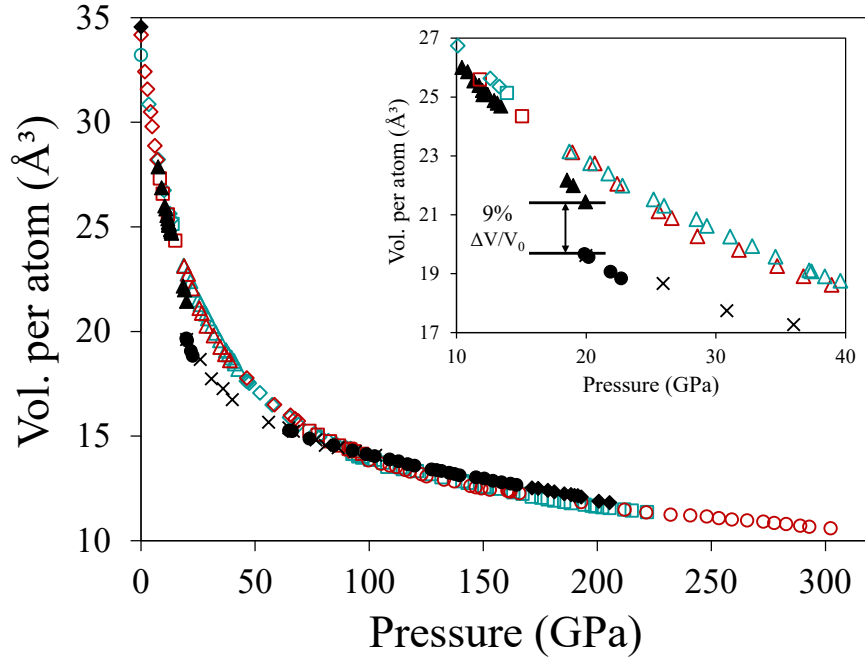


Figure 7.4 *The compressibility of Pr to 205 GPa. The data from our previous measurements to 22 GPa [23] and the current study from 65 to 205 GPa are plotted with solid symbols, while the data for oC4-Pr from the study of Chesnut and Vohra [24] are shown as crosses. The compressibilities of Nd (open red symbols) [4] and Sm (open cyan symbols) [2] have been added for comparison. The inset highlights the 9 % volume collapse seen in Pr and, as can be inferred, the deviation in the compressive behaviour of Pr versus that of Sm and Nd.*

A P–V curve of Pr is shown in Figure 7.4 along with the published compression data from Nd [4] and Sm [2]. It is observed that the compressibility of Pr is significantly different to that of both Nd and Sm, where the onset of the $oC4$ -Pr phase brings about a significant reduction in compressibility (see the inset in Figure 7.4) that carries forward into the near-continuous transition to the $tI2$ phase. For the cases of Nd and Sm, this reduction in compressibility is seen to occur in the $hP3$ phase [2, 4]. Furthermore, owing to a larger bulk modulus, the volume per atom above ~ 90 GPa of $oC4$ -Pr becomes greater than that of the $oF8$, $oC4$ phases of Nd and the $oF8$ phase of Sm.

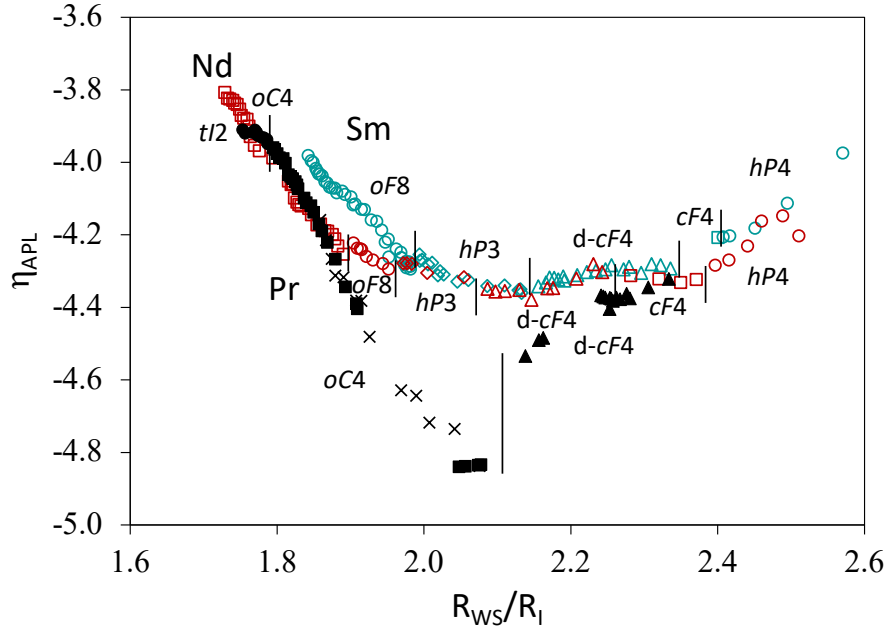


Figure 7.5 *Linearisation of the compression of Pr shown in the form of an η_{APL} - R_{WS}/R_{5p} plot, where R_{WS} is the Wigner-Seitz radius in Å, and R_{5p} is the 5p ionic radius in Å [25]. The data from the different phases of Pr are plotted using different symbols, and the phase boundaries are marked with vertical lines. The compressibility data from Pr is shown using solid symbols black, while the data from Nd and Sm are shown using red and cyan hollow symbols, respectively. The $hR24$ -Sm phase and the $hR24$ and $oI16$ phases of Pr and Nd are labelled as ‘d-cF4’. Data for the compressibility in Nd and Sm are taken from Refs [2, 4], and the data represented by crosses are taken from Ref [20].*

To highlight the similarities and differences in compression data of Pr, Nd and Sm, and to also highlight the systematics in phase transition pressures, the APL linearisation formalism [142] with respect to the radius ratio R_{WS}/R_I [40] has

been applied, where R_{WS} is the pressure dependent Wigner–Seitz radius

$$R_{WS} = \frac{3}{4\pi}(V_{\text{atom}})^{\frac{1}{3}} \quad (7.1)$$

and R_I is a pressure independent individual value for the ionic radius of each element [143]. The pressure dependent values of R_{WS} were determined from the measured atomic volumes, while R_I were taken to be the R_{5p} radii [42], as tabulated by Waber & Cromer [25].

Figure 7.5 shows the APL linearised compression data for Pr in the form of a $\eta_{APL} - R_{WS}/R_{5p}$ plot, along with the published data for Nd and Sm to 302 and 222 GPa, respectively [2, 4]. The data for Pr exhibit significant curvature, very similar to that observed in Nd and Sm [2, 4], up to the transition to the α -U ($oC4$) phase. However, unlike in Nd and Sm, there is an abrupt change in behaviour within the $oC4$ -Pr phase, contrary to the more subtle behavioural changes in the $hP3$ phases in Nd and Sm. The $oF8$ phases of both Nd and Sm, the $oC4$ phases of Nd and Pr ($R_{WS}/R_I < 2$) and the $tI2$ phase in Pr display the linear behaviour expected of a “regular” metal [152].

7.3.3 Electronic Structure Calculations

Zero-temperature DFT calculations performed by our collaborators at KCL examined the enthalpy change in the $oC4$ and $tI2$ phases at high pressures [27]. The results revealed that the $tI2$ phase had lower enthalpy above 130 GPa. These results agree reasonably well with the experimental ones, where the $oC4 \rightarrow tI2$ transition occurs at 170(2) GPa.

7.4 Conclusions

The post- $oC4$ (α -U) structure of Pr has been reassigned to a bct structure with 2 atoms in the unit cell, spacegroup $I4/mmm$, contrary to that which has been published by Velisavljevic *et al.* [22]. This structure is also found in the high-pressure phases of Ce [48, 83, 84], Th [85, 86] and U [50].

Measurements of the compressibility of Pr reveal that it becomes less compressible after the transition to the $oC4$ phase at 19 GPa and that in the $oC4$ phase at

higher pressures and $tI2$ phase its compressibility is that of a “regular metal”. Linearisation of the compressibility in Pr is found to have similar behaviour as that previously seen in Nd [4] and Sm [2].

Chapter 8

The Pressure-Induced Phase Transition Sequence of Yttrium

8.1 Introduction

The transition metal Y is considered a rare earth element, along with Sc and the lanthanides (La to Lu). Y exhibits the same structural sequence as the trivalent lanthanides (all lanthanides except Ce, Eu and Yb): hcp $\rightarrow$ Sm-type $\rightarrow$ dhcp $\rightarrow$ fcc $\rightarrow$ dfcc $\rightarrow$ “volume-collapsed” [11, 98], yet it does not have any f electrons.

Above 100 GPa, Y is reported to transform to the $mC4$ structure – the same as that previously assigned to all the post-dfcc phases of the trivalent lanthanides [11]. However, after reassigning this structure to a face-centred orthorhombic structure with either 8 or 16 atoms in the unit cell in the trivalent lanthanides, it is necessary to determine whether Y also exhibits this orthorhombic structure or deviates from the common, structural phase transition sequence of the trivalent lanthanides and adopts the $mC4$ structure or another crystal structure.

The ultra-high pressure phases of Y have been of keen interest to theoreticians, particularly in the field of superconductivity [155]. Finding a room temperature superconductor has been a goal in the area of superconductivity for a long time, and, at only 262 K, a superhydride of Y has been found to be superconducting at a pressure of 182 GPa – a pressure at which this thesis has confirmed Y exhibits the $oF16$ structure [156]. Furthermore, DFT calculations performed by Chen *et al.* predicted the existence of the $P6_222$ and $Fddd$ structures at pressures of

206 and 97 GPa, respectively [150, 157]. Both these predictions are particularly interesting considering the findings presented in Chapters 5 and 6 on Sm and Nd.

In order to assess the structural phase transitions of Y, studies were conducted on Y from 1 to 180 GPa using ADXD techniques. The data analysed in this chapter have been published in Physical Review B [3].

8.2 Experimental Details

High-purity distilled samples of Y supplied by Ulrich Schwarz at the Max-Planck-Institut für Chemische Physik fester Stoffe in Dresden were loaded into four DACs in a dry argon atmosphere (<1 ppm O_2 and <1 ppm H_2O) to prevent oxidation. Two DACs were equipped with bevelled diamonds, both with $100\text{ }\mu\text{m}$ diameter culets. The other two DACs were equipped with $300\text{ }\mu\text{m}$ and $180\text{ }\mu\text{m}$ diameter culets, respectively, and W gaskets. The samples were loaded without any pressure medium. All samples were loaded with a small (few μm) copper (Cu) sphere to act as a pressure calibrant, using the published Cu equation of state of Sokolova *et al.* [132]. Two of the samples were loaded by Dr Edward Pace, and the low pressure data between 1 and 63 GPa used in the P-V diagram (see Figure 8.7) were collected by him during one experiment.

Diffraction data were collected in two experiments on three samples on the Extreme Conditions P02.2 beamline at the Petra-III synchrotron in Hamburg, Germany and on one sample on the high-pressure I15 beamline at the Diamond Light Source (DLS) synchrotron, United Kingdom, Monochromatic x-ray beams of wavelength $0.2898\text{\AA}$ – $0.4832\text{\AA}$ (Petra-III) and $0.4246\text{\AA}$ (DLS), focused down to $3\text{ }\mu\text{m} \times 6\text{ }\mu\text{m}$, $0.85\text{ }\mu\text{m} \times 0.85\text{ }\mu\text{m}$ (Petra-III) and $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ (DLS) were used, and the powder-diffraction data were recorded on Perkin-Elmer (Petra-III) and Mar345 (DLS) area detectors, placed 300–400 mm from the sample. In the first experiment conducted at Petra-III, the area detector was moved from ~ 400 mm to ~ 600 mm from the sample in order to improve the low-angle peak resolution. CeO_2 and LaB_6 diffraction standards were used to calibrate the exact sample-detector distances and the detector tilts in each experiment. The 2D diffraction images collected at each pressure were integrated azimuthally using Dioptas [135] to obtain standard 1D diffraction profiles, which were then analysed using Rietveld [138] and Le Bail profile-fitting methods.

8.3 Experimental Results

Data were collected on three samples of Y from 1.2 to 180 GPa in order to confirm that its pressure-induced phases have the same structures as those found in the phases of the trivalent lanthanides under the same changing conditions and, in particular, the pressure-induced phases of the heavy trivalent lanthanides.

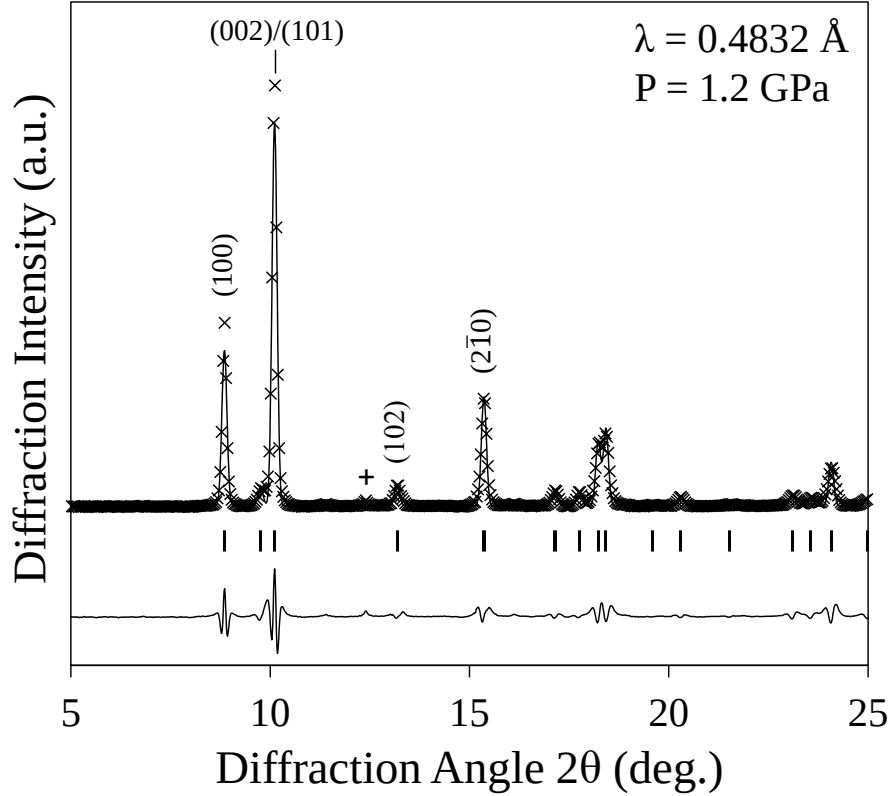


Figure 8.1 *Le Bail refinement of the hP2 structure to a diffraction profile from Y at 1.2(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first five peaks of the hP2 phase are labelled with their Miller indices.*

8.3.1 Low-Pressure Phases

The initial integrated diffraction data showed single phase hcp patterns. Figure 8.1 displays a Le Bail refinement of the *hP2* structure to a diffraction pattern at 1.2(2) GPa. The diffraction pattern displays very sharp peaks, likely to be a result of very little strain on the Y sample as pressures are still relatively low.

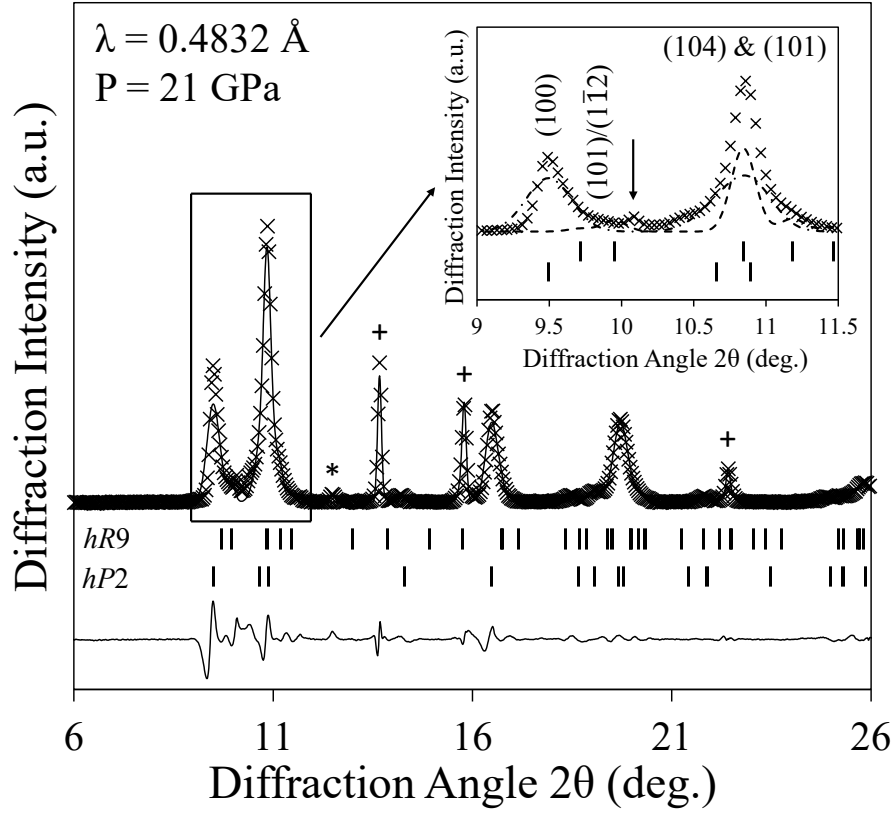


Figure 8.2 *Le Bail refinement of the hR9 and hP2 structures to a mixed-phase diffraction profile from Y at 21(1) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The (100) and (101) (second in parentheses) peaks of the hP2 phase (dot-dash) and the (101), ($\bar{1}\bar{1}2$) and (104) of the hR9 phase (dash) are labelled in the inset. The arrow labels a misfitting peak from the hR9 phase that is thought to arise from stacking faults. The asterisk identifies the (110) peak from the W gasket and the + signs mark peaks from the Cu pressure calibrant.*

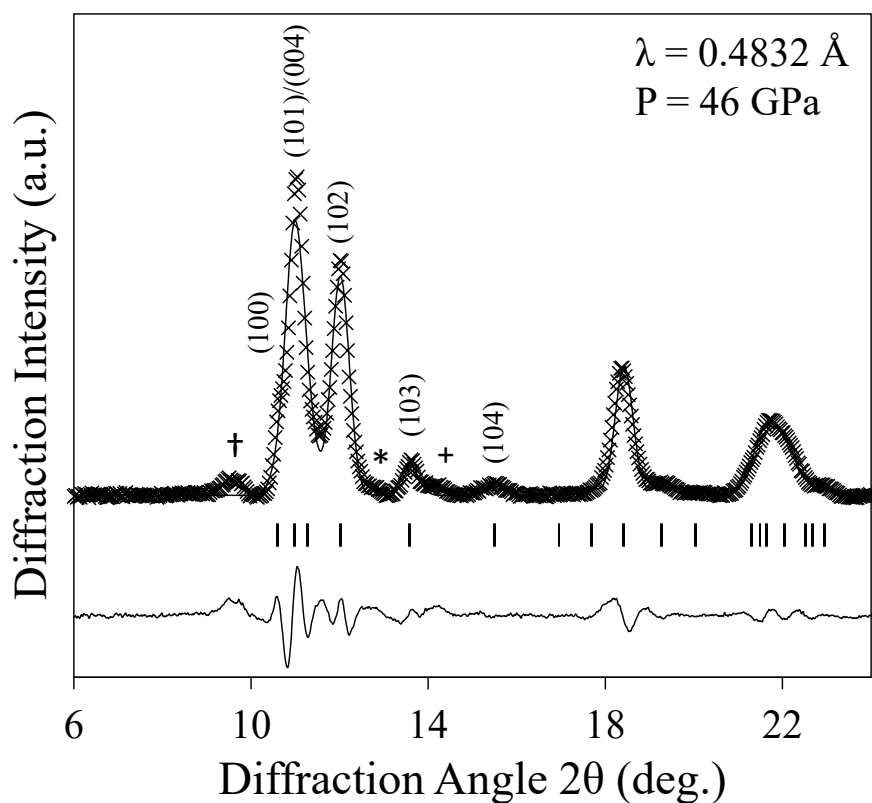


Figure 8.3 *Le Bail refinement of the hP4 structure to a diffraction profile from Y at 46(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first six peaks of the hP4 phase are labelled. The dagger identifies a peak from a contaminant, the asterisk identifies the (110) peak from the W gasket and the + sign marks a peak from the Cu pressure calibrant.*

At 14.2(5) GPa, a transition to the α -Sm phase was observed in agreement with previous studies, and adopts the $hR9$ structure. Figure 8.2 displays a Le Bail refinement of the $hR9$ and $hP2$ structures to a mixed-phase pattern at 21(1) GPa. The inset shows the extent of phase mixing occurring halfway through the region of stability (14–27 GPa) for the $hR9$ phase, where the $hP2$ phase still exhibits strong intensity from the (100) and (104) peaks. The arrow in the inset highlights peak misfitting from the α -Sm phase that is thought to arise from stacking faults within the $hR9$ structure, causing asymmetry in the peak profiles of, in this case, the (101) and ($1\bar{1}2$) reflections.

This phase remains stable until 27 GPa, where a transition to the dhcp phase occurs. Figure 8.3 displays a Le Bail refinement of the $hP4$ structure to a diffraction profile of Y at 46(2) GPa. The sluggish phase transition from $hP2 \rightarrow hR9 \rightarrow hP4 \rightarrow hR24$ arise from the slight differences in stacking of the hexagonal layers.

At 47(5) GPa, a transition to the rhombohedral dfcc phase, $hR24$, was observed in agreement with previous studies. This study found that the $hP4$ phase remains phase-mixed with the $hR24$ phase up to almost the $hR24 \rightarrow$ volume-collapsed transition. Figure 8.4 shows a Le Bail refinement of the $hR24$ and $hP4$ structures to a diffraction profile from Y at 98(2) GPa.

8.3.2 Lower Symmetry Structures

Above 100 GPa, marked changes in the diffraction patterns revealed the onset on a transition to a new phase. Previously, this phase has been assigned to the $mC4$ structure that was assigned to all the trivalent lanthanides except Lu [11].

Figure 8.5 shows a Rietveld fit of the $oF16$ structure to the diffraction profile from Y at 150(4) GPa, where the refined lattice parameters are $a = 16.668(8)$ Å, $b = 4.5977(5)$ Å, and $c = 2.6950(4)$ Å, $V/V_0=0.391(9)$, with atoms on the $16e$ site at $(\frac{3}{16}, 0, 0)$. The fit is excellent, with all of the observed diffraction peaks accounted for. Buhot *et al.* [154] reanalysed the x-ray diffraction data from samples of Y published by Samudrala *et al.* [11] at 123 GPa using Rietveld methods and showed that it can be fitted with the $oF16$ structure.

Figure 8.6 displays profiles from each phase of Y. The profiles are the same as those presented in Figures 8.1–8.5.

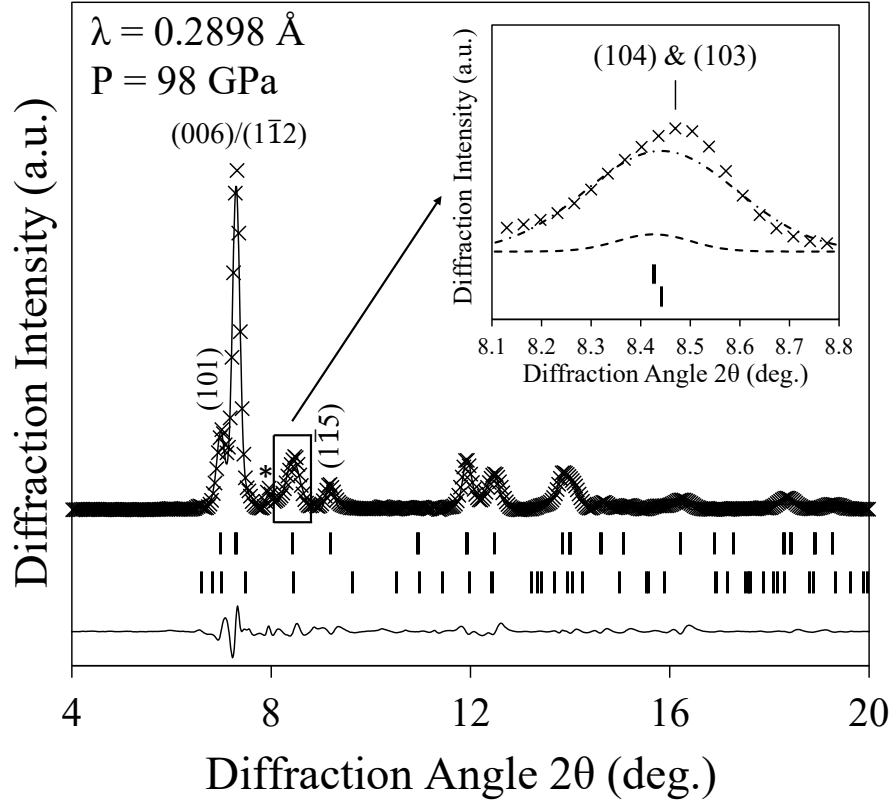


Figure 8.4 *Le Bail refinement of the hR24 and hP4 structures to a mixed-phase diffraction profile from Y at 98(2) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first five peaks of the hR24 phase are labelled with their Miller indices. The (104) peak from the hR24 phase (dash) and the (103) peak from the hR9 phase (dot-dash) are labelled in the inset. The asterisk identifies the (110) peak from the W gasket.*

Table 8.1 *Structural data for five different pressure-induced phases of Y observed at room temperature, including spacegroups, lattice parameters and pressures with their uncertainties.*

Structure	Lattice Parameters (Å)	Pressure (GPa)
<i>hP2</i>	$a = 3.61514(14), c = 5.6816(9)$	1.2(2)
<i>hR9</i>	$a = 3.2993(7), c = 21.676(3)$	21(1)
<i>hP4</i>	$a = 3.0185(3), c = 9.833(5)$	46(2)
<i>hR24</i>	$a = 5.5457(2), c = 13.791(2)$	98(2)
<i>oF16</i>	$a = 16.668(8), b = 4.5977(5), c = 2.6950(4)$	150(3)

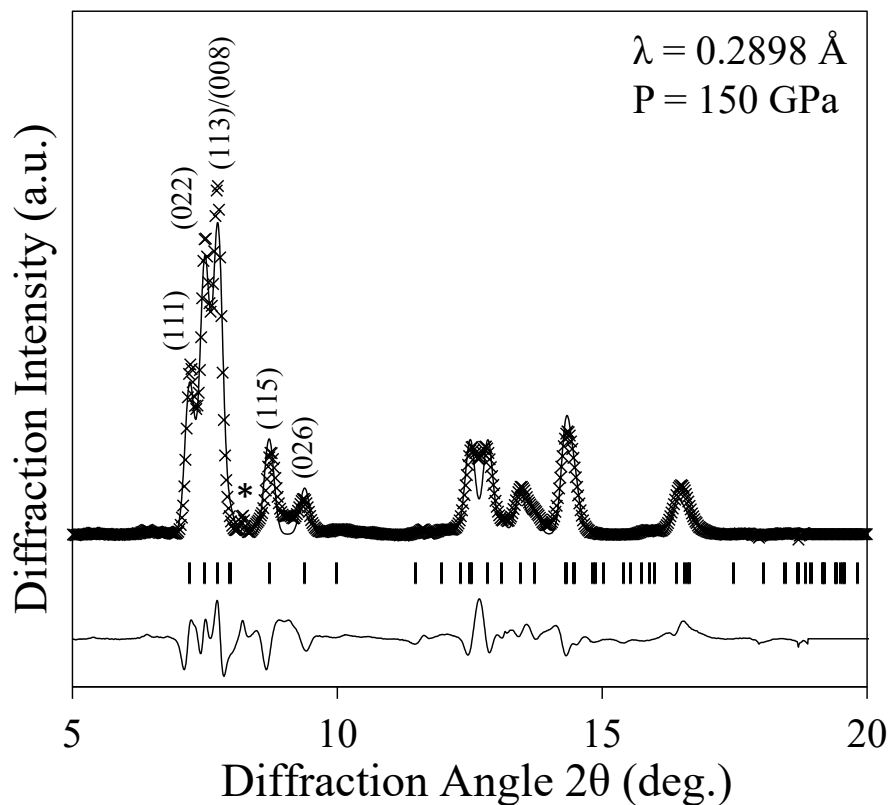


Figure 8.5 *Rietveld refinement of the oF16 structure to a diffraction profile from Y at 150(3) GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The first six peaks of the oF16 phase are labelled with their Miller indices. The asterisk identifies the (110) peak from the W gasket. The peaks at ~ 5 , ~ 6 , ~ 9 and ~ 13 degrees are unexplained, but likely arise from contaminants in the sample.*

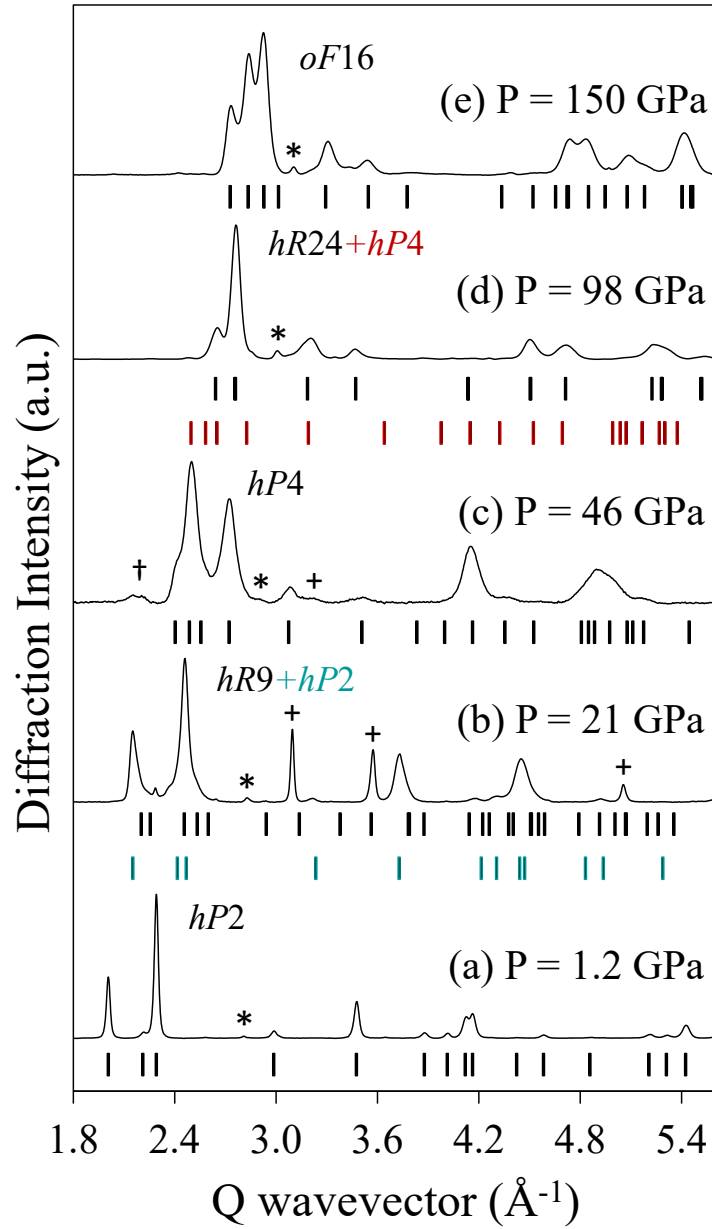


Figure 8.6 Diffraction profiles collected from *Y* on pressure increase. The data were collected from two different samples during two different synchrotron visits, and so are plotted as a function of wavevector (Q) in order to take account of the two different x-ray wavelengths used. Profiles (a)–(e) display the five different phases seen in *Y* upon pressure increase: *hP2*, *hR9*, *hP4*, *hR24* and *oF16*. Reflection positions of each phase are labelled beneath each profile. The peaks marked with asterisks are from the *W* gasket, and the + signs marks peaks from the *Cu* pressure marker.

8.3.3 APL Equation of State

The compressibility of Y up to 180 GPa is shown in Figure 8.7 and is almost continuous. An AP3 EOS has been fitted from the $hP2$ to $hR24$ phases. However, there is a small volume change of 1.8% at the $hR24 \rightarrow oF16$ transition and, therefore, the $oF16$ phase was fitted with an AP1 EOS.

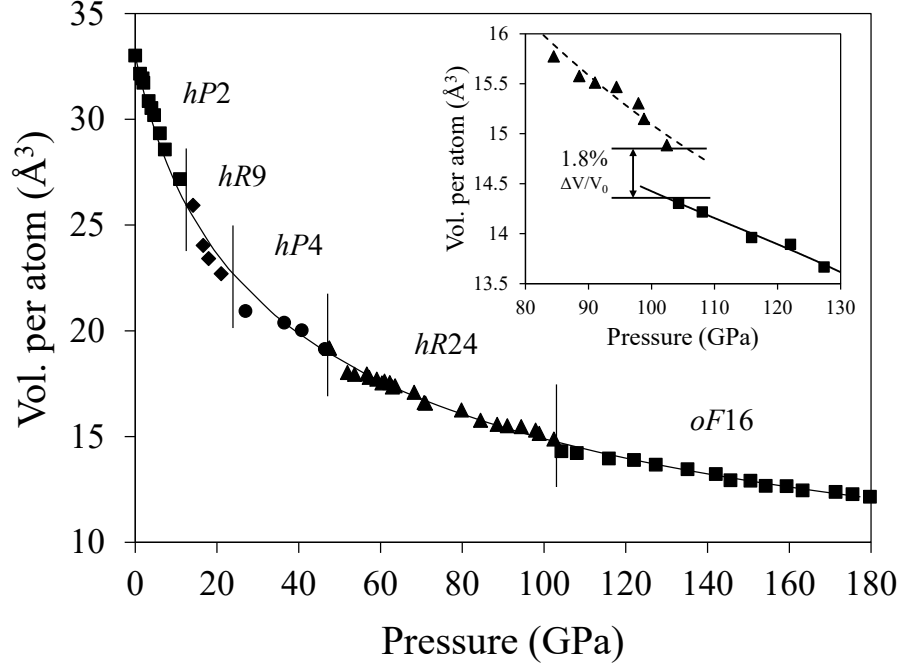


Figure 8.7 *The compressibility of Y up to 180 GPa. The dashed line shows the best fitting third-order AP3 EOS to the compression curve from the $hP2$ to $hR24$ phases. The solid line shows the best fitting first-order AP1 EOS to the $oF16$ phase.*

Holzappel’s Adapted Polynomial of order L (APL) EOS formalism was utilised to analyse the compressibility of Y [152]. The compression data can be fitted using the second order (AP2) form of the APL EOS [142, 143] described in detail in Chapters 3 and 5.

To realise the similarities and differences in compression data of Y with respect to “ideal” behaviour, and to also highlight the systematics in phase transition pressures in Y and Nd & Sm, an APL linearisation with respect to the radius ratio R_{WS}/R_I [40] was used. The description of the radius ratio is provided in Chapter 6.

The linearised $\eta_{APL} - R_{WS}/R_I$ data for Y is shown in Figure 8.8, along with

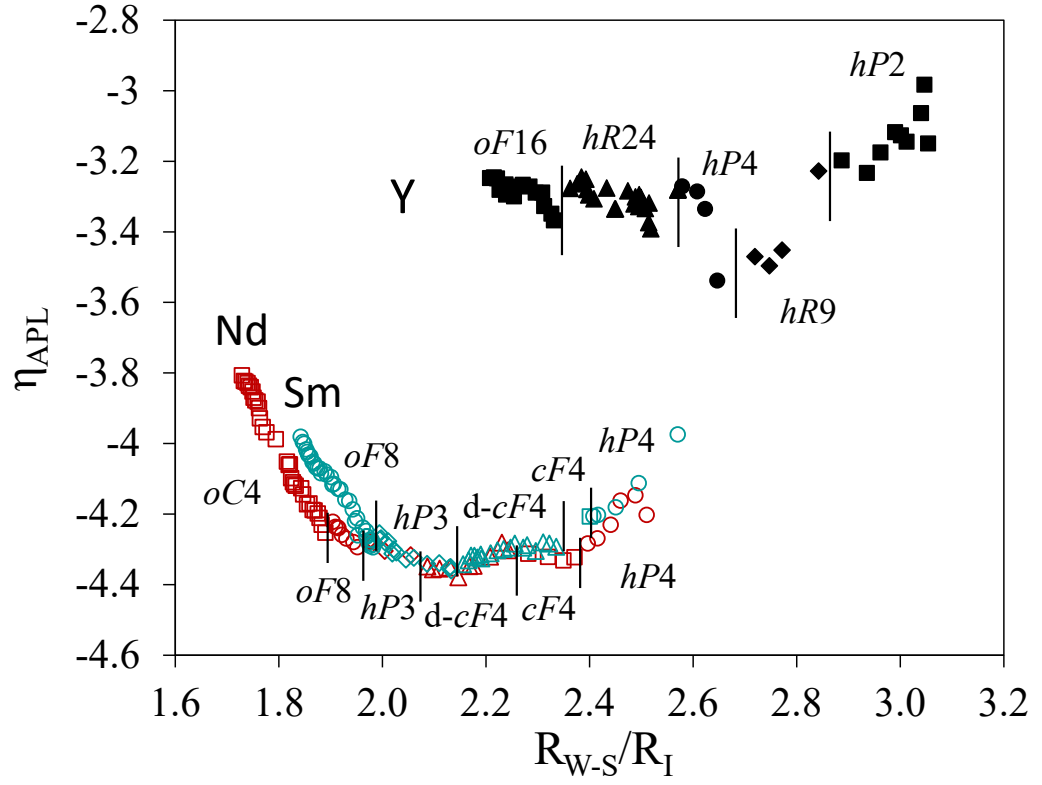


Figure 8.8 *Linearisation of the compression of Sm shown in the form of an $\eta_{\text{APL}}-x$ plot. The data from the different phases of Sm are plotted using different symbols, and the “regular” compressibilities of Au and Pt, as calculated from the compression data of Dewaele et al. [21], are shown for comparison.*

the similarly-linearised data reported for Nd [4] and Sm [2]. In such a plot, materials undergoing “normal” compressive behaviour will show linear or quasi-linear behaviour with the correct theoretical limit of $\eta_{\text{APL}}(0) = 0$. This behaviour is demonstrated by Nd and Sm in Figure 8.8, providing excellent examples of materials whose compressibilities are initially ‘irregular’ as a result of $s-d$ electron transfer, but which become ‘regular’ after they transform to the $oF8$ structures in Nd and Sm. Although the data from the lower-pressure phases of Y exhibit some scatter amongst the linearised η_{APL} values, a general positive gradient can be identified. However, on entering the $oF16$ phase, there is a clear shift to linear behaviour with a negative gradient reasonably similar, yet not as obvious, to that observed in Nd and Sm. Although the pressure range over which we have compression data for $oF16$ -Y (80 GPa) is somewhat smaller than the 100+ GPa pressure range over which we have compression data for $oF8$ -Sm, the linearised data in Figure 8.8 suggest that $oF16$ -Y, like $oF8$ -Sm, is a metal with ‘regular’ compressibility.

The continually-shifting gradient exhibited by the phases of Y in Figure 8.8 suggests that the compression curve shown in Figure 8.7 would be well fitted by a 3rd-order AP3.

8.3.4 Electronic Structure Calculations

Regular compressive behaviour in the $oF16$ phase of Y may arise from discrete changes in the electronic structure. Indeed, calculations performed by Li *et al.* showed increased occupation of the $4d$ -band as a result of transitions of electrons from the $4s$ -band [158].

The DFT calculations performed by Plekhanov *et al.* on the $oF16$ and $oF8$ phases of Y [3] have demonstrated that the $oF16$ phase is lower in enthalpy than the $oF8$ phase between 40 and 240 GPa. These findings have corroborated what was previously demonstrated by Chen *et al.* who have shown that the $oF16$ phase is more energetically favourable than the $hP3$ phase [150] – a phase previously seen at high pressures in Nd [18] and Sm [75].

8.4 Conclusions

The structure of Y metal above 104(2) GPa is found to be face-centred orthorhombic, *oF16*, and isostructural with that observed in the collapsed phases of the trivalent lanthanides Tb [1], Gd, Dy, Ho and Er. It is also the likely structure of the superconducting phase in Y [150] and the structure of the post-*hR24* of Tm and Lu. This result confirms the close structural relationship between the lanthanides and Y, showing that *f* electrons are still not participating in the bonding and, therefore, not influencing the pressure-induced, structural phase transitions up until at least the *oF16* (Tb–Lu, except Yb) and *oF8* (Nd and Sm) phases.

High precision measurements of the compressibility of Y reveal similar anomalous behaviour at lower pressures as that seen at low pressures in Pr, Nd and Sm. In fact, Y is shown to begin behaving as a ‘regular’ metal from the onset of the post-*hR24* phase, *oF16*, again showing analogous behaviour to the post-*hR24* phases of Pr, Nd and Sm.

DFT calculations performed by Plekhanov *et al.* revealed that the *oF16* structure has lower enthalpy above 100 GPa relative to the *oF8* structure observed in Nd and Sm, and thus more likely to be the correctly assigned structure to the post-*hR24* phase.

Chapter 9

Conclusions & Future Work

9.1 The Trivalent Lanthanides & Other Rare Earths

The literature published previously on x-ray diffraction studies of the lanthanide and rare earth elements has reported the following structural phase transition sequence with increasing pressure: hcp $\rightarrow$ Sm-type $\rightarrow$ double-hcp $\rightarrow$ fcc $\rightarrow$ dfcc. At pressures above the dfcc phases, a C-centred monoclinic structure has been previously reported to exist in all the lanthanide metals, except Eu and Yb, and in Y at high pressures. Angle dispersive, x-ray powder diffraction studies were performed on Y, Pr, Nd, Sm, Gd, Tb and Dy to investigate the common structural sequence, and to identify the structures, both observed and not yet observed, at ultra-high pressures. This thesis has reported that the previously-assigned monoclinic structure is incorrect, and that a more highly-symmetric, face-centred orthorhombic structure, spacegroup $Fddd$, is the correct assignment to the corresponding, high-pressure phase in all the trivalent lanthanides and Y.

9.2 The Heavy Trivalent Lanthanide Elements

The post- $hR24$ phases of Gd, Tb and Dy have been confirmed, via analysis of the data presented in this thesis, as having a higher-symmetry orthorhombic structure with 16 atoms in the unit cell, $oF16$ in Pearson notation. From reanalysis of

studies from Ho [26] and comparisons of the published diffraction data on Er [9] and Tm [63], it has also been confirmed that these elements also exhibit the $oF16$ structure at higher pressures rather than the reported $mC4$ structure.

Lu would make an excellent candidate for future work using a toroidal DAC. Thus far, it has been studied up to 202 GPa where it still remains in the $hR24$ phase [11]. Therefore, to observe a full transition to the expected $oF16$ structure pressures in excess of 300 GPa would be required.

Tb was seen to transition to a new phase above 160 GPa, which remained phase-mixed with the $oF16$ structure to the maximum pressure reached in this work of 247 GPa. An *ab initio* refinement of the $oF8$ and $oF16$ structures to a diffraction pattern of Tb at 247 GPa suggests that Tb, and therefore the other heavy trivalent lanthanides, may transition to the same structure as that of Am-III, Cm-IV and Cf-IV [19, 87, 88]. It would be intuitive to perform further toroidal diamond anvil studies to achieve single-phase patterns of this new phase and, therefore, provide a definitive answer of the correct structural assignment.

9.3 The Light Trivalent Lanthanide Elements

The $hP3$ phases of Nd and Sm have been assigned to the $P6_222$ spacegroup, rather than the less-symmetric $P3_121$ spacegroup previously assigned in the literature.

The post- $hR24$ phases of Pr and the post- $hP3$ phases of Nd and Sm have been confirmed as having lower symmetry structures than the $hR24$ and $hP3$ phases, but with a structural assignment to a more symmetrical structure than the monoclinic structure $mC4$ previously assigned to the post- $dfcc$ phase as reported in the literature.

At 74 and 93 GPa, Nd and Sm, respectively, transition to a lower-symmetry, face-centred orthorhombic structure with 8 atoms in the unit cell, $oF8$, from a hexagonal phase. This hexagonal phase is known to adopt the $hP3$ structure, however this thesis has assigned a more highly-symmetric spacegroup, $P6_222$ as opposed to $P3_121$, to the phase.

Nd transitions from the $oF8$ phase to another phase, adopting the α -U or $oC4$ structure, at pressures above 100 GPa. The α -U structure was known to occur in Nd above 100 GPa [18], however this work has shown it transforms from a

different structure than that seen previously.

Pr transitions from an orthorhombic *dfcc* phase, *oI16*, to the α -U at 20 GPa, which persists to ~ 170 GPa. Previously, it was reported that a transition to a primitive orthorhombic occurred at 147 GPa [22]. However, this study reports that Pr transforms to a body-centred tetragonal structure, *tI2*, at pressures above 170 GPa, which has considerably higher symmetry than the α -U structure. This is isostructural with the body-centred tetragonal structure seen in a high pressure phase of Ce after the α -U phase at pressures above 12 GPa [48, 83, 84] and from ambient conditions in Th [85, 86].

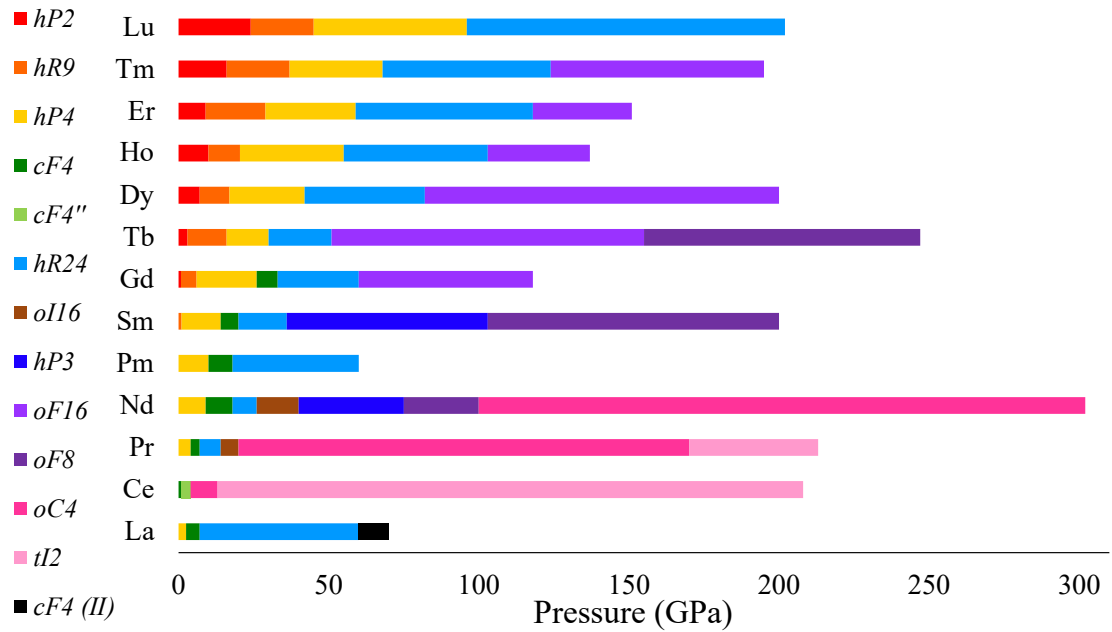


Figure 9.1 The pressure-induced, structural phase transition sequences of the trivalent lanthanides and Ce to 302 GPa, taken from Ref. [10] and references therein, with updated results from this thesis and Refs. [1, 2, 4, 26, 27].

9.4 The Rare Earth Elements

Structural studies of Y above 100 GPa have revealed that it exhibits the *oF16* structure [3, 154] that is observed in the post-*hR24* phases of Gd, Tb [1] and Dy, and not the *mC4* structure that was previously assigned [11]. Studies of the compressibility of Y have shown that it behaves like a ‘regular’ metal after transition to the *oF16* phase, thus displaying similar behaviour to that of Pr, Nd

and Sm in the $oC4$ (Pr) and $oF8$ (Nd and Sm) phases.

The structural phase transitions of Y emulates the transition sequence of the heavy trivalent lanthanides with increasing pressure. It therefore draws into question whether or not Sc, La and Ac have more similar phase transitions with increasing pressure than published previously in the literature.

It has been long understood that, eventually, the f electrons in the lanthanide elements would become itinerant and participate in the bonding. However, as already mentioned, Y does not have any f electrons yet produces the same pressure-induced, structural sequence. The question then remains: at what point will the common structural phase transition sequence of Y and the heavy trivalent lanthanides part ways and become two distinct sequences? To study this, ultra-high pressure studies into the structures of Y above the $oF16$ are required to reveal whether or not Y transitions to either the α -U ($oC4$) or $tI2$, or to something different.

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Structure and magnetism of collapsed lanthanide elements

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Using synchrotron x-ray diffraction, we show that the long-accepted monoclinic structure of the “collapsed” high-pressure phases reported in seven lanthanide elements [Nd, Tb, Gd, Dy, Ho, Er, and (probably) Tm] is incorrect. In Tb, Gd, Dy, Ho, Er, and Tm we show that the collapsed phases have a 16-atom orthorhombic structure (*oF16*) not previously seen in the elements, whereas in Nd we show that it has an eight-atom orthorhombic structure (*oF8*) previously reported in several actinide elements. *oF16* and *oF8* are members of a new family of layered elemental structures, the discovery of which reveals that the high-pressure structural systematics of the lanthanides, actinides, and group-III elements (Sc and Y) are much more related than previously imagined. Electronic structure calculations of Tb, combined with quantum many-body corrections, confirm the experimental observation, and calculate that the collapsed orthorhombic phase is a ferromagnet, nearly degenerate with an antiferromagnetic state between 60 and 80 GPa. We find that the magnetic properties of Tb survive to the highest pressures obtained in our experiments (110 GPa). Further calculations of the collapsed phases of Gd and Dy, again using the correct crystal structure, show the former to be a type-A antiferromagnet, whereas the latter is ferromagnetic.

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I. INTRODUCTION

The lanthanide (Ce to Lu) and actinide (Th to Lr) series of metals are characterized by the monotonic increase in the number of their *4f* and *5f* electrons, respectively. As electron interactions can be readily modified by changing interatomic distances, studies of the lanthanide and actinide elements under compression have been critical in developing an understanding of *f*-electron behavior at high densities [1–6]. The *f* electrons in both series of elements are usually classified as being either localized and characterized by tightly bound shells or narrow bands of highly correlated electrons near the Fermi level or itinerant and able to participate in the metallic bonding [5]. In the predominantly trivalent lanthanides (La to Lu, excluding Ce, Eu and Yb), the *4f* electrons are localized at ambient conditions, and, on compression, an increase in *d*-band occupancy resulting from *s-d* electron transfer gives rise to a common phase-transition sequence between structures comprising different stackings of close-packed layers: hcp- (space-group *P6₃/mmc* and *hP2* in Pearson notation) → Sm-type (*R $\bar{3}m$* and *hR3*) → double-hcp (*P6₃/mmc* and *hP4*) → fcc- (*Fm $\bar{3}m$* and *cF4*) → distorted-fcc (*R $\bar{3}m$* and *hR24*) (Refs. [5,6], and references therein). Although there are no measurable volume changes between any of these different phases, neither do any of them have group-subgroup relationships. Indeed, Porsch and Holzapfel studied the symmetry changes at the *cF4* → *hR24* transition in detail and showed that it must be first order [7].

When compressed further, the *hR24* phases transform to lower-symmetry “collapsed” phases, often via a sudden decrease in atomic volume (Ref. [6], and references therein). Similar behavior is observed in the trans-Pu “heavy” actinide elements (Am [8], Cm [9], and Cf [10]) on compression, each of which transforms via volume discontinuities to complex structural forms seen in the lighter actinides (Th–Pu). Volume discontinuities and the appearance of low-symmetry structures are commonly associated with the pressure-induced delocalization of the *4f/5f* electrons and their subsequent participation in bonding. However, recent x-ray spectroscopy measurements on Tb to extreme pressure reveal that neither a valence change nor *4f* delocalization occur at the volume collapse pressure of 53 GPa [11]. Rather, the collapsed phases of both Tb and neighboring Dy exhibit anomalously high magnetic ordering temperatures suggestive of an unconventional magnetic state [12,13]. Understanding the mechanism(s) responsible for these high-ordering temperatures might enable their reproduction in a suitable compound at ambient pressure, leading to the synthesis of superior permanent magnet materials.

The collapsed phases in the regular lanthanides are most commonly reported to have a four-atom monoclinic structure with space-group *C2/m* (*mC4* in the Pearson notation) first observed in Ce 40 years ago [16]. Since then, the collapsed phases of Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm have all been reported to have the same *mC4* structure (Ref. [6], and references therein) such that it is now *the* key structure in the

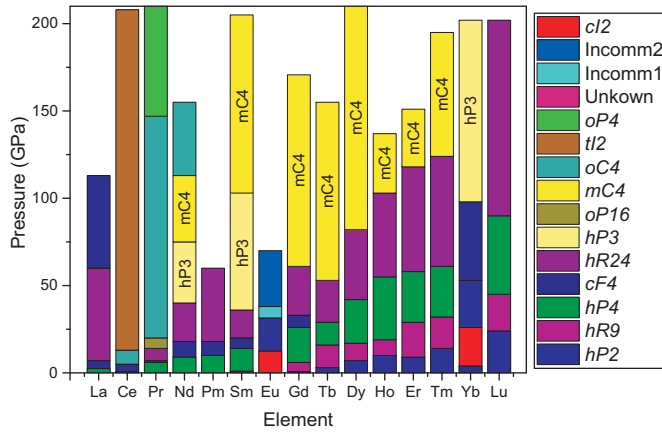


FIG. 1. The different phases reported in the lanthanide elements up to 210 GPa at ambient temperature. Transition pressures are taken from Refs. [6,14,15] and references therein. The collapsed *mC4* and *hP3* phases are highlighted in full and pale yellow, respectively, and are labeled. Of the low-symmetry phases, only the *oC4* and *tI2* phases are also seen in the actinides.

lanthanide elements at high densities (see Fig. 1). In Nd and Sm, the *mC4* phase is obtained via an intermediate rhombohedral *hP3* phase (space-group $P3_121$, but see later) seen only in these two elements [17,18] and Yb [19]. And in Ce, Pr, and Nd, a collapsed phase with the orthorhombic structure found in uranium at ambient conditions (space-group *Cmcm* and Pearson notation *oC4*) is also found [20–22]; somewhat surprisingly, this and the tetragonal *tI2* phase seen in Ce and Th [23,24] are the only noncubic crystal structures that the lanthanides and actinides have in common on compression.

There is, thus, a consensus, constructed over decades, as to the structural behavior of the lanthanides on compression as illustrated in Fig. 1 and the phases which are common to both lanthanides and actinides. However, although the similarity of many of the published diffraction patterns from the collapsed phases of the lanthanides suggests they do share a common structure, the widely reported *mC4* monoclinic structure provides an inadequate fit to many, if not all of them—as detailed in the Supplemental Material [25].

Using high-quality synchrotron x-ray-diffraction data, we have determined the correct structure of the collapsed phase of Tb as orthorhombic with space-group *Fddd* and 16 atoms per unit cell (*oF16*). Furthermore, we show that the same *oF16* structure better fits the published diffraction data from the collapsed phases of Dy, Ho, Er, and Tm as well as data we have collected from the collapsed phase of Gd. The *oF16* structure comprises a stacking of eight quasi-close-packed layers and is isosymmetric with the structures found previously in Pu, Cf, Am, and Cm—although with a four-layer stacking sequence in those cases (*oF8*). We show that the *hP3* structures of Nd, Sm, and Yb comprise a similar three-layer stacking sequence of the same quasi-close-packed layers, and hence that the *hP3*, *oF8*, and *oF16* structures form a new family of layered elemental crystal structures, differing only in the stacking sequence of their atomic layers.

The correct determination of the structures of the collapsed phases of Nd, Gd, Tb, Dy, Ho, Er, and Tm greatly strength-

ens the structural systematics within the lanthanide series, whereas also revealing very much stronger structural links with the actinide elements. Electronic structure calculations using the correct structure for the collapsed phases of Tb, Dy, and Gd provide new insight into the behavior of the 4*f* electrons at high density and provide an explanation for the unusual magnetism seen in the collapsed phases of these elements.

II. EXPERIMENT

We focused our experimental study on the collapsed phase of Tb, which is obtained at a lower pressure (~ 50 GPa) than in other lanthanides [26] thereby enabling the highest-quality diffraction data to be collected and which is reported to have an unusual magnetic state [12]. We conducted experiments on two separate Tb samples, reaching a maximum pressure of 110 GPa at 300 K. High-purity distilled samples were loaded into two diamond-anvil cells in a dry argon atmosphere (< 1 ppm O_2 and < 1 ppm H_2O) to prevent oxidation. The first sample was loaded without a pressure medium but with a small piece of Ta foil as a pressure calibrant. The second sample was loaded in a He pressure medium without any pressure calibrant. Diffraction data were collected on the high-pressure ID09 beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble, (samples 1 and 2) and on the high-pressure I15 beamline at the Diamond Light Source (DLS) in the United Kingdom (sample 1). Monochromatic x-ray beams of wavelength $\lambda = 0.411\,77\text{ \AA}$ (ESRF) and $0.424\,54\text{ \AA}$ (DLS), focused down to a FWHM of $10\text{ }\mu\text{m}$ (ESRF) and $20\text{ }\mu\text{m}$ (DLS) were used, and the powder-diffraction data were recorded on MAR345 (DLS) and Mar555 (ESRF) area detectors, placed ~ 350 mm from the sample. The sample pressure in sample 1 was derived from the published Ta equation of state [27], whereas the pressure in sample 2 was determined from the Tb equation of state established using sample 1. The data used to solve the structure were obtained from sample 2. The two-dimensional (2D) diffraction images were integrated using FIT2D [28], and the resulting one-dimensional profiles were analyzed using Rietveld and Le Bail fitting techniques [29] as well as least-squares fitting to the positions of individual diffraction peaks.

III. EXPERIMENTAL RESULTS

On compression, the onset of the transition to the collapsed phase was seen at 54(1) GPa, and single-phase diffraction patterns from it was seen above 64 GPa. The diffraction pattern from Tb at 64 GPa is shown in Fig. 2 with inset (a) showing a Rietveld fit of the reported *mC4* structure to the midangle region of this profile. This structure completely fails to fit the pattern above $2\theta = 16^\circ$ (see Fig. S1 for the *mC4* fit to the full profile in the Supplemental Material [25]). In particular, there is a clear doublet at $2\theta = 18^\circ$, the higher-angle peak of which cannot be unaccounted for by the *mC4* structure. The same doublet is evident in the published diffraction patterns from the collapsed phases of Dy, Ho, Er, and probably Tm (as detailed in the Supplemental Material [25]), whereas the diffraction data we have collected from the collapsed phase of Gd also exhibit the same doublet (Fig. S2 of the Supplemental

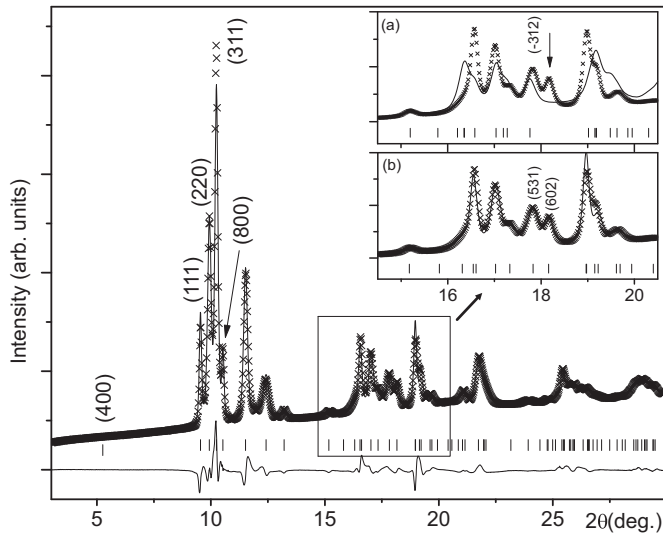


FIG. 2. Rietveld refinement of the *oF16* structure to the Tb diffraction data at 64 GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions (vertical lines), principal Miller indices, and difference profile (lower line). Space-group *Fddd*, Tb on $16e(x, 0, 0)$ sites with $x = 3/16$ (fixed), $a = 17.950(2)$, $b = 4.933(1)$, $c = 2.899(1)$ Å. The insets show Rietveld fits to the midangle region of the profile using (a) the *oC4* structure and (b) the *oF16* structures. The fit in (a) is clearly very poor, and among other misfits, the *mC4* structure cannot account for the clear doublet at 18° . The fit provided by the *oF16* structure is much better, and the doublet arises from the (531) and (602) peaks.

Material [25]). The presence of this doublet shows that *none* of the collapsed phases of Gd to Tm have the long-reported *mC4* structure.

Ab initio indexing of the Tb data obtained at 64 GPa showed that all of the peaks could be accounted for by an orthorhombic unit cell with $a = 17.950(2)$, $b = 4.933(1)$, $c = 2.899(1)$ Å. The same cell fitted data collected to 110 GPa. The observed peaks and density uniquely identified the space group as *Fddd* with 16 atoms/cell. Placing the atoms on the $16e$ site at $(x, 0, 0)$ gave an excellent fit with x refining freely to 0.1874(4). The resulting structure comprises eight layers of quasi-close-packed atoms stacked along the a axis. If $x = 3/16 = 0.1875$, then these layers are evenly spaced at $x = 1/16, 3/16$, etc., and the intensity of the low-angle (400) peak at $\sim 5^\circ$ (see Fig. 2) is exactly zero. Lengthy x-ray exposures revealed no evidence of the (400) peak at any pressure, and so we have fixed $x = 3/16$. The final Rietveld refinement with the *oF16* structure is shown in Fig. 2.

This *oF16* unit cell is closely related to that of the previously reported *mC4* cell, which is pseudo-orthorhombic [25] and fits all observed peaks, including the problematic doublet with high precision [see inset (b) in Fig. 2]. The *oF16* structure also fits our own data from the collapsed phase of Gd [25], and it explains the doublets visible in the reported diffraction patterns from Gd, Ho, Er, and (probably) Tm [25]. The collapsed phases of Gd-Tm, therefore, all have the *oF16* structures.

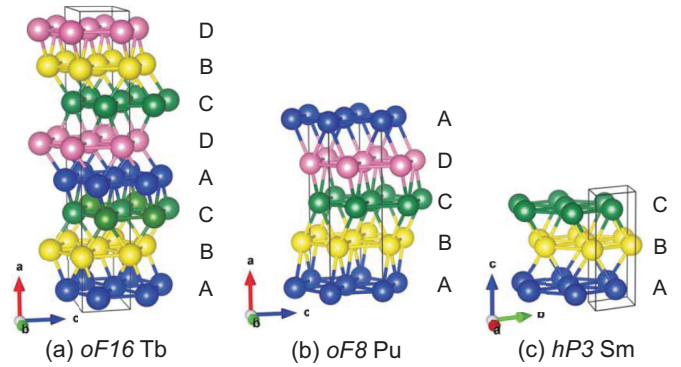


FIG. 3. The *oF16* structure of Tb at 64 GPa, the *oF8* structure of Pu at ambient pressure, and the *hP3* structure of Sm at 47 GPa, all shown on the same scale. The structures each comprise stackings of quasi-close-packed hexagonal planes but with different stacking sequences. In all three structures, the atoms within each layer are stacked over the saddle point of two atoms in the preceding layer, resulting in tenfold coordination. This differs from the stacking of the layers of hcp and fcc, etc., where the atoms are stacked over the midpoint of three atoms in the previous layer and the resulting coordination is 12-fold.

The *oF16* structure of Tb comprises eight quasi-close-packed layers ($b/c \sim \sqrt{(2.9)} \sim \sqrt{3}$) stacked along the a axis [see Fig. 3(a)]. Rather than the stacking seen in fcc, hcp, dhcp, etc., where atoms in the close-packed layers are located above the midpoint among three atoms in the previous layer, in the *oF16* structure, the atoms are located above the saddle point between two atoms in the previous layer. This results in tenfold ($6 + 2 + 2$) coordination, and the possibility of each layer to choose among three different positions relative to the previous layer. As a result, the *oF16* structure of Tb has an eight-layer ABCADCBD repeat. Exactly the same type of layer stacking is seen in the isosymmetric *oF8* structure of Pu (which is also seen in Am, Cm, and Cf on compression [8–10]), although this structure has only a four-layer ABCD repeat [Fig. 3(b)].

It is possible to predict other members of the same structural family, such as structures having three-layer (ABC) or six-layer (ABCADC) stacking sequences. Analysis of the *hP3* structure reported in Nd, Sm, and Yb shows that this is the three-layer ABC structure [Fig. 3(c)] [30]. We note that the *hP3* phase of Nd has recently been reported to exhibit the same rapid increase in magnetic ordering temperature seen in the *oF16* phases of Tb and Dy [31], whereas the ordering temperature in *hP3*-Sm is relatively unchanged with pressure [32].

Furthermore, the monoclinic phase of Cm-III (space-group *C2/c*), which is stabilized by spin polarization of its $5f$ electrons, has a very similar structural motif to *hP3* [9], whereas the structure of Sc found above 240 GPa is only slightly distorted from *hP3* [33]. The collapsed phases of the regular trivalent lanthanides, divalent Yb, Pu at ambient pressure and high temperature, Am, Cm, and Cf on compression, and Sc at extreme pressures are, thus, all members of this new family of elemental structures. The six-layer ABCADC structure, and other possible members, remain to be identified.

The *oF*16 structure has not been reported previously in the elements, but was predicted to be a high-pressure form of Y, with the *oF*16 and *hP*3 phases being energetically favorable at pressures over 97 GPa [34]. Although the similarity in the enthalpies of these two structures is perhaps not surprising given the structural similarities revealed here, the same calculations showed that the *oF*8 form of Y would have a somewhat higher enthalpy and was unlikely to be observed. We note that the experimentally determined structure of collapsed Tb above 100 GPa is the same *mC*4 structure of collapsed Tb, etc. [35]. New data are required to determine whether this phase too has the *oF*16 structure, which would further strengthen the structural systematics of Y and Sc with those of the lanthanides and actinides.

Finally, we address the structures of the collapsed *mC*4 phases of Nd and Sm which are obtained via a transition from the lower-pressure *hP*3 phase (Fig. 1). The diffraction patterns of *mC*4-Nd [36] and *mC*4-Sm [37] are both very different from each other and from those reported in the higher-Z lanthanides. The lattice parameters of *mC*4-Nd and *mC*4-Sm are also very different ($\beta = 118.6^\circ$ in Nd at 89 GPa [36], and $\beta = 112.8^\circ$ in Sm at 109 GPa [37]). However, the published diffraction pattern from *mC*4-Nd is strikingly similar to that reported for *oF*8-Am [8], and there is a clear relationship between the *mC*4 and the *oF*8 unit cells [25]. As a result, Nd at 89 GPa can be fitted with the *oF*8 structure of γ -Pu with $a = 2.7160(1)$, $b = 4.8473(2)$, and $c = 8.8618(2)$ Å [25]. The $P6_22$ and $Fddd$ space groups of *hP*3-Nd and *oF*8-Nd are not group-subgroup related, but the previous determination of the equation of state of Nd to 155 GPa [22] revealed that there is no volume discontinuity at the *hP*3 $\rightarrow$ *oF*8 transition, a result which, due to the close similarities of the lattices of the *mC*4 and *oF*8 structures [25], is unaffected by whether the higher-pressure phase is indexed as orthorhombic or monoclinic.

This first observation of the *oF*8 structure in a lanthanide element further strengthens the structural similarities of the lanthanide and actinide series and reveals that the three-, four-, and eight-layer structure types are all observed in the lanthanide elements. Further studies will be required to determine the true structure of the post-*hP*3 phase of Sm, which has recently been shown to exhibit the rapid increase in magnetic ordering temperature seen in the *oF*16 phases of Tb and Dy [32].

IV. ELECTRONIC STRUCTURE CALCULATIONS

The calculations of Chen *et al.* on Y showed that the shift of the *d*-electron energy levels and *s*-to-*d* electron transfer gave rise to the stability of the *oF*16 and *hP*3 structures. As Y has no *f* electrons, their role in stabilizing the *oF*16 structure in the lanthanides was undetermined. To address this, we have performed extensive density-functional theory (DFT) and dynamical mean-field theory (DMFT) calculations of the *oF*16 phases of Tb, Gd, and Dy.

Structural optimization of bulk Tb in the *mC*4 and *oF*16 phases was accomplished by using spin-polarized DFT calculations with the help of the VASP [38] package using the Perdew-Burke-Ernzerhof functional [39]. The many-body properties of the *mC*4 and *oF*16 phases were further investigated by using a recent implementation of DFT + DMFT

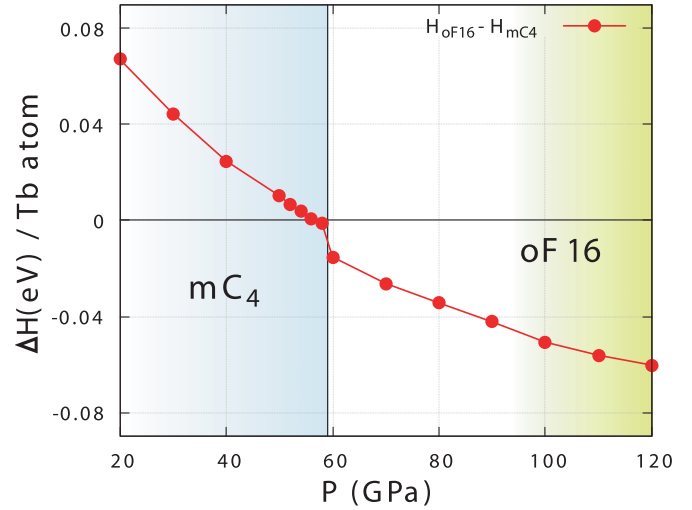


FIG. 4. The enthalpy difference per Tb atom as a function of pressure as predicted by magnetic DFT. The calculations were performed at 0 K.

in the CASTEP code [40–42]. The *k*-point sampling was performed using a Monkhorst-Pack mesh of $8 \times 8 \times 8$ for the *oF*16 and $10 \times 10 \times 6$ for the *mC*4 structures, respectively, and a Gaussian smearing of 0.1 eV. Convergence in DFT over the *k* points was achieved within 1 meV per atom, and the energy cutoff was 800 eV. Scalar relativistic spin-orbit coupling was taken into account within the Koelling-Harmon approximation [43].

In the DMFT, we used the Hubbard I solver, valid for *f* elements. In this paper, we focused on the DMFT approach within the framework of fixed Kohn-Sham potentials, the so-called “one-shot” DFT + DMFT method. This has been shown to predict the equilibrium volume and bulk modulus for *f* materials that are in excellent agreement with experimental data [40]. We use typical values for the Coulomb repulsion ($U = 6$ eV) and Hund’s coupling ($J = 1$ eV). Throughout this paper, we performed DFT + DMFT calculations with fixed charge and used the fully localized limit type of double-counting corrections.

Zero-temperature DFT calculations for Tb confirmed that the *oF*16 phase is stable with respect to *mC*4 above 60 GPa (see Fig. 4), and the predicted atomic volume of the *oF*16 phase is in good agreement with the room-temperature experimental data. Calculations of the phonon spectrum of *oF*16-Tb at 80 GPa (see Fig. S6 of the Supplemental Material [25]) structure verified its stability (no soft phonons). We see no evidence of the *mC*4 phase at any pressure in our (room-temperature) diffraction studies. The ground states of both the *mC*4 and the *oF*16 phases are calculated to be ferromagnetic, but in the *oF*16 phase between 60 and 80 GPa, the energy difference between the ferromagnetic and antiferromagnetic (AF) state is on the order of room temperature, suggesting that competition between these different magnetic states might occur in this pressure range. This may account for the highly nonmonotonic behavior of the magnetic ordering temperature observed in Tb near 70 GPa by Lim *et al.* [44]. Remarkably, the AF phase in Tb is stabilized via a gain of internal electronic energy but at the cost of a lattice expansion. This

rules out the possibility for AF order at higher pressures. In Gd, however (see the discussion below), the AF order is concomitant with a reduction of the volume and, hence, is naturally stabilized at higher pressures.

We emphasize that the remarkable agreement between theory and experiments can only be achieved within spin-polarized DFT which accounts for the strong magnetic moments due to f electrons: The simpler nonmagnetic DFT approach does not provide a reasonable equation of state, confirming the importance of magnetism for the structural properties above 60 GPa. Indeed, the volume obtained at 60 GPa in nonmagnetic calculations is 14% lower than the experimental value, whereas magnetic calculations calculate the atomic volume to within 1.5% of the experimental value.

Although the magnetism in Tb is not stable at room temperature, at which our experiments have been carried out, a local fluctuating magnetic moment due to f states is expected to persist in the paramagnetic state at 300 K. It is, therefore, important to properly describe the dynamical fluctuations of local magnetic moments within the theoretical framework, which is not achievable within DFT calculations and requires extensions.

For this, we carried out DFT + DMFT calculations at room temperature. Figure 5 shows the calculated spectral weight in the paramagnetic DFT + DMFT solution. Although the DMFT approximation does not have long-range magnetic order, it describes the fluctuations of the local magnetic moment of the Tb atoms. Note that, in DMFT, we observe sharp resonances corresponding to the splitting of the f states into magnetic multiplets [see Fig. 5(a)] with the majority spin states at -5 eV and the minority spin states at $+7$ eV.

Additionally, we also obtain a sharp peak at the Fermi level [at $\omega = 0$, see Fig. 5(a)]. This narrow feature is absent at simpler levels of approximations (such as DFT), and, although it does not impact on averaged quantities, such as forces or magnetism, it sheds light on possible emerging excitations, important for thermomechanical constants and specific-heat coefficients.

The picture of the collapsed phase of Tb that emerges from our calculations is that of a lattice of unscreened weakly coupled local moments embedded in a delocalized d -conduction band with a large bandwidth. As discussed in the DFT context, the unscreened moments are key for the correct description of the structure at high pressure. On compression (see Fig. S5 in the Supplemental Material [25]), we observe only minor changes in the overall spectral weight, and the magnetic moment remains a sextet $S = \frac{5}{2}$ at all pressures studied.

Our finding that the collapsed phases of Dy and Gd also have the $oF16$ structures prompted us to expand our DFT calculations to these two elements, which are reported to exhibit different magnetic behaviors under pressure [44]. At 90 GPa and 0 K, our calculations confirm the $oF16$ phase is energetically favorable compared to the $mC4$ phase in both Dy and Gd—although, in Gd, the $mC4$ phase is calculated to be more stable below 90 GPa. Our room-temperature diffraction studies of Gd see no evidence of the $mC4$ phase at any pressure.

At 90 GPa and 0 K, $oF16$ -Gd is calculated to be a type-A antiferromagnet, whereas $oF16$ -Dy is calculated to be a ferromagnet. This contrasts with the results for Tb which

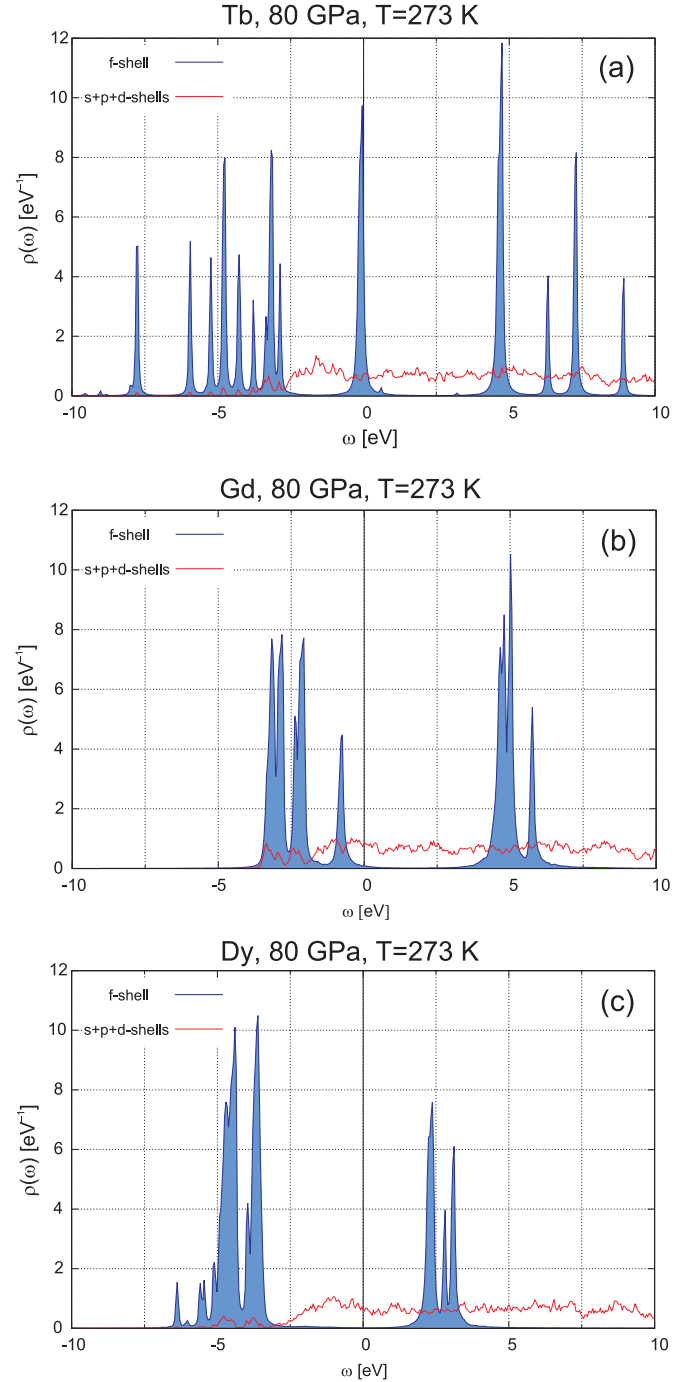


FIG. 5. DMFT spectral weight $\rho(\omega)$ obtained at room temperature and 80 GPa for the $oF16$ phases (a) Tb, (b) Gd, and (c) Dy. The sums of the s , p , and d orbitals are shown in red, and the sums of the f orbitals are shown in blue.

identify it as a Kondo ferromagnet, nearly degenerate with an antiferromagnetic state between 60 and 80 GPa. Our calculations show that the magnetic order in Dy is much more robust than in Tb and Gd, in agreement with the higher magnetic ordering temperature observed by Lim *et al.* [44]. Indeed, the enthalpy difference in Dy between the ferromagnetic and antiferromagnetic states is 0.14 eV/atom, whereas in Tb and Gd it is $\approx |0.06|$ eV/atom at 110 GPa.

For all three elements, the spin magnetic moment of the f shell persists at room temperature at 80 GPa— $S = 3\mu_B$ in Gd, $S = 2.5\mu_B$ in Tb, and $S = 2\mu_B$ in Dy, although the long-range magnetic order is lost. These magnetic moments are approximately $0.5\mu_B$ smaller as compared to the respective free ions due to the transfer of approximately one electron from the f shell to the d shell as a consequence of applied pressure. However, the different magnetic behaviors of the materials can be inferred by their different paramagnetic properties. In particular, as antiferromagnetism is stabilized by Ruderman-Kittel-Kasuya-Yosida processes [45,46] mediated by conduction electrons, the hybridization between f and d states is key to obtaining antiferromagnetic order. Our calculations reveal that the f and d states are indeed hybridized in Gd [see Fig. 5(b)], whereas such hybridization is absent in Dy [see Fig. 5(c)]. Indeed, in Dy, the f states are below the Fermi level (between -7 and -3 eV) and are very weakly hybridized to the d states as the weight of these states is weak in this energy window [see the red curve in Fig. 5(c) between -7 and -3 eV].

V. CONCLUSIONS

The assignment of the $oF16$ structure to the collapsed phases of Tb, Gd, Dy, Ho, Er, and Tm rewrites the long-established structural systematics of the lanthanide elements, whereas the $oF16$ structure's close similarity to the isosymmetric $oF8$ structure seen in Pu, Am, Cf, and Cm reveals a previously unrecognized relationship between the high-pressure phases of the lanthanide and actinides series. This is reinforced further by the discovery that the highest-pressure phase of Nd also has the same $oF8$ structure and that the $oF16$ and $oF8$ structures and the $hP3$ structure found in Nd, Sm, and Yb, are all members of a new family of elemental crystal structures. Further members of this family are predicted and remain to be discovered.

State-of-the-art quantum many-body calculations using the correct structure for the collapsed phase provide new insights into the physics of f elements at high pressure and, in particular, highlight that Kondo-type physics, and more generally magnetism, can be sustained at extreme pressure, a question that has long eluded scientists of the field as emergent quantum phenomena, such as the Kondo effect, are associated with exponentially low-energy scales. The joint experimental and theoretical approach confirms that magnetism of the $4f$ electrons is correctly accounted for, and a classification of typical lanthanides has been obtained in terms of ferromagnetism, antiferromagnetism, and Kondo behaviour for Dy, Gd, and Tb, respectively. The interplay between structural properties and electronic properties accounts for the stability of antiferromagnetism in Gd, absent in Tb.

Note added in Proof. New diffraction data from the collapsed phases of Sm at 175 GPa and Y at 125 GPa suggest that they have the $oF8$ and $oF16$ structures, respectively [54].

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High-pressure structural systematics in samarium up to 222 GPa

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Angle-dispersive x-ray powder diffraction experiments have been performed on samarium metal up to 222 GPa. Up to 50 GPa we observe the Sm type (*hR9*) → *dhcp* (*hP4*) → fcc (*cF4*) → distorted fcc (*hR24*) → *hP3* transition sequence reported previously. The structure of the high-pressure phase above 93 GPa, previously reported as having a monoclinic structure with space group *C2/m*, is found to be orthorhombic, space group *Fddd*, with eight atoms per unit cell (*oF8* in Pearson notation). This structure is the same as that found in Am, Cm, and Cf at high pressures. Analysis of samarium's equation of state reveals marked changes in compressibility in the *hP3* and *oF8* phases, with the compressibility of the *oF8* phase being that of a “regular” metal.

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I. INTRODUCTION

The lanthanide series of elements is characterized by the monotonic filling of the 4*f* electron shell, and the members of the series play an important role in many modern technologies, including high-performance permanent magnets, catalysts, and computer memories. As one traverses the series, the predominantly trivalent lanthanide elements (La to Lu, excluding Ce, Eu, and Yb) exhibit a reduction in their atomic radii, the well-known lanthanide contraction, and a change in the ambient-conditions crystal structure that correlates with changes in the *d*-band occupancy [1]. The same structural sequence—*hcp* → Sm type → *dhcp* → fcc → distorted fcc (*hP2* → *hR9* → *hP4* → *cF4* → *hR24* in Pearson notation)—can be induced via compression in individual lanthanide elements as a result of increased occupation of the 5*d* states arising from pressure-induced *s*- to *d*-electron transfer [2,3]. The structures of all these phases comprise different stackings of close-packed or quasi-close-packed layers, and Raman scattering studies on Sm to 20 GPa [4] have reported that the structural sequence involves softening of optical and acoustic modes, implying also anomalies in the elastic behavior of the different phases. There are no measurable volume changes between the phases, but further compression of the *hR24* phase results in first-order phase transitions to the

so-called collapsed phases, the lower-symmetry structures of which have long been reported to arise from the participation of 4*f* electrons in the bonding [5], although more recent studies have questioned this [6–9].

In Nd and Sm, the initial post-*hR24* phase is reported to be rhombohedral with space group *P3₁21* and three atoms per unit cell (*hP3* in Pearson notation) and is obtained via a small volume change of ~0.4% [10]. On further compression, these two elements are then reported [11] to transform into a monoclinic structure (space group *C2/m*, *mC4* in Pearson notation) first observed in Ce at high pressure over 40 years ago [12]. The same *mC4* structure is reported in the collapsed phases of Gd, Tb, Dy, Ho, Er, and Tm, all of which are obtained via a direct first-order transition from the *hR24* phase rather than via the intermediate *hP3* phase [13–17].

We recently showed that the long-reported *mC4* structure is incorrect in Tb and also in Gd, Dy, Ho, Er, and Tm and that the true structure of these collapsed phases is orthorhombic, space group *Fddd*, with 16 atoms per unit cell (hereafter *oF16*) [18]. While isosymmetric with the eight-atom *Fddd* structure (hereafter *oF8*) found in Am, Cm, and Cf at high pressures [19–21], the *oF16* structure comprises an eight-layer ABCADCBD stacking of quasi-*hcp* layers, as opposed to the four-layer ABCD repeat seen in *oF8* (see Fig. 1). However, the nature of the stacking in the two structures is the same, with the atoms in each layer centered above the midpoint of two atoms in the previous layer, resulting in both having tenfold (6+2+2) coordination. We have also

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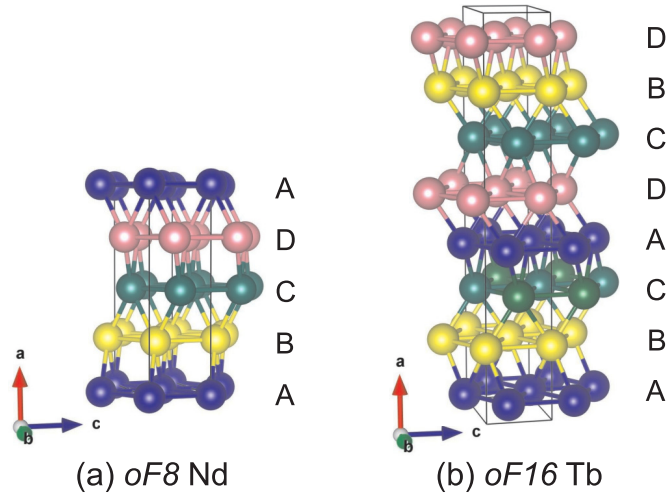


FIG. 1. The crystal structures of (a) *oF8*-Nd at 89 GPa and (b) *oF16*-Tb at 64 GPa. The structures are isosymmetric with the *Fddd* space group and differ in the stacking of their flat, hcp-like atomic layers: the stacking sequence in *oF8* is ABCD, while in *oF16* it is ABCADCBD.

reported that the *hP3* structure of Sm actually has space group *P6₂22* rather than *P3₁21* and that it has the same stacking as the *oF8* and *oF16* structures, although with a three-layer ABC stacking sequence [18]. Finally, we have noted that the reported diffraction profiles from the *mC4* phase of Nd [22] are remarkably similar to those from the *oF8* phase of Am, Cm, and Cf and that the published *d* spacings of Nd at 89 GPa [22] can be fitted perfectly with this orthorhombic structure [18]. The collapsed *oF8*, *oF16*, and *hP3* phases are thus all members of the same family of quasi-close-packed layer structures, differing only in the stacking sequence of the layers. The same structures are also seen in both the lanthanide and actinide elements.

The single trivalent lanthanide element whose high-pressure behavior does not seem to follow the same structural sequence is Sm [11]. While the post-*hP3* phase is reported to have the same *mC4* structure initially found in Nd [22], the reported diffraction patterns from Sm are dissimilar to those obtained from any other collapsed phase [11], including Nd, suggesting it has neither the *oF16* nor the *oF8* structure. To investigate whether Sm does, indeed, have a different sequence of high-pressure phases to any other lanthanide element, we have performed x-ray powder diffraction studies of Sm to 222 GPa. We find that the post-*hP3* phase does, indeed, have the same *oF8* structure seen in Nd, Am, Cm, and Cf and that this phase is stable to at least 222 GPa. We suggest that the diffraction pattern reported previously as coming from the *mC4* phase was, in fact, from a mixed-phase sample of *hP3* and *oF8*.

II. EXPERIMENTAL DETAILS

High-purity distilled samples of Sm supplied by Ulrich Schwarz at the Max-Planck-Institut für Chemische Physik fester Stoffe in Dresden were loaded into three diamond-anvil cells (DACs) in a dry argon atmosphere (<1 ppm O₂ and <1 ppm H₂O) to prevent oxidation. The DACs were equipped

with beveled diamonds with 100- μ m culets and tungsten gaskets. The samples were loaded without any pressure medium but with a small copper sphere to act as a pressure calibrant, using the recently published Cu equation of state of Sokolova *et al.* [23].

Diffraction data were collected in two experiments on the Extreme Conditions P02.2 beamline at the PETRA III synchrotron in Hamburg and in a third experiment on the high-pressure I15 beamline at the Diamond Light Source (DLS) in the United Kingdom. Monochromatic x-ray beams with wavelengths of 0.2898 and 0.4808 Å (PETRA III) and 0.4248 Å (DLS), focused down to $3 \times 6 \mu\text{m}^2$ and $0.85 \times 0.85 \mu\text{m}^2$ (PETRA III) and $20 \times 20 \mu\text{m}^2$ (DLS), were used, and the powder-diffraction data were recorded on Perkin-Elmer (PETRA-III) and Mar345 (DLS) area detectors, placed 300–400 mm from the sample. CeO₂ and LaB₆ diffraction standards were used to calibrate the exact sample-detector distances and the detector tilts. The two-dimensional diffraction patterns collected at each pressure were integrated azimuthally using FIT2D [24] and DIOPTAS [25] to obtain standard one-dimensional diffraction profiles, which were then analyzed using Rietveld and Le Bail methods or by fitting to the *d* spacings of individual diffraction peaks.

The submicron-diameter beam on the Extreme Conditions P02.2 beamline is a recent development ideally suited to high-pressure diffraction experiments above 200 GPa. The small beam minimizes parasitic scattering from the high-Z metallic gasket surrounding the sample, minimizes pressure gradients in the diffracting sample volume, and also enables calibrant-free diffraction patterns to be obtained from the sample if required. Focusing is achieved by first cutting down the x-ray beam size ~ 35 m from the source to approximately $0.05 \times 0.05 \text{ mm}^2$ before using 136 Be compound refractive lenses [26], optimized for use at a fixed x-ray wavelength of 25.6 keV (~ 0.48 Å), to focus only the coherent part of the beam to $0.85 \times 0.85 \mu\text{m}^2$ (FWHM) over a focal length of 360 mm (Fig. 2). Finally, the focused beam is passed through a 15- μ m-diameter pinhole immediately before the DAC in order to trim its tails. We have found that a 15- μ m pinhole provides the optimum trade-off between x-ray flux and the intensity of the parasitic scattering from the W gasket.

III. DISCUSSION

Diffraction patterns were first collected from the *hP3* phase below 50 GPa to ensure results consistent with those collected previously by Husband *et al.* [27]. The transition to the *hP3* phase was observed at 42(5) GPa, in excellent agreement with previous studies [27]. Analysis of the *hP3* patterns confirmed that the systematic absences were consistent with space group *P6₂22* rather than *P3₁21*.

On further compression above 50 GPa (see Fig. 3), evidence of the post-*hP4* phase was first observed at 93(4) GPa [Figure 3, profile (c)]. The peaks from the post-*hP3* phase increased in intensity on further compression [Figure 3, profiles (d)–(f)], and single-phase profiles were obtained above 157 GPa [Figure 3, profile (g)]. No further changes were observed up to 222(2) GPa, the highest pressure reached in this study.

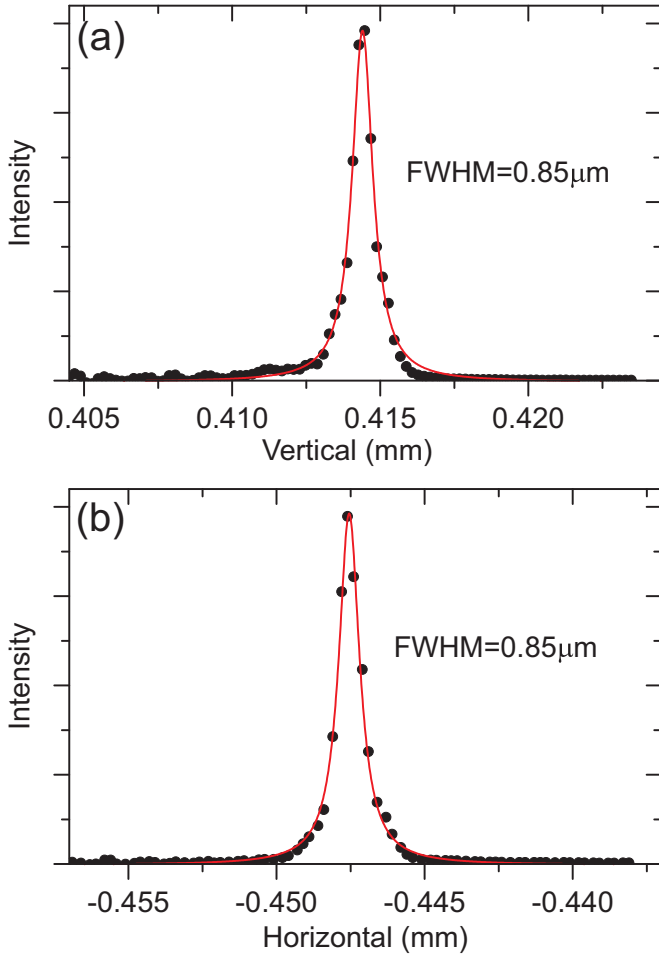


FIG. 2. Scans across the microfocused x-ray beam on the P02.2 beamline, both (a) vertically and (b) horizontally. The exact beam size in each direction varies from experiment to experiment but is typically $0.85 \times 0.85 \mu\text{m}^2$ FWHM, as shown by the two Lorentzian curves.

The single-phase diffraction profiles obtained above 157 GPa are remarkably similar to those obtained from the *oF8* phase of Nd [22]. Figure 4 shows a Rietveld fit of the *oF8* structure to the diffraction profile from Sm at 175(2) GPa, where the refined lattice parameters are $a = 8.4250(9)$ Å, $b = 4.5531(3)$ Å, and $c = 2.5227(2)$ Å and $V/V_0 = 0.364(2)$, with atoms on the $8a$ site at (0,0,0). The fit is excellent, with all of the observed diffraction peaks being indexed.

The *oF8* structure of Sm and Nd and the *oF16* structure of Tb (see Fig. 1) both comprise stackings of flat, quasi-close-packed layers, the distortion of which from hexagonal symmetry can be quantified by the deviation of the b/c ratio from the ideal orthohexagonal value of $\sqrt{3} = 1.732$. The pressure dependence of the b/c ratio in *oF8*-Sm is shown in Fig. 5, along with the ideal value of $\sqrt{3}$ in the *hP3* phase. There is a clear discontinuity in the “hexagonality” of the atomic layers from 1.732 to ~ 1.78 at the *hP3* $\rightarrow$ *oF8* transition, after which the distortion grows slowly and monotonically to reach a maximum value of 1.818(5) at 222 GPa. Our fit to the Nd diffraction pattern reported by Akella *et al.* at 89 GPa [22]

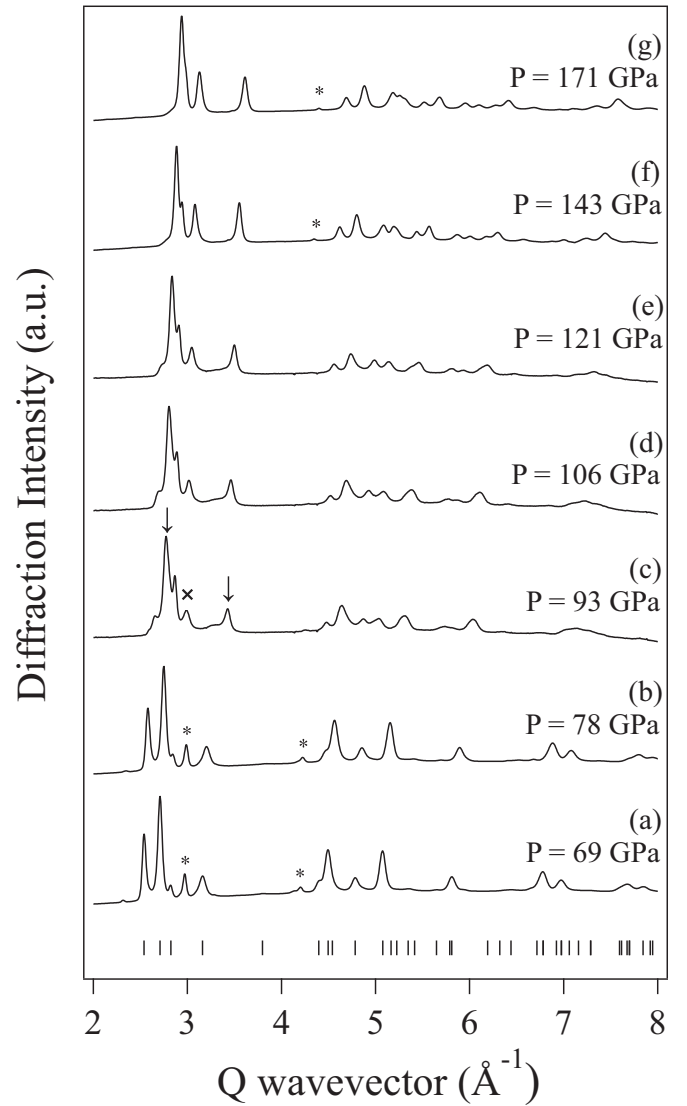


FIG. 3. Diffraction profiles collected from Sm on a pressure increase. The data were collected from the same sample during two different synchrotron visits and so are plotted as a function of wave vector Q in order to take into account the two different x-ray wavelengths used. Tick marks beneath profile (a) mark calculated peak positions from the *hP3* phase. The peaks marked with asterisks are from the W gasket. The arrows in profile (c) mark the first appearance of peaks from this phase. The reflections labeled with a cross in profile (c) indicate a doublet including the (101) peak from the W gasket and a peak from the post *hP3* phase. A single phase pattern of the post-*hP3* phase is seen in profile (g).

revealed a ratio of 1.7847(1) at that pressure [18], the same as that observed in *oF8*-Sm at ~ 132 GPa.

The similarity of the *oF8*-Sm diffraction patterns reported here to those published previously from *oF8*-Nd above 75 GPa [22] raises the question of why the reported *mC4* structures from the two phases were previously very different [11,22]. However, it is clear that the diffraction pattern reported from Sm at 109 GPa [11] is not from a single-phase sample of *oF8*-Sm. Comparison of the 109 GPa diffraction pattern reported by Chesnut [11] with the mixed *hP3*-*oF8* profile obtained in the current study at 106 GPa [see Fig. 3,

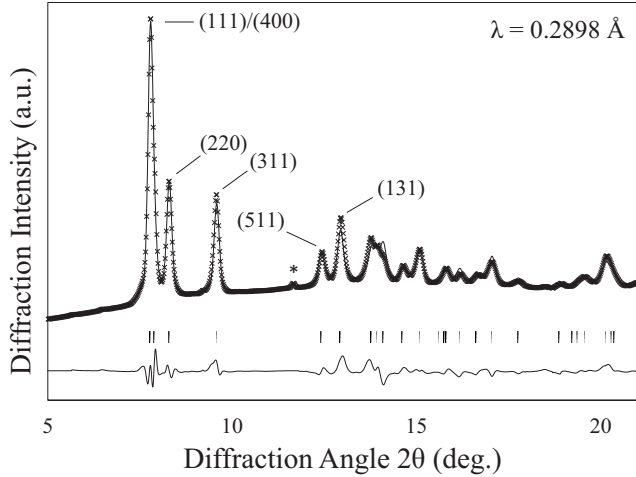


FIG. 4. Rietveld refinement of the *oF8* structure to a diffraction profile from Sm at 175 GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile ($R_p = 2.1\%$, $R_{wp} = 3.1\%$, $R_E = 2.8\%$, goodness of fit (GoF) = 1.09, and $R(F^2) = 7.2\%$). The first six peaks of the *oF8* phase are labeled with their Miller indices, and the asterisk identifies the (200) peak from the W gasket [the (110) peak from the gasket is overlapped by the (220) reflection from Sm].

profile (d)] reveals them to be very similar. A two-phase *hP3-oF8* Le Bail fit to this profile is shown in Fig. 6, which reveals that all of the observable peaks are explained by the two-phase model. We therefore suspect that Chesnut's analysis at 109 GPa was hampered by the use of a profile

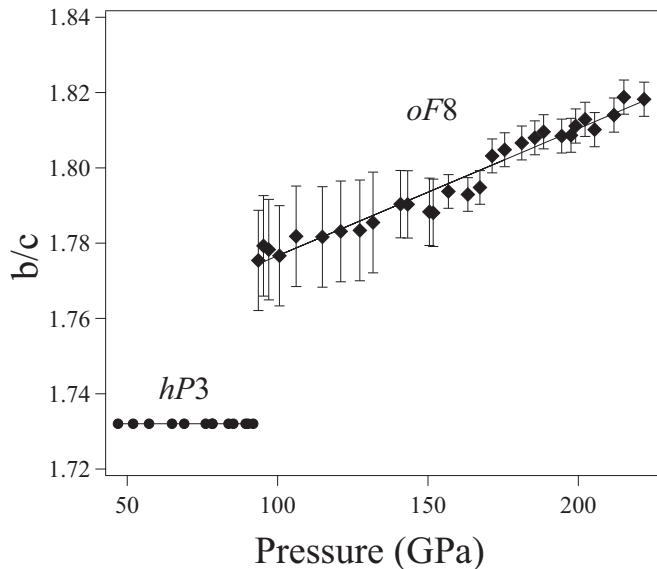


FIG. 5. The pressure dependence of the hexagonality of the atomic layers in the *oF8* phase of Sm. The distortion in the *oF8* phase can be quantified by the deviation of the b/c ratio from the ideal orthohexagonal value of $\sqrt{3}$ (1.732). The atomic layers in the *hP3* phase have perfect hexagonal symmetry and hence have the ideal orthohexagonal value. The discontinuity in the geometry of the layers at the *hP3* $\rightarrow$ *oF8* transition at 93 GPa is very clear and suggests that the transition is not continuous.

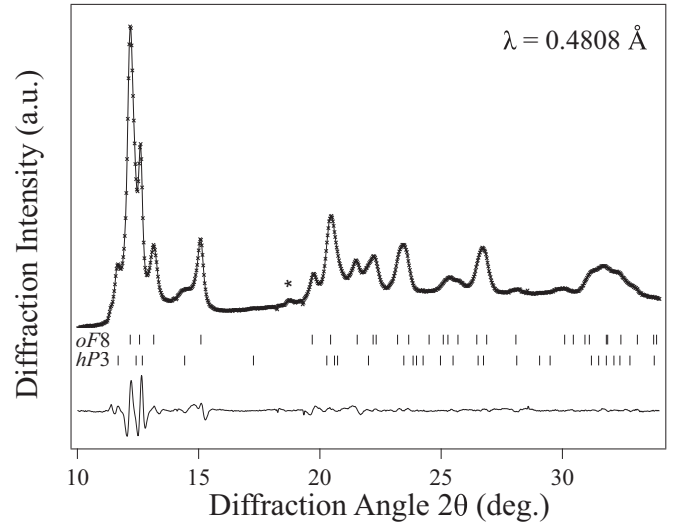


FIG. 6. Le Bail fit of the *hP3* and *oF8* structures to a mixed-phase diffraction profile from Sm at 106 GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated peak positions of the two phases, and the difference profile. The asterisk identifies the (200) peak from the W gasket. This is the same profile as that shown in Fig. 3(d).

from a mixed-phase sample. Unfortunately, while that study attained pressures of 200 GPa, where single-phase patterns from the *oF8* phase might be expected, no diffraction profiles were shown above 109 GPa.

The compressibility of Sm to 222 GPa, including the data of Husband *et al.* below 50 GPa [27], is shown in Fig. 7. The similarities of the *hP3* and *oF8* structures, which differ only in the stacking sequence of their hcp-like layers [18], result in a sizable pressure range (for example, 93–157 GPa in one of our samples; see Fig. 3) over which mixed *hP3-oF8* profiles are observed and in extensive peak overlap in this

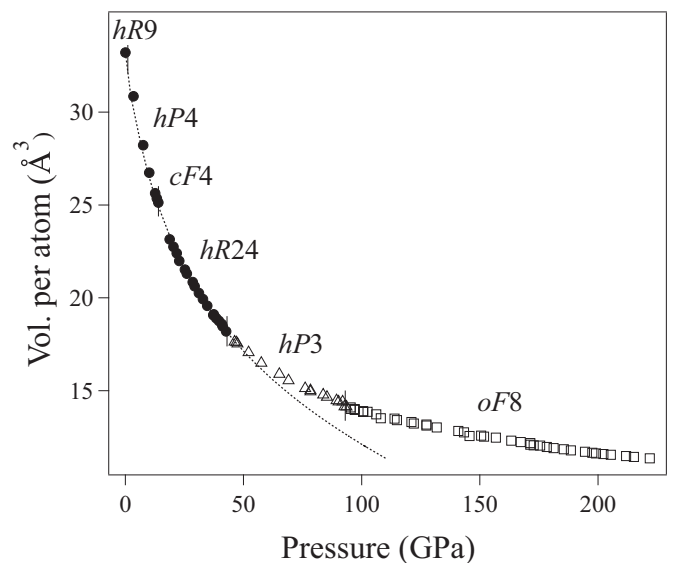


FIG. 7. The compressibility of Sm up to 222 GPa. The dotted line shows the AP2 equation of state obtained from fitting the data to 43 GPa. The misfit beyond 43 GPa can be clearly observed.

mixed-phase region. The $P6_222$ and $Fddd$ space groups are not group-subgroup related, and so the transition between the $hP3$ and $oF8$ structures need not be second order. Indeed, the sharp discontinuity observed in the geometry of the atomic layers at the $hP3 \rightarrow oF8$ transition (Fig. 5) suggests that the transition is not continuous. However, careful analysis of mixed-phase profiles reveals that there is no measurable volume change at the transition, despite the discontinuity in the shape of the atomic layers.

Fits to the compression data of Sm up to 43 GPa (that is, up to the $hR24 \rightarrow hP3$ transition) were made with the second-order (AP2) form of the adapted polynomial of order L (APL) equation of state (EOS) [28]

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

where K_0 is the zero-pressure bulk modulus, K' is its pressure derivative, $x = (V/V_0)^{1/3}$, $c_0 = -\ln(3K_0/p_{FG})$, $c_2 = (3/2)(K' - 3) - c_0$, $p_{FG} = a_{FG}(Z/V_0)^{5/3}$ is the Fermi-gas pressure, Z is the atomic number, and $a_{FG} = [(3\pi^2)/5](\hbar^2/m_e) = 0.02337 \text{ GPa nm}^5$ is a constant. This gave an excellent fit with $K_0 = 33.4(5) \text{ GPa}$ and $K' = 3.08(3)$ [29] (see Fig. 7). However, extrapolation of this EOS to higher pressures revealed an increasingly poor fit, with the compressibilities of both the $hP3$ and $oF8$ phases above 43 GPa being considerably smaller than that predicted from the extrapolation of the AP2 EOS obtained from the data below that pressure (see Fig. 7).

Fits to the full compression curve to 222 GPa using a single AP2 EOS were poor, and the inability of second-order EOSs to fit the Sm compression curve was noted previously by both Zhao *et al.* [30] and Chesnut [11], who subsequently fitted third-order Birch and modified universal EOSs, respectively, to their data. Anomalies in the EOS data for the individual phases of Sm can be most readily visualized by using a simple “linearization” procedure whereby anomalies arising from changes in electronic structure can be distinguished from the “normal” compressive behavior of regular metals [31].

Figure 8 shows the APL linearized compression data for Sm in the form of a $\eta_{APL} - x$ plot,

$$\eta_{APL}(x) = \ln(px^5/p_{FG}) - \ln(1-x), \quad (2)$$

where $x = (V/V_0)^{1/3}$, $p_{FG} = a_{FG}(Z/V_0)^{5/3}$, and $a_{FG} = 0.02337 \text{ GPa nm}^5$, along with similarly linearized data for the “regular” metals Au and Pt [32]. In such a plot, materials undergoing normal compression will show linear or quasilinear behavior, with the correct theoretical limit of $\eta(0) = 0$ at $x = 0$. The behavior of Au and Pt clearly exhibits this form. In marked contrast to the very linear behavior of Au and Pt, the data for Sm exhibit significant curvature, as noted previously by Zhao *et al.* for Sm [30] and by Grosshans and Holzapfel [33] for the trivalent lanthanides in general, and there is a clear change in gradient after the $hR24$ to $hP3$ transition at 43 GPa ($x \sim 0.81$) such that above 65 GPa ($x \sim 0.78$) the data from the $hP3$ and $oF8$ phases show normal linear behavior, extrapolating to $\eta(0) \sim 0$. The $oF8$ phase of Sm might then be regarded as a regular metal.

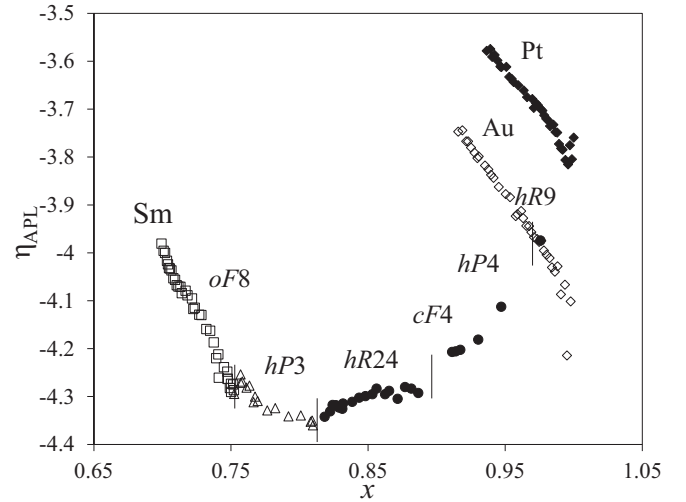


FIG. 8. Linearization of the compression of Sm shown in the form of an $\eta_{APL} - x$ plot. The data from the different phases of Sm are plotted using different symbols, and the “regular” compressibilities of Au and Pt, as calculated from the compression data of Dewaele *et al.* [32], are shown for comparison.

Zhao *et al.* drew attention to these changes in gradient using their data collected over a smaller compression range and using the incorrect structure for Sm above 90 GPa and suggested that they arose from the change in the nature of the bonding in the different phases: from d bonding in $hR24$ to intermediate $4f$ bonding in $hP3$ to itinerant $4f$ bonding in the $oF8$ phase [30]. The valence state of Yb metal has long been known to change on pressure increase [34,35], and Herbst and Wilkins [36] predicted a valence transition in Sm from $3+$ to $2+$ at $\sim 100 \text{ GPa}$, close to the $hP3 \rightarrow oF8$ transition pressure of 92 GPa. Such a divalent state is reported to contribute to the high-temperature magnetic susceptibility of Sm at ambient pressure [37]. Any valence change might be expected to have an effect on the compressibility of Sm, but as shown in Fig. 8, there is no change in behavior at the $hP3 \rightarrow oF8$ transition. Recent L_3 x-ray appearance near-edge structure measurements on Tb to 65 GPa [38] and on Dy to 115 GPa [39] explicitly ruled out the presence of a valence transition in either of these higher- Z lanthanide elements at high pressure. Similar studies are required on Sm to see if it too remains trivalent to the highest pressures.

The data shown by Zhao *et al.* were from a variety of sources and exhibited considerable scatter and, as mentioned, used an incorrect structure for the $oF8$ phase. Our data, collected from three samples of the same ingot, the pressures for which were obtained using the same Cu EOS, show greater consistency, and the changes in gradient in the linearized plot are therefore clearer. Our data to 222 GPa suggest that the discontinuity in incompressibility occurs between 45 and 65 GPa within the $hP3$ phase, with no further change being observed at the $hP3 \rightarrow oF8$ transition at 93 GPa.

As mentioned previously, both Zhao *et al.* [30] and Chesnut [11] found that third-order EOSs provided a better fit to their data, and Fig. 9 shows the fit [29] of a third-order APL (AP3) EOS to the full Sm compression curve with $K_0 = 40.6(11) \text{ GPa}$, $K' = 1.58(6)$, and $K'' = -0.0524(3)$. While

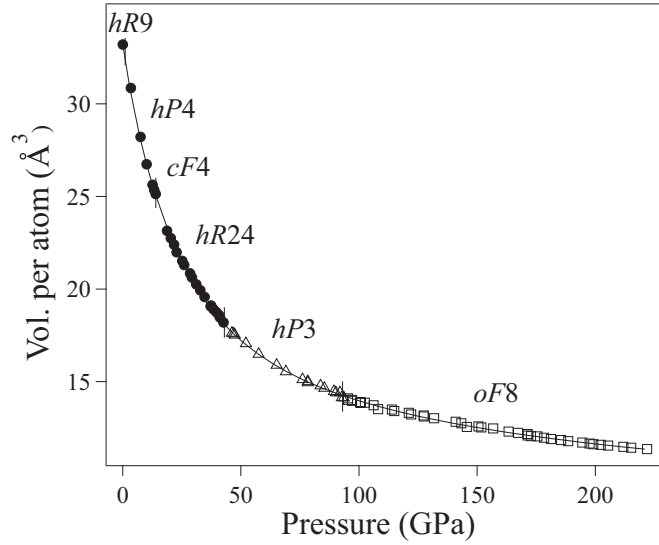


FIG. 9. The compressibility of Sm up to 222 GPa. The solid line shows the best-fitting third-order AP3 EOS to the full compression curve.

the AP3 form fits the full compression curve much better than the AP2 form, the K_0 value of 40.6 GPa is larger than the value of 31.6 GPa obtained by fitting only the data up to 43 GPa and the value of 33 GPa reported previously [33]. Close analysis of the AP3 fit reveals that it slightly underestimates the compressibility of the lower-pressure ($hR9$, $hP4$, $cF4$, and $hR24$) phases to 43 GPa (and therefore overestimates K_0) in order to better fit the higher-pressure ($hP3$ and $oF8$) phases over the larger pressure range of 43 to 222 GPa.

For many regular solids, such as the $oF8$ phase of Sm above 93 GPa, c_2 and all the higher-order terms c_k ($k > 2$) of the APL EOS [see Eq. (1)] are zero [40], which implies, for the corresponding AP1 form, that

$$K'_{AP1} = 3 + (2/3)c_0. \quad (3)$$

The AP1 form thus has only two variables (V_0 and K_0), and it has been used to fit compression data from high-pressure phases when the pressure values for the first data points from that phase are small relative to the total pressure range for data for that phase [40]. Despite having no data below 93 GPa, the 100+ GPa pressure range over which we have compression data for the $oF8$ phase meant that fitting the AP1 EOS to the $oF8$ phase was straightforward, giving values of $V_0 = 37.9(7) \text{ Å}^3/\text{atom}$, $K_0 = 4.0(4) \text{ GPa}$, and $K' = 7.07(6)$. Since the $oF8$ phase is unstable at low pressures, there is no experimental value of V_0 with which to compare the fitted value. However, the *calculated* value for this phase at ambient pressure and 0 K, as obtained from electronic structure calculations, is $35.95 \text{ Å}^3/\text{atom}$ [41]. Fixing V_0 at this calculated value, the AP1 fit gave $V_0 = 35.95 \text{ Å}^3/\text{atom}$ (fixed), $K_0 = 5.08(1) \text{ GPa}$, and $K' = 6.96(2)$, values not too dissimilar from those obtained from the free fit. While the small value of K_0 is that of an alkali metal, such as potassium ($K_0 = 3.1 \text{ GPa}$) or sodium ($K_0 = 6.3 \text{ GPa}$), the large value of K' results in a bulk modulus of $\sim 390 \text{ GPa}$ for the $oF8$ phase at 95 GPa

Low-temperature magnetic studies of Sm to 50 GPa have shown that the magnetic transition temperatures closely follow the crystallographic symmetry during the $hR9 \rightarrow hP4 \rightarrow cF4 \rightarrow hR24$ transition sequence at high pressures and low temperatures [42]. More recently, Deng and Schilling measured the magnetic ordering temperature T_0 of Sm metal up to 150 GPa and observed a strong increase in T_0 with pressure above 85 GPa from ~ 60 to $\sim 140 \text{ K}$ [9]. This pressure is close to that of the $hP3 \rightarrow oF8$ transition in Sm at 300 K, and so it is likely that it is the $oF8$ phase of Sm that has a highly correlated electron state, such as a Kondo lattice [9]. Given the very similar structural behavior of Nd and Sm reported here, it is perhaps then surprising that the magnetic ordering temperature T_0 of Nd *decreases* sharply from 180 to 120 K between 70 and 110 GPa, where it has the $oF8$ structure at 300 K, before decreasing toward 0 K near 150 GPa [6]. Electronic structure calculations are needed both to cast light on the different magnetic behaviors seen in Sm and Nd and to determine why the $oF16$ structure of Tb and the higher-Z trivalent lanthanides is not seen in either Sm or Nd.

IV. CONCLUSIONS

The structure of Sm metal above 93 GPa is found to be face-centered orthorhombic ($oF8$), isostructural with that observed in Nd, Am, Cm, and Cf at high pressures, and isosymmetric with the $oF16$ structure observed in Tb, Gd, Dy, Ho, Er, and (probably) Tm [18]. High-precision measurements of the compressibility of Sm reveal that it becomes less compressible after the transition to the $hP3$ phase at 43 GPa and that above 65 GPa its compressibility is that of a regular metal such as Au or Pt. Previous studies of Sm have linked changes in its crystal structure and compressibility to changes in its electronic structure, particularly changes from d bonding in the $hR24$ structure to intermediate $4f$ bonding in the $hP3$ structure to itinerant $4f$ bonding in the $oF8$ structure. Previous calculations which have suggested a delocalization of the $4f$ shell in the 100-GPa pressure range were performed on the assumption that the post- $hP3$ phases of Sm has a body-centered tetragonal structure ($tI2$) rather than the $oF8$ structure reported here [43]. Further calculations using the correct crystal structure are therefore now required.

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Structural phase transitions in yttrium up to 183 GPa

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Angle-dispersive x-ray powder diffraction experiments have been performed on yttrium metal up to 183 GPa. We find that the recently discovered *oF*16 structure observed in the high-*Z* trivalent lanthanides is also adopted by yttrium above 106 GPa, pressures where it has a superconducting temperature of ~ 20 K. We have also refined both tetragonal and rhombohedral structures against the diffraction data from the preceding “distorted-fcc” phase and we are unable to state categorically which of these is the true structure of this phase. Finally, analysis of yttrium’s equation of state reveals a marked change in the compressibility upon adoption of the *oF*16 structure, after which the compression is that of a “regular” metal. Electronic structure calculations of *oF*16-Y confirm its stability over *oF*8 structure seen in Nd and Sm, and provide insight into the nature of the shift of orbital character from *s* to *d* under compression.

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I. INTRODUCTION

The trivalent transition metals yttrium (Y) and scandium (Sc) are considered members of the rare-earth elements, along with the lanthanide series (La to Lu). The unique structural and material properties exhibited by the rare-earth elements at extreme pressures has incentivized a great number of experimental and theoretical studies [1–7]. The regular trivalent lanthanides (La to Lu, excluding Ce, Eu and Yb) each exhibit a common phase transition sequence on compression, the structures of which differ only in the stacking arrangement of their close-packed atomic layers: hcp (space group $P6_3/mmc$, *hP*2 in the Pearson notation) $\rightarrow$ α -Sm type ($R\bar{3}m$, *hR*9) $\rightarrow$ double-hcp ($P6_3/mmc$, *hP*4) $\rightarrow$ face-centred cubic ($Fm\bar{3}m$, *cF*4) $\rightarrow$ distorted-*cF*4 ($R\bar{3}m$, *hR*24) [1,8,9]. As the reverse sequence of structures (*hP*4–*hR*9–*hP*2) is adopted by the same elements at ambient conditions as one traverses them with increasing atomic number (*Z*), it was initially thought to arise from changes in the occupancy of the *f*-band with *Z* or with pressure. However, Y, which has no *f* electrons, was later shown to exhibit the same transition sequence on compression [10,11], and the subsequent reassessment of the structural changes found that they arise from an increase in the *d*-band occupancy, as a result of *s* $\rightarrow$ *d* electron transfer [9]. Y has thus historically been used as a benchmark for

comparing the electronic character of the structural transitions in the rare-earth metals [10–13].

None of the phase transitions listed above results in a measurable volume change [6]. However, upon further compression, the distorted-*cF*4 phase transforms to a “collapsed” phase accompanied by a discontinuity in the atomic volume [3,5,6]. This transition occurs at ~ 95 GPa in Y with a volume change of -2.6% [13]. For the last 20 years, the structure of the collapsed phases was generally perceived to be either orthorhombic ($Cmcm$, *oC*4) in Ce, Pr, Nd and Sm, or monoclinic ($C2/m$, *mC*4) in Ce, Nd, Sm, Tb, Gd, Dy, Ho, Er, Tm, and Y (see Ref. [6], and references cited therein). The fits of the *mC*4 structure to the reported diffraction data were typically poor, except in the case of Ce [14,15], and we have recently shown that the true structure of the collapsed phase in Tb, Gd, Dy, Ho, Er, and Tm is orthorhombic, space group $Fddd$ with 16 atoms per unit cell (*oF*16) [7], while in Nd and Sm it is also orthorhombic with space group $Fddd$, but with eight atoms per unit cell (*oF*8) [16]. The *oF*8 structure was previously found in the actinides Cf, Am, and Cm at high pressure [17–19] and the *oF*16 and *oF*8 structures, along with the *hP*3 structure observed in Nd, Sm, and Yb [20,21], form a new family of structures which differ only in the stacking sequence of their quasi-close-packed layers [7].

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Remarkably, while the *oF*16 structure had not previously been observed experimentally in any element, although it has recently been confirmed as the stable phase of Ho above 103 GPa [22], both it and the *hP*3 structure were calculated to be the stable phase(s) of Y above 97 GPa [12,23,24], pressures at which Y has a remarkably high superconducting transition temperature (T_c) of 19.5 K at 115 GPa [25]. It is then a reasonable assumption that the superconducting phase adopts one of these two structures, as both *oF*16 and *hP*3 are estimated to have a T_c in the range of 16–19 K at 97 GPa [23,26]. Furthermore, electronic structure calculations have found that shifts of the *d* electron states to low-energy levels, and a significant decrease in the density of states (DOS) at the Fermi level, contribute to the stabilities of both the *oF*16 and *hP*3 structures [23]. In addition, the accumulation of electrons into interstitial sites in both structures was also reported to play an important role in their stability [23].

The diffraction patterns from the *mC*4 and *oF*16 structures are somewhat similar, which led to the incorrect assignment of the former to the collapsed phases of the high-*Z* trivalent lanthanides [7]. The previous determination of the structure of Y above 100 GPa as being *mC*4 [13] then suggests that the structure is more likely to be *oF*16 rather than *hP*3, which has a different and much simpler diffraction pattern [20]. In order to determine the true structure of Y above 100 GPa, we have made diffraction studies to 183 GPa using x-ray powder diffraction and synchrotron radiation. We find that Y does indeed adopt the *oF*16 structure above 95 GPa, in agreement with computational studies [23,24]. Our result confirms that the high-pressure structural behavior of Y and the trivalent lanthanides is indeed very similar, but different to that of the other rare-earth element Sc [27].

The high quality of our diffraction data also enabled us to address another long-standing issue with the rare-earth series, that is, the crystal structure of the distorted-*cF*4 phase (*d-cF*4). Although the most widely accepted structure, including in Y, is *hR*24 (space group $R\bar{3}m$) [28,29], other possibilities have been suggested in order to explain peak splittings which are forbidden by the rhombohedral symmetry of this structure, for example in Dy [30]. In Y, recent *ab initio* density functional theory (DFT) calculations have suggested tetragonal or triclinic distortions of *hR*24 as being the true structure of the *d-cF*4 phase [31], and we have tested these new models against our diffraction data.

II. EXPERIMENT

We conducted synchrotron x-ray diffraction experiments on four separate Y samples, attaining a maximum pressure of 183 GPa at 300 K. Diamond anvil cells (DACs) equipped with diamond culets ranging in diameter from 80 to 300 μm were prepared with tungsten (W) gaskets and the sample chamber was filled with Y powder (99.9% purity, Sigma Aldrich) under a dry Ar atmosphere (<1 ppm O_2 and <1 ppm H_2O) to prevent oxidation. A Cu sphere $\sim 5 \mu\text{m}$ in diameter was loaded into three of the DACs as a pressure calibrant, while a small ruby sphere was used as a calibrant in the fourth. Angle-dispersive diffraction data were collected at the high pressure beamlines P2.02 at PETRA-III in Hamburg, at beamline I15 at the Diamond Light Source (DLS), and at beamline

9.5HP at the now-closed Synchrotron Radiation Source (SRS) at Daresbury Laboratory in the UK. Monochromatic x-rays of wavelength 0.34439 Å (PETRA-III), 0.42454 Å (DLS), and 0.44379 Å (SRS) were focused down to a FWHM of 2 μm (PETRA), 20 μm (DLS), and 50 μm (SRS). Diffraction data were recorded on a Perkin-Elmer area detector (PETRA-III) and a MAR345 image-plate detector (DLS and SRS). In one run at PETRA-III the detector was initially placed ~ 400 mm from the sample, and later increased to ~ 600 mm to improve the low-angle peak resolution, while in other runs at PETRA-III the detector was maintained at ~ 400 mm. At DLS and SRS the detectors were maintained at ~ 300 mm from the sample. The exact sample-detector distance and the detector tilts were determined using diffraction standards (LaB_6 , CeO_2 and Si). The sample pressures were derived from the published Cu equation of state (EoS) [32] and standard ruby fluorescence calibration data [33,34]. The 2D diffraction images were integrated to 1D profiles using DIOPTAS [35], and these were analysed using Rietveld and Le Bail profile fitting [36,37], and least-squares [38] to individual peak positions.

III. RESULTS AND DISCUSSION

At ambient pressure, Y crystallizes in the *hP*2 structure and this produced sharp, well-defined diffraction peaks (Fig. 1) and atomic volumes in excellent agreement with previous compression studies [10,11]. The transition from *hP*2 to the *hR*9 structure has been described previously as sluggish, starting at 13 GPa and becoming complete at 16 GPa [13]. We observed the transition to start at 14 and 16 GPa in two different samples, and observed the *hR*9 phase only as a minority component in mixed-phase samples along with either *hP*2 (at lower pressures) or *hP*4 (at higher pressures). Indeed, the similarities of the *hP*2, *hR*9, *hP*4 and *cF*4 structures, which differ only in the stacking of their close-packed atomic layers—e.g., AB in *hP*2 and ABACACBCB in *hR*9—resulted in significant overlap of diffraction peaks from the different phases, and sluggish transitions that produced mostly mixed-phase diffraction patterns.

These effects were perhaps exacerbated by the absence of any pressure transmitting medium (PTM) in our samples, which typically increases non-hydrostaticity. However, we note that neither Vohra *et al.* [10] nor Samudrala *et al.* [13] reported the use of a PTM in their previous studies of Y. Using the 2 μm diameter x-ray beam at PETRA-III we used ‘grid-scans’ to map out the pressure gradients within the samples at a number of pressures. These scans revealed not only pressure variations of 4 GPa within the sample volume at 89 GPa, and 7 GPa at 125 GPa, but also revealed that these variations resulted in different phase mixtures being present at different locations within the samples. We obtained accurate compressibility data, and reduced the effects of pressure gradients and mixed-phase samples, by ensuring that our diffraction patterns contained diffraction peaks from both the Y sample and Cu pressure marker, and utilizing the small x-ray beam size available at PETRA-III to ensure that the pressure gradients within the sampled volume were minimal. Preliminary experiments using the larger (20 μm) x-ray beam at the DLS resulted in both more complex mixed-phase diffraction patterns, and

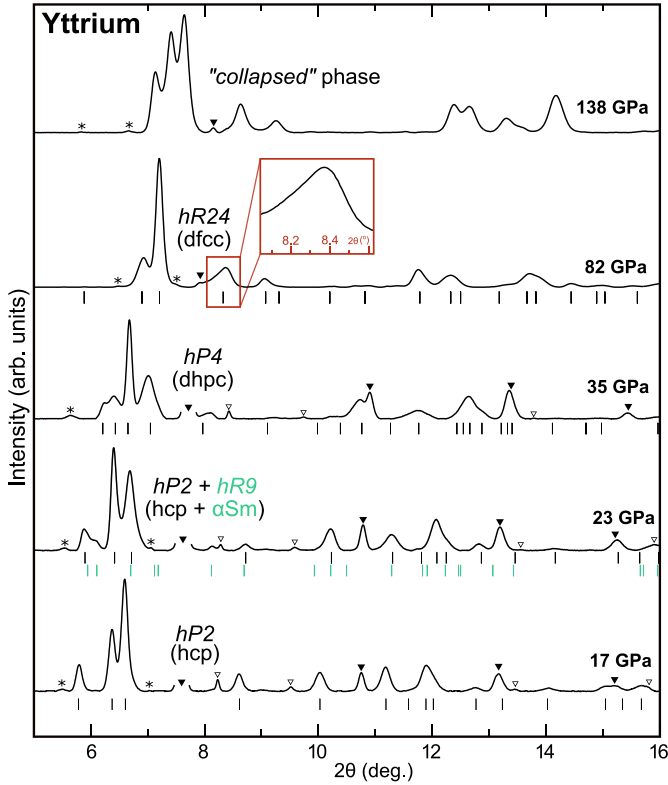


FIG. 1. Background-subtracted angle-dispersive diffraction profiles from Y collected on compression showing the diffraction patterns obtained from each of the different phases. For the four profiles collected below 95 GPa, the reflection positions predicted by the different phases ($hP2$, $hP2 + hR9$, $hP4$ and $hR24$, respectively) are indicated by vertical bars below each profile. The profile collected at 138 GPa is from the “collapsed” phase. The ▼ symbols identify peaks from the W gasket, ∇ denotes peaks from the Cu calibrant and asterisks identify weak peaks from a sample impurity. The (224) peak in the $hR24$ profile at 82 GPa is enlarged in the inset to highlight the asymmetric shape that may indicate it is a closely spaced doublet—something that is forbidden by the rhombohedral symmetry of the $hR24$ structure.

discrepancies in the compressibility data due to the pressure gradients within the much larger ($\sim 100\times$) sampled volume.

While complex mixed-phase samples were often observed below 52 GPa, only single-phase diffraction patterns from the $d\text{-}cF4$ phase were observed above that pressure. If the $d\text{-}cF4$ phase of Y has the $hR24$ structure, then the $cF4 \rightarrow hR24$ transition produces two changes to the diffraction pattern. Firstly, the distortion from cubic to rhombohedral symmetry results in the peaks of the cubic $cF4$ structure splitting at the transition. Importantly, the (200) peak in the $cF4$ pattern remains a singlet in $hR24$ [where it indexes as the (204)—see inset to Fig. 2(a)], while the most intense (111) $cF4$ peak splits into a doublet [which index as the (202) and (006) peaks]. Secondly, additional diffraction peaks appear at the transition as a result of the enlarged unit cell of the $hR24$ structure and the movements of the atoms at the transition to lower-symmetry sites.

Studies of single-phase $d\text{-}cF4$ profiles from Y between 52 and 102 GPa using the $hR24$ structure revealed that the

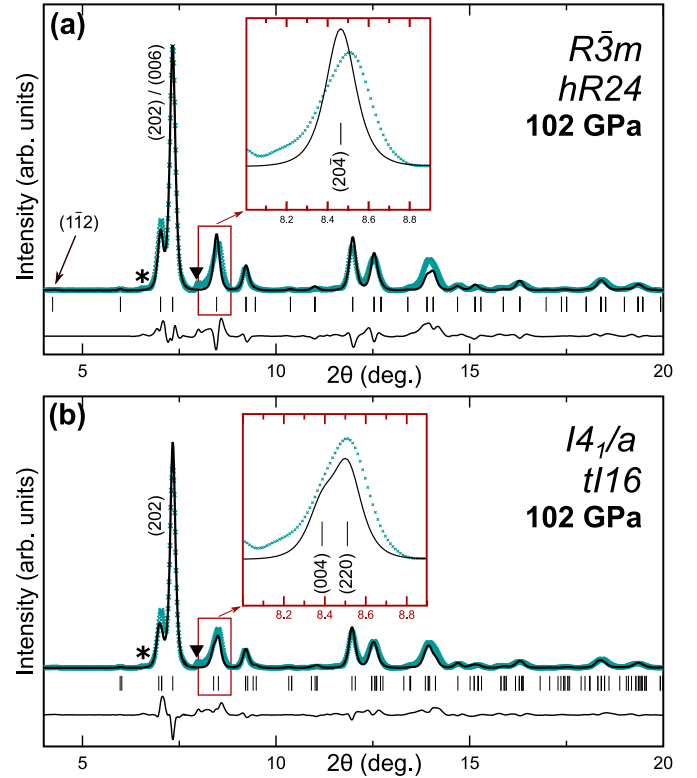


FIG. 2. Rietveld refinements of the (a) $hR24$ and (b) $tI16$ structures to a diffraction profile of Y obtained at 102 GPa, showing the observed (cyan crosses) and calculated (black line) diffraction patterns. The calculated reflection positions (vertical bars), principal Miller indices, and difference profiles (lower lines) are shown. The ▼ symbols identify a weak peak from the W gasket, and the asterisks identify a weak peaks from a sample impurity. The same diffraction peak is highlighted in both profiles illustrating how it is fitted as a singlet in $hR24$ and a doublet in $tI16$. The (112) peak, which is predicted by the $hR24$ structure at 4.2° but not by the $tI16$ structure, is highlighted in (a). The refined structural parameters are (a) $a = 5.554(1)$ Å, $c = 13.604$ Å, atoms at (0.521(1), −0.521(1), 0.243(1)) and (0, 0, 0.269(1)) and (b) $a = 5.524(1)$ Å, $c = 7.926(2)$ Å, atoms at (0.528(1), 0.219(1), 0.890(1)).

(202)/(006) doublet remains unresolved at all pressures, and the same is true for the higher-angle (404)/(00,12) doublet, which would have a larger splitting than the (202)/(006). The overlap of the peaks in these doublets implies that the c/a ratio is indistinguishable from $\sqrt{6}$ at all pressures. This is in marked contrast to the behavior seen in the $hR24$ phases of Pr [39], and Sm [40], where the (202)/(006) and (404)/(00,12) peaks are clearly resolved into doublets, and the c/a ratio increases rapidly with pressure. Importantly, the (200) peak in the $cF4$ phase (which indexes as the (204) in the $hR24$ structure) shows some evidence of being a closely spaced doublet in the $d\text{-}cF4$ diffraction profiles in Y, as highlighted in the 82 GPa profile in Fig. 1. A similar doublet, which is forbidden by the $hR24$ structure, was seen in diffraction profiles from the $d\text{-}cF4$ phase of Dy, and this was used by Shen *et al.* to argue that $d\text{-}cF4$ phase of Dy has orthorhombic rather than rhombohedral symmetry [30].

The computational study of Y by Chen *et al.* [18] suggested that the $d\text{-}cF4$ phase of Y has the $hR24$ structure [12], and

this was confirmed experimentally soon afterwards by Samudrala *et al.* [13]. However, more recently, Ishikawa *et al.* [31] have reported that two distortions of the *hR24* structure, with tetragonal and triclinic symmetry, also have low enthalpies over the relevant pressure range, with the former having the slightly lower enthalpy between 40 and 80 GPa. Analysis of the atomic coordinates of the tetragonal structure listed by Ishikawa *et al.* [31] reveal it to be body-centred rather than primitive, and to have spacegroup $I4_1/a$ (*tI16*) with atoms on the 16*f* sites at (0.5295, 0.2327, 0.8918). This structure becomes *cF4* when $c = \sqrt{2}a = 2a_{\text{FCC}}$ and the atoms are at (0.5, 0.25, 0.875). A key feature of the *tI16* structure is that the (111) reflection in *cF4* remains a singlet in *tI16*, while the (200) reflection becomes a doublet. In contrast, if the *d-cF4* phase of Y were to adopt the *oS8* structure, first proposed by Porsch and Holzapfel [41] and reported to be the structure of the *d-cF4* phase of Dy [30], then both the (111) and the (200) peaks would become doublets. In the triclinic structure suggested by Ishikawa *et al.* [31], the (111) and the (200) peaks would split into 4 and 3 peaks, respectively. The *tI16* structure therefore provides a high-symmetry, few-parameter solution to the structure of the *d-cF4* phase when the (111) peak of *cF4* remains a singlet while the (200) becomes a doublet.

As highlighted in Fig. 1, there is some evidence of the (200) peak of the *cF4* becoming split in the *d-cF4* phase of Y, although this is evident only as an asymmetry on the low-angle side of the peak. A Rietveld fit of the *tI16* structure to a profile obtained at 102 GPa [see Fig. 2(b)] is excellent, and the refined structure is shown in Fig. 3(a). The relationship of the *tI16* structure to that of *cF4* is illustrated in Fig. 3(b).

However, despite the excellent fit of the *tI16* structure, there are no clear features (apart from the possible doublet at 8.5°) not also accounted for in a fit using the *hR24* structure with $c/a = \sqrt{6}$ [see Fig. 2(a)]. While higher resolution profiles would make distinguishing the two structures straightforward, since they have different symmetry and predict a multitude of different peak splittings, our current data are unable to decide definitively between the two structural models. The *hR24* structure also predicts an additional low-angle peak at $\sim 4.2^\circ$ [the (1 $\bar{1}$ 2)] not accounted for by *tI16*, but it is predicted to be extremely weak, and was not observed previously in either Pr or Sm [39,40]. We are thus unable to determine the structure of the *d-cF4* phase of Y definitively, despite the quality of our diffraction data, and to obtain its compressibility we have refined it as having the *hR24* structure with the constraint $c/a = \sqrt{6}$ [see Fig. 2(a)].

We observe the transition to the “collapsed” phase of Y at 106 GPa (Fig. 5), which is much closer to the most recently predicted transition pressure of 109 GPa [24], than the 95 GPa reported by Samudrala *et al.* [13]. The onset of the transition is clearly evident from the splitting of the (202)/(006) doublet (of *hR24*), see Fig. 1, and is complete by 117 GPa. A Rietveld refinement of the *Fddd* (*oF16*) structure to the diffraction profile obtained at 138 GPa is shown in Fig. 4, and the fit is excellent. The *oF16* structure comprises eight quasi-close-packed layers with a b/c axial ratio of $\sqrt{2.9}$ —ideal packing would give an axial ratio of $\sqrt{3}$. In *oF16* the atoms of each layer are located above the saddle point between two

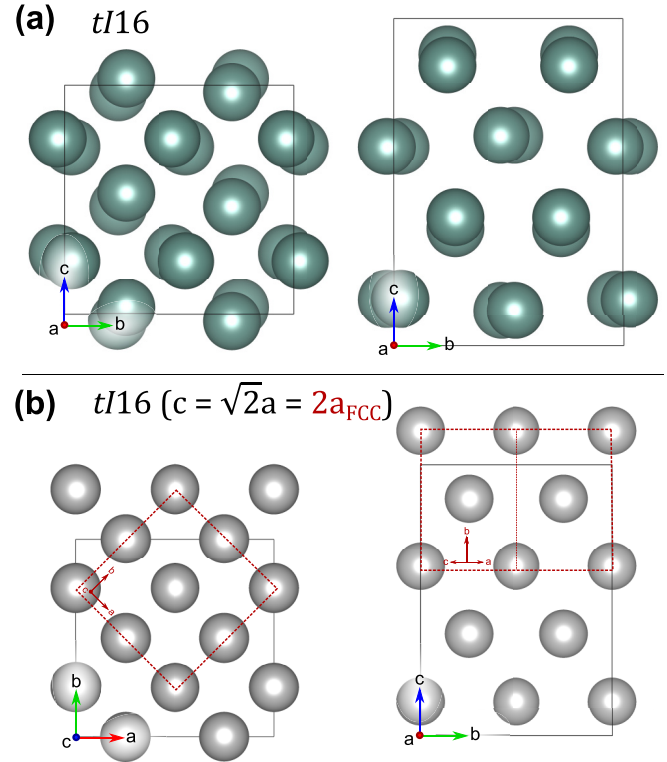


FIG. 3. (a) The *tI16* structure of Y at 102 GPa with $a = 5.524(1)$ Å and $c = 7.926(2)$ Å, $c/a \sim \sqrt{2.06}$, and atoms located on the 16*f* site at (0.528(1), 0.219(1), 0.890(1)). (b) The *tI16* structure with $c = \sqrt{2}a = 2a_{\text{FCC}}$, which reproduces the *cF4* structure when the atoms are at (0.5, 0.25, 0.875). The cubic FCC unit cell highlighted by dotted lines.

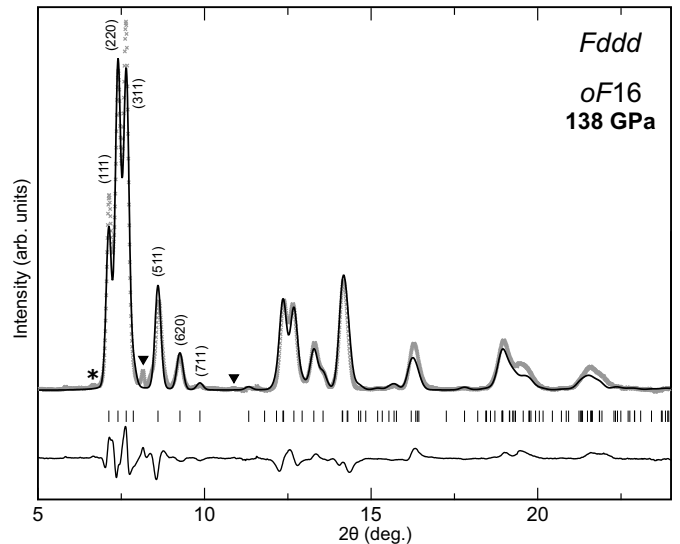


FIG. 4. Rietveld refinement of the *oF16* structure to a diffraction profile from Y at 138 GPa, showing the observed (cyan crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile. The ▼ symbols identify peaks from the W gasket, and the asterisk identifies a weak peak from a sample impurity. Space group *Fddd* with Y atoms on the 16*e* ($x, 0, 0$) Wyckoff sites with $x = 3/16$ (fixed), $a = 4.611(3)$ Å, $b = 4.656(1)$ Å, and $c = 2.728(1)$ Å.

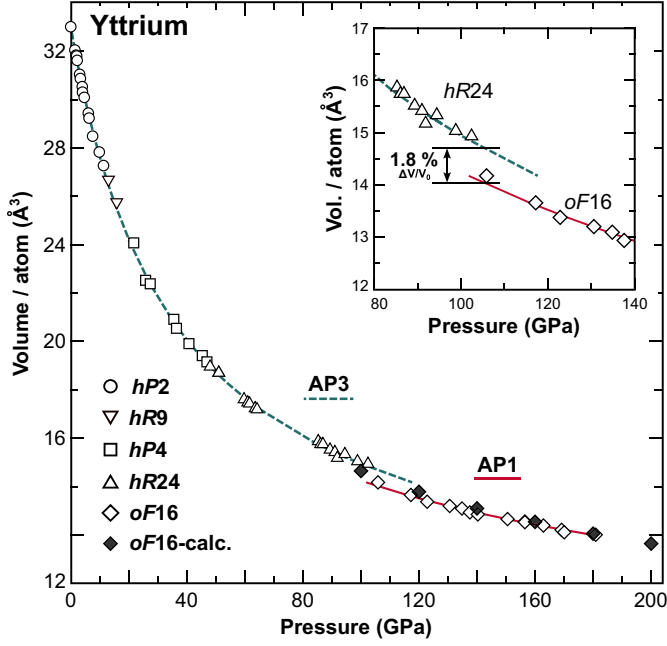


FIG. 5. The compressibility of Y to 183 GPa, shown as the volume per atom versus pressure (GPa). Open symbols refer to experimental data while the filled diamonds are atomic volumes of the *oF16* phase determined from our DFT calculations. The inset shows an enlarged view of the region near the *hR24* → *oF16* transition, highlighting the -1.8% volume change ($\Delta V/V_0$). The dashed line through the data points below 100 GPa is the best-fitting AP3 equation of state (EoS) with $V_0 = 33.0177 \text{ Å}^3$ (fixed), $K_0 = 47.3(6) \text{ GPa}$, $K' = 1.90(13)$, and $K'' = -0.017(6)$. The solid line through the data from the *oF16* phase is a best-fitting AP1 EoS with $K_0 = 11.56(4) \text{ GPa}$, $K' = 6.02(2)$ and V_0 is fixed at $32.42 \text{ Å}^3/\text{atom}$, the value for *oF16*-Y at ambient pressure and 0 K as determined from our DFT calculations.

atoms in the preceding layer, resulting in ten-fold coordination ($6 + 2 + 2$), whereas in close-packed *hP2*, *hP4*, *hR9* and *cF4*, each atom is located at the central point between the three closest atoms in the previous layer, resulting in twelve-fold coordination ($6 + 3 + 3$). The *oF16* structure has an eight-layer stacking sequence - ABCADCBD - twice that of the four-layer ABCD repeat sequence of the isosymmetric *oF8* structure observed in Sm, Nd, Am, Cm, and Cf [7,16–19].

The compressibility of Y up to 183 GPa is shown in Fig. 5. A volume change ($\Delta V/V_0$) of -1.8% (see inset to Fig. 5) is observed at the transition to the “collapsed” phase, much closer to typical volume changes observed in the equivalent transition amongst the other rare-earth elements than the discontinuity of -2.6% reported by Samudrala *et al.* when using the *C2/m* structure to analyze the collapsed phase [13]. The theoretical work of Chen *et al.* reported that the stability of the *oF16* structure in Y arises from the shift in the *d*-electron energy levels, which results in the transfer of *s* electrons to the *d* band [23]. Such changes in the electronic structure can result in changes in compressibility, which are most easily visualizing by linearizing the compressibility curve, enabling one to distinguish anomalies arising from changes within the electronic structure from the standard compressive behavior expected of a “normal” metal [44].

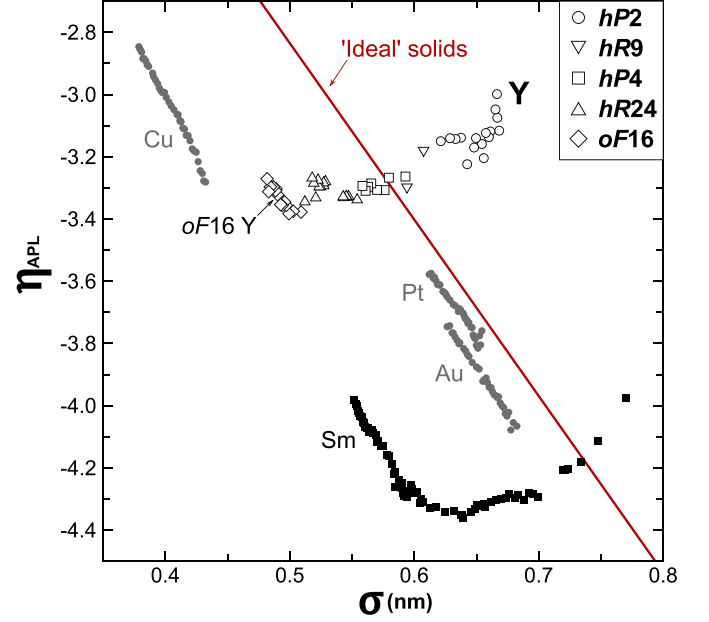


FIG. 6. Linearization of compressibility of Y in the form of an $\eta_{\text{APL}} - \sigma$ plot, where $\sigma = \sigma_0 x$, $x = (V/V_0)^{1/3}$ and σ_0 is the Thomas-Fermi radius $(3ZV_0/4\pi)^{1/3}$. The data from the different phases of Y are plotted using different symbols, alongside the same plot for Sm (irregular compressibility, black filled squares) and the “regular” compressibilities of Cu, Au and Pt (grey filled circles), as determined from the compression data of Dewaele *et al.* [42] for comparison. The red line labeled “ideal solids” has the gradient $\bar{\eta} = -5.67 \text{ nm}^{-1}$, and is the average gradient expected for all elements with regular compression [43,44].

If one fits the compression data using the second order (AP2) form of the adapted polynomial of order L (APL) EoS [43,44]:

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

where K_0 is the zero pressure bulk modulus, K' is its pressure derivative, $x = (V/V_0)^{1/3}$, $c_0 = -\ln(3K_0/p_{\text{FG}})$, $c_2 = (3/2)(K' - 3) - c_0$, $p_{\text{FG}} = a_{\text{FG}}(Z/V_0)^{5/3}$ is the Fermi-gas pressure, Z is the atomic number, and $a_{\text{FG}} = [(3\pi^2)/5](\hbar^2/m_e) = 0.02337 \text{ GPa nm}^5$ is a constant, then the compression data can be linearized in a so-called $\eta_{\text{APL}} - x$ plot:

$$\eta_{\text{APL}}(x) = \ln\left(\frac{px^5}{p_{\text{FG}}}\right) - \ln(1-x), \quad (2)$$

where $x = (V/V_0)^{1/3}$, the Fermi-gas pressure $p_{\text{FG}} = a_{\text{FG}}(Z/V_0)^{5/3}$, and $a_{\text{FG}} = 0.02337 \text{ GPa nm}^5$.

To realize differences in compression data of different materials with respect to “ideal” behavior, it is most convenient to use an APL linearization not with respect to x but rather to $\sigma = \sigma_0 x$, with σ_0 being the Thomas-Fermi radius $(3ZV_0/4\pi)^{1/3}$, because this scaling brings out common trends more clearly [44].

The linearized $\eta_{\text{APL}} - \sigma$ data for Y is shown in Fig. 6, along with the similarly linearized data we have recently reported for Sm [16] and the data for the “regular” metals Cu,

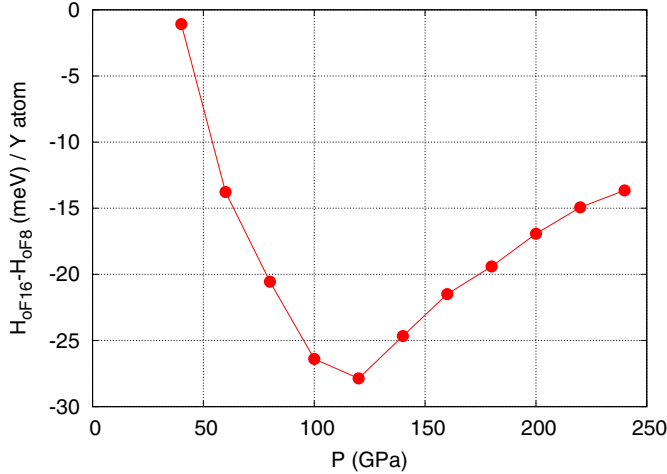


FIG. 7. The enthalpy difference between *oF* 16-Y and the *oF* 8-Y as a function of pressure, as calculated within DFT. The difference is normalized per Y atom and exhibits a minimum around $P = 120$ GPa.

Au, and Pt [42]. In such a plot, materials undergoing “normal” compressive behavior will show linear or quasi-linear behavior with an average “ideal” gradient of -5.67 nm^{-1} and with the correct theoretical limit of $\eta_{\text{APL}}(0) = 0$. This behavior is clearly demonstrated by Cu, Au, and Pt in Fig. 6, while Sm provides an excellent example of a material whose compressibility is initially “irregular” as a result of *s-d* electron transfer, but which becomes “regular” after it transforms to the *oF* 8 structure. Although the data from the lower-pressure phases of Y exhibit some scatter amongst the linearized η_{APL} values, a general positive gradient can be identified, similar to that shown by Sm. However, on entering the *oF* 16 phase, there is a clear shift to linear behavior with a negative gradient very similar to that found in Sm, Cu, Au, and Pt. Although the pressure range over which we have compression data for *oF* 16-Y (80 GPa) is somewhat smaller than the 100+ GPa pressure range over which we have compression data for *oF* 8-Sm, the linearized data in Fig. 6 suggest that *oF* 16-Y, like *oF* 8-Sm, is a metal with ‘regular’ compressibility.

The positive gradient exhibited by the lower-pressure phases of Y in Fig. 6 suggests that the compression curve shown in Fig. 5 would not be well fitted by an AP2 EoS. This was indeed the case, and we found that a 3rd-order AP3 form was required, as shown in Fig. 5. However, the regular compression of the *oF* 16 phase means that it could be well fitted using a 1st-order AP1 EoS (Fig. 5).

IV. ELECTRONIC STRUCTURE CALCULATIONS

As said, the transition to regular compressive behavior in the collapsed *oF* 16 phase may arise from a discrete change in the electronic structure of Y. Indeed the recent electronic band structure calculations of Li *et al.* for *oF* 16-Y exhibited metallic features, with the majority of the DOS at the Fermi level collected in the *4d*-band, transferred from the *4s* band [24]. This supports prior models predicting high critical Coulomb pseudopotentials for *oF* 16, and it would be interesting to obtain a linearized plot (similar to Fig. 6) from compression

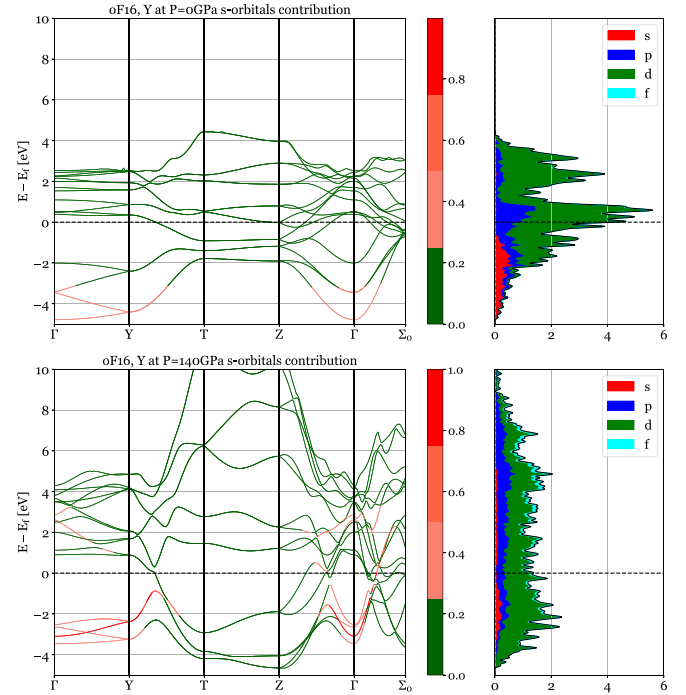


FIG. 8. Band structure (BS) and density of states (DOS) for *oF* 16-Y at ambient pressure (top) and at 140 GPa (bottom). The color code of the BS plot reflects the predominant orbital character: either *s* (red) or *d* (green). The color code of the “stacked” DOS plots corresponds to the orbital character: ‘red for *s*-orbital, blue for *p*-orbital, ‘green for *d*-orbital, and cyan for *f*-orbital. These plots were made by using the PYPROCAR package [45].

data collected below the predicted superconducting transition pressure, to observe if such treatment of standard compressibility data could provide additional insight into other material behaviours affected by its electronic structure.

To gain further insight, we have performed extensive DFT calculations of the *oF* 16 and *oF* 8 phases of Y. Structural optimization of bulk Y in the *oF* 8 and *oF* 16 phases was accomplished by using the DFT calculations with the help of the VASP [46] package using the Perdew-Burke-Ernzerhof functional [47]. The *k*-point sampling was performed using a Monkhorst-Pack mesh of $8 \times 16 \times 2$ for the *oF* 8 and $8 \times 12 \times 2$ for the *oF* 16 structures in the tetragonal unit cell, respectively, and a Gaussian smearing of 0.1 eV. During the DFT structural optimization, the convergence on internal forces and stress tensor of 0.01 eV/Å was reached, and the energy cutoff was set to 500 eV. Scalar relativistic spin-orbit coupling was taken into account within the Koelling-Harmon approximation [48].

Our zero-temperature DFT calculations for Y demonstrate that the *oF* 16 phase is lower in enthalpy than the *oF* 8 phase at all pressures between 40 and 240 GPa, as shown in Fig. 7, with the maximum enthalpy gain being reached near 120 GPa. The agreement of our DFT zero-temperature volume calculations for *oF* 16-Y as a function of pressure with the room-temperature experimental data is also very good, as can be seen from Fig. 5. The absence of the imaginary phonon modes in the *oF* 16 phase was previously established in the work of Chen *et al.* [23].

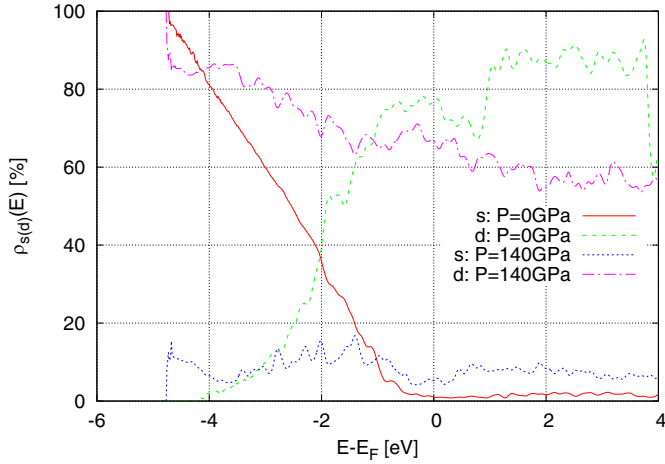


FIG. 9. Relative contribution to the total DOS of the s and d states at $P = 0$ GPa (solid red line: s states, dashed green line: d states) and at $P = 140$ GPa (dotted blue line: s states, dashed-dotted magenta line: d states).

The qualitative change of the valence electrons' orbital character in the $oF16$ - $Fddd$ can be best seen from the combined band structure and density-of-states plots at ambient and at high pressures, as shown in Fig. 8. It can be seen that the major contribution to the band structure in the energy range of $[-5 : 10]$ eV comes from the s and d states, while the main effect of the pressure on Y is to increase dramatically the bandwidth of the d states. Indeed, by applying pressure from 0 to 140 GPa, the d state's bandwidth increases by a factor of two. At the same time, the s states, located around 4 eV below the Fermi energy, are slightly raised by around 1 eV and are strongly hybridized with the d states, as a result of applied pressure.

In order to underline the difference in contribution of the s and d states to the total DOS at high and low pressure, in Fig. 9, we plot the quantities

$$\rho_s(E) = \frac{D_s(E)}{D_{\text{tot}}(E)}, \quad \rho_d(E) = \frac{D_d(E)}{D_{\text{tot}}(E)}, \quad (3)$$

where $D_s(E)$, $D_d(E)$, and $D_{\text{tot}}(E)$ are the partial s , partial d and the total DOS, respectively. It can be seen that at $P = 0$ GPa, the total DOS is dominated by the s states, reaching 100% at -5 eV, and the s states contribution gradually goes to zero as one approaches Fermi energy. At the same time, the d -state contribution gradually grows until it reaches a value of the order of 80% at E_F . Conversely, at high pressure, the s -state contribution remains approximately constant and small (below 20%), while the d -state contribution, starting at 100%

at -5 eV, decreases slightly, but remains higher than 60% until few eV above Fermi energy. Thus, in our calculations, the $s \rightarrow d$ charge transfer appears more like a d bandwidth increase rather than a real transfer of the charge between the orbitals, which is ill-defined in a metallic system.

V. CONCLUSIONS

The structure of Y metal above 100 GPa, and thus the likely structure of the superconducting phase, is found to be face-centered orthorhombic ($oF16$), isostructural with that observed in the collapsed phases of the trivalent lanthanides Tb, Gd, Dy, Ho, Er, and (probably) Tm. This result confirms the close structural relationship between the lanthanides and yttrium, which has no f electrons. High-precision measurements of the compressibility reveal anomalous values at lower pressures, very similar to those seen in Sm, but that the compressibility of the $oF16$ phase is that of a regular metal, such as Au, Pt, or Cu. DFT calculations confirm the lower enthalpy of the $oF16$ structure relative to that of $oF8$ structure seen in Sm and Nd, and reveal that the $s \rightarrow d$ charge transfer occurs via a d -bandwidth increase, which enhances the relative contribution of the d -states to the density of states near the Fermi level.

Note added in proof. Buhot *et al.* [49] have recently re-analyzed the x-ray diffraction data of Samudrala *et al.* [13] at 123 GPa using Rietveld methods and shown that it can be fitted with the $oF16$ structure, while their superconductivity measurements show that the $oF16$ phase can be stabilized without partially occupied f states.

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The phase diagram of Ti-6Al-4V at high-pressures and high-temperatures

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Abstract

We report results from a series of diamond-anvil-cell synchrotron x-ray diffraction and large-volume-press experiments, and calculations, to investigate the phase diagram of commercial polycrystalline high-strength Ti-6Al-4V alloy in pressure–temperature space. Up to ~ 30 GPa and 886 K, Ti-6Al-4V is found to be stable in the hexagonal-close-packed, or α phase. The effect of temperature on the volume expansion and compressibility of α -Ti-6Al-4V is modest. The martensitic $\alpha \rightarrow \omega$ (hexagonal) transition occurs at ~ 30 GPa, with both phases coexisting until at ~ 38 –40 GPa the transition to the ω phase is completed. Between 300 K and 844 K the $\alpha \rightarrow \omega$ transition appears to be independent of temperature. ω -Ti-6Al-4V is stable to ~ 91 GPa and 844 K, the highest combined pressure and temperature reached in these experiments. Pressure–volume–temperature equations-of-state for the α and ω phases of Ti-6Al-4V are generated and found to be similar to pure Ti. A pronounced hysteresis is observed in the ω -Ti-6Al-4V on decompression, with the hexagonal structure reverting back to the α phase at pressures below ~ 9 GPa at room temperature, and at a higher pressure at elevated temperatures. Based on our data, we estimate the Ti-6Al-4V α - β - ω triple point to occur at ~ 900 K and 30 GPa, in good agreement with our calculations.

Keywords: Ti-6Al-4V, x-ray diffraction, high-pressure, high-temperature, phase transformation, equation-of-state

(Some figures may appear in colour only in the online journal)

1. Introduction

Ti-6Al-4V (wt.%, and hereafter referred to as Ti64) is a two-phase ($\alpha + \beta$) alloy of titanium (Ti) and substitutional aluminium (Al) and vanadium (V). Originally created to stabilise the α -phase character of Ti, Ti64 finds itself utilised across a wide range of industrial and commercial applications,

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where superior strength-to-weight ratio, resistance to corrosion and ease of machinability are desirable material properties [1, 2]. Compared with commercial Ti, Ti64 possesses a greater hardness, yield strength and tensile strength [3]. This makes Ti64 particularly attractive to the defence, aerospace and automotive sectors, where there is a constant drive to improve performance by means of greater fuel efficiencies and component fatigue mitigation. Ti64 is also broadly used for

biomechanical applications, including prostheses and implants. Since the mechanical properties of a material are strongly influenced by the underlying microstructure (crystal structures, defects, impurities, grain boundaries), design engineers require materials models that accurately represent these properties. However, without adequate experimental data to constrain and validate these models, uncertainties will inevitably remain. Surprisingly, the crystal structure of Ti64 has rarely been studied under extreme pressure and temperature conditions. This scarcity of data renders the development of a truly predictive Ti64 model challenging. Therefore, there is a clear requirement for more experimentation to address this data deficiency.

At ambient conditions, Ti64 crystallises predominantly in the hexagonal-close-packed (hcp) structure, or α phase (space group $P6_3/mmc$). Around the α phase grain boundaries there exists a smaller fraction by volume of body-centred-cubic (bcc), or β phase (space group $Im3m$) Ti64. The alloying of substitutional elements Al and V, and the presence of interstitial impurities (mostly oxygen, carbon and iron) increases the strength of near- α (hereafter referred to as just α) Ti64 relative to pure Ti [1, 2].

At ambient pressure, Ti64 transforms from α to the mixed ($\alpha + \beta$) phase at ~ 1070 K and then to the more ductile β phase at ~ 1280 K [2]. Melting occurs at 1943 K [4]. Pure Ti, which also crystallises in the α phase at ambient conditions, transforms to β -Ti at 1155 K and melts at ~ 1940 K.

At room temperature (RT), and under static compression in combined diamond-anvil-cell (DAC) and x-ray diffraction (XRD) studies, commercially pure α -Ti64 is stable up to at least 26 GPa [5–8]. The bulk modulus (K_0) and pressure derivative (K_0') for α -Ti64 embedded in neon, a quasi-hydrostatic pressure-transmitting-medium (PTM), were found to be $K_0 = 101(3)$ GPa, and $K_0' = 4.1(3)$ [6, 7], respectively. With no PTM present, thus resulting in the α -Ti64 sample experiencing a strong uniaxial stress along the direction of load, $K_0 = 154(11)$ GPa and $K_0' = 5(1)$ [8], suggesting a link between compressibility and the hydrostaticity of the pressure environment [8]. α -Ti64 martensitically transforms to the more brittle hexagonal ω -phase (space group $P6_3/mmm$) at 26–33 GPa [5–7]. The $\alpha \rightarrow \omega$ transition is sluggish and completely transforms by ~ 45 GPa [6]. The corresponding volume reduction at $\alpha \rightarrow \omega$ is $-\Delta V/V \sim 1\%–2\%$ [5–7]. The Ti64 samples studied were of the commercial variety, and hence low purity [5–8]. On decompression from 70 GPa back to 0.8 GPa, α -Ti64 was recovered from ω -Ti64 [6]. This $\alpha \rightarrow \omega$ transition sequence is common to group IVB metals Ti, zirconium (Zr) and hafnium (Hf) [9, 10]. In Ti, the $\alpha \rightarrow \omega$ transition occurs at 3–14.6 GPa [11–20] and appears to be sensitive to impurity content and the presence of non-hydrostatic stress conditions [16]. For α -Ti, $K_0 = 102–117$ GPa, and for ω -Ti, $K_0 = 107–142$ GPa [13–20], depending on the PTM. Just like Ti64, Ti has a higher compressibility in a more hydrostatic environment. Unlike Ti64, the $\alpha \rightarrow \omega$ transition is strongly dependent on the PTM, with the transition taking place at higher pressures in more hydrostatic environments [16, 19]. The $\alpha \leftrightarrow \omega$ transformation exhibits a considerable hysteresis in a hydrostatic environment, with ω -Ti remaining after decompression [12,

13, 19], though in the presence of shear stress, ω -Ti reverts to α -Ti after pressure release [16].

Under further compression at RT, ω -Ti64 transforms sluggishly to a bcc-type phase, which is isomorphic to high-temperature (HT) β -Ti64 and has been proposed (but not probed yet) to be the same phase. To distinguish the two phases, we will name the RT high-pressure phase as β' -Ti64. This transition occurs at ~ 94 GPa, and completes at 127–128 GPa, with a reduction in volume at $\omega \rightarrow \beta'$ of $-\Delta V/V < 2\%$ [6]. The transition to β' -Ti64 is characterised by the gradual reduction in intensity of the (001), (101), (111), (002) and (112) ω -Ti64 peaks in the XRD patterns until only β' phase peaks remain. At RT, β' -Ti64 is stable to at least 220 GPa [6, 7]. Density functional theory calculations confirm the $\alpha \rightarrow \omega \rightarrow \beta'$ transformation pathway to be the most likely sequence for Ti64 at RT, but the transition pressures are only consistent with experiment if calculations are performed on the assumption that significant local atomic ordering occurs during compression [6].

Ti does not undergo the $\alpha \rightarrow \omega \rightarrow \beta'$ RT pathway followed by Ti64 and the other Group IVB metals, Zr and Hf [9, 10]. ω -Ti transforms to an orthorhombic (space group $Cmcm$) γ phase (distorted hcp) at 115–128 GPa, and then to an orthorhombic (space group $Cmcm$) δ phase (distorted bcc) at 135–145 GPa [13, 14, 17]. The δ phase has been reported to transform back to the β' phase at 243 GPa, which is stable to at least 290 GPa [22]. In one study [15], a mixed phase ω -Ti and β' -Ti was reported between 40 GPa and 80 GPa. After laser-heating at 78–80 GPa, an orthorhombic η -Ti (space group $Fmmm$) structure emerged that reverted back to pure β' -Ti below 40 GPa after quenching to RT, and then finally transformed to ω -Ti below 30 GPa [15]. The thermal properties of Ti have been studied up to 200 GPa and 3500 K [15, 19–23]. Thermal equations-of-state (EoSs) have been generated for α -Ti, ω -Ti [21] and β -Ti [20], and the α - β - ω triple point was estimated to lie at ~ 8.0 GPa and > 900 K [19, 20]. The hysteresis in the $\alpha \leftrightarrow \omega$ transformation at HT is reduced compared with RT, with partial ω -Ti reportedly still present at ~ 2 GPa and 737 K [20]. After quenching β -Ti from 3000 K, the δ -Ti phase subsequently reappeared under compression, suggesting the δ phase is not metastable [20].

Shock experiments have yet to verify the $\alpha \rightarrow \omega$ transition in Ti64 [24–30] though this may be due to the difficulty in detecting the small volume change across the phase boundary [24, 26]. Sollier *et al* [29] shock compressed Ti64 up to 52 GPa and observed a dip in the release isentrope at ~ 27 GPa. This feature may correspond to the α - β - ω triple point at 30 GPa and 850 K, predicted using the particle swarm optimization (PSO) technique [31, 32]. α -Ti has been observed to transform to ω -Ti at 10.1–14.3 GPa under shock compression [34–37]. The presence of impurities in Ti, notably interstitial oxygen, strongly influences the shock $\alpha \rightarrow \omega$ transition pressure: for high purity Ti (oxygen content 360 ppm), the transition pressure was 10.4 GPa, whereas for low purity Ti (oxygen content 3700 ppm), no transition was observed up to 35 GPa [36].

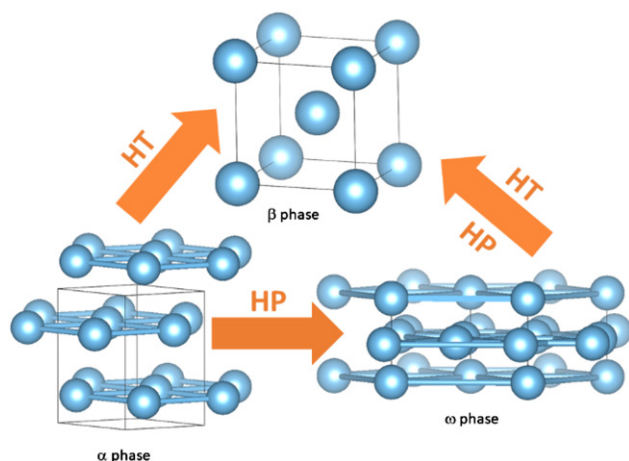


Figure 1. The transformation pathway of Ti-6Al-4V at high-pressure and HT.

Very few calculations of the Ti64 pressure–temperature (P – T) phase diagram have been attempted (see section 3.2 for a discussion of the PSO method), primarily due to a lack of experimental data to constrain the models [32, 34]. On the other hand, considerable effort has been expended on the Ti phase diagram and on developing a better understanding of the $\alpha \rightarrow \omega$ transition mechanism [38–50]. Cold curve calculations agree with the sequence $\alpha \rightarrow \omega \rightarrow \gamma$ [40, 42, 43, 45, 46], but disagreements exist concerning the subsequent pathway as either $\gamma \rightarrow \beta'$ [40, 43] or $\gamma \rightarrow \delta \rightarrow \beta'$ [42, 46], largely based on considerations of phase stability under hydrostatic conditions. At RT, Joshi *et al* predict $\omega \rightarrow \beta'$ [38], and in a joint experimental and theoretical study, $\omega \rightarrow \beta'$ has also been proposed as the structural pathway [15].

The energetics and kinetics driving the martensitic $\alpha \rightarrow \omega$ transformation have been considered and intermediate metastable states have been contemplated [47–51]. The so-called TAO-1 pathway was found to have the lowest activation enthalpy for the $\alpha \rightarrow \omega$ transformation [47–49]. In addition, interstitial and substitutional impurities have been calculated to suppress the transition by increasing the energy barrier of the TAO-1 transformation [49].

Interstitial oxygen has more significance than nitrogen and carbon in suppressing the $\alpha \rightarrow \omega$ transition in pure Ti [49], as borne out by experiment [36]. Even a low density body-centred orthorhombic (bco) metastable structure might be stabilised through the manipulation of impurities [51].

In summary, given its widespread utility across industry and commerce, it is surprising how seldom Ti64 has been studied experimentally and theoretically at extreme pressures and temperatures [5–8, 24–30, 32–34]. By contrast, the available literature on Ti is quite extensive [11–23, 33–51]. Here we report results from a series of high-pressure high-temperature (HP–HT) experiments to investigate the structural pathway of Ti64 (see figure 1) and benchmark these results against published Ti data.

2. Experimental details

Powdered samples of commercial polycrystalline Ti64, possessing an impurity level of 0.123 wt.%, were procured from Goodfellow. The purity level of the Ti64 was equivalent to an oxygen content of approximately 3700 ppm in pure Ti. Produced by Goodfellow using a patented approach known as plasma atomization, these samples can be characterised as low purity [52]. The Ti64 samples used in this study were sourced from the same batch used in a previous RT study performed by us [6, 7].

2.1. DAC experiments

Samples of Ti64 powder were loaded into eight gas membrane-driven piston and cylinder DACs, together with one or more of the following: potassium chloride (KCl), sodium chloride (NaCl), magnesium oxide (MgO), and copper (Cu), as the PTM and/or pressure marker. The thermal EoSs for these materials are known and can be used to determine pressure values from XRD patterns at HP–HT [53–56]. Spark-eroded rhenium (Re) discs were used as the gasket material (pressure chamber). We chose a variety of pressure media to reduce the risk of potential chemical reactions at HT. Diamond culet diameters ranged from 200 μm to 300 μm and the pressure chamber diameters <100 μm .

For HP–HT measurements, our DACs were placed inside a dedicated water-cooled vacuum vessel and heated with a coiled Watlow resistive heater (rated at 4.65 W cm^{-2}), wrapped around the outside of the DACs [57]. To prevent diamond oxidation and convective heating inside the vessel, vacuum pressures <10^{−5} mbar level were maintained using a rotary-backed turbo pump. Water cooling the vacuum vessel limits the effects of thermal transfer from the heater and improves the positional stability of the sample relative to the x-ray microfocus. Temperatures were measured using a K-type thermocouple attached to the DAC piston, close to the diamond anvils. The accuracy of temperature measurements is better than 0.4%. In our experience, the practical upper limit in temperature that samples can be heated to using this apparatus is ~ 900 K (for example, [58–60]). To ensure the conditions inside the DACs were as close to thermal equilibrium as practicable, the Ti64 samples were initially compressed to a low pressure (<5 GPa) in the α phase and then heated up slowly at a rate of ~ 100 K hr^{-1} to a target temperature. Isotherms were then collected in small pressure steps (<1 GPa) at the target temperature.

Data were mostly collected at beamlines I15 at diamond light source (DLS) and BL04-MSPD at the ALBA synchrotron [61]. The monochromatic x-ray wavelength was 0.4133 Å (30 keV) at I15 and 0.4246 Å (29.2 keV) at BL04. The FWHM of the x-ray beam microfocus at I15 and BL04 was ≤ 20 μm . The detector used at I15 was a Mar345 image plate detector and at BL04 a Rayonix CCD. Additional data were collected at the high pressure collaborative access team beamline 16-

BMD, at the advanced photon source (APS). The x-ray wavelength was 0.4133 Å (30 keV) and the detector used was a Mar345 CCD.

In total, eight isotherms were collected from initial temperatures of 298, 418, 517, 586, 642, 713, 844 and 886 K. All of the 2D angle-dispersive XRD (ADXRD) patterns were integrated azimuthally using Fit2D [62] or DIOPTAS [63]. The resulting 1D profiles were analysed by applying a Le Bail refinement using GSAS [64] or by performing a least-squares fitting of the d spacings of individual peaks using the JADE 9 [65] and unitcell [66] programs. Only XRD patterns containing reflections from both the sample and the pressure marker were analysed.

2.2. Bridgman-type cell experiments

To complement the DAC experiments, we performed lab-based experiments using a Bridgman-type belt apparatus. This device consists of a 150 ton oil-press containing steel-belted Bridgman-type opposed tungsten-carbide anvils. The sample is contained in a pyrophyllite gasket with hexagonal boron nitride acting as the PTM. The sample pressure is determined by calibrating the load applied to the anvils against high-pressure resistivity transitions in calibrant materials, see for example [67, 68]. Though the calibrant data is limited in range, for pressures above 10.5 GPa a linear extrapolation can be applied to the calibration [68]. The heating element consists of a graphite block connected to a 100 A power supply. Temperatures in the pressure chamber are measured using a shielded K-type thermocouple with an accuracy <3% [69].

This device is capable of pressurising samples to 13 GPa at temperatures up to 1600 K [69, 70]. Resistivity measurements are made across samples using the four probe method. Discontinuities in the measured electrical resistance are indicative of a material phase change. For this study, three experiments were performed on samples of Ti64 sourced from the same batch used in the DAC experiments.

3. Results and discussion

3.1. HP RT DAC XRD experiment

We performed one compression run at 298 K from 2.95(6) GPa to 66(1) GPa. The Ti64 sample was embedded in KCl, which acted as both the PTM and pressure marker. A Sanchez-technologies pressure control system (maximum output 1000 bar) was used to regulate the DAC membrane-pressure. A time interval of 2–3 min between membrane-pressure increase and data collection ensured the sample pressure was always close to equilibrium. At 6.4 GPa, the pressure gradient across the pressure chamber (gasket hole diameter <100 μm) was 0.3 GPa. The results at RT are in excellent agreement with previous studies [5–7]. Thus, for the sake of brevity (and to avoid redundancies) we do not show a selection of RT XRD patterns. In our experiments, the emergence of the dominant ω -Ti64 (110/101) peaks at 30(1) GPa signified the onset of the $\alpha \rightarrow \omega$ transformation. This sluggish transformation to the ω phase was completed at 40.7(8) GPa. The measured volume reduction $-\Delta V/V$, from α - to ω - was <2%.

The KCl B2 Vinet EoS parameters used to generate pressure values at 298 K, as a function of volume, were: $V_0 = 54.5 \text{ Å}^3$, $K_0 = 18.3(3) \text{ GPa}$ and $K'_0 = 5.60(3)$ [53], where V_0 is the ambient cell volume.

The c/a axial ratio for α -Ti64 was found to be almost invariant under pressure, fluctuating between 1.595 and 1.602 between 2.95(6) GPa and 33.1(6) GPa, again in good agreement with previous measurements [6, 7]. These values are smaller than the ideal value of 1.633 for the α phase. For ω -Ti64, c/a has a slightly positive slope, rising from 0.612 (the ideal value) to 0.617 between 34.8 GPa and 65.5 GPa. The calculated c/a ratio for ω -Ti64 at 0 K, due to local ordering of Al and V, rises from 0.616 at 20 GPa to 0.618 at 60 GPa, and then drops to 0.615 at 100 GPa [6].

The sample was slowly decompressed from 66(1) GPa, to reveal a strong hysteresis, with the ω phase stable to $\sim 9.1(1)$ GPa. A sudden jump in pressure to 3.2(1) GPa resulted in the Ti64 completely reverting back into the α phase. But unlike ω -Ti under quasihydrostatic conditions [11, 12], ω -Ti64 is not metastable at ambient pressure after pressure release [6]. Errandonea *et al* [16] recovered α -Ti from ω -Ti at RT, after decompressing a Ti sample embedded in NaCl, a similar PTM to KCl. But α -Ti was not detected after pressure release for ω -Ti embedded in the more hydrostatic PTMs argon and 4:1 methanol–ethanol [16] and helium [19]. In our earlier study of Ti64, we decompressed ω -Ti64 from 70 GPa to 0.8 GPa in a methanol–ethanol PTM and recovered α -Ti64 [6].

A discussion of the RT EoS will be conducted in section 3.3 in combination with the analysis of the HP–HT results. Here we would like just to mention that a 3rd order Birch–Murnaghan (BM3) EoS [71] fit to the α -Ti64 data generated the EoS parameters, $V_0 = 17.25(4) \text{ Å}^3$, $K_0 = 110(2) \text{ GPa}$ and $K'_0 = 3.8(2)$. For ω -Ti64, a BM3 fit generated $V_0 = 16.8(2) \text{ Å}^3$, $K_0 = 115(8) \text{ GPa}$ and $K'_0 = 4.6(8)$. A Vinet [72] fit to the data returned similar values. These EoS results are consistent with published data for Ti64 [5–7] and pure Ti [13–17, 20].

3.1.1. HP–HT DAC XRD experiments. Seven HP–HT isotherms were collected at 418(2), 517(2), 586(2), 642(3), 713(1), 844(5) and 886(2) K. All DACs were precompressed to ~ 5 GPa in the α phase at RT and then heated to a target temperature and compressed into the ω phase. To control the gas-membrane pressure to our DACs, we used a Sanchez-technologies control system at ALBA and a Druck PACE 5000 (maximum output 210 bar) at DLS and the APS. With the exception of the isotherms collected at 418 K and 642 K, all samples were compressed until diamond or gasket failure.

The first set of HP–HT experiments were performed at DLS (isotherms at 517, 642 and 886 K). All DACs were loaded with α -Ti64, NaCl as the PTM, and Cu as the pressure marker. The Cu P – V – T EoS used to generate pressure values comprised a BM3 for RT and a Mie–Grüneisen–Debye (MGD) term for the thermal effects [56].

In figure 2, a waterfall plot of integrated ADXRD patterns, collected at 642 K, shows the $\alpha \rightarrow \omega$ transition and demonstrates the sluggish nature of the transition. The XRD patterns

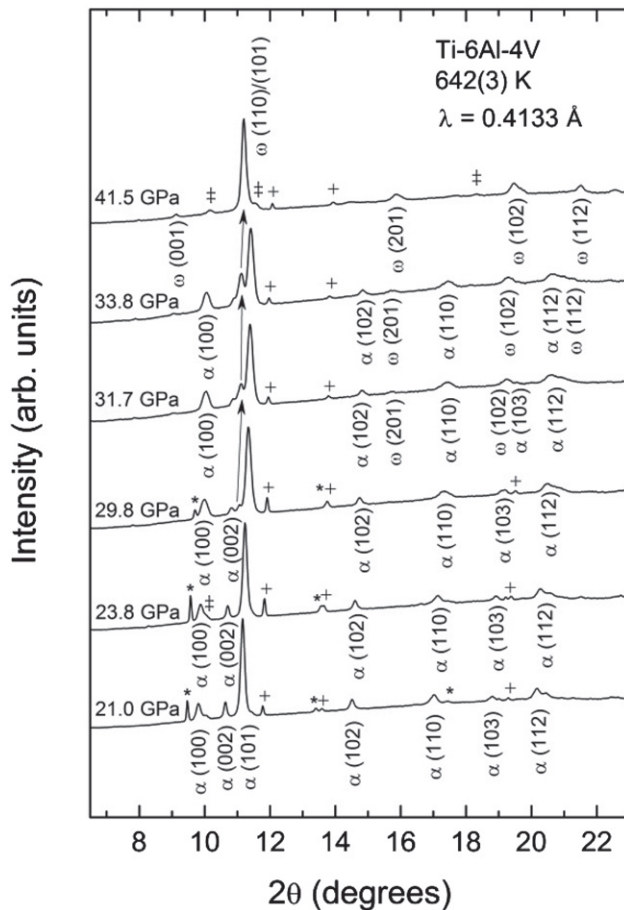


Figure 2. A waterfall plot of integrated ADXRD patterns showing the $\alpha \rightarrow \omega$ transformation in Ti-6Al-4V with increasing pressure at 642(3) K. The vertical arrow at 29.8 GPa points to the emergent ω (101)/(110) peaks. * represents reflections from B1 NaCl, + reflections from Cu, and ‡ reflections from Re. Less prominent peaks are not labelled.

are affected by preferred orientation due to limitations in the experimental apparatus. However, this does not affect phase identification. The dominant ω phase (101)/(110) peaks appear at $\sim 29(1)$ GPa (the peak positions are indicated by the vertical arrow at 29.8 GPa) and grow in intensity with increasing pressure, while simultaneously the α phase peaks gradually diminish in intensity, until at ~ 40 GPa the transformation is complete. The volume change from α to ω phase, $-\Delta V/V \sim 1.7\%$. The pressure range of $\alpha + \omega$ phase coexistence of ~ 10 GPa at 642 K matches that observed at RT. This DAC was compressed to 65 GPa at 642 K into the ω phase. On decompression back to 32 GPa and 642 K, Ti64 was still stable in the ω phase. An unexpected drop in pressure to 8 GPa resulted in the complete transformation back into α -Ti64. Piston and cylinder DACs often seize, then jump, during decompression at HT, leading to irregular intervals in sample pressure. This DAC was cooled down to 517 K and recompressed back into the ω phase at 30(1) GPa, with a phase coexistence extending over a range of ~ 9.5 GPa. Diamond failure in the ω phase occurred at ~ 45 GPa. For both isotherms the volume reduction from α -Ti64 to ω -Ti64, $-\Delta V/V < 2\%$. Pure

Ti remains in the ω phase if released back to ambient pressure at 444 K, but at 737 K there is a partial recovery of the α phase after decompression [19]. An isotherm collected at 886 K, the highest temperature reached in our DAC experiments, terminated early at ~ 23 GPa in the α phase due to gasket failure.

A second series of HP-HT DAC experiments were performed at ALBA (isotherms at 418, 586 and 713 K). Samples of α -Ti64 were embedded in KCl, which acted as both the PTM and pressure marker. Pressure values were generated using a B2 KCl EoS consisting of a Vinet RT term and an MGD thermal term [53]. The transition pressures for $\alpha \rightarrow \omega$ were: 30.0(3) GPa at 418 K, with a phase coexistence of ~ 8.3 GPa; 31(1) at 586 K, with a coexistence of ~ 8.5 GPa; and $\sim 31(1)$ GPa at 713 K, with a coexistence of ~ 8 GPa. Again, $-\Delta V/V$ from α -Ti64 to ω -Ti64, was $< 2\%$. The sample at 418 K was compressed to 49.4 GPa in the ω phase and then released back to 21.9 GPa, still in the ω phase. Upon cooling to RT and 24.7 GPa, the sample still retained the ω phase. Seizure of the cell prevented any further measurements. The 586 K and 713 K isotherms were terminated at 44 GPa and 67 GPa due to gasket failure. At 713 K, the pressure gradient across the chamber (gasket hole $< 100 \mu\text{m}$) at 22.7 GPa was 1.4 GPa. At 713 K and 48.6 GPa, the pressure gradient was 1.7 GPa. To avoid contamination of the XRD patterns from the gasket, we collected all of our patterns as close to the centre of the pressure chamber as possible and to reduce the effects of the pressure gradient.

An additional isotherm at 844 K was collected at the APS, this time using MgO as the PTM and pressure marker. The onset of the $\alpha \rightarrow \omega$ transition was observed at 29(2) GPa, with a coexistence region of ~ 8 GPa before completion of the transformation to the ω phase. ω -Ti64 was stable up to the highest pressure achieved, 93(1) GPa. Due to peak overlap and Re contamination it was not possible to measure the volume reduction across the α - ω phase boundary. In figure 3 we show an integrated ADXRD pattern of ω -Ti64 at 91(1) GPa and 848 K. The unit-cell parameters for the ω -Ti64 pattern in figure 3 are $a = 3.9617(27) \text{ \AA}$ and $c = 2.4666(12) \text{ \AA}$.

Pressure values were generated using a combined BM3 and modified MGD thermal EoS for MgO [55]. Unfortunately we did not detect a measurable lowering in intensity of the (001), (101), (111), (002) and (112) ω peaks to indicate the onset of the predicted $\omega \rightarrow \beta'$ transformation. However, based on our analysis, the simulated intensity of the (101) peak relative to the (110) begins to decrease at ~ 85 GPa. In figure 3, as the (101) and (110) start to separate, the (101) peak becomes a shoulder and introduces an asymmetry into the overall profile, which is consistent with the behaviour we observed at ~ 88 GPa in our previous RT experiment as ω -Ti64 transformed to β' -Ti64 [6]. In the current experiment, the run terminated at ~ 93 GPa due to diamond failure.

For all HP-HT experiments, the c/a axial ratio trend for α -Ti64 is effectively invariant under pressure, indicating isotropic compression, see figure 4. In the plot, the c/a ratio for the α phase at RT, 586 and 844 K averages as 1.597(8). The c/a ratio for ω -Ti64, on the other hand, appears to increase monotonically from the ideal ratio $\sim 0.613(1)$ at ~ 30 GPa to

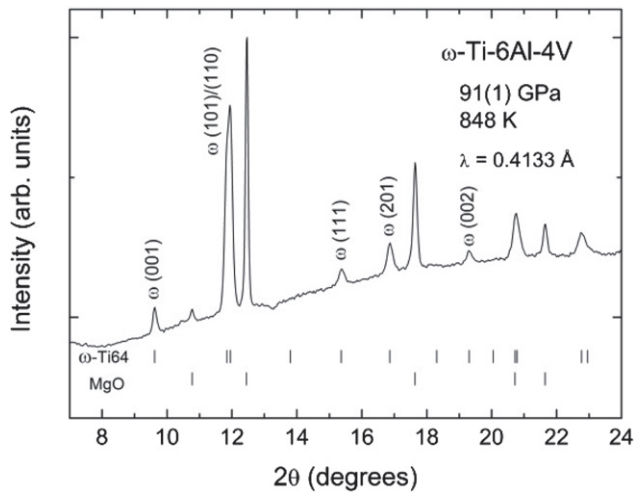


Figure 3. An integrated ADXRD pattern showing ω -Ti-6Al-4V at 91(1) GPa and 848 K. MgO was used as the pressure marker and pressure transmitting medium. The prominent ω phase peaks are indexed. The tick marks beneath the profile indicate the ω phase and MgO diffraction peaks. Note the splitting of the dominant ω (101)/(110) peaks at $\sim 12^\circ$.

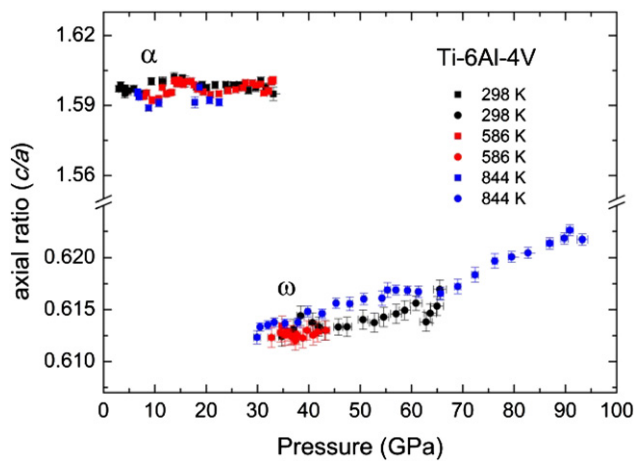


Figure 4. A plot of axial ratios for α -Ti-6Al-4V and ω -Ti-6Al-4V, as a function of pressure, at 298, 586 and 844 K. Square datapoints represent α -Ti-6Al-4V and circular datapoints represent ω -Ti-6Al-4V.

$\sim 0.622(1)$ at ~ 91 GPa. The slope also seems to be independent of temperature. This behaviour is not universally observed in Ti HP experiments. A constant c/a ratio ~ 0.6125 for ω -Ti was reported up to 8.1 GPa in a large press at RT [20], whereas in DAC experiments at RT, the c/a ratio for ω -Ti rises in a similar fashion to our ω -Ti64 data, but starting from a much lower $\alpha \rightarrow \omega$ transition pressure [17–19].

3.1.2. Bridgman-type cell experiment. Three isobaric experimental runs were performed using the Bridgman-type cell apparatus and resistivity measurements were made using the four-probe method. In figure 5, the change in electrical resistivity as a function of temperature is shown for Ti64 at 4.0(2), 8.0(2) and 12.0(2) GPa. The sudden decrease in the measured resistivity is indicative of a material transformation. This

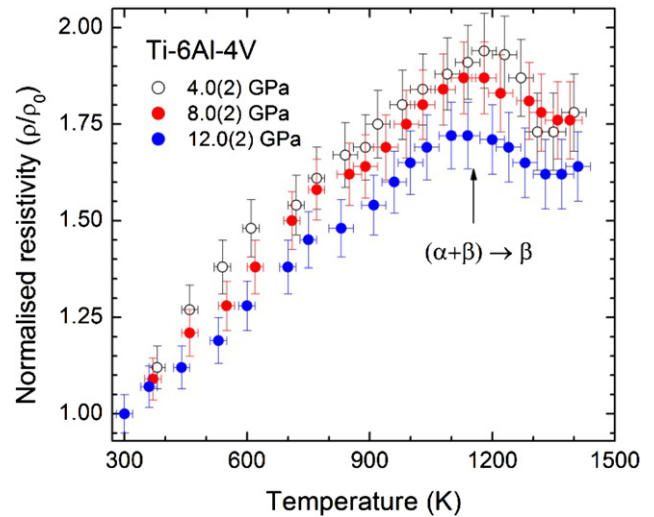


Figure 5. A plot showing the measured changes in resistivity of Ti-6Al-4V at 4.0(2), 8.0(2) and 12.0(2) GPa, as a function of temperature. ρ_0 corresponds to the ambient conditions resistivity measurement.

change of resistivity on its own does not provide evidence for the $\alpha \rightarrow \beta$ phase transition in Ti64. However, since Ti64 is a near- α two-phase $\alpha + \beta$ alloy at ambient conditions, and is known to transform at ambient pressure to the $\alpha + \beta$ phase at ~ 1070 K [2], the modest change observed in the slope for $((d\rho/\rho_0)/dT)$ at 1230(30) K at 4.0(2) GPa; 1180(30) K at 8.0(2) GPa; and 1140(30) K at 12.0(2) GPa, is likely caused by the growth of β phase grains. Similar experiments performed on hcp Ti, Zr and Gd at HP-HT in a large press found the measured resistivity increased with increasing temperature and decreased with increasing pressure [73]. The slight change in slope for isobaric data collected at temperatures up to ~ 900 K suggested the $\alpha \rightarrow \omega$ transformation in Ti occurred above 2 GPa at HT [73]. The α -Ti64 plots in figure 5 appear to confirm the relationship between resistivity and temperature, and resistivity and pressure.

3.2. HP-HT phase diagram

The Ti64 pressure–temperature (P – T) phase diagram is shown in figure 6. The DAC data and Bridgman-type cell data from this study are shown alongside RT data collected by us in an earlier study [6]. Based on the DAC data, the α – ω phase boundary appears to be almost vertical in P – T space. The slope of the α – ω phase boundary, $dT/dP \sim 550$ K GPa $^{-1}$. The slope of the α – ω phase boundary for pure Ti was reported by Zhang *et al* to be 345 K GPa $^{-1}$ [22]. The Bridgman-type cell data lie on a slope given by $dT/dP \sim -11.3$ K GPa $^{-1}$. The black dashed line denotes the proposed solid–solid boundaries for the α – ω and $(\alpha + \omega)$ – β phases. Extrapolating the black dashed line from the Bridgman cell data towards the proposed α – ω phase boundary suggests the α – β – ω triple point occurs at ~ 30 GPa and ~ 910 K.

The black dot-dot-dash line indicates the upper pressure bound of the mixed-phase $(\alpha + \omega)$ region, beyond which, ω -Ti64 is stable. The width of this region of coexistence does not change significantly with increasing temperature. It

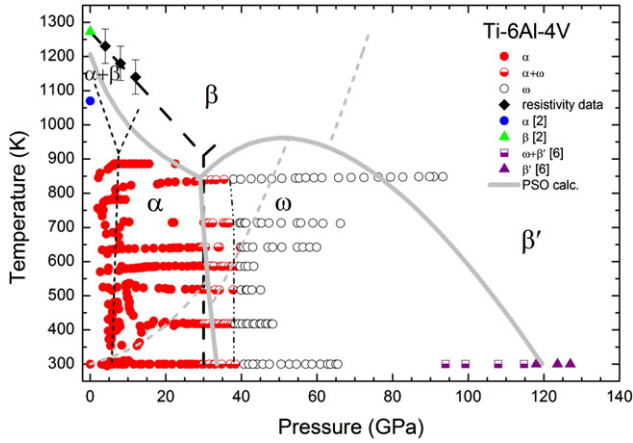


Figure 6. The P - T phase diagram of Ti-6Al-4V. Experimental data from this study are represented by: red circles, α -Ti64; half-red half-white circles, mixed phase ($\alpha + \omega$)-Ti64; white circles, ω -Ti64; black diamonds, phase changes measured using the Bridgman-type cell. Experimental data from previous work are represented by: blue circle, α -Ti64 [2]; green triangle, β -Ti64 [2]; half-purple half-white squares mixed phase ($\omega + \beta'$)-Ti64 [6]; purple triangles β' -Ti64 [6]. The black dashed lines act as a visual guide for the proposed α - ω and ($\alpha + \beta$)- β phase boundaries based on our data. The black dashed-dot line indicates the complete transition to ω -Ti64 from the mixed phase ($\alpha + \omega$)-Ti64. The solid grey lines represent the solid-solid phase boundaries calculated using the PSO technique; and the dashed grey lines the Hugoniot, also calculated using the PSO. The black short dashed lines represent the solid-solid phase boundaries of pure Ti measured by Zhang *et al* [21].

reduces from ~ 10 GPa at RT to ~ 8 GPa at 844 K, which suggests the kinetic barrier in the transformation to the preferred ω phase is weakly dependent on temperature and hydrostaticity. Once transformed, ω -Ti64 extends to at least ~ 93 GPa and 850 K. In this P - T diagram there are regions where we have observed the coexistence of the α and ω phases. Phase coexistence could be affected by Al redistribution between the α and ω phase. However, the exact Al content in each phase cannot be accurately determined from our experiments. Since the quantity of Al in Ti64 is known to vary between 5.7 and 6.5%, we expect the Al redistribution to not significantly affect our results.

The solid and dashed grey lines in figure 6 represent the solid-solid phase boundaries and the Hugoniot, calculated using the PSO technique [31, 32]. The PSO is a stochastic analysis technique that fits statistical mechanics-based condensed matter models to wide ranging datasets. For solid phases, an EoS can be generated by combining contributions to the Helmholtz free energy from a cold curve calculation, thermal ion term, and thermal electron term. In this study, the cold curve was calculated using the augmented stabilised jellium EoS (ASJEOS) [74], which requires only three inputs: ρ_0 , K_0 and K'_0 , where ρ_0 is the density. The thermal ion term combines a mean field model [75] with an Einstein density of states model, where the Einstein temperature is given by

$$\theta_E = \frac{h}{2\pi k} \epsilon^{1/3} \rho^{5/6} (2(2 - \lambda) E'_C + 3\rho E''_C)^{1/2}, \quad (1)$$

Table 1. Multiphase EoS parameters for Ti-6Al-4V, generated using the PSO technique. Parameters λ and ϵ represent model choices for the solid phase and do not change during the PSO calculations.

Parameter	α -Ti-6Al-4V	β -Ti-6Al-4V	ω -Ti-6Al-4V
ρ_0 (g/cc)	4.4615	4.5075	4.6578
K_0 (GPa)	119.78	131.01	156.58
K'_0	3.2518	2.7469	2.7799
λ	-1	-1	-1
ϵ	0.70711	0.76980	0.70711
Boundary	Ambient	α - β	α - ω
P_1 (GPa)		0.0001	33
T_1 (K)		1207	300
P_2 (GPa)		29	29
T_2 (K)		846	846

where the derivatives of the cold curve energy E_C , are with respect to density; ϵ is a constant dependent on the lattice structure; λ takes the value -1, 0, or +1, which gives rise to the Slater, Dugdale-MacDonald, or Vaschenko-Zuborov Grüneisen functions when calculated using $\Gamma = -\partial \ln \theta_E / \partial \ln V$, where Γ is the Grüneisen parameter and V is the volume. The Thomas-Fermi model represents the electronic term. The EoS along a phase boundary is calculated using the method of mixtures [76]. To predict a phase boundary, the Gibbs free energies are forced to be equal at two specified starting P - T points, which are constraints described by experimental data. No constraints exist for subsequent calculated points in P - T space.

Since the PSO method does not incorporate metastable or two-phase regions in calculations, phase boundaries in P - T space are generated as single points only [32]. As such, the PSO α - β phase boundary in figure 6 is a little misleading. The ($\alpha + \beta$) mixed phase region is currently treated as β -Ti64 using the PSO technique, hence the apparent disagreement between the predicted α - β phase boundary and our proposed ($\alpha + \beta$)- β phase boundary. Nonetheless, the α - β - ω triple point, predicted by PSO to occur at 30 GPa and 850 K [32], is in reasonable agreement with our inferred triple point. The parameters obtained from the PSO fitting process are presented in table 1. In figure 6, the calculated value for the RT ω - β' phase boundary appears to be a little high at ~ 120 GPa, compared with our previous measurement for $\omega \rightarrow \beta'$ of ~ 95 -120 GPa [6].

At 848 K, there is a suggestion in our current dataset that the $\omega \rightarrow \beta'$ transition may be occurring at ~ 85 GPa, but PSO predicts the transition below 80 GPa. This could be related to the use of the Einstein model, which neglects anharmonicity, and which has been found to be relevant for the bcc structure (β -phase) in metals at HP-HT [77]. An alternative explanation for the β' -phase at higher pressures is the presence of kinetic barriers [78]. To close this discussion we would like to emphasise the point that the PSO technique takes into account shock data as well as static data in the fitting process, and that the overall result includes a misfit with some of the experimental data [32]. The PSO calculated P - T phase boundaries, shown in grey in figure 6, are therefore generated as a balance of best fits to the available experimental data.

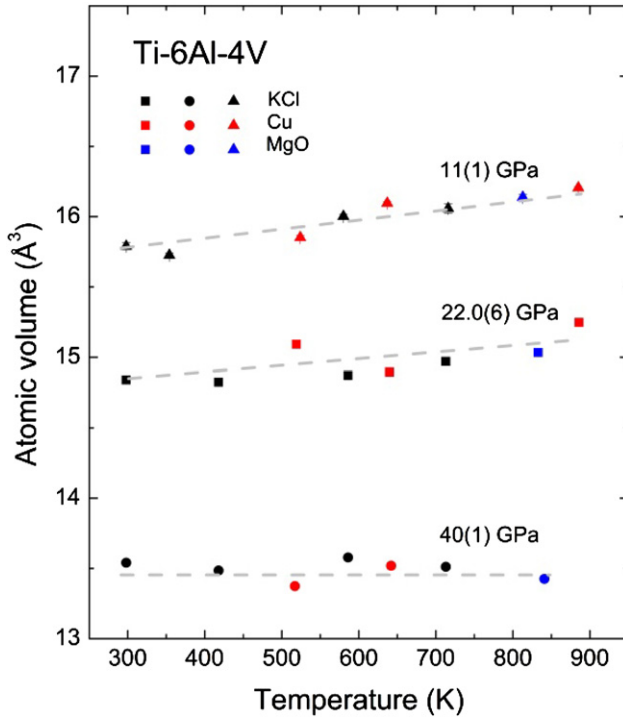


Figure 7. The variation in the atomic volume of Ti-6Al-4V as a function of temperature, at pressures 11(1), 22.0(6) and 40(1) GPa generated using KCl, Cu and MgO thermal EoSs. Ti-6Al-4V is in the α -phase at 11 and 22 GPa and in the ω -phase at 40 GPa. The uncertainties are absorbed into the data-points. The dashed grey lines have been added as a visual guide.

3.3. P - V - T EoS

Since our data were collected from three synchrotron visits, it is worth considering the impact an analysis of three separate datasets may have on the overall P - V - T EoS. Firstly, errors inadvertently introduced during the setting up of the beamlines could lead to systematic errors propagating into the data. These effects are difficult to quantify but are assumed to be negligible since detector calibrations were performed using x-ray standards (CeO₂, LaB₆ and Si) at the start of each experiment. Secondly, the selection of a range of pressure media and markers for these experiments may give rise to dissimilar pressure environments and inconsistent pressure values. We used thermal EoSs for KCl [53], MgO [55] and Cu [56] to determine sample pressures. In figure 7, the measured atomic volumes for Ti64 are plotted against temperature, at pressures 11(1), 22.0(6) and 40(1) GPa, generated using the KCl, MgO and Cu thermal EoSs. The effects of thermal expansion on atomic volume decrease with increasing pressure. The lack of scatter in the data suggests the overall impact of the different DAC loadings on the volume analysis is not critical and therefore these variations can be discounted as limiting factors in the determination of a P - V - T EoS for Ti64.

The thermal EoS of a material can be defined as:

$$P(V, T) = P(V, T_0) + P_{th}(V, T), \quad (2)$$

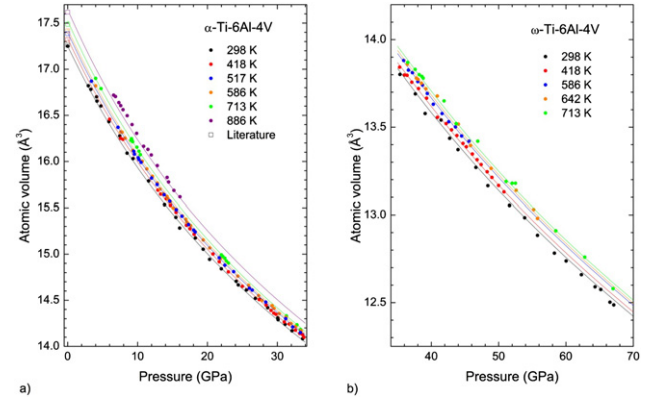


Figure 8. Pressure–volume–temperature data for (a) α -Ti-6Al-4V and (b) ω -Ti-6Al-4V. The solid lines correspond to EOS fits to the data. To ease interpretation of the data, we have omitted a number of isotherms from these figures.

where $P(V, T_0)$ represents the RT isothermal EoS component and $P_{th}(V, T)$ the thermal component. The thermal expansion of a material is given by

$$V_{0T} = V_{00} \exp \int_{T_{ref}}^T \alpha(T) dT \quad (3)$$

where T_{ref} is 298 K, V_{00} is the volume at 298 K, and $\alpha(T)$ is the coefficient of thermal expansion. The Berman model [79] can be used to describe the effects of non-linear thermal expansion on the variation of the volume with temperature, and at constant pressure:

$$V_{0T} = V_{00} \left(1 + \alpha_0 (T - T_{ref}) + \frac{1}{2} \alpha_1 (T - T_{ref})^2 \right), \quad (4)$$

where α is treated as a constant. For small changes in volume, the thermal expansion can be approximated to

$$\alpha \approx \alpha_0 + \alpha_1 (T - T_{ref}), \quad (5)$$

where α_0 is the thermal expansion coefficient at 298 K [80].

A P - V - T EoS was generated for α -Ti64 and ω -Ti64 using the least-squares fitting programme *EoSFit7* [80, 81]. Isothermal data generated at 298, 418, 517, 586, 713 and 886 K were used to generate the thermal EoS for α -Ti64, and isotherms at 298, 418, 586, 642 and 713 K were used for ω -Ti64. For both Ti64 phases, a BM3 EoS was fit to the RT data, giving the EoS parameters reported in section 3.1.

The isotherms for α -Ti64 are shown in figure 8(a) along with the best fits to the data. In figure 8(b), we show the isotherms and fits for ω -Ti64. The corresponding EoS parameters for both phases are presented in table 2 alongside previously published parameters for pure Ti at HP-HT [20]. There is good agreement with the values reported for pure Ti [20]. The negative value for $(\partial K_0 / \partial T)_P$ in Ti64 indicates a reduction in the bulk modulus with increasing temperature. Between RT and ~ 900 K, this corresponds to a decrease in the bulk modulus of $\sim 15\%$ for α -Ti64 and $\sim 6\%$ for ω -Ti64.

Table 2. P – V – T EoS parameters generated using a 3rd order Birch–Murnaghan model at RT and a Berman model for the thermal component.

	V_0 (Å ³)	K_0 (GPa)	K'_0	α_0 (K ^{−1})	α_1 (K ^{−2})	$(\partial K_0/\partial T)_P$ (GPa K ^{−1})
α -Ti-6Al-4V	17.25(4)	110(2)	3.8(2)	4.1(6) 10 ^{−5}	3(2) 10 ^{−8}	−0.028(3)
ω -Ti-6Al-4V	16.8(2)	115(8)	4.6(8)	3.0(9) 10 ^{−5}	1.0(4) 10 ^{−8}	−0.011(2)
α -Ti [20]	17.64(1)	114(3)	4.0 ^a	1.2(6) 10 ^{−5}	2.5(1.1) 10 ^{−8}	−0.011
ω -Ti [20]	17.29(1)	107(3)	—	6.5(3.5) 10 ^{−6}	2.8(6) 10 ^{−8}	−0.0095

^a K'_0 was fixed to derive a value for K_0 .

4. Conclusion

Commercial powdered polycrystalline Ti64 has been investigated at HP–HT using DACs and a Bridgman-type cell. ADXRD data up to 95 GPa and between RT and 886 K were collected using membrane-driven DACs. Resistivity data up to 12 GPa, and at temperatures between RT and 1500 K were collected using a Bridgman-type cell.

The data has been combined to generate for the first time a phase diagram in P – T space for Ti64. This work confirms the suppression of the $\alpha \rightarrow \omega$ transition in Ti64 up to ~ 30 GPa. For low purity Ti64 (this sample), the $\alpha \rightarrow \omega$ transition appears to be insensitive to the pressure environment in a DAC and also to temperatures between RT and ~ 900 K. On decompression, there is a pronounced hysteresis in ω -Ti64. The $\omega \rightarrow \alpha$ transition is sensitive to temperature, and transforms back into the α phase at higher pressures than is the case at lower temperatures. Our calculated solid–solid phase boundaries using the PSO method are consistent with these results and with previously published shock and static Ti64 data. Our proposed α – β – ω triple point appears to occur at the same temperature as that proposed for pure Ti, but shifted from ~ 8 GPa to ~ 30 GPa. In addition, we have derived the thermal EoSs for α -Ti64 and ω -Ti64 and found the agreement with α -Ti and ω -Ti to be good.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Acknowledgments

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High-Pressure Structural Systematics in Neodymium to 302 GPa

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Angle-dispersive x-ray powder diffraction experiments have been performed on neodymium metal to a pressure of 302 GPa. Up to 70 GPa we observe the $hP4 \rightarrow cF4 \rightarrow hR24 \rightarrow oI16 \rightarrow hP3$ transition sequence reported previously. At 71(2) GPa we find a transition to a phase which has an orthorhombic structure ($oF8$) with 8 atoms in the unit cell, space group $Fddd$. This structure is the same as that recently observed in samarium above 93 GPa, and is isostructural with high-pressure structures found in the actinides Am, Cf and Cm. We see a further phase transition at 98(1) GPa to a phase with the orthorhombic α -U ($oC4$) structure, which remains stable up to 302 GPa, the highest pressure reached in this study. Electronic structure calculations find the same structural sequence, with calculated transition pressures of 66 and 88 GPa, respectively, for the $hP3 \rightarrow F8$ and $oF8 \rightarrow C4$ transitions. The calculations further predict that $oC4$ -Nd loses its magnetism at 100 GPa, in agreement with previous experimental results, and it is the accompanying decrease in enthalpy and volume that results in the transition to this phase. Comparison calculations on the $oF8$ and $oC4$ phases of Sm show that they both retain their magnetism to at least 240 GPa, with the result that $oC4$ -Sm is calculated to have the lowest enthalpy over a narrow pressure region near 200 GPa at 0 K.

I. INTRODUCTION

The predominantly trivalent lanthanide metals (La to Lu, excluding Ce, Eu, and Yb) exhibit a common series of structural phase transformations with increasing pressure: hcp ($hP2$ in Pearson notation) $\rightarrow$ Sm-type ($hR9$) $\rightarrow$ dhcp ($hP4$) $\rightarrow$ fcc ($cF4$) $\rightarrow$ distorted-fcc ($hR24$, $oI16$, or $oS8$)^{1–4}. This transition sequence is thought to arise from increases in occupation of the $5d$ states as a result of pressure-induced s - to d -electron transfer⁵. Under further compression, the distorted-fcc phases undergo first-order volume collapse transitions into more complex phases, the low-symmetry structures of which are reported to be a result of the participation of $4f$ electrons in the bonding⁶, although this has been questioned in more recent publications^{7–10}.

In Nd and Sm, the structure of the initial phase seen after the volume collapse is reported to be hexagonal with spacegroup $P6_222$ and 3 atoms per unit cell ($hP3$), a structure otherwise seen only in Yb¹¹. On further compression, both Nd and Sm are then reported¹² to transform into a monoclinic structure (spacegroup $C2/m$, $mC4$) first observed in Ce at high pressure over 40 years ago¹³, and subsequently reported in Gd, Tb, Dy, Ho, Er and Tm^{14–19}.

However, we have recently shown^{20,21} that the $mC4$ structure does not account for all of the observed peaks in the diffraction profiles from Gd-Tm, and that a better fit

can be obtained with a 16-atom orthorhombic structure, space group $Fddd$ ($oF16$), that is isosymmetric with the $oF8$ structure seen in the actinides Cf, Am and Cm at high pressure. A comparison of the published diffraction pattern from Nd at 89 GPa²² with those from the $oF8$ phases of Cf, Am and Cm^{23–25} revealed them to be very similar, suggesting that the post- $hP3$ phase of Nd has the $oF8$ structure rather than the $oF16$ structure seen in the higher- Z lanthanides. A subsequent diffraction study of Sm to 222 GPa revealed that the post- $hP3$ phase of Sm also has the $oF8$ structure at pressures above 93 GPa²¹.

Unlike in Sm, however, the $oF8$ phase of Nd is known to undergo a further transition at 113 GPa to the orthorhombic $oC4$ structure seen in Ce and Pr at only 5 GPa and 20 GPa, respectively^{3,26–28}. This would then appear to be the next structure in the general lanthanide transition sequence, but with a transition pressure that increases greatly with atomic number (from 5 GPa for $Z=58$ to 113 GPa for $Z=60$). Here we describe diffraction studies on Nd to above 300 GPa which were performed (i) to confirm that the post- $hP3$ phase has the $oF8$ structure, (ii) to determine the nature of the $oF8$ structure immediately prior to the transition to the $oC4$ phase, thereby providing information from which we might predict where the same transition will occur in Sm, and (iii) to determine whether Nd undergoes a further transition over this pressure range to the post- $oC4$ phase reported in Pr above 147 GPa²⁹. We have also conducted elec-

tronic structure calculations of the *hP3*, *oF8* and *oC4* phases of both Nd and Sm to provide insight into the observed structural behaviour, to calculate the magnetic behaviour of Nd, and to estimate the pressure of the *oF8*→*oC4* transition in Sm.

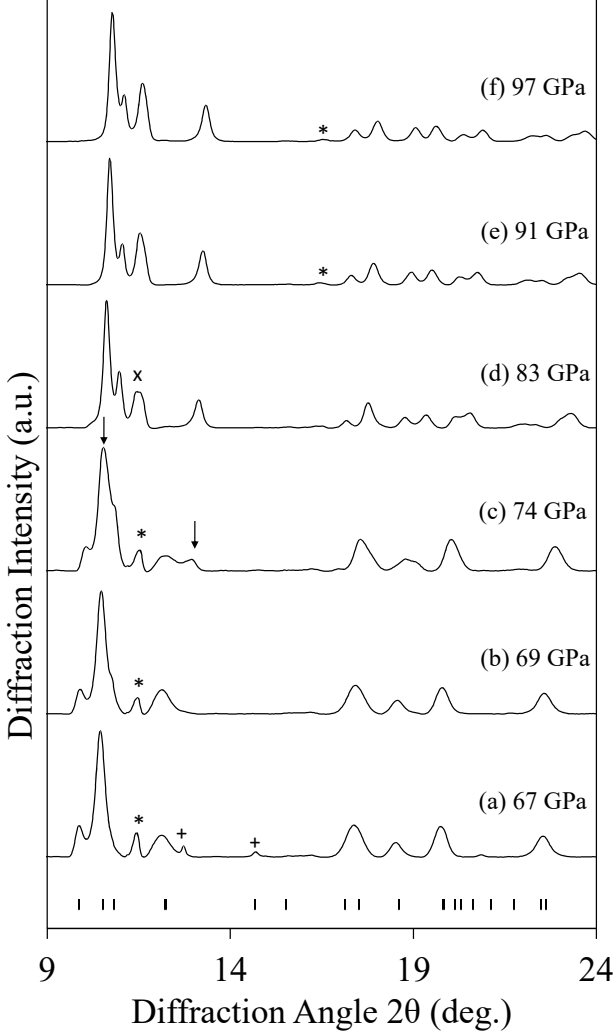


FIG. 1. Diffraction profiles collected from Nd on pressure increase to 97 GPa. The data were collected from the same sample at DLS using a wavelength $\lambda = 0.4246$ Å. Tick marks beneath profile (a) mark the calculated peak positions in the *hP3* phase at this pressure. The peaks marked with asterisks are from the W gasket, and the peaks marked with a + are from the Cu calibrant. The two arrows in profile (c) mark the first appearance of peaks from the post-*hP3* phase. The peak labelled with a 'x' in profile (d) is a closely-spaced doublet which includes the (110) peak from the W gasket and a peak from the new phase. Single-phase patterns from the post-*hP3* phase are seen in profiles (e) and (f).

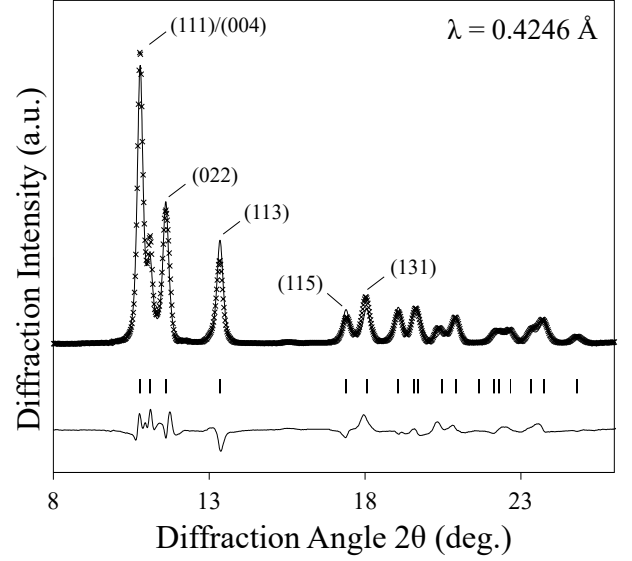


FIG. 2. Rietveld refinement of the *oF8* structure to a diffraction profile from Nd at 97 GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile ($R_P = 1.8\%$, $R_{wP} = 2.5\%$, goodness of fit (GoF) = 0.46, $R(F^2) = 6.1\%$). The first six peaks of the *oF8* phase are labelled with their Miller indices.

II. EXPERIMENTAL DETAILS

High-purity distilled samples of Nd supplied by Ulrich Schwarz at the Max-Planck-Institut für Chemische Physik fester Stoffe in Dresden were loaded into two diamond-anvil cells (DACs) in a dry argon atmosphere (<1 ppm O_2 and <1 ppm H_2O) to prevent oxidation. The DACs were equipped with diamonds with 300 μm culets, bevelled to diameters of 50 μm and 100 μm , and tungsten (W) gaskets. The samples were loaded without any pressure transmitting medium to prevent contamination. Both samples were loaded with a small (few μm) copper (Cu) sphere to act as a pressure calibrant, using the recently-published Cu equation of state of Sokolova *et al.*³⁰. However, in one cell the Cu sphere was lost on closing the DAC, and the sample pressure was subsequently determined using the diamond Raman mode method³¹.

Diffraction data were collected in two experiments on the high-pressure I15 beamline at the Diamond Light Source (DLS), United Kingdom, and in a further two experiments on the Extreme Conditions P02.2 beamline at the PETRA-III synchrotron in Hamburg, Germany. Further low-pressure data were obtained in 2008 on beamline 9.5HPT at the now-closed Synchrotron Radiation Source (SRS) at Daresbury Laboratory in the UK. Monochromatic x-ray beams of wavelength 0.4246 Å (DLS), 0.2898 Å and 0.4830 Å (PETRA-III) and 0.4438 Å (SRS), focused down to 20 $\mu m \times 20 \mu m$ (DLS), 0.85 μm

$\times 0.85 \mu\text{m}$ and $3 \mu\text{m} \times 6 \mu\text{m}$ (PETRA-III) and $50 \mu\text{m} \times 50 \mu\text{m}$ (SRS) were used, and the powder-diffraction data were recorded on Perkin-Elmer (PETRA-III) and Mar345 (DLS and SRS) area detectors, placed 300-400 mm from the sample. LaB_6 and CeO_2 diffraction standards were used to calibrate the exact sample-detector distances and the detector tilts in each experiment. The 2D diffraction images collected at each pressure were integrated azimuthally using Fit2D³² and Dioptas³³ to obtain standard 1D diffraction profiles, which were then analysed using Rietveld and Le Bail profile-fitting methods³⁴ or by fitting to the measured d -spacings of individual diffraction peaks³⁵. The sub-micron beam available at PETRA-III enabled us to map the pressure distribution in each sample at 166 GPa and the results are given in Figs. S1 and S2 in the Supplementary Information³⁶.

III. RESULTS AND DISCUSSION

Diffraction patterns were initially collected up to 40 GPa and the data confirmed the phase transition sequence reported previously, including the existence of the orthorhombic $oI16$ phase, previously observed between the $hR24$ and $hP3$ phases^{3,37}. Evans reported the transition to $oI16$ to start at 25.8 GPa, with a transition to the $hP3$ phase above 40 GPa, in agreement with current study.

On compression above 40 GPa (see Figure 1), the $hP3$ phase was found to be stable to 71(2) GPa where a transition to the post- $hP3$ phase was observed (as illustrated in Figure 1 (c)). Above this pressure, the diffraction peaks from the $hP3$ phase decreased in intensity while those from the post- $hP3$ phase became more intense (see Figure 1 (d)). Single-phase profiles of the higher-pressure phase were seen above 90 GPa (see Figure 1 (e) and (f)), and these are strikingly similar to those obtained from the $oF8$ structure of Sm at pressures above 157 GPa²¹.

Figure 2 shows a Rietveld fit of the $oF8$ structure to the background-subtracted diffraction profile obtained from Nd at 97 GPa, where the refined lattice parameters are $a = 2.681(1) \text{ \AA}$, $b = 4.781(1) \text{ \AA}$, and $c = 8.783(1) \text{ \AA}$, $V/V_0=0.413(2)$, with atoms on the $8a$ site of spacegroup $Fddd$ at (0,0,0). The fit is excellent, with all of the observed diffraction peaks being accounted for.

Further compression of the sample (see Figure 3) showed that the $oF8$ phase was stable to 98(1) GPa, where the appearance of new diffraction peaks signalled a phase transition to the post- $oF8$ phase. This transition was sluggish, and single-phase profiles from the higher-pressure phases, which were very similar to those reported previously by Chesnut *et al.*³⁸, were obtained only above 170 GPa.

Figure 4 shows a Rietveld fit of the $oC4$ structure to the background-subtracted diffraction profile from Nd at 302 GPa, the highest pressure reached in this study. The refined lattice parameters at this pressure

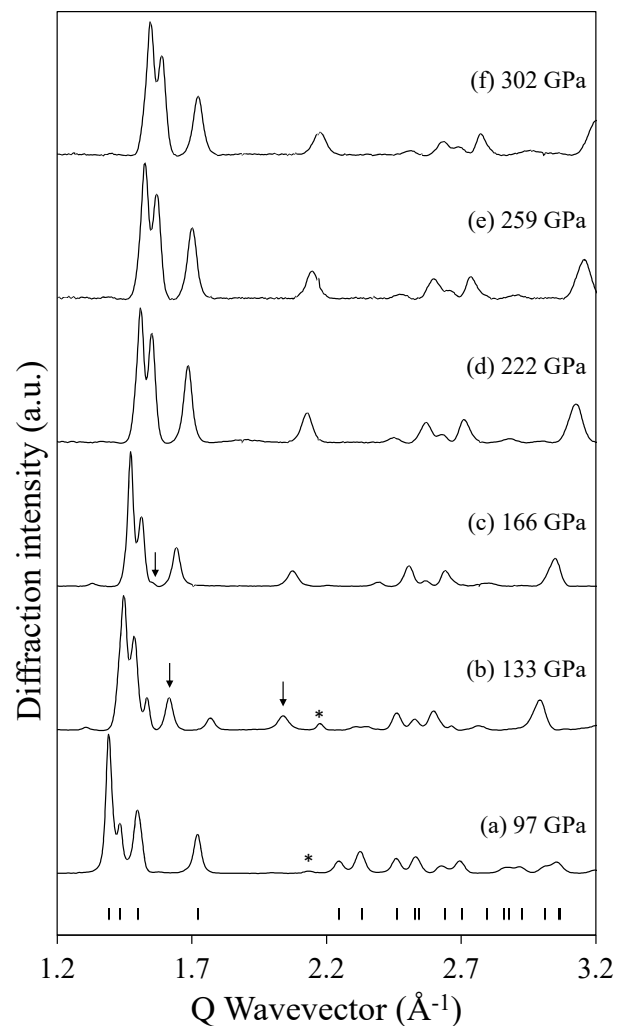


FIG. 3. Diffraction profiles collected from Nd on pressure increase to above 300 GPa. The data were collected from two samples at DLS and PETRA-III using wavelengths of $\lambda = 0.4246 \text{ \AA}$ (DLS) and $\lambda = 0.4830 \text{ \AA}$ (PETRA-III) and so are plotted as a function of wave vector Q so as to take into account the two different wavelengths. Tick marks beneath profile (a) mark the calculated peak positions of the $oF8$ phase. The peaks marked with the asterisks in profiles (a) and (b) are from the W gasket. The two arrows in profile (b) mark the appearance of peaks from the $oC4$ phase, and the arrow in profile (c) marks the almost complete disappearance of a peak from the remainder of the $oF8$ phase. Single-phase patterns are seen in profiles (d), (e) and (f).

are $a = 2.280(1) \text{ \AA}$, $b = 4.515(1) \text{ \AA}$, and $c = 4.129(2) \text{ \AA}$, $V/V_0=0.312(6)$, with atoms on the $4c$ site of spacegroup $Cmcm$ at (0,0.114(6),0.25). The fit is again very good, with all of the observed diffraction peaks being accounted for. The misfits in peak intensities arise from the textured nature of the sample.

Nd is the only lanthanide in which the $oF8 \rightarrow oC4$

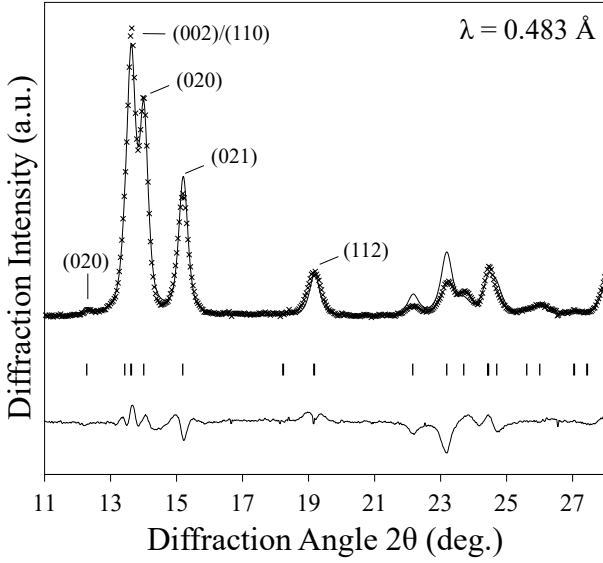


FIG. 4. Rietveld refinement of the *oC4* structure to a diffraction profile from Nd at 302 GPa, showing the observed (crosses) and calculated (line) diffraction patterns, the calculated reflection positions, and the difference profile ($R_P = 0.7\%$, $R_{wP} = 1.1\%$, $\text{GoF} = 0.33$, $R(F^2) = 8.2\%$). The first six observable peaks of the *oC4* phase are labelled with their Miller indices.

transition has been observed to date. However, the similarity of the phase transition sequences in Nd and Sm at lower pressures suggests that the latter will also transform to the *oC4* structure, but at pressures higher than have been reached to date (222 GPa)²¹. It is therefore of interest to determine whether the structural data obtained from the present study might enable us to predict at which pressure *oF8*-Sm will become unstable and transform to the *oC4* structure.

The *oF8* structure comprises a 4-layer ABCDA stacking of flat, quasi-close packed layers, the distortion of which from hexagonal symmetry can be quantified by the deviation of the b/c axial ratio from the ideal ortho-hexagonal value of $\sqrt{3} = 1.732$. The *hP3* structure comprises a 3-layer ABC stacking of the same layers, which are exactly hexagonal in this case. The *oC4* structure can also be described as a 2-layer stacking of heavily-distorted hcp layers with their distortion being quantified by deviations of the b/a ratio from the ideal ortho-hexagonal value of 1.732. The structures of *oF8*-Nd at 100 GPa and *oC4*-Nd at 105 GPa are shown in Figure 5, presented so as to highlight the arrangement of the quasi-hcp layers in each.

The pressure dependence of the b/c ratio in *oF8*-Nd is shown in Figure 6, along with the ideal value of $\sqrt{3}$ in the *hP3* phase, and the b/a ratio in the *oC4* structure. As was seen previously in Sm²¹, there is a clear discontinuity in the “hexagonality” of the atomic layers

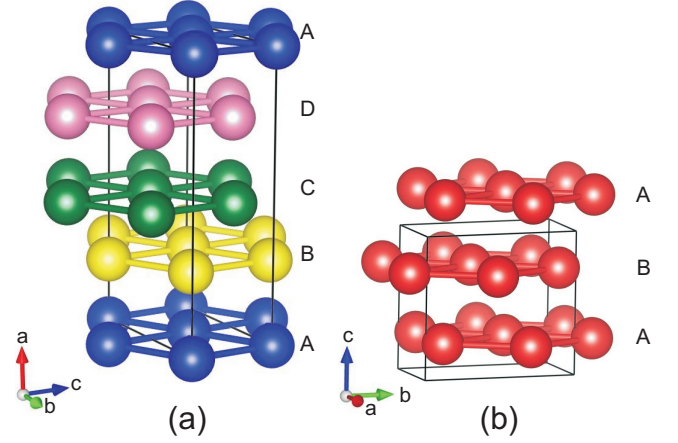


FIG. 5. The crystal structures of (a) *oF8*-Nd at 100 GPa and (b) *oC4*-Nd at 105 GPa. Both structures comprise stackings of flat, distorted-hcp atomic layers: the 4-layer stacking sequence in *oF8* is ABCD, while *oC4* has a 2-layer ABAB repeat. The distortion of the layers from hexagonal symmetry can be quantified by the deviation of the b/c axial ratio in *oF8*-Nd, and the b/a axial ratio in *oC4*-Nd, from the ‘ideal’ ortho-hexagonal value of $\sqrt{3}=1.732$.

from 1.732 to ~ 1.78 at the *hP3* $\rightarrow$ *oF8* transition. However, in contrast to Sm, where the b/a ratio of *oF8*-Sm increases monotonically with pressure, reaching a value of 1.82 at 222 GPa²¹, the b/a ratio of *oF8*-Nd remains constant with pressure at ~ 1.79 up to 100 GPa where the transition to the *oC4* structure results in a further sharp increase in the axial ratio to ~ 1.92 , increasing to ~ 1.98 at 120 GPa, after which the ratio is little changed by pressure up to 302 GPa. As the b/a ratio of *oF8*-Sm passes through the value of 1.79 at ~ 140 GPa without undergoing a transition to the *oC4* structure, the hexagonality of the atomic layers in the *oF8* structure would seem to offer no insight into either the *oF8* $\rightarrow$ *oC4* transition pressure or the transition mechanism.

The compressibility of Nd up to 302 GPa is shown in Figure 7. There are no detectable volume changes at any of the phase transitions up to the *hP3* phase at 50 GPa, but at the *hP3* $\rightarrow$ *oF8* and *oF8* $\rightarrow$ *oC4* transitions there are small volume changes ($\Delta V/V_0$) of 0.4(2)% and 0.4(1)%, respectively. Despite these, the full compression curve can be fitted with a single equation of state (EoS) with little loss of accuracy.

In our recent studies of Sm²¹ and Y⁴⁰, we utilised Holzapfel’s APL equation of state (EoS) formalism to analyse the compressibility. This EoS has several advantages over other formalisms, and enables the compressibility to be linearised straightforwardly. Non-linear behaviour can then be interpreted as arising from deviations from “regular” compressive behaviour expected from a “normal” metal, perhaps arising from changes in the electronic structure⁴¹.

If one fits the compression data using the second order

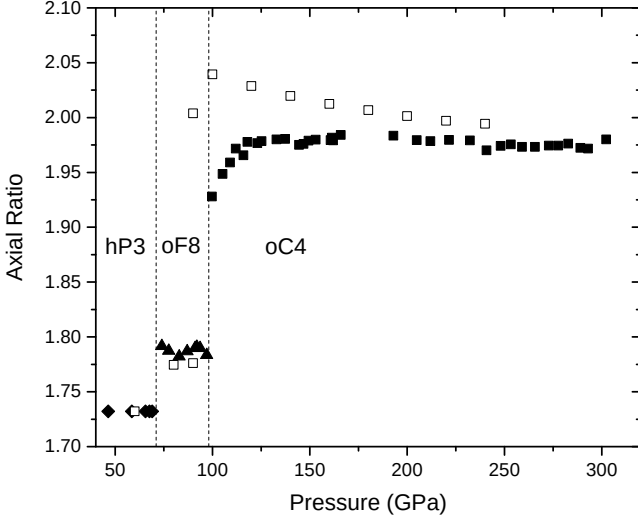


FIG. 6. The pressure dependence of the hexagonality of the atomic layers in the *hP3*, *oF8* and *oC4* structures of Nd, as quantified by the b/a (*hP3* and *oC4*) and b/c (*oF8*) axial ratios - see Figure 5. Because of the extended y -scale, the error bars on the axial ratios are smaller than the symbols used to plot the points, and have therefore been omitted. The experimental data points are shown with filled symbols, while the computed values are shown using unfilled symbols.

(AP2) form of the Adapted Polynomial of order L (APL) EoS^{42,43}:

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

where K_0 is the zero pressure bulk modulus, K' is its pressure derivative, $x = (V/V_0)^{1/3}$, $c_0 = -\ln(3K_0/p_{FG})$, $c_2 = (3/2)(K' - 3) - c_0$, $p_{FG} = a_{FG}(Z/V_0)^{5/3}$ is the Fermi-gas pressure, Z is the atomic number, and $a_{FG} = [(3\pi^2)/5](\hbar^2/m_e) = 0.02337 \text{ GPa nm}^5$ is a constant, then the compression data can be linearised in a so-called $\eta_{APL} - x$ plot:

$$\eta_{APL}(x) = \ln\left(\frac{px^5}{p_{FG}}\right) - \ln(1-x) \quad (2)$$

To highlight the similarities and differences in compression data of different lanthanides with respect to “ideal” behaviour, and to also highlight the systematics in phase transition pressures, it is most convenient to use an APL linearisation not with respect to x but rather with respect to the radius ratio R_{WS}/R_I^1 , where R_{WS} is the pressure dependent Wigner–Seitz radius

$$R_{WS} = \frac{3}{4\pi} (V_{\text{atom}})^{1/3} \quad (3)$$

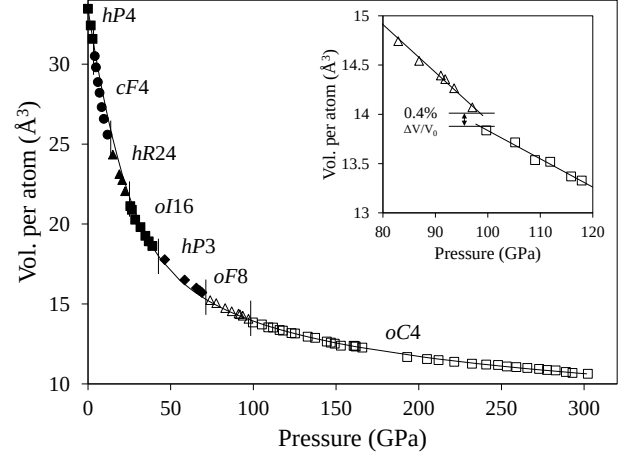


FIG. 7. The compressibility of Nd up to 302 GPa. The solid line shows the best fitting third-order APL EoS to the full compression curve. The inset shows an enlarged view of the volume near 100 GPa, illustrating the small volume discontinuity ($\Delta V/V_0$) of 0.4% and change in compressibility at the transition.

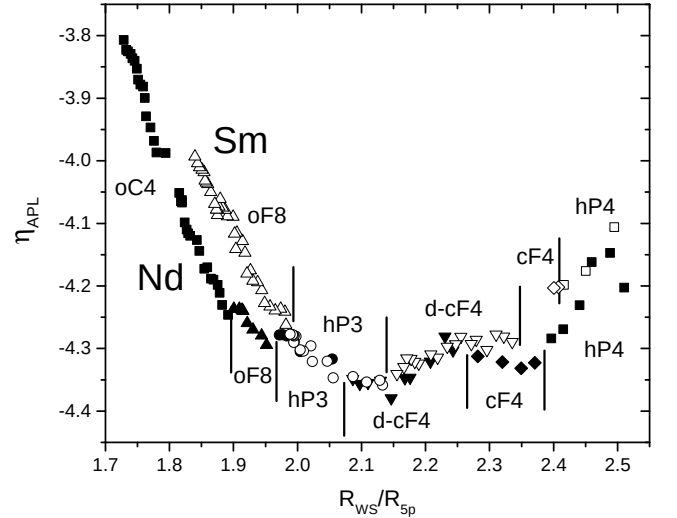


FIG. 8. Linearisation of the compression of Nd shown in the form of an $\eta_{APL} - R_{WS}/R_{5p}$ plot, where R_{WS} is the Wigner–Seitz radius in angstroms and R_{5p} is the $5p$ ionic radius³⁹. The data from the different phases of Nd are plotted using different symbols, and the phase boundaries are marked with vertical lines. The *hR24* (Sm) phase, and the *hR24* and *oI16* phases (Nd), are labelled as ‘d-cF4’.

and R_I is a pressure independent individual value for the ionic radius of each element⁴³. The pressure dependent values of R_{WS} were determined from the measured atomic volumes, while R_I were taken to be the R_{5p} radii⁴⁴, as tabulated by Waber and Cromer³⁹.

Figure 8 shows the APL linearised compression data

for Nd in the form of a $\eta_{APL} - R_{WS}/R_{5p}$ plot, along with the recently-published data for Sm to 222 GPa²¹. In such a plot, materials undergoing regular compression will show linear or quasi-linear behaviour, with the correct theoretical limit of $\eta(0)=0$. This is certainly not the case for Nd, the data for which exhibit significant curvature, very similar to that observed in Sm²¹. As in Sm, there is a striking change in behaviour within the *hP3*-Nd phase, such that both *oF8*-Nd and *oC4*-Nd display the linear behaviour expected of a “regular” metal, and with a gradient very similar to that exhibited by *oF8*-Sm⁴¹.

Kruger *et al.* have previously reported⁴⁴ that constant critical radii ratios R_{WS}/R_{5p} are observed for the equilibrium values of the three transitions between the *hP2*, *hR9*, *hP4* and *cF4* structures of the regular trivalent lanthanides, suggesting that these transitions arise from changes in the *d*-band occupancy without any essential contributions from *4f* electron bonding. At that time, the evidence suggested that the transitions to the ‘special’ low-symmetry structures at higher pressures, that is *hR24*, *oF8*, *oF16* and *oC4*, did not occur at similarly critical radii, perhaps suggesting the role of *4f* electron delocalization in these transitions⁴⁴.

Figure 8 shows the locations of all the now known phase transitions in Nd and Sm. The *oI16* phase is seen only in Nd and, as a distorted-*cF4* phase³, it has been combined with the *hR24*-Nd phase in Figure 8 and labelled “d-*cF4*”.

The phase boundaries in Nd are displaced systematically to lower values of R_{WS}/R_{5p} (i.e. higher pressures) compared to those observed in Sm, with a displacement of 0.1 or less. What then stands out is the extended stability range of *oF8*-Sm, which extends down to $R_{WS}/R_{5p}=1.84$, whereas Nd transforms into the *oC4* structure at $R_{WS}/R_{5p}=1.90$. Taking into account the offset in R_{WS}/R_{5p} between the transitions in Nd and Sm, Figure 8 suggests we would expect a transition to *oC4*-Sm at $R_{WS}/R_{5p} \sim 1.91$, equivalent to a pressure of ~ 145 GPa.

The non-linear behaviour of Nd illustrated in Figure 8 means that its compressibility cannot be fitted by a single second-order AP2 EoS (see Figure S3). However, as was the case with Sm and Y, the compression curve of Nd *can* be fitted with the third-order AP3 EoS, as illustrated in Figure 7, which shows both the compression curve to 302 GPa, and the AP3 fit. The best-fitting parameters are $K_0 = 37.2(2)$ GPa, $K' = 1.57(2)$ and $K'' = -0.051(2)$. It can be seen from the curve that the AP3 fit slightly underestimates the compressibility of the *hP4*, *cF4* and *hR24* phases in order to more accurately fit the higher-pressure data.

IV. ELECTRONIC STRUCTURE CALCULATIONS

To gain further insight into the behaviour of Nd at high compression, we have performed extensive DFT calcula-

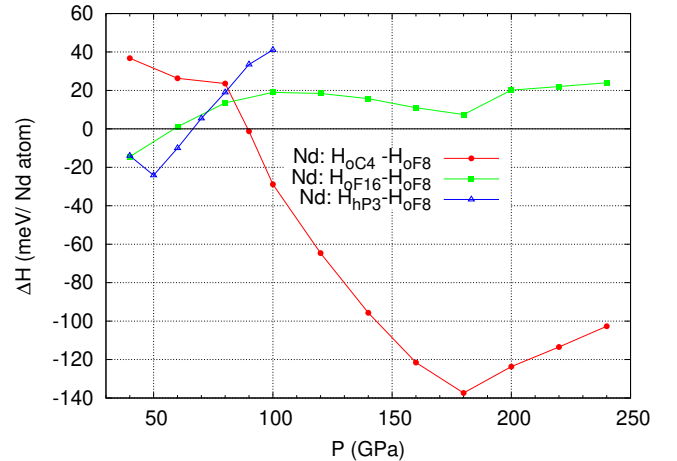


FIG. 9. The enthalpy gain of the *hP3*, *oC4* and *oF16* phases relative to that of the *oF8* phase. Notice the range of pressure between 60 and 90 GPa where the *oF8* phase appears to be most stable. The *oC4* phase becomes the most stable at pressures above 90 GPa. *hP3* phase is most stable below 60 GPa. The kinks on the curves correspond the loss of magnetisation.

tions of the *oF16*, *oF8*, *oC4* and *hP3* phases. Structural optimisation of bulk Nd in each phase was accomplished by using DFT calculations with the VASP⁴⁵ package, utilising the Perdew-Burke-Ernzerhof functional⁴⁶. The *k*-point sampling was performed using Monkhorst-Pack meshes, ensuring a *k*-point density of at least $0.2\text{\AA}^{-1}$ for all the structures and a Gaussian smearing of 0.1 eV. During the DFT structural optimization, a convergence on internal forces and stress tensor of 0.01 eV/Å was reached, and the energy cutoff was set to 500 eV. Scalar relativistic spin-orbit coupling was taken into account within the Koelling-Harmon approximation⁴⁷.

Our zero-temperature DFT calculations for Nd reveal a series of phase transitions on compression as shown in Figure 9. Namely, by comparing the total enthalpy of the three phases examined (*hP3*, *oF8* and *oC4*) we find that the *hP3* phase has the lowest enthalpy up to 66 GPa, after which the *oF8* has the lowest enthalpy to 88 GPa, with the *oC4* phase having the lowest enthalpy above that pressure. The calculated transition pressures of 66 GPa and 88 GPa are 5-10 GPa lower than the experimentally observed transition pressures of 71(2) and 98(1) GPa seen experimentally at room temperature.

The relative enthalpy gain for the *oF8* and *oC4* phases shown in Figure 9 exhibits a number of kinks which can be traced back to the loss of magnetisation, as illustrated in Figure 10. The two lowest-enthalpy phases above 70 GPa, *oC4* and *oF8*, exhibit a profoundly different magnetisation behaviour as a function of pressure: while *oC4*-Nd loses its magnetic order at 100 GPa, *oF8*-Nd does so only at 200 GPa, well outside its calculated stability range of 66-88 GPa. The loss of the magnetisation in *oC4*-Nd leads to a reduction in its atomic volume, which is clearly visible at 90 GPa in the calculated compress-

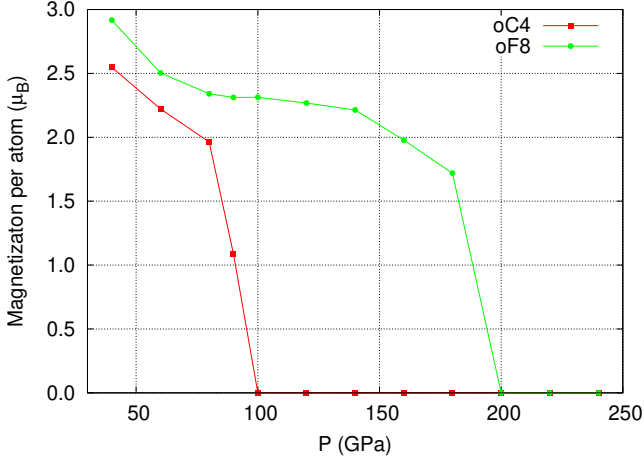


FIG. 10. The calculated magnetisation, in μ_B/atom , of *oF8*-Nd and *oC4*-Nd as a function of pressure. The magnetisation in *oC4*-Nd is greatly reduced at 90 GPa, and is zero at 100 GPa - the pressure where it is first observed experimentally. The magnetisation of *oF8*-Nd decreases rapidly only above 180 GPa, well beyond the upper pressure at which it is stable.

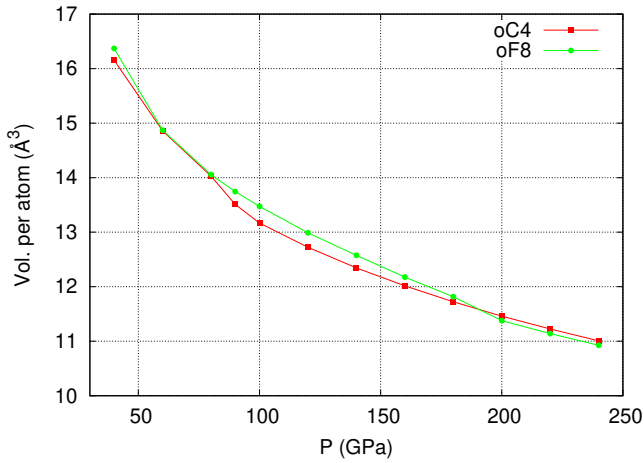


FIG. 11. The calculated volume per atom of *oF8*-Nd and *oC4*-Nd over the pressure range 40-240 GPa. The loss of magnetisation in *oC4*-Nd at 90 GPa is accompanied by a volume change ($\Delta V/V_0$) of 0.9% and a reduction in the compressibility.

ibilities of the *oC4* and *oF8* phases shown in Figure 11, and also a sharp reduction in its enthalpy such that it becomes lower than that of the *oC4* phase above 90 GPa. Without this loss of magnetisation, the enthalpy curves (Figure 10) suggest that *oF8*-Nd would have remained the most stable phase to much higher pressures.

The *oF8* $\rightarrow$ *oC4* transition occurs at 98(1) GPa at 300 K, and our calculations therefore suggest that the experimentally-observed *oC4* phase has no net magnetization. This is in agreement with the low temperature resistivity measurements of Song *et al.*⁷, which showed the magnetic ordering temperature (T_0) of Nd to drop to

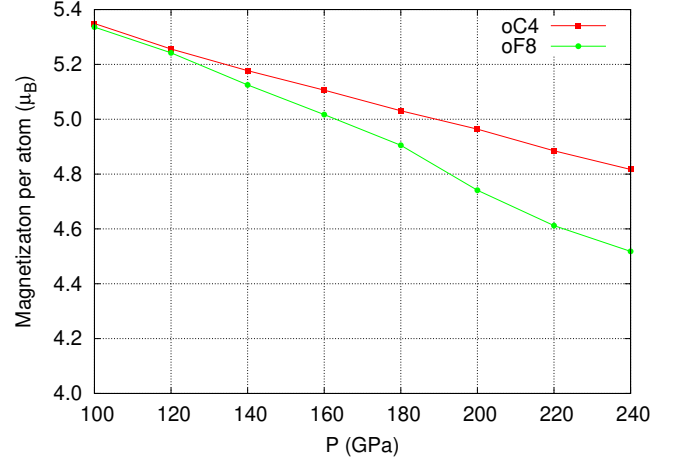


FIG. 12. The calculated magnetisation, in μ_B/atom , of the *oC4* and *oF8* phases of Sm over the pressure range from 100 to 240 GPa. In contrast to the behaviour seen in Nd, the magnetisation, although decreases, is non-zero in both phases at all pressures.

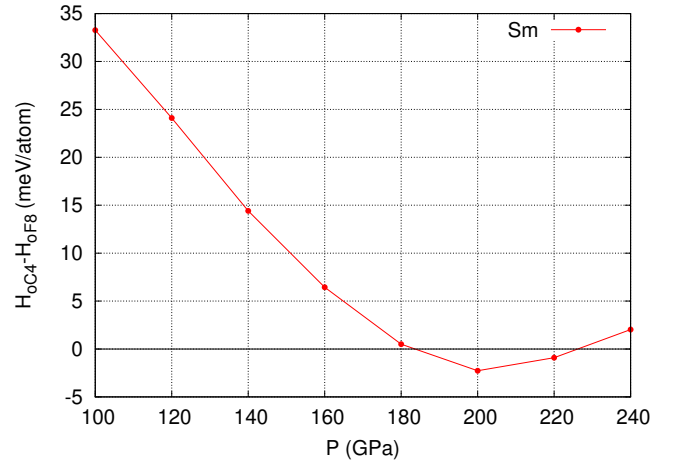


FIG. 13. The enthalpy gain of *oC4*-Sm relative to that of the *oF8*-Sm over the pressure range 100 – 240 GPa. The *oC4* phase is more stable over only a narrow pressure range between 185 and 225 GPa, above which the *oC4* phase is favoured. Note the greatly reduced y -scale in comparison to Figure 9.

0 K above ~ 130 GPa. The lack of a sharp drop in T_0 at 100 GPa might arise from the sluggish nature of the *oF8* $\rightarrow$ *oC4* transition, such that the sample is mixed-phase until 170 GPa. This same argument was made by Velisavljevic *et al.* to explain the gradual decrease in resistivity they observed in Nd above 100 GPa⁴⁸.

The calculated magnetic transition and associated volume change in *oC4*-Nd is intriguing, as the volume change ($\Delta V/V_0$) of 0.9% at 100 GPa should be easily detectable by x-ray diffraction. The sluggishness of the *oF8* $\rightarrow$ *oC4* transition on pressure increase at 300 K means that *oC4*-Nd is only a minority component of the sample

near 100 GPa. However, there are still sufficient Bragg peaks to determine its volume with high precision, as demonstrated in Figure 7, and these measurements show no evidence of any volume discontinuity after the transition to *oC4*, although there is a reduction in compressibility, as highlighted in the inset to Figure 7. This may suggest that the sample is already in the higher-density, non-magnetic state, and that the transition within the *oC4* phase takes place at a pressure below 100 GPa. In that case, the sluggishness seen on compression suggests that the reverse *oC4*→*oF8* transition will also take place over a large pressure range on decompression. As a result, a single-phase *oC4*-Nd sample obtained above 170 GPa on compression might be retained as single-phase *oC4*-Nd below 100 GPa on decompression. If there is a magnetic transition in *oC4*-Nd at these lower pressures, then this might be apparent from changes in the resistivity of the sample on cooling, as has been used to measure the ordering temperature in the lower-pressure *oF8* and *hP3* phases of Nd⁷. Simultaneous x-ray diffraction measurements would both ensure that the sample remained single-phase *oC4*-Nd, and enable the 0.9% volume change predicted to accompany the magnetic transition (Fig. 12) to be observed and measured. Further studies at both room- and low-temperature are thus required.

For comparison with our calculations on Nd, we have also made DFT calculations of the *oF8* and *oC4* phases of Sm, which reveal very different behaviour. *oC4*-Sm and *oF8*-Sm are very close in volume and energy at all pressures, and, crucially, while the magnetisation of *oF8*-Sm and *oC4*-Sm decreases with pressure, it does not go to zero in either phase up to 240 GPa (see Figure 12). The *oC4* phase is calculated to have the lower enthalpy over only a small pressure range of 185-225 GPa (see Figure 13), and, even then, the enthalpy gain per atom is very small, 2 meV/atom at most (compare the *y*-axis scales of Figs 13 and 9). This small stability range, and the very small enthalpy gain at 0 K, probably explains why *oC4*-Sm has not been observed experimentally over this pressure range at room temperature. It is also possible, of course, that the *oF8*→*oC4* transition in Sm takes place at a pressure higher than calculated, which is close to the highest pressure at which Sm has been studied to date (222 GPa).

In either case, it is clear that the *oF8*→*oC4* transition pressure in Nd and Sm has little correlation with the R_{WS}/R_{5p} ratio. While we originally interpreted the different behaviour as *oF8*-Sm having a greatly extended stability range, it is perhaps more correct to see the stability range of *oF8*-Nd as greatly reduced. As said, it is the loss of magnetisation in *oC4*-Nd that results in its rapid decrease in enthalpy relative to the *oF8* phase, and without this the transition pressure between the two

phases would have been very much higher. As *oC4*-Sm is calculated to remain magnetic to at least 240 GPa, this greatly extends the stability range of the *oF8*-Sm phase.

V. CONCLUSIONS

The structure of Nd metal above 71(2) GPa is found to be face-centred orthorhombic (*oF8*) rather than monoclinic as reported previously. The same structure is observed in Am, Cm and Cf at high pressure, and also in Sm²¹. However, this structure is different to the isosymmetric *oF16* structure observed in the heavy trivalent lanthanides Gd-Tm (except Yb)²⁰ and also in Y^{40,49}. *oF8*-Nd is stable to 98(1) GPa, where it transforms to the *oC4* phase, which is itself stable to 302 GPa, the highest pressure reached in this study. High-precision measurements of the compressibility of Nd reveal that it becomes less compressible after the transition to the *hP3* phase at 43 GPa and that in the *oF8* and *oC4* phases its compressibility is that of a regular metal.

Electronic structure calculations of the *hP3*, *oF8* and *oC4* phases of Nd predict that the *hP3*→*oF8* and *oF8*→*oC4* transitions take place at 66 and 88 GPa, respectively, and that the latter transition results from the loss of magnetism in *oC4*-Nd which reduces both its volume and enthalpy. Comparison calculations on the *oF8* and *oC4* phases of Sm, in which the *oC4* phase has not been seen experimentally at pressures up to 222 GPa at 300 K, predict that *oC4*-Sm is the more stable of the two over only a small pressure range of 185-225 GPa at 0 K, and that the enthalpy difference between the two structures is very small. The calculations predict no loss of magnetism in *oC4*-Sm to at least 240 GPa, greatly extending the stability range of the *oF8* phase.

VI. ACKNOWLEDGEMENTS

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