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Novel Materials Under Extreme Conditions

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Abstract

Materials under extreme conditions often exhibit novel behaviours that differ widely from those observed at room pressure and temperature. These novel behaviours include metal to insulator transitions, insulator to metal transitions, pressure induced superconductivity, valency changes and structural phase transitions.

Structural phase transitions are seen in many simple elemental materials when exposed to variations in pressure and temperature. In germanium, a number of well studied room temperature solid to solid phase transitions are known however few studies have been carried out on the high temperature behaviour of these phases. A study of high temperature germanium is presented at pressures up to 111 GPa using powder x-ray diffraction techniques showing evidence of a novel high temperature crystalline phase, Ge-VIII. Alongside this new phase, further extensions to the phase diagram are proposed, exploring the Ge-II/Ge-IV phase boundary.

Another phenomenon often observed under extreme conditions is the introduction of novel reaction pathways. One such material group of interest within the area of novel reaction pathways is the formation of hydrides. These hydrides formed under high pressure often have high hydrogen densities and as such are of potential interest as potential superconducting materials as well as some hydrides having predicted behaviours analogous to those of atomic solid metallic hydrogen. Some experimental results are presented from investigations into the formation group XIV hydrides under high pressure which show no evidence of hydride formation up to 135 GPa along with evidence of the formation of a potentially superconducting hydride of Co.
Lay summary

Most of human existence occurs in a very narrow range of pressure and temperature conditions, and yet these conditions are not the norm across the known universe; for example, below the surfaces of planets, pressures can readily reach millions of times that of the earths’ atmosphere. As we cannot directly access these environments, it is through the field of extreme conditions sciences that we are able to explore the mysteries of these environments.

Within the realms of extreme conditions, many interesting phenomena can be seen to occur. Materials can change from insulators to metals, chemical reactions that would not ordinarily occur can be instigated, and atomic structures can adopt different arrangements. These changes include such phenomena as the well known transformation of coal into diamonds or commonly occurring transformations of elements (such as oxygen, silicon and many others) into metals (and superconductors) with pressure. The basis of much of extreme conditions sciences and this thesis, is in trying to determine the arrangements of the atoms. Understanding these atomic arrangements then allows us to comprehend many of the material physical and chemical properties in these conditions and offers the ability to better grasp the behaviours of matter in environments outside of those in which humans inhabit.

Typically, to achieve the pressures required to observe many of these changes, samples of materials are compressed between the surfaces of two diamonds in specially designed apparatus referred to as diamond anvil cells (DACs). With DACs, pressures can readily be reached that are several millions times that of the earth’s atmosphere, with the added benefit that, through various techniques, the temperatures of samples within DACs can also be easily controlled. Through this ability to control changes in temperature and pressure, materials can be, in essence, ‘cooked’ into new phases and compounds that would not normally occur
within chemistry at room temperature and pressure.

This kind of high pressure ‘cooking’ is well understood to have the potential to bring about the formation of super-hard materials or materials with interesting electronic properties such as superconductivity in materials. Superconductivity in itself is an interesting phenomenon in which a conductive material undergoes a change that causes it to have no resistance to electrical current, a feature which has great potential for industrial applications. It is well established that these extreme conditions ‘cooking’ techniques can be a great tool when forming new hydrogen containing materials, or hydrides, of which many are expected to exhibit superconducting behaviours. Recent experimental studies have shown that hydrides of lanthanum have shown that attainable temperatures for this superconducting behaviour may be achievable with the phenomenon being seen at temperatures as high as −23.15 °C, only slightly below the temperature of the average household freezer.

Throughout this thesis, the hydride formation of several materials was investigated with cobalt, germanium and lead all being tested using DAC techniques combined with laser heating across a range of pressures and temperatures. These projects concluded with different degrees of success. As was predicted, cobalt was seen to form a hydride (CoH\textsubscript{3}) which is predicted to show superconducting behaviours. The attempted formation of lead and germanium hydrides showed that under the conditions explored, no hydrides formed but these experiments may be used as a basis from which further studies can be undertaken. As is often the case with science, the investigations into germanium, whilst not yielding the expected results, showed interesting and previously unobserved behaviour across an unexplored range of conditions. This led to a change in direction to better map out the high temperature behaviour of pure germanium under compression.
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][2].

(Liam Carl Kelsall, 24th October 2021)
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Contents

Abstract i

Lay summary ii

Declaration iv

Acknowledgements v

Contents viii

List of Figures x

List of Tables xix

1 Introduction 1

1.1 High Pressure Science ............................................. 1

1.2 Thesis Outline ..................................................... 2

1.2.1 Chapter 2: Experimental Apparatus and Techniques ... 3

1.2.2 Chapter 3: Studies of High Temperature Elemental Germanium at High Pressure ............................................. 3

1.2.3 Chapter 4: Mixed Group XIV and Hydrogen Systems ... 4

1.2.4 Chapter 5: Investigations into the Cobalt-Hydrogen System 4

2 Overview of Experimental Apparatus and Techniques 5

2.1 The Diamond Anvil Cell ............................................. 5
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.1)</td>
<td>Cross section depicting a flat (left) and bevelled (centre) brilliant cut diamonds as used in diamond anvil cell (DAC) experiments alongside a Boehler-Almax IIa (BA) (right) cut flat diamond. The diamonds’ tables (a), facets (b), culets (c) and bevel (d) are labelled to clarify the terms used when describing DACs. Notice should be given to the key difference between BA and brilliant cut diamonds to the rear facets (e) which are smooth and conical on the BA diamonds to facilitate self levelling in the seat. The bottom two images show the view of these two cut styles from above the culets.</td>
</tr>
<tr>
<td>(2.2)</td>
<td>Simplified schematic of a diamond anvil cell showing the key components. The central sample environment comprises of a hole in the gasket material hermetically sealed between the two diamond culets.</td>
</tr>
<tr>
<td>(2.3)</td>
<td>Example sketch of DACs in different states of alignment. The size difference between the top (pink) and bottom (blue) diamond has been exaggerated for clarity in this illustration. A cell with good alignment (left) has a clear set of concentric circles when looking through the diamond culets indicating the two culet centres are aligned. The poorly aligned cell (right) show the two diamonds clearly off centre in a position where the load force will be uneven, leading to shear when a load is applied, likely causing anvil failure.</td>
</tr>
<tr>
<td>(2.4)</td>
<td>Example spectra of the stressed first order Raman mode at approximately 86 GPa.</td>
</tr>
<tr>
<td>(2.5)</td>
<td>Example schematic of a dual-sided laser heating setup for DAC XRD experiments with an optical setup for emission spectroscopy from the high-pressure beamline ID-27, ESRF. The blue line represents the beam paths of the Nd:YAG lasers, the red line the beam path of the Co2 and HeNe laser and the green line the path of the x-ray source. This figure is reproduced from Petitgirard et al. [39], ©2014 Petitgirard et al. [CC-BY-4.0].</td>
</tr>
</tbody>
</table>
(2.6) Sketches of typical temperature distributions associated with the laser heating process relative to the heating beam (green dashed lines) red areas indicate high temperatures with blue areas denoting colder temperatures with the general temperature of the sample decreasing with distance from the central heating point (adapted from the studies presented by Du et al., Kiefer et al., Dewaele et al., and Goncharov et al. [42–45]). Profiles are presented viewing from within the beam path looking down on the sample (left), and as a cross-section of the heated material for both single-sided (centre) and double-sided (right) laser heating.

(2.7) An example of a typical raw diffraction plate (insert) and its corresponding integrated diffraction pattern. The diffraction sample is a CeO₂ calibration sample with incident x-rays of wavelength λ = 0.3344 Å. The red rectangle indicates the region enlarged within the smaller insert.

(2.8) Geometric illustration of Bragg’s law. Atomic Bragg planes spaced by lattice spacing $d_{hkl}$ are struck by an incoming wave which is specularly reflected at an angle $\theta$ giving the diffracted angle $2\theta$. The additional path travelled by the lower wave is $d_{hkl} \sin \theta$ on both the inbound and outbound path giving a total path difference of $2d_{hkl} \sin \theta$.

(2.9) Example of a synchrotron XRD beamline configuration at beamline P02 at PETRA III. This figure is reproduced from the work of Liermann et al. [60] ©2015 Liermann et al. [CC-BY-4.0].

(2.10) Visualisation of changes in energy levels of electrons during commonly occurring scattering effects.

(3.1) Accepted phase diagram of Ge before the investigations contained within this chapter. Data points marked with filled symbols represent the data points provided in the work of Prakapenka et al. [97], unfilled data points represent room temperature compression samples conducted in the following experiments.

(3.2) X-ray diffraction patterns showing room temperature compression of elemental Ge in a H₂ environment. It can be seen that there is clear evidence that under room temperature compression, elemental Ge matches that expected from previous literature as summarised in Table 3.1.
Example of XRD patterns from a heating run conducted at 56 GPa with elemental Ge in MgO pressure transmitting medium. From these diffraction patterns, it is clear that at 1560(110) K that there is a broadening in the Ge-II peak at around 8.3° caused by the appearance of the Ge-IV 200 peak before the appearance of the characteristic triplet at around 8.8° from the Ge-IV Imma structure at 1850(130) GPa. Alongside evidence of the transition is there an apparent pressure increase over the transition temperature of around 4 GPa, calculated from MgO, which is observed in all experimental runs in which the Ge-II/Ge-IV transition is present. 

High-pressure high-temperature X-ray diffraction patterns ($\lambda = 0.3344 \text{Å}$) at 76 GPa showing the IV-VIII transition.

2D image plates, $\lambda = 0.3344 \text{Å}$ measured with a Pilatus detector with a 2s acquisition time at room temperature (left) and 1757(50) K (right) at 76 GPa. The blue lines indicate contributions to the diffraction image plate from Ge-VIII along with their corresponding Bragg peak indices. The existence of ‘spotty’ features in the diffraction pattern at high temperature from Ge-IV can still be seen along with strong Debye-Scherrer rings from MgO in both low and high-temperature images.

This figure shows the ball and stick model of the determined atomic structure associated with the Ge-VIII phase at 76 GPa and 1750 K.

Diffraction patterns at 76 GPa demonstrating the reversibility of the Ge-IV/VIII transition with temperature. The two room-temperature diffraction patterns are from immediately before (bottom) and after (top) laser heating (middle) in which it is clear that there are no contributions to the patterns from the novel phase Ge-VIII. MgO was used as the pressure transmitting medium.

(Top) Le Bail refinement of Ge-VIII at 76 GPa and 1757(130) K with lattice parameters of $a = 2.978(5) \text{ Å}$, $c = 2.732(3) \text{ Å}$ and a single atomic position for Ge resting on the origin. The wavelength used was 0.3344 Å with residuals shown as a continuous black line and the fit to the Ge-VIII phase shown as a continuous red line, and the experimentally observed diffraction pattern as black crosses. Experimental peaks observed from untransformed Ge-IV and MgO incorporated in the full pattern fit with Ge-IV having lattice parameters of $a = 4.577(4) \text{ Å}$, $b = 4.376(3) \text{ Å}$ and $c = 2.4731(15) \text{ Å}$. (Bottom) In blue shows the expected peak intensities of the Ge-VIII structure with atomic occupations on the 2a Wyckoff site. As can be seen, whilst not a perfect match, there is visual similarity within the peak ratios.
a) Rietveld refinement of Ge-VIII at 76 GPa and 1757(130) K with lattice parameters of $a = 2.980(5)$ Å, $c = 2.718(13)$ Å and a single atomic position for Ge resting on the origin. b) shows a Rietveld refinement of the HT phase Ge-VIII at 76 GPa and 2000(200) K in MgO with lattice parameters of $a = 2.978(5)$ Å, $c = 2.731(3)$ Å. In a and b, the wavelength used was 0.3344 Å residuals are shown as a continuous black line, with the fit to the Ge-VIII phase shown as a continuous red line and experimentally observed diffraction pattern as black crosses. Experimental peaks observed from untransformed Ge-IV and MgO are not included in the Rietveld refinement. Untransformed Ge-IV and MgO are marked with red and blue asterisks, respectively. c) shows a Rietveld refinement of the HT phase Ge-VIII at 68 GPa and 1600(300) K in hydrogen with lattice parameters of $a = 3.021(12)$ Å, $c = 2.849(19)$ Å. The wavelength used is 0.4066 Å. No evidence was seen of a reaction between the Ge and hydrogen under these conditions again, contributions from Ge-IV were not included in the fitted pattern. The peaks marked with the red asterisk correspond to those associated with ReH. In all of the figures, a March-Dollase model was used to account for preferred orientation on the (100) plane with the final fits having a $wR_p$ of 3.21%, 0.66% and 0.63% and a $wR_{obs}$ of 10.81%, 2.98% and 2.14% in figure a), b) and c) respectively.

(3.8) (top) Relative enthalpies of the room temperature phases of Ge and the novel high temperature phase from 40 GPa to 140 GPa relative to Ge-VI with the inset showing a zoomed view of the pressure range from 70 GPa to 80 GPa, the region over which much of the Ge-IV/VIII transition is experimentally observed.

(3.9) Mean square displacement (MSD) (black line) and temperature (cyan dots) of the 80 GPa MD run of Ge-IV at 80 GPa. The continuous blue line represents the 200-step temperature running average. Clear fluctuations in the MSD appear 2 ps after increasing the temperature to 1500 K. The structure finally melts after switching to an NPT ensemble at 10 ps. The inset shows the atomic trajectory of NVT Ge-IV at 750 K (cyan) and 1500 K after the MSD fluctuations (magenta). Spheres depict the initial positions. Arrows are a guide to the eye, labelling some of the antiparallel displacement of planes resulting from the phase transition.

(3.10) Phonon dispersions for various structures of Ge at 80 GPa: $P6/mmm$ (left), $Cmca$ (middle) and $I4/mmm$ (right). The lower maximum and higher relative weight of the peak below 100 cm$^{-1}$ in $I4/mmm$ indicate a competitive free energy at high temperatures.
(3.12) Trajectories of Ge-IV at 80 GPa on the NVT ensemble. Purple spheres show the initial positions of the Ge atoms, and the green dots show the trajectories at 750 K. The silver dots show the trajectories after the MSD fluctuations are added. Arrows have been added to the figure showing the antiparallel displacement of the planes.

(3.13) Diffraction patterns of Ge sample laser heated at 110 GPa with MgO pressure transmitting medium. From these diffraction patterns it can be observed that there is no evidence of Ge-VIII with increasing temperature up to temperatures of 2080(150) K. The unindexed peak at 8.5° is assumed to be from MgGeO₃.

(3.14) Selected raw diffraction patterns of Ge in MgO pressure medium collected for 2s at (left) 44 GPa; (centre) 60 GPa; (right) 68 GPa. The insets correspond to the zoomed in regions of the diffraction patterns with the region of interest associated with the diffuse liquid scattering. Unexplained peaks correspond to reaction products between MgO and Ge, as a chemical reaction has been observed for some heating series when hot spots had been generated.

(3.15) Diffraction patterns of germanium in MgO pressure transmitting medium while increasing temperature at: (left) 44 GPa; (middle) 60 GPa and (right) 68 GPa. Diffraction patterns shown have been background subtracted by the fitted room temperature Legendre background polynomial. Asterisks show peaks attributed to MgGeO₃ and the blue area shows the smoothed difference between the room temperature and high-temperature background. The bottom pattern shows the diffuse scattering from the melts obtained from subtracting the room temperature diffraction pattern to the high-temperature background.

(3.16) 2D images collected with the Pilatus CCD detector for 2 s of: a) Crystalline Ge-II at 44 GPa at room temperature (left); molten Ge and partially crystalline Ge-II at 44 GPa at 1600 K (right). b) Crystalline Ge-II at 60 GPa at room temperature (left); molten and partially crystalline Ge-IV at 68 GPa and temperatures of 2030 K (right) c) Crystalline Ge-II at 68 GPa at room temperature (left); molten and partially crystalline Ge-IV at 68 GPa and temperatures of 2750 K (right). The strong powder lines passing through the image plates correspond to the MgO pressure transmitting medium.
Proposed extensions to the Ge P-T phase diagram, phase boundaries added in collaboration with Dr Ross Howie. For clarity, due to the density of the points, the error bars have been omitted from the figure. The full figure with error bars can be found in fig. A.1. Filled data points represent the data previously collected and presented in the work of Prakapenka et al. [97], unfilled data points are those presented in this chapter.

Low frequency Raman shifts with increasing pressure after laser heating. Due to a drop in intensity with pressure the spectra shown in scale by a factor of 3. The peak at around 50 cm$^{-1}$ may be attributable to thin layers of PbO on the sample material [146].

Raman shift of the hydrogen vibron and the mid-frequency modes in position 1 with increasing pressure after laser heating. The splitting in the hydrogen vibron is also seen in position 2 of the sample at a much lower intensity. The mid-frequency (left) region appears to comprise of contributions from a number of modes in two main bands separated by around 100 cm$^{-1}$.

Raman shift of the mid frequency modes and hydrogen vibron in the laser heated region of the sample upon decompression at ESRF. The low signal to noise ratio makes it difficult to determine accurately the presence of the Raman mode at around 3300 cm$^{-1}$ but an indication of its presence can be seen.

Raman shift of the mid-frequency modes and hydrogen vibron in the laser-heated region (position 2) of the sample collected upon compression. An additional frequency band is visible in this sample region when comparing to position 1 fig. 4.2 at a higher frequency than that of the hydrogen vibron seen at position 1. The fitted frequency shifts agree with those seen in position 1 for both the hydrogen vibron and the observed splitting at the same pressure. The peaks seen around 4550 cm$^{-1}$ at 25 GPa can be attributed to ruby fluorescence visible in the sample.

Raman shift as a function of the pressure of the vibrational modes of the laser-heated regions of the sample around the 3000 – 3500 cm$^{-1}$ region (left) and around the hydrogen vibron (right). The data presented by grey triangles correspond to the Raman signal seen on in-house spectroscopy facilities at ESRF. All other data shown was collected in a high-resolution Raman system. The two positions refer to two regions with a distinct Raman fingerprint. The expected Raman signal of bulk hydrogen is shown by the dashed yellow line.
Diffraction patterns with increasing pressure of Pb in excess hydrogen. Peaks marked with a black asterisks are attributed to diffraction from outside of the sample chamber. In this sample heatings were conducted at 86 GPa and 120 GPa with the data collected at 120 GPa and 135 GPa being collected 24 hours after the preceding data sets. No notable changes within the XRD patterns were observed beyond the expected appearance of Pb(bcc) at around 104 GPa.

XRD patterns of Pb in H$_2$ on decompression from 87 GPa to the point of diamond failure at 54.4 GPa. Tic marks show the indexed location of peaks attributable to the hcp-Pb phase. No notable structural changes were observed within Pb on decompression which is consistent with all other experimental data sets collected in this study. Unindexed peaks are assumed to be from the delaminated cell coating of Al$_2$O$_3$ as these peaks were not seen when in the absence of the coating when laser heating at similar pressures (see fig. 4.6).

(a) High pressure x-ray diffraction patterns ($\lambda = 0.2895$ Å) taken on compression of the fcc Fm$\overline{3}$m CoH and CoH$_2$. Subsequent laser heating above 75 GPa leads to the synthesis of new cobalt hydride CoH$_3$ Pm$\overline{3}$m. CoH$_3$ diffraction patterns in compression are showing up to 110 GPa. b) Rietveld fit of CoH$_3$ structures, unfitted peaks belong to ReH and Re. The fit matches the structure with a wRp of 0.39 and a wR$_{obs}$ of 2.9. c) Figure showing the diffraction plates of the sample at 70 GPa before (1) and after (2) laser heating. Coloured lines are a guide to the eye to the most intense for the structures seen in each pattern with each phase being denoted by the corresponding colour: CoH (grey), CoH$_2$ (green), CoH$_3$ (blue). In all panels, tick marks indicate the reflections of CoH (grey), CoH$_2$ (green), CoH$_3$ (blue). Asterisks correspond to Re and ReH, whilst crosses correspond to W.
(5.2) a) Absolute volumes of the different stoichiometries of CoHx compounds per Co atom with pressure. Pluses represent data collected in the study by Wang et al. [12] and diamonds representing data collected in this study. Dotted lines show the expected volume of the elemental constituents, and the combined dash-dot line is the theoretically calculated equation of state (EOS) for each compound through DFT using ultrasoft potentials (calculated using QuantumESPRESSO code). For CoH3 the light blue dashed-dotted line was calculated with VASP, using ‘hard’ PAW pseudopotentials and the optB88-vdW dispersion-corrected functional. The solid line representing a third-order Birch Murnahan fit to the experimental data set with the parameters as found in table 5.1 b) Stick and ball models of the Pm3m CoH3 and the Fm3m structures of CoH and CoH2.

(5.3) Convex hull calculations showing the relative enthalpies of the various composition ratios of Co-H compounds at pressures up to 200 GPa.

(5.4) Room temperature diffraction patterns on decompression of the ‘contaminated’ Co+H regions of the sample chamber. Within these regions, several distinct structures can be observed with two distinct. Potential structures discussed in this chapter are included (I4/mmm CoH5 and Pm3m CoH3), along with the expected peak positions for the P1 structure of the Co3H7 simulation. As can be seen, there is potential for the CoH5 structure to be valid, but due to the poor powder averaging and relatively low intensities of the peaks, it is not possible to fully solve these structures. By inspection of the peak positions, it seems unlikely that the P1 structure is valid as many of the major peaks can be attributed to Re and ReH.

(A.1) Proposed extensions to the Ge P-T phase diagram inclusive of error bars. Filled data points represent the data previously collected and presented in the work of Prakapenka et al. [97], unfilled data points are those presented chapter 3 of this work.

(A.2) A plot showing the lattice parameters of Ge-IV (triangles) and Ge-VIII (diamonds) with varying temperature at 77 GPa. Open symbols represent data points collected with the laser operating in continuous mode and filled symbols represent those with the laser operating in pulsed mode. It is reasonably likely that due to the thermal gradients within the sample and the presence of Ge-IV being observed long after the transition temperature, particularly when operating in pulsed mode, that the temperature in regions of Ge-IV is considerable lower than those of Ge-VIII at the heating spot.
List of Tables

(3.1) A summary of known room temperature phases of Si and Ge.
* denotes formation on gradual decompression and presence of shear from Ge-II and Si-II and † denotes formation on rapid decompression, ‡ denotes that the structure forms from the bc8 structure at room temperature in Ge and 573 K in Si. . . . . . . 59

(5.1) EOS parameters for the various hydrides of Co and elemental Co. . 109
Chapter 1

Introduction

1.1 High Pressure Science

Materials under extremes of pressure and temperature often exhibit a wide range of interesting behaviours not observable at ambient conditions. These behaviours include alterations to the electronic configuration, loss of magnetic properties, insulator-metal transitions, structural transitions and novel reaction pathways and are of great interest to the scientific community’s understanding of the material universe. This is due, in no small part, to the fact that whilst most of human existence occurs within a narrow range of pressure and temperature conditions (1 atm \{0.1 \text{ MPa}\} and average annual temperatures between \(-15\) and \(25 \degree \text{C}\) \{258.15 and 298.15 K\} [3]), which is not the norm for most of the universe. For example, conditions within the planetary interior range estimates of 1900 K and 28 GPa at the upper-lower mantle boundary to 5500 K and 360 GPa at the earth’s core [4]. Additionally, a wide range of pressure conditions are also applicable for exoplanet interiors which may greatly exceed the pressure and temperature conditions of the earth’s interior. The desire to study these conditions led to the creation of several techniques and apparatus which allow these conditions to be attained. These apparatus include the Diamond Anvil Cell (DAC) [5] which is the main experimental tool within this work.

Further to the ability offered by high-pressure experimental techniques to explore the conditions of planetary interiors, it is widely understood that the application of non-ambient conditions, in particular high pressure and temperature, can open...
novel reaction pathways. This is particularly of interest in materials such as hydrides, of which many are predicted to show superconducting behaviours.

With many metals, notably the transition metals, having very low hydrogen solubility at ambient pressure, transition metal hydrides are rarely observed under ambient conditions. However, different reaction pathways can be achieved with the introduction of pressure, offering new and interesting pathways to create metal hydrides. This has shown to be valid for a number of metals that under ambient conditions do not create hydrides such as magnesium (Mg) [6], platinum (Pt) [7], and rhenium (Re) [8].

In addition to their interest to industrial development, extreme conditions science allows interesting developments in the understanding of fundamental science. For example, it has already been observed that the presence of high hydrogen density has interesting effects on the electronic properties of a material with lanthanum decahydride (LaH$_{10}$) having been reported to have the highest superconducting transition temperature observed in all materials at 260 K at 160 GPa [9]. It is also proposed by Ashcroft [10] that through the use of chemical pre-compression, various hydrogen-rich materials will form hydrogen environments similar to those predicted for solid metallic hydrogen [11] but considerably lower pressure. Reaching conditions analogous to those of the theorised metallic hydrogen state would hopefully allow for further understanding of properties of the most fundamental and abundant element in our known universe at considerably more experimentally accessible pressure ranges.

1.2 Thesis Outline

As is often the case within science in general, when searching for the answers to one question, another equally interesting question is generated, or an unexpected result provides an interesting tangent worth pursuing. This leads to the general name of this thesis ‘Novel Materials Under Extreme Conditions’ as the theme of extreme conditions and its experimental techniques in the form of powder x-ray diffraction, laser heating and diamond anvil cell compression, unifies the different components of this work. The topic of extreme conditions science covers a wide range of areas far beyond the reach of those covered above. The initial aim of this work was to explore the formation of hydrides of various elemental materials, with a focus being given to those predicted by Ashcroft [10] within the group
XIV elements alongside studies into transition metal/hydrogen mixtures. Whilst limited success was observed with the attempted fabrication of novel hydrides, unexpected novel behaviour was observed in elemental germanium, which became a key focus of this work leading to the discovery of a novel structural phase in elemental germanium. As a result, this thesis is divided into four main components, followed by a concluding chapter summarising the key findings of the different studies, and offering potential routes for future studies.

1.2.1 Chapter 2: Experimental Apparatus and Techniques

This chapter provides an overview of the techniques and underlying physical principles associated with the work contained within this thesis. Focus is given to the sample preparation techniques, determination of pressure, generation of heating effects, temperature measurement, and determination of scattering through x-ray diffraction techniques. This aims to be a general overview of all the techniques throughout this work used in the context of their physical and theoretical backgrounds. Areas adjacent to the central thesis are also mentioned to provide the context of alternate techniques alongside direction to sources of further detailed discussions of these methods.

1.2.2 Chapter 3: Studies of High Temperature Elemental Germanium at High Pressure

This chapter focuses on high temperature and high-pressure studies of elemental germanium (Ge) in a number of different pressure mediums. It opens with a brief overview of germanium in its industrial context, along with a summary of previous studies into the high-pressure and high-temperature behaviours of elemental germanium. The remainder of this chapter then focuses on the findings of the experimental studies conducted on elemental germanium under extreme conditions. The presence of a new phase of germanium (Ge-VIII) is presented at pressures between 56 GPa and 88 GPa at temperatures exceeding 1500 K alongside computation evidence showing the stability of this structure. Additionally, evidence is presented of the Ge-II/IV phase transition at temperatures above ambient temperature, providing an indication of the phase boundaries location with changing pressure. Evidence is also presented supporting an extension to the Ge-II melt line alongside suggestions for the melt boundary beyond the Ge-
II/IV/liquid triple point. These studies combine to provide an extension to the phase diagram of elemental germanium to temperatures exceeding 2000 K and pressures up to 110 GPa. This work was published in [1].

1.2.3 Chapter 4: Mixed Group XIV and Hydrogen Systems

This chapter focuses on studies of the group XIV elements, predominantly focusing on lead (Pb) and their interactions with hydrogen at high pressure. These experiments show evidence of no novel hydride formation across the pressure conditions observed.

1.2.4 Chapter 5: Investigations into the Cobalt-Hydrogen System

This chapter focuses on studies of cobalt (Co) in an excess of hydrogen with increasing pressure. Previous theoretical studies of this system indicated a high likelihood that higher hydrogen content hydrides of cobalt could be achieved than those which were previously observed in the work of Wang et al. [12]. Experimental studies are presented showing evidence of the formation of cobalt trihydride (CoH₃) alongside an unknown structure observed in one experimental run which may be interesting to attempt to replicate in future studies as it appears that it may have a still higher hydrogen content. Components of this work were published in [2].

In the interest of clarity to the reader, when presented throughout this work vectors are notated in the form $\vec{A}$. 
Chapter 2

Overview of Experimental Apparatus and Techniques

This chapter is intended to provide an overview of the apparatus and techniques used throughout this work for the extreme condition studies of different systems. This is not intended to be an exhaustive overview of high-pressure techniques but will contain some relevant background theory and history covering diamond anvil cells (DACs), sample loading techniques, pressure calibration techniques, laser heating and x-ray diffraction (XRD). Supplementary techniques such as surface coating and Raman spectroscopy will also be briefly discussed.

2.1 The Diamond Anvil Cell

2.1.1 Background

Pressure is of great importance as a thermodynamic variable for exploring a wide range of environments in the known universe. Prior to the invention of the diamond anvil cell, the two main methods of pressure production in the static high-pressure large-volume WC presses and Bridgman style cells. In 1949, Lawson and Tang proposed that diamonds would be an excellent material to replace the WC materials used in other pressure cells because it is both transparent to x-rays and optically alongside its high material strength. They drilled a hole into two halves of diamond and used the hole as a sample chamber, referring to the setup
as the ‘split diamond bomb’. With this apparatus, it was possible for them to gather x-ray data at pressures up to 2 GPa. In the late 1950s, two research groups independently came up with modifications to the Bridgeman style anvil cells, which at that time were using WC anvils. A group at the University of Chicago created a cell intended for XRD whilst the group of Weir et al. developed a different style of cell for infra-red absorption experiments. The latter of the two cells forms the basis for the cells used in much of the research done in the field to date.

If the DAC is simplified to its most fundamental components, much like Bridgeman style pressure cells, the DAC consists of two parallel anvils. However, the main difference from the Bridgman cells is the replacement of the WC anvils with anvils made of diamond. A metallic gasket is then placed between the two diamonds to act as a container for the sample area, which then has a load force applied to it to until the gasket material until ductile deformation ceases. A section of the gasket material between the two culets is then removed to act as a sample chamber for the materials that are to be studied (fig. 2.2). To apply pressure using this setup, a load force is applied to the cell perpendicular to the diamond culet planes, with several different methods being typically used. These include gas membranes, load screws and lever arms. Due to the underlying physics of the geometry setup, the modest load forces applied by these techniques (typically of the order of 1 kN) allows the generation of pressures greatly exceeding those generated by other static compression techniques. With this setup and the use of various diamond cuts (fig. 2.1), including high precision multi-stage anvils, there are now recorded pressure experiments with pressures of over 700 GPa.

2.1.2 Cell Types

Two main DAC designs were used during this work: a type of 4 pin symmetric DAC referred to in this work as GG-type cells and modified Mao-Bell type piston-cylinder cells. The piston-cylinder style of cell comprises of a tight-fitting long piston and cylinder pair, each holding one of the two diamonds. This design of DAC allows for easily repeatable positioning of the two diamonds after closing the cell due to the additional stability afforded by the piston shaft. This repeatability means that it is possible to consistently return the cell within 1 µm after the initial indentation, and the high stability decreases the likelihood of alignment shifts during the experiment. This design does come with its own set of limitations.
Figure 2.1  Cross section depicting a flat (left) and bevelled (centre) brilliant cut diamonds as used in DAC experiments along side a Boehler-Almax (BA) (right) cut flat diamond. The diamonds tables (a), facets (b), culets (c) and bevel (d) are labelled to clarify the terms used when describing DACs. Notice should be given to the key difference between BA and brilliant cut diamonds to the rear facets (e) which are smooth and conical on the BA diamonds to facilitate self levelling in the seat. The bottom two images show the view of these two cut styles from above the culets.

Due to the length of the piston and the asymmetry of the cell body, there is a large distance between the sample environment and the top aperture of the DAC which creates difficulties when optically viewing the diamond on the interior of the piston with optics with working lengths shorter than the piston length. For most standard microscope objective lenses and infra-red (IR) grade lenses, this working distance is usually somewhere in the order of 2-3 cm. This means that without specially chosen optics or shorter piston lengths that lose some of the benefits of the cell type, it is often not possible to conduct dual-sided heating experiments with piston cylinders. Alongside this, the length of the cell means that it is not ideal for wide-angle XRD experiments because the large quantity of cell body material on one side of the cell can create shadows in the collected data, significantly limiting the 2θ that can be collected. To some extent, this can be mitigated by having the main cell body on the incident side, widening the available collection angles. Often, however, a compromise must be made between the pinhole size and the cell length, meaning that ultimately the spatial resolution of the sample volume needs to be lower than that of a shorter symmetric cell.

In contrast to the asymmetric piston/cylinder composition of the modified Mao-Bell cells, the GG-type cells comprise of a cell body made of two separate diamond backing plates, both with wide angle openings behind the region in which the seat is mounted. These two plates are connected to one another through the use of four
Figure 2.2 Simplified schematic of a diamond anvil cell showing the key components. The central sample environment comprises of a hole in the gasket material hermetically sealed between the two diamond culets.

metal pins which act as guide rails to encourage the application of uniaxial load force. This load force is applied, much like in the modified Mao-Bell cells through the use of load bearing screws between the two components of cell body. These cells are configured such that they can also easily be used with gas membranes to allow remote pressure control.

In contrast to the modified Mao-Bell type cells, GG-type symmetric cells afford a much larger 2θ to be collected at the expense of overall cell stability. This reduction in stability of the closing action of the cell is related to the four narrow posts, which due to the geometry of the cell closing, are much more susceptible to imbalances of forces during closing. This means that the cell may pitch slightly, in essence, moving the cell alignment fractionally (of the order of 10µm). However, due to the symmetry of the DAC it is much easier to see the sample environment from both top and bottom, greatly improving the ability to ensure that sample bridging between diamonds is not occurring. This ability to observe sample bridging is of great importance in the preparation of samples for laser heating experiments. The reduced steel volume within the cell and much wider angle openings also make the GG-type cells considerably more useful for XRD experiments. This reduction in volume means that the effects of ‘shadowing’ from the DAC are greatly reduced or non-existent, and the wider cell aperture means that a wider 2θ can be collected.
2.1.3 Sample Preparation

Diamond Types and Seats

Before preparing a diamond anvil cell for experiments, several factors should be considered to determine that a suitable cell configuration is attained. These can be summarised into two main categories of consideration, the geometry of the diamond anvils and the seat’s geometry. These two factors have some degree of impact on the suitability of one another in the sample preparation process. However, first, we will consider the possibility of offering geometries of diamonds available for use as diamond anvils.

When selecting diamonds for use as anvils, both the intended pressure range of the sample and the intended method of probing the sample needs to be taken into consideration. The more simple factor of these to consider is the desired pressure range to attain during the experiment. As the cross-sectional area of the culet governs the overall attainable pressure creation, the expected pressure can be approximated by the equation $P = F/A$. Given that within the diamond anvil cell, forces of the order of 1 to 10 kN can be readily attained, it is possible to attain pressures of the order of 100 GPa with diamonds of around 100 µm culet size.

Due to a need to affix the diamonds to the cell body, seats need to be used to hold the diamonds in position whilst minimising the amount of lateral strain placed through the weaker planes of the diamond. This typically means that the diamonds will be glued to a relatively hard and incompressible material such as WC or BN. However, for lower pressure experiments, it is possible to use hardened steel. Several different diamond cut types are available for DAC research; however, only two styles were used throughout this research, the ‘flat’ brilliant cut and the conical [Boehler-Almax IIac (BA)] design [15]. These two different cuts have several key differences, but, as shown in fig. 2.1, both cuts share the presence of a large flat surface known as the table, a smaller flat surface parallel to the table referred to as the culet and a number of facets. Brilliant cut diamonds refer to the diamonds most commonly thought of when thinking of jewellery diamonds with a large, flat table on the diamond. As a result of this, brilliant-cut diamonds are typically mounted on flat seats with the culet positioned above an aperture in the seat. Due to the need to have a strong seat that will not deform or break under pressure, these flat seats are...
often limited to relatively small aperture angles. Whilst this is not a problem for optical experiments, when conducting powder XRD experiments, it is often beneficial to gather the widest $2\theta$ range possible and may be necessary to sweep through a range of incident angles to attain better powder averaging. With these ‘narrow’ seat apertures, these confines often cause signal loss above the angle of the aperture or the inclusion of ‘shadows’ in the collected diffraction patterns from the seat. This can be avoided through the use of BN seats, which are transparent to x-rays, instead of the heavily absorbing WC seats. This issue of the signal being cut by the seat can also be minimised by increasing the aperture of the seat itself, which, with a change in the geometry of the diamonds themselves, is possible. BA diamonds are cut with a conical back to the diamonds instead of the flat facets on the table side, allowing corresponding conical recess to be cut into the seat itself. This allows for a different distribution of load forces through the seat to that on a flat seat, meaning a much wider aperture can be attained.

**Alignment**

Due to the susceptibility of diamonds to structural failure when under the application of shear stress, it is of great importance to ensure that the load force on the diamonds is as uniaxial as possible. A major step in attaining this uniaxial load force can be achieved by carefully aligning the opposing anvils. As the anvils are resting on a WC or BN seat, which is not permanently attached to the structure of the cell (see fig. 2.2), when initially placing the diamonds into the DAC, it is highly unlikely that the two diamond culets will be centrally aligned with one another.

To make this alignment possible, the DACs used throughout these experiments have a number of grub screws located in the base of the cell, which can be used to adjust the position of the seat whilst also holding the seat in place. Firstly, the grub screws are tightened to lock the seat in place on one side of the DAC in an approximately central location relative to the cell body. The grub screws are then loosely tightened on the opposing seat to hold it in an approximately central location. Once this is achieved, the cell can be carefully closed under observation until the diamonds are within approximately 50 $\mu$m of one another. At this point, whilst observing the cell from the side on, the culet of the loosely fastened diamond can be approximately lined up with the culet of the other diamond. This is then repeated for the other grub screw axis. After this is
Figure 2.3  Example sketch of DACs in different states of alignment. The size difference between the top (pink) and bottom (blue) diamond has been exaggerated for clarity in this illustration. A cell with good alignment (left) has a clear set of concentric circles when looking through the diamond culets indicating the two culet centres are aligned. The poorly aligned cell (right) show the two diamonds clearly off centre in a position where the load force will be uneven, leading to shear when a load is applied, likely causing anvil failure.
achieved, the diamonds are then brought closer still (approximately 10-20 µm apart), and through observations of diamonds through the table, the position of the loosely fitted diamond is adjusted further until the two diamonds are aligned fully. This is deemed to have been completed when the approximately circular cross-sections of the two diamond culets are arranged such that they create the image of concentric circles if the diamond size is mismatched, or if as one diamond culet if they are the same size or concentric circles if the diamonds have noticeably different culet sizes (see fig. 2.3). At this point, the grub screws on the loosely fitted diamond are tightened to lock the position.

Gasket Preparation

As the aim of DAC experiments is to attain extreme pressures and the vast majority of materials will deform or flow under pressure, it is necessary to create a chamber of some kind to contain the sample material. This is particularly important with powder and non-solid samples. Typically, this sample environment is created with the use of a gasket material located between the two diamond culets. In addition to forming an integral part of the sealing of the sample environment, the gasket material also acts as a barrier between the two diamonds preventing contact between the two diamond culets and acting to distribute the load forces around the diamond culets. This is of great importance as, when under load forces, contact between the two diamonds often leads to scratches and chips on the diamond surface, which undermine the structural integrity of the diamonds, commonly leading to failure of the diamond anvils.

To prepare a gasket, a small sheet of metal, typically between 100 µm and 300 µm thick, is placed between the two diamond culets and the cell closed just beyond pinch tight to allow the shallow preindent to form within the gasket material. This shallow preindent minimises the chances of the pressure calibrant shifting off the culet when the gasket material undergoes ductile flow. Typically the gasket then undergoes a full preindentation to 20–25 GPa after which pressure is released from the cell, and a hole is then drilled using a pulsed Nd:YAG IR laser drilling configuration to approximately 50% of the culet diameter. Alternatively, focused ion beam (FIB) or spark eroding techniques can be used to create the hole within the compressed region of the gasket; however, these techniques were not used throughout this work. Upon replacing the gasket within the DAC, it is then possible to attain the thickness of gasket material between the two culets using
white light interferometry. By shining the light from the upstream end of the DAC, the two diamond culets act as the mirrors in a Fabry-Perot interferometer creating distinct interference fringes across the distinct wavelengths of light. Using a wavelength resolved CCD detector, it is possible to measure the distance between neighbouring peaks of maximum intensity, allowing the gasket’s thickness to be calculated using the Fabry-Perot interferometry techniques. This technique uses the interference relationships of light between two reflective surfaces to determine the distance $d$ between the two surfaces, in this case, the diamond culets. The Fabry-Perot relationship is denoted as,

$$2d \cos \alpha = m \lambda$$

(2.1)

where $m$ is the order of the interference and has resolution of

$$\frac{\lambda}{\Delta\lambda} = \frac{m \sqrt{r}}{1 - r}$$

(2.2)

As $\alpha$ represents the angle from the normal of the two plane surfaces, when using light source perpendicular to the culet surfaces, this tends to 0, giving the $\cos \alpha$ term a value of 1. This means to calculate the distance between the two culets the following equation can be used.

$$2d = m_0 \lambda_0 - m_{0+n} \lambda_{0+n}$$

(2.3)

Where $\lambda_0$ is the wavelength of an arbitrarily selected interference peak and $\lambda_{0+n}$ is the wavelength of an interference peak $n$ fringes away. As $m$ is an integer value the equations can be manipulated to the form:

$$d = \frac{n(\lambda_0 - \lambda_{0+n})}{2}$$

(2.4)

which allows experimental determination of the spacing between culets with only one measurement.

### 2.1.4 Sample Loading

After gasket preparation, the DAC is ready for sample loading. In the case of solid samples, this technique involves placing small chips or powder of the material centrally within the sample chamber to minimise the risk of observing gasket
material when conducting XRD experimentation. In addition to the sample material, it is necessary to load in a pressure transmitting medium (PTM) and is often ideal for adding to the sample environment a pressure calibrant that is appropriate to the techniques being used, as is discussed in section 2.2. For the pressure calibrant, as these materials are often solid, these materials can be loaded in the same way as with a solid sample material. However, when preparing samples for optical experiments, if using ruby as a pressure calibrant, it is necessary to ensure there is some separation between the area of interest and the ruby due to the strength of ruby fluorescence compared to Raman scattering effects. This is particularly the case if optical spectra from the sample are expected to have components at or around 700 nm. When loading a PTM, the technique used is highly dependent upon the state of the material. For solid powder PTMs such as NaCl and MgO, one method of sample preparation involves the placement of a small amount of the PTM into the gasket hole using a needle before closing the DAC to compact the PTM. After this step, a small hole is made in the disk of PTM into which the sample can be placed before a further small quantity of PTM is placed over the sample and the DAC hermetically sealed. For both of these materials, the process of adding more material over the sample can be repeated until the sample chamber becomes translucent upon sealing to reduce gasket collapse upon compression. This is particularly important for dual-sided heating experiments as the presence of PTM on both sides of the sample reduces the risk of the heated surface being directly in contact with the diamond culets. However, it should be noted that in the event of overloading of the PTM in solid form, if the material is less compressible than the gasket, the sample chamber is likely to expand in diameter when compressed.

For gaseous PTMs such as noble gasses or as was used in the case of the hydride synthesis experiments contained within this thesis H₂ an alternate technique must be used. At its simplest, the gas loading technique comprises of ‘trapping’ gas within the sample chamber in pre-compressed state at a pressure of around 0.15–0.2 GPa. To perform this loading technique, the DAC in its loaded state must be placed within a high-pressure steel chamber attached to a gearbox. After the chamber is sealed, all air is replaced with the desired gaseous mix compressed to the desired loading pressure. By remotely turning the load screws on the DAC using a gearbox fitted to the inside of the loading chamber, the sample chamber is hermetically sealed, trapping the gaseous mixture within the sample chamber. The use of different gases is limited by the compression system used within the gas loader due to safety reasons. The apparatus used for gas loading in these
experiments are designed specially to allow the safe loading of hydrogen gas.

2.2 Pressure Calibrants

Due to the extreme range of pressures, small areas and the enclosed nature of DACs, it is not possible to measure the pressure directly using conventional macroscale techniques. As such, pressure calibrants need to be used to establish the pressure in the sample volume. There are three main calibration techniques used for this purpose, diamond edge Raman, ruby fluorescence and x-ray compression equations of state (EOSs).

2.2.1 X-ray Diffraction and Equations of State

Within collected XRD data from materials at high pressure, a variety of different behaviours can be observed within the crystal structure. One such behaviour occurs due to the increase in potential energy on the systems when exposed to an extreme load force generated by the internal pressures within the pressure cell. The additional external pressures balance against the internal electro-repulsive forces within the material, which are typically focused down the lattice planes, via the movement of atoms. This typically manifests in a decrease in unit cell volume with increasing pressure. Due to the pressure dependence of this volume change, as long as there is no change of symmetry within the crystalline structure, it is possible to determine a relationship mapping the observable crystal unit cell dimensions to the pressure of the sample chamber, which is not possible to measure directly.

There are a number of accepted relationships between the pressure and volume of a crystalline unit cell under pressure, referred to as EOSs. The simplest EOS for solids undergoing isothermal compression is that of the classical description of bulk modulus denoting the relationship between the isothermal bulk modulus $K_T$, pressure $P$ and volume $V$ at a constant temperature as described by equation 2.5:

$$K_T = -V \left( \frac{\partial P}{\partial V} \right)_T$$  \hspace{1cm} (2.5)

When observing systems at high pressure under the assumption of infinitesimal strain, the dimensions of the compressed materials would vary linearly. Experi-
mentally within solids it is observed that this is not the case as typical P-V plots of materials under pressure show that there is a decrease in incompressibility, and thus an increase in bulk modulus, with increasing pressure. As such, a number of different models of equations of state have been formulated accounting for the finite strain terms. Of these formulations, within DAC static compression experiments, two of the main equation of states are typically used, the Vinet EOS and the Birch-Murnaghan EOS (B-M EOS).

These two equations of state from the basis of those used within the work contained in the latter chapters of this thesis, with the main EOS used being the 3rd order B-M EOS. The 3rd order B-M EOS was formulated in 1947 by A.F. Birch [16] based on the early work of F.D. Murnaghan in 1944 [17]. Using the previously derived Murnaghan EOS which was limited to low compression systems by its modelling of Eulerian strain, the B-M EOS was adapted to incorporate 3-dimensional tensors into the model in an attempt to constrain better the compression behaviour of the earth’s mantle. The 3rd order B-M EOS at constant temperature [16] can be described by the equation

\[
P_T(V) = \frac{3 K_{T_0}}{2} \left\{ \left( \frac{V_0^{\frac{2}{3}}}{V} \right) - \left( \frac{V_0^{\frac{5}{3}}}{V} \right) \right\} \left\{ 1 - \frac{3}{4} \left( K'_{T_0} - 4 \right) \left( \frac{V_0^{\frac{2}{3}}}{V} \right) - 1 \right\} \quad (2.6)
\]

Where \( P \) is the pressure, the deformed volume \( V \) and \( V_0 \) the reference volume. The two bulk modulus terms derived from the relationship in Equation 2.5 can be defined as

\[
K_{T_0} = -V \left( \frac{\partial P}{\partial V} \right)_{p=0,T} \quad (2.7)
\]

and

\[
K'_{T_0} = -V \left( \frac{\partial K}{\partial P} \right)_{p=0,T} \quad (2.8)
\]

with the values of \( K_0 \) and \( K'_{T_0} \) typically being obtained from fits to experimental P-V data points or the simulated behaviour of structural models.

Similarly, the Vinet EOS [18] (also referred to as the Rose-Vinet EOS) is a modification of the B-M EOS with a reduced stiffness in the solid modelling, typically giving a slightly lower pressure than that of the B-M EOS. The Vinet EOS...
EOS can be described by the equation

\[ P_T = 3K_T \left( \frac{1 - \eta}{\eta^2} \right) e^{\frac{3}{2}(K'_T - 1)(1 - \eta)} \]  

\[ (2.9) \]

where \( \eta \) is the shorthand notation of cube root specific volume

\[ \eta = \left( \frac{V}{V_0} \right)^{\frac{1}{3}}. \]  

\[ (2.10) \]

As these two EOSs only accurately model isothermal compression, additional modifications to these equations must be made to account for the effects of thermal expansion if these equations are to be used to determine the pressure on non-isothermal data sets. Typically this is conducted by the addition of a thermal pressure term within the pressure calculations using the general equation of state in the form

\[ P(V, T) = P_T(V, 0) + P_{Th}(V, T). \]  

\[ (2.11) \]

with the \( P_T \) being previously discussed isothermal EOS and the second term, \( P_{Th} \) representing the thermal pressure. As is explained by Anderson in his 1999 paper [19], applying the operator \( \left( \frac{\partial P}{\partial T} \right)_V \) to the general EOS yields the relationship

\[ \left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial P_{Th}}{\partial T} \right)_V. \]  

\[ (2.12) \]

integrating this with respect to \( dT \) gives,

\[ P_{Th} = \int_{T_b}^{T_1} \alpha K_T \, dT \]

\[ (2.13) \]

where \( \alpha \) is the thermal expansivity and \( K_T \) is the thermal bulk modulus. Assuming the quasiharmonic approximation holds [20] pp. 34–35] and the assumption that \( P_{Th} \) is linearly related to \( T \) this integral can be expressed in the form

\[ \Delta P_{Th} = \alpha K_T (T - T_0) \]

\[ (2.14) \]

and thus it is apparent that the volume dependence in \( P_{Th} \) is derived exclusively from the \( \alpha K_T \) term.
Calibrant Selection

Each structural transition within crystalline solids has some effect on both the thermal and isothermal EOS. Alongside this, different materials have different compressibilities at different pressure ranges dependent on the bulk moduli of materials. This means that to ascertain pressure through the use of a pressure calibrant using XRD techniques; it is necessary to extract the volume of the crystalline unit cell of the chosen material, the complete technique of which is explained in section 2.4.2, for use in the above EOS. To achieve this, the observation of the diffraction peaks of the calibrant material must be readily distinguishable from the sample material. This means that calibrant materials are typically preferable when of a higher symmetry group, for example, some variant of the cubic or hexagonal space groups, due to the lower density of Bragg reflections within those space groups. Additional considerations should be given when selecting a pressure calibrant for XRD experiments when the expected position of the Bragg reflections of the calibrant material is close to the expected position of the key reflections of interest within the sample material are known. This is because an overlap in the Bragg reflections of the two materials at a key point such as phase transition or reaction limits the potential extraction of data from a given experiment. Additionally, the degree of volume change over the desired experimental range must be large enough such that the volume change can be observed within the experiment with the available wavelength resolution. This means that for low-pressure experiments in which pressure change is only be observed over a few GPa, materials should be chosen with high compressible in that region to increase the accuracy of the pressure determination.

Finally, the potential of a reaction with the sample must be considered when choosing a calibrant material. This is particularly true in high-temperature experiments when the increased energy within the sample environment can generate novel reaction pathways, rendering previously inert materials at ambient conditions reactive. Obviously, an unintentional reaction within the sample environment between the pressure calibrant and sample should be avoided where possible, not least because of the potential of material changes and thus a loss of accuracy in pressure measurements within the sample environment. A number of materials readily available fulfil the majority of these requirements meaning that a wide variety of pressure calibrants can be considered for this purpose, including Pt, Au, W, Cu, MgO and many others [21].
2.2.2 Ruby Fluorescence

Rubies are a naturally occurring gemstone made of primarily Corundum (Al$_2$O$_3$) containing inclusions of Cr within the crystal structure. It is these inclusions that give rubies their $^4T_2$ and $^4T_1$ absorption bands which cause the distinctive red appearance both in the body colour of the gems and lead to its usefulness as a pressure calibrant in high-pressure physics as outlined in an extensive review by Syassen [22]. Incident photons are absorbed by the electrons within the ruby within these levels; however, instead of remitting a photon with the same energy as the incident photon, the electrons pass through an intermediate energy level ($^2E$) before reaching the ground state. These electrons then return to the ground state from the excited $^2E$ which, due to spin-orbit coupling, creates two distinct emission bands which fall within the visible region of the electromagnetic spectrum. These emissions, $R_1$ and $R_2$, occur at 692.8 nm and 694.2 nm respectively at ambient conditions. It is these emission bands in the fluorescence spectra that can be harnessed for the purposes of pressure determination.

With an increase in pressure, there is a shift in the wavelength of the ruby $R_1$ fluorescence, which is linear in its relation up to 10 GPa [23]; however, this linear relationship becomes increasing non-linear with pressure. Several pressure relationships have been suggested over the years [21, 24] with the most recent being proposed by Shen et al. [25] calibrated against a number of other pressure scales using XRD EOS of accepted pressure calibrants including Cu, Mo, MgO and C$_{diamond}$. This relationship claims to be accurate to within 2.5% at pressure up to 150 GPa and allows the calculation of pressure from the relationship,

$$ P \ [GPa] = 1.87 \ (\pm 0.01) \times 10^3 \left( \frac{\Delta \lambda}{\lambda_0} \right) \left( 1 + 5.63 \ (\pm 0.03) \left( \frac{\Delta \lambda}{\lambda_0} \right) \right) $$

(2.15)

with $\lambda_0$ representing the $R_1$ fluorescence band for a given ruby at ambient pressure and $\Delta \lambda$ being the change in wavelength of the same fluorescence band at pressure. The experiments within thesis were conducted prior to the publication of this incarnation of the pressure calibration relationship and instead used the pressure calibration of Dewaele et al. [21] which can be expressed in the form presented by Mao and Bell [24] as

$$ P \ [GPa] = \frac{1904}{9.5} \left[ \left( 1 + \frac{\Delta \lambda}{\lambda_0} \right)^{9.5} - 1 \right] \approx 200.42 \left[ \left( 1 + \frac{\Delta \lambda}{\lambda_0} \right)^{9.5} - 1 \right]. $$

(2.16)
A limitation to this calibration method occurs with increasing pressure in that the $^4T_2$ and $^4T_1$ energy states increase in energy when undergoing compression. This, in turn, decreases the likelihood of absorption when using green laser excitation. This means that with increasing pressure, the overall intensity of the ruby fluorescence decreases as a lower proportion of the electrons pass through the $^2E$ state. To combat this, it is possible to increase the fluorescence efficiency at higher pressure through the use of red lasers, which absorb more strongly with the $^2T_1$ state, which also decays through the $^2E$ states as is outlined by Syassen [22]. Despite this, due to the relative chemical inertness and the very small quantities of material needed, ruby is one of the most commonly used pressure markers in optical high-pressure experiments.

### 2.2.3 The Diamond Raman Gauge

The use of the first-order Raman mode of diamond as a pressure gauge was first proposed by Hanfland and Syassen [26]. In this paper, they suggest a linear relationship in the first-order Raman mode relative to the ruby fluorescence scale at pressure up to 40 GPa. At ambient pressure, the first-order Raman mode of diamond can be observed at 1333.0(5) cm$^{-1}$ with this frequency increasing with increasing pressure. The change in Raman shift with pressure has been extensively studied, and calibration up to pressures of 410 GPa [27–30] with the most recent of these studies having been carried out by Akahama et al. [28]. This experiment provides a fit to the increase in Raman shift of the first order diamond mode with pressure when calibrated against a Pt pressure marker in the form of:

$$P(GPa) = A \frac{\Delta \omega}{\omega_0} \left[ 1 + \frac{1}{2} (B - 1) \frac{\Delta \omega}{\omega_0} \right],$$ \hspace{1cm} (2.17)

where $\Delta \omega$, $\omega_0$ and $\frac{\Delta \omega}{\omega_0}$ correspond to the frequency shift, frequency at ambient pressure and the relative frequency change respectively whilst $A$ and $B$ are fitting parameters with values of 574(11) GPa and 3.75(20) respectively. This relationship holds up to pressures of 300 GPa around which point the uncertainty in pressure exceeds the 3% that is claimed, and an alternate quadratic relationship [28] must instead be used. However, the breakdown of this relationship is beyond the pressure range used within this work and, as such, will not be included here. It is proposed that the validity of these models for pressure determination are at least partially dependent on culet geometry as outlined by Baer et al. [31] which may impact the assumption of uniaxial strain within the anvils leading to variance.
in the relative Raman shift.

With these factors considered, the diamond Raman pressure gauge is an incredibly useful tool within DAC experiments, allowing for the determination of pressure in samples beyond the pressures at which ruby fluorescence becomes more difficult to stimulate. Additionally, it provides a pressure diagnostic tool for experiments where otherwise, due to the small sample volumes, access to synchrotron radiation sources is required to determine cell volume EOS or the presence of non-sample calibrant materials may alter the sample through reaction or catalytic effects.

![Raman Shift Graph](image)

**Figure 2.4** Example spectra of the stressed first order Raman mode at approximately 86 GPa.

### 2.3 High Temperature Tools

Whilst the application of pressure alone often allows for structural changes or the reaction of materials that would not ordinarily occur under ambient conditions, it is often the case that with a different amount of thermal energy within the system, a variety of different structural and reaction pathways can be observed. In the case of reaction pathways, this is often due to a requirement to overcome a potential barrier. This has been observed in a number of experiments,
particularly the formation of hydride and nitride materials with a plethora of higher stoichiometries of compounds formation \[32–36\]. The effect of temperature on structural pathways is also well known, with both low and high temperatures often leading to a variety of solid-solid structural pathways. Famously, one such low-temperature transition, the metastable transition into the brittle α-tin (or grey tin) structure of tin occurring at ambient pressure at temperatures below 13 °C is the subject of great historical debate. It is this structural transition which, in urban legend, is proposed to have been a major contributing factor in the defeat of the Grand Armée in Napoleon’s 1812 campaign against the Russian Empire. It is claimed that the extremely low temperatures of the winter potentially leading to the tunic buttons becoming brittle and disintegrating; however, these claims are likely untrue \[37\] as very little evidence is present to suggest that tin buttons were used on mass for the uniforms and it was typical of the era to instead use brass buttons for officers and bone buttons for the enlisted soldiers.

Returning to the subject at hand, two main techniques can be implemented to attain the high temperature required in many high-pressure experiments. These methods are resistive heating and laser heating, with each of the two methods having temperature regions in which they provide their most efficient results. Typically resistive heating techniques limit experiments to temperatures between 300–1100 K based on the limitations of the heating elements used with laser heating techniques providing much higher temperatures, typically in excess of 800 K. The latter of these methods provides the primary method of temperature generation throughout this thesis. The details and limitations of this technique will be explained below in more detail. However, firstly resistive heating will be briefly discussed.

2.3.1 Resistive Heating

Resistive heating, also referred to as Joule heating, is the process in which an electrical current passing through a conductor generates heat. This, in daily life, forms the basis of many household objects such as electric toasters, incandescent light bulbs and even electrical fuses, among other applications. As defined by the Joule-Lenz law

\[ W' = I^2 R \]  

the amount of power, \( W' \), output by the conductive material is proportional to the product of the square of the current, \( I \), passed through it and resistance, \( R \), of
the conducting material. The electrical energy imparted into the heating element is then transferred into thermal energy, which further increases the material’s resistance as the thermal motion adds more opposition to the flow of electrons. This additional heat is then dissipated from the heating element in two main ways, conduction into the surrounding materials, typically the air or materials in direct contact with the heating element and thermal radiation. All material above absolute zero emits some quantity of thermal radiation as the presence of any charge motion or dipole oscillations induce electromagnetic radiation emission as per the principles of electromagnetism. The exact details of the spectrum of electromagnetic radiation emitted are described by Kirchoff’s law which is discussed in further detail in section 2.3.4.

Typical constructions of resistive heaters comprise of coils of conducting material, often a metal with low reactivity and high melting temperature wound around an insulating core for structural and electrical reasons. Often these heating coils are internal to the DAC surrounding the gasket. This allows as much thermal energy to be transferred to the sample environment with temperature measurements possible to be taken by the inclusion of a thermistor placed between the diamonds and the gasket or in larger DAC sample chambers within the sample chamber itself. With these techniques and variants of them, temperatures are limited to below 1300 K and can take some time to reach these temperatures stably. With the recent developments in internal and external resistive heating devices and techniques, it is now possible to reach very high temperatures of around 3000 K in low-pressure systems, and reasonable temperatures of around 1200 K at pressures above 100 GPa consistently and stably. As it may be apparent, there are limitations inherent to this as a heating technique. Two fundamental limitations are that it is not possible to attain temperatures above the melt temperature of the heating element for obvious reasons and the increased risk of oxidation with increasing temperature.

In the case of many of the metal hydrides, due to the high energy barriers involved, resistive heating is often not adequate for the creation of temperatures required which can be in excess of 2000 K. To achieve these pressures, we must instead look to laser heating techniques.
2.3.2 Laser Heating

As previously mentioned, to reach temperatures above 1200 K readily, alternative techniques to conventional resistive heating need to be used. One such technique capable of this is laser heating. In its most simple terms, laser heating is the transfer of energy from a photon beam to energy in the form of heat within the target material. The interactions of the incident laser beam with the surface of the target material (typically through the absorption of the incident photons) generates an excess of kinetic energy across the exposed region. Through interactions caused by the induced randomised motion of the energetic atoms, this excess of kinetic energy is dissipated to neighbouring atoms and throughout the sample environment, increasing the overall heat within the sample. The continued transfer of energy from the laser creates a localised ‘hot-spot’ within the target material, often at temperatures in excess of those at which visible emission is observed, with a sharp gradient of heat decreasing from the central ‘spot’ to regions outside of the lasers focal area. Whilst emission may be occurring from a wide radius in the sample, the visible emission of the ‘hot-spot’ typically dominates the emission profile of the sample area. Through the collection of the emission spectra, it is possible to calculate an upper estimate for the sample temperature as is explained in subsection 2.3.4.

The main advantage to this method over other heating techniques is the ability to readily generate temperatures of $\sim 5000K$ within the DAC whilst under compression, with these temperatures being approximately in the range expected of the earth’s core boundary ($\sim 5600K$). Through the use of a beam splitter on the incident heating beam path or two separate heating lasers, it is possible to have heating of the sample from two sides simultaneously with an example of an optical setup for this style of the system being shown in fig. 2.5. This allows the creation of much larger homogeneous heated areas than with conventional single-sided laser heating experiments, as well as the potential for higher temperatures as the lower thermal gradients across the sample slow the rate of cooling. This can be very useful for studies, particularly those in which XRD is being used as inhomogeneity within the samples will have a noticeable effect on the diffraction patterns, minimising the amount of unheated sample within the beam path.

There are several limiting factors with the efficiency of laser heating techniques, however. These mostly pertain to the absorption efficiency of the target material due to the need for absorption to occur for heat transfer from the beam. With
Figure 2.5  Example schematic of a dual-sided laser heating setup for DAC XRD experiments with an optical setup for emission spectroscopy from the high-pressure beamline ID-27, ESRF. The blue line represents the beam paths of the Nd:YAG lasers, the red line the beam path of the Co2 and HeNe laser and the green line the path of the x-ray source. This figure is reproduced from Petitgirard et al. [39], ©2014 Petitgirard et al.[CC-BY-4.0].
metals, due to the prevalence of free electrons, there typically is a high degree of absorption capacity. However, with other non-metallic materials, the absorption will only occur if the energy of the incident photons exceeds the bandgap of the material outside of multi-photon events or impurity states. When absorbed, additional limitations arise in the dissipation of the energy into the phonon modes of the material as to release the energy; the electrons need to return to a lower energy state (the thermalisation rate) which requires a finite amount of time to occur, which is typically longer in non-metals than metals. If the rate of incident photons exceeds this thermalisation rate, the incident photons may instead impart energy into liberating electrons and breaking chemical bonds over transferring thermal energy. This limits the increase in temperature within the material leading to phenomena such as surface ablation. Further information surrounding the phenomenon of photon absorption can be found in [41].

2.3.3 Limitations of Laser Heating in Diamond Anvil Cells

Whilst laser heating is a very useful tool in the creation of extreme temperatures, particularly within the DAC sample chamber, there are a number of potential issues and limitations that occur. The first and largest limitation occurring with laser heating in DACs is in the temperature distribution profile of the heated region. Due to the focused laser’s relatively small size, a relatively small area of the sample surface is often directly heated by the incident beam. Whilst the overall impact of this can be lessened by the movement of the main heating point across the sample to more evenly distribute the maximum temperature, a factor which is of great importance when attempting to induce a chemical reaction, this often leads to high-temperature gradients across the sample. A number of studies have been conducted over the years into the distribution of heat within the DAC [42, 43, 46, 47] whilst undergoing laser heating with a number of these studies carrying out finite element modelling of the temperature distribution within the sample itself [44, 45, 48, 49]. As is illustrated in the sketches presented in fig. 2.6 the areas of highest temperatures occur closest to the heated spot, with temperatures decreasing rapidly towards the bulk temperature of the material with distance from the central heating spot. This can be a particular issue when it comes to the propagation of heat throughout the sample perpendicular to the heated surface as temperatures are observed to rapidly decrease with depth into the heated material [41, 45]. This means that the side furthest away from the heating spot can potentially be marginally above room
Figure 2.6 Sketches of typical temperature distributions associated with the laser heating process relative to the heating beam (green dashed lines) red areas indicate high temperatures with blue areas denoting colder temperatures with the general temperature of the sample decreasing with distance from the central heating point (adapted from the studies presented by Du et al., Kiefer et al., Dewaele et al., and Goncharov et al. [42–45]). Profiles are presented viewing from within the beam path looking down on the sample (left), and as a cross-section of the heated material for both single-sided (centre) and double-sided (right) laser heating.
temperature whilst the heated spot is of the order of 1000 K. This presents a unique challenge when performing heated XRD experiments as heated regions of the sample and unheated bulk material are often visible simultaneously, creating complex diffraction patterns comprising of multiple phases. Additionally, with samples that exhibit a wide range of polymorphisms or in which reactions to differing stoichiometries across different energy pathways, these thermal gradients can cause the creation of complex mixed products.

There are several ways with which the effects of the thermal gradients can be reduced. The first and simplest of these solutions involves the setup of the sample chamber itself. Through the use of insulating materials with heat capacities higher than the sample material (often MgO, Al₂O₃, NaOH or Ar) the amount of heat lost from the sample through conduction can be minimised. This means that overall, with adequate time, this will allow for a more distributed heat profile across the sample. Alternatively, particularly for thicker samples, the amount of the sample at temperatures close to the peak temperature can be improved using double-sided heating techniques. As is shown in fig. 2.6 (right), with the introduction of heating from the opposite side of the sample, the warmer areas of the thermal gradient meet within the sample, creating a much more significant proportion of the sample at increased temperature. With thin samples, the use of double-sided heating techniques allows for the vast majority of the sample to be at temperatures near to the peak temperature throughout the sample depth.

In addition to the limitations created by the presence of thermal gradients within the sample, there are also several limiting factors associated with the geometry of the sample environment. One of these factors, which can often prove to be the most damaging, is ‘bridging’. In this context, bridging refers to the situation in which the sample material that is due to be the target of laser heating is arranged within the sample chamber so that it is in contact with both culets when under compression. This creates a situation in which, in a best-case scenario, the heat transfer from the heated region of the sample has a direct connection to the anvils. Due to the high heat capacity of diamond, in these situations, heat is rapidly transferred into the anvils, decreasing the effectiveness of laser heating. In a non-ideal situation, the complications bought on by the effects of bridging are much more severe. Due to the proximity of the target sample to the surface of the culet, it is possible for the focal point of the heating laser to align with the culet itself or for the hot spot created by heating to be in direct contact with the culet. This leads to a localised hot-spot on the surface of the diamond anvil, which
can exceed the graphitisation temperature of diamond \([50]\) (∼1200 K at ambient pressure). The formation of graphite on the culet of the anvil can then spread deeper into the anvil or act as a coupling point for the heating laser creating more graphite an ultimately leading to the spontaneous structural failure of the anvil. To mitigate the risk of this occurring within the experiments conducted in this work, samples were precompressed to pressures beyond the point of ductile flow for the gasket material after loading to ensure no evidence of bridging could be observed before laser heating was conducted.

As a result of the extremely harsh conditions created when laser heating samples environments within DACs, it is advisable to provide the diamond culets with some degree of thermal insulation. This particularly advisable when conducting experiments at the upper limits of stress for the given diamond pairs. This is particularly true of sample environments containing low Z elements due to the risks associated with diamond embrittlement through quantum tunnelling effects, which are often a potential problem even at low temperatures \([51, 52]\), or materials which are known to react readily with carbon as the increased energy allows these behaviours to become more prevalent. Whilst it is possible to lay the insulating layer below or around the sample with conventional loading techniques, this leaves a much lower sample volume for the sample itself and, for gaseous samples, can interfere with the sample itself, particularly in synthesis experiments. A solution to this is the use of various diamond tip coating techniques in which layers of material are directly adhered to the diamond surface. Several different techniques can be used to achieve these coatings including, evaporation deposition, chemical vapour deposition and sputter coating alongside simple brush application of materials suspended in solvents. Some attempts to use sputter coating techniques to generate a protective layer across the culet were used during the projects contained within this work to limited success, with the coating layer often delaminating under compression. As such, it would be interesting to explore the conditions under which the laminated layer remained stable under compression; however, these studies were not possible within the confines of this thesis.

2.3.4 Temperature Determination Using Blackbody Emission

Due to the steep temperature gradients with laser heating alongside the incredibly small sample volumes, conventional temperature measurement techniques relying on contact with the heated material, such as thermistors, are not fit for
purpose. Due to the difficulties associated with temperature measurements directly within the sample chamber, indirect temperature determination methods are often necessary. Two key methods can be used in DAC experiments for this purpose, both of which have their own limitations. These techniques rely on the relationship between the Raman Stokes and Anti-Stokes ratios or measurement of the thermal emission from the heated sample. As the calculation of temperature using the ratio of Stokes and anti-Stokes modes was not used in these studies, it will not be discussed here. However, an overview of the method can be found in the work of Han et al.\cite{53} and references therein. With the use of thermal emission spectra as the primary method of temperature determination in this work, this shall form the focus of this discussion.

The following derivation is adapted from several sources, including \cite{54,57}. As is widely understood, at any temperature above absolute zero, thermal motion within materials and the movement of electrons between quantum energy states causes the emission of photons. For any given system, so long as the particles are distinguishable, the likelihood of a system occupying a specific energy state can be described using the Boltzmann distribution,

$$p_j = \frac{e^{-\varepsilon_j/kT}}{\sum_{j=0}^{M} e^{-\varepsilon_j/kT}}$$

(2.19)

where $p_j$ is the probability of a given energy state $j$, $\varepsilon_j$ represents the energy of the energy state $j$, $k$ is the Boltzmann constant, $T$ is the temperature of the system, and $M$ is the total number of available energy states within the system. Knowing the number of particles within the system, $N$, it is possible to determine the number of particles occupying a given energy state, $n_j$, with $n_j = Np_j$. This gives the relationship,

$$n_j = N \frac{e^{-\varepsilon_j/kT}}{\sum_{j=0}^{M} e^{-\varepsilon_j/kT}}$$

(2.20)

From this, determination of the energy distribution within the system is possible with total energy $U = \sum_{j=0}^{M} n_j \varepsilon_j$. Looking at this in terms of photons, each state then can be described as having an energy of $\varepsilon_j = hv$, where $h$ is Planck’s constant and $v$ is the frequency of the photon. Thinking in terms of the average energy of the mode of frequency, $E_v$, then gives the relationship

$$E_v = \frac{\sum_{j=0}^{M} \varepsilon_j n_j}{N} n_j = \frac{\sum_{j=0}^{M} \varepsilon_j n_j e^{-\varepsilon_j/kT}}{\sum_{j=0}^{M} e^{-\varepsilon_j/kT}}$$

(2.21)
which though the use of series expansions can be simplified to

\[
E_v = \frac{\varepsilon_j}{e^{\varepsilon_j/kT} - 1} = \frac{hv}{e^{hv/kT} - 1}.
\] (2.22)

These frequency modes refer to the groups of waves that are energetically indistinguishable. As such, it is necessary when considering the macroscopic energies within the system to consider the density of states of the system, \( g(v) \). Thinking of these frequency modes as harmonic oscillators in a box of volume \( V \), the density of states can be considered as the function describing the number of possible states within an infinitesimal shell of in a 3d wave space \( \vec{k} + d\vec{k} \). The number of states possible can be calculated as the ratio of the volume of the shell in \( k \)-space and the volume of the states themselves. Considering only positive magnitudes of the orthogonal components of \( \vec{k} \), due to physical restraints of the system allows the system to be limited to one quadrant of \( k \)-space with each state having two possible polarities.

\[
V_{\text{shell}} = 4\pi k^2 dk
\] (2.23)

\[
V_{\text{state}} = \pi^3 V^{-1}
\] (2.24)

\[
N = g(k)dk = \frac{1}{4} \frac{V_{\text{shell}}}{V_{\text{state}}} = \frac{V}{\pi^2} k^2 dk
\] (2.25)

which when converting the units to frequency \( v \) gives with the relationship \( k = \frac{2\pi v}{c} \)

\[
N = g(v)dv = V \frac{8\pi v^3}{c^3} dv
\] (2.26)

This can then be substituted in to normalise the energy of the frequency modes \( E_v \) per unit volume \( V \) such that \( \int_0^\infty g(v)E_v dv = U(v,T) = \frac{4\sigma T^4}{c} \) inline with the Steffan-Boltzmann law of radiative power. This gives the expression for the
spectral energy $U(v)$ as

$$U(v, T) = \frac{1}{V} \int_{0}^{\infty} g(v) E_v dv = \int_{0}^{\infty} 8\pi h v^3 \frac{1}{c^3} \frac{1}{e^{h v / k T} - 1} dv \quad (2.27)$$

which using the relationships $c = \lambda v$ and $dv = c\lambda^{-2} d\lambda$ can be expressed in terms of wavelength $\lambda$ as

$$U(\lambda, T) = \frac{1}{V} \int_{0}^{\infty} 8\pi h c \frac{1}{\lambda^5} \frac{1}{e^{hc / \lambda k T} - 1} d\lambda. \quad (2.28)$$

Due to the quantised nature of photons, it is possible and much more helpful to describe the system in such a way that the total emitted energy need not be measured. This can be done by instead looking at the spectral energy density per unit volume $B_v$ or $B_\lambda$ which can be given as

$$B_v(v, T) = \frac{1}{V} \frac{dU(v, T)}{dv} = \frac{8\pi h v^3}{c^3} \frac{1}{e^{h v / k T} - 1} \quad (2.29)$$

$$B_\lambda(\lambda, T) = \frac{1}{V} \frac{dU(\lambda, T)}{d\lambda} = \frac{8\pi h c}{\lambda^5} \frac{1}{e^{hc / \lambda k T} - 1} \quad (2.30)$$

in terms of frequency and wavelength, respectively, with this being Planck’s Law of blackbody emission as described in 1900 [58].

To convert this into a more useful form from an experimental perspective, it is helpful to convert these equations to be evaluated in terms of spectral intensity ($I$), defined as the amount of energy passing per unit solid angle per second per unit frequency or wavelength. The first step is to convert from energy to power which, due to the lack of time dependence of the equation, can be done by dividing by the time period of 1s. If we consider only the emitted photons heading in the observer’s direction, assuming that the emission is uniformly distributed about the sphere of radiance, half of the total energy will be observable within this hemisphere. These observable emitted photons will all be distributed about the
hemisphere of solid angles $2\pi$ steradians at a radius of $tc$ m where $c$ is the speed of light. This means that to determine the power per unit solid angle, a factor of $\frac{1}{2}\frac{c}{2\pi}$ should be applied to the equation, giving:

$$I_\lambda(\lambda, T) = \frac{1}{2}\frac{c}{2\pi}B_\lambda(\lambda, T) = \frac{1}{2}\frac{c}{2\pi} \cdot \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda kT} - 1} = \frac{2hc^2}{\lambda^5} \cdot \frac{1}{\exp\left(\frac{hc}{\lambda kT}\right) - 1} \quad (2.31)$$

$$I_\lambda(\lambda, T) = \frac{2hc^2}{\lambda^5} \cdot \frac{1}{\exp\left(\frac{hc}{\lambda kT}\right) - 1} \quad (2.32)$$

Within known materials, there are no perfect blackbody emitters and most materials can instead be modelled as a greybody emitter. That is to say that there is a scaling factor referred to as emissivity applied to the blackbody emission profile of the material. Emissivity is often denoted as $\varepsilon(\lambda, T)$ but will be denoted as $\alpha(\lambda, T)$ to avoid confusion with energy states. This value represents the ratio of emitted light compared to that which is expected of a perfect blackbody emitter having a value between 0 for no emission and 1 for perfect blackbody emission. Applying this to the spectral emission distribution as seen in eq. (2.31) to give the equation in the form of

$$I_\lambda(\lambda, T) = \alpha(\lambda, T) \cdot \frac{2hc^2}{\lambda^5} \cdot \frac{1}{\exp\left(\frac{hc}{\lambda kT}\right) - 1} \quad (2.33)$$

Due to the electronic interactions within the material, it is possible for $\alpha(\lambda, T)$ to vary across both wavelength and temperature. These materials are referred to as selective emitters. However, it is much more common for materials to have a near-constant emissivity ratio across all wavelengths, meaning that a constant value of $\alpha$ can be assigned to the material. Materials where this assumption is valid are referred to as greybody emitters and form the majority of naturally occurring metals.

For materials with which the greybody assumption holds, it is possible to use the thermal emission profile to determine temperatures within a moderate degree of uncertainty. Using the same optical system as that used for the laser heating process, with appropriate alignment, it is possible to collect the thermal emission profile from the heated area through the use of a CCD. The collected emission profile can then be integrated into a 1D intensity profile; however, due to the
nature of optical components, there is a distortion on the emission profile caused by the optical path $f_{\text{dist}}(\lambda)$. To correct for this distortion to the emitted spectra, it is necessary to know the distortion function; however direct measurement or calculation of this profile is difficult and changes with any adjustments of the optical system. By using a thermal calibration lamp, typically a tungsten filament bulb, it is possible to indirectly determine the distortion profile ($f_{\text{dist}}(\lambda)$).

Expressing the collected emission profile, $I_{\text{co}}(\lambda, T)$, in terms of the distortion profile, $f_{\text{dist}}(\lambda)$, and the original emission, $I_{\text{em}}(\lambda, T)$, gives the relationship,

$$ I_{\text{co}}(\lambda, T)_T = f_{\text{dist}}(\lambda) I_{\text{em}}(\lambda, T)_T, \quad (2.34) $$

which can be rearranged in to the form

$$ f_{\text{dist}}(\lambda) = \frac{I_{\text{co}}(\lambda, T)_T}{I_{\text{em}}(\lambda, T)_T}. \quad (2.35) $$

As all light passing through the optical system is affected by the same optical distortion function so long as it takes the same optical pathway. That is to say for two different sources of emission placed into the system the ratio of the collected and emitted profiles will be equal and equivalent to the distortion profile ($f_{\text{dist}}(\lambda)$), expressed mathematically as

$$ f_{\text{dist}}(\lambda) = \frac{I_{\text{co}1}(\lambda, T)_T}{I_{\text{em}1}(\lambda, T)_T} = \frac{I_{\text{co}2}(\lambda, T)_T}{I_{\text{em}2}(\lambda, T)_T}. \quad (2.36) $$

Through the use of a calibration collection from a known source using the optical system, it is possible to correct collected emissions from calibrated sources to provide the original emission profile. Typically a tungsten lamp at 2 A providing emission at around 2700 K is used for these calibration purposes. With source 1 representing the calibration source and 2 representing the sample, rearranging eq. (2.36) gives an equation for an unknown emission profile,

$$ I_{\text{em, sample}}(\lambda, T)_T = \frac{I_{\text{em, cal}}(\lambda, T)_{T_{\text{cal}}}}{I_{\text{co, cal}}(\lambda, T)_{T_{\text{cal}}}} \frac{1}{I_{\text{co, sample}}(\lambda, T)_T}. \quad (2.37) $$

With this method of correcting the thermal emission profile via the removal of the distortions from the optical system, it is possible to use fitting algorithms to determine the temperature of the emitting object. Using eq. (2.33) both $\alpha$ and $T$ can be used as variables in the fitting process.
Several different fitting algorithms exist, but due to the non-linear nature of Planck’s Law, a geometric fitting technique must be used. Within these fitting algorithms, often, the variables are iteratively altered, with the modelled curve being compared to the experimental data using regression analysis. Typically for geometric fitting, either $\chi^2$ or $R^2$ goodness of fit tests are used for the regression analysis, with the aim of the iterative process being to minimise the results of these regression tests. When the iterative process reaches a minimum, the final result of the regression analysis combined with a visual inspection of the fitted curve can be used to evaluate the overall goodness of the fit. The temperature fits throughout this thesis were conducted using one of two pieces of software: T-Rax maintained by Clemens Prescher (available at https://github.com/CPrescher/T-rax) and a custom MATLAB script produced by the author for use with the in-house laser heating setup.

With spectral temperature analysis, there are several sources of uncertainty in the determined temperature which should be considered. One such source is with the fitting algorithms themselves. The statistical uncertainties within the algorithms arise based on the number of data points collected across the collected spectra and are output by the fitting algorithm itself. These statistical uncertainties are much worse with low-intensity profiles as the signal to noise ratio is much lower in these cases, which leads to the noise affecting the fit itself. With an adequate intensity emission profile (typically over 1000 counts), these statistical uncertainties are often relatively small, $<50 \text{ K}$, compared to the expected temperatures. Additionally, the heating technique itself can cause uncertainties within the temperature, which is much harder to quantify. When conducting pulsed heating, due to the discontinuous nature of the heating process, there will naturally be fluctuations in the heating of the sample, often leading to visible ‘wobbling’ in the intensity of the heated spot. This leads to a situation in which the peak temperature and the bulk temperatures have a mismatch. To combat this, it is possible to collect a number of temperature readings across the heating run and then average the fitted temperature value across the collected values. Typically this includes averaging 3-8 spectra from the heating before averaging the temperature with a lower bound on the uncertainty of the temperature given by the standard deviation of this averaged data set. Uncertainties in temperature measurements can also be compounded by discrepancies in beam placement and the spectral collection as, due to the temperature profiles of laser-heated samples as discussed in section 2.3.3, the further from the centre of the heating beam, the more the temperature drops off back to the bulk apparatus temperature. To
mitigate the effects of this, it is imperative that the collected data comes from as close to the heating laser spot as possible, which means that the optical alignment of the system should be regularly checked on systems in which emission spectra analyses are to be collected.

2.4 X-ray Diffraction

2.4.1 Elementary Scattering Theory

At its simplest, scattering is the phenomenon by which an incident particle or wave is deflected or diffused upon integration with some material object. This phenomenon of scattering ranges from the macroscopic scale interactions of snooker balls all the way down to the interaction of photons and materials at the atomic scale but all of which can be simplified to a transfer of momentum and energy between scattering components. This can be described mathematically for an incident particle with wavevector $\mathbf{k}_i$ and angular frequency $\omega_i$ and post
scattering event wavevector $\mathbf{k}_f$ and angular frequency $\omega_f$ with the momentum transfer of the scattering event expressed as

$$\mathbf{p} = \hbar \mathbf{k}_i - \hbar \mathbf{k}_f = \hbar \Delta \mathbf{k}$$

(2.38)

where the Plank constant $\hbar = \hbar/2\pi$ and the scattering vector

$$\Delta \mathbf{K} = \mathbf{k}_i - \mathbf{k}_f$$

(2.39)

and the energy transfer of the scattering event described as

$$\Delta E = \hbar \omega_i - \hbar \omega_f = \hbar \Delta \omega$$

(2.40)

As diverse as they are, these interactions can be categorised into two main groups, elastic and inelastic scattering. In the case of elastic scattering, no internal energy states are changed within the scatterer or the scattered component, which can be expressed mathematically as

$$\Delta E = 0 \leftrightarrow \Delta \omega = 0,$$

(2.41)

and in the case of inelastic scattering, energy is transferred between the two parties during the scattering event resulting in a change in the internal energy states of both the scatterer and scattered component.

Of these two regimes, x-ray diffraction falls into the domain of elastic scattering, with the resultant scattering events being characterised by a scattering event in which momentum is transferred, but no exchange of energy occurs between the scattering photon and the material. Applying the parameters of elastic scattering as described in Equation 2.41 to the definition of the wavenumber $k = |\mathbf{k}| = 2\pi/\lambda$ it holds that the modulus of the wavevector and subsequently the wavelength $\lambda$ remains constant throughout the scattering event

$$|\mathbf{k}_i| = |\mathbf{k}_f| = \frac{2\pi}{\lambda},$$

(2.42)

which can be shown more formally by substituting the photon dispersion relation $c = \omega/k$, where $c$ is the speed of light, in to Equation 2.40.

As crystals are periodic lattices with consistent spacing between atoms across the structural planes, for an incident beam for scattering with a wavelength
Figure 2.8  Geometric illustration of Bragg’s law. Atomic Bragg planes spaced by lattice spacing $d_{hkl}$ are struck by an incoming wave which is specularly reflected at an angle $\theta$ giving the diffracted angle $2\theta$. The additional path travelled by the lower wave is $d_{hkl}\sin\theta$ on both the inbound and outbound path giving a total path difference of $2d_{hkl}\sin\theta$.

comparable to the atomic spacing, the crystal lattice will behave as a diffraction grating when struck by a monochromatic photon source. When considering the periodicity of crystal structures, it can be helpful to outline the nomenclature of the structural planes in the form of the Miller indices $h$, $k$ and $l$ which describe the intersection of the lattice planes with the unit cell axis $\vec{a}$, $\vec{b}$ and $\vec{c}$. These relationships are defined such that the plane denoted $(hkl)$ intersects the unit cell axis at the points $\vec{a}/h$, $\vec{b}/k$ and $\vec{c}/l$.

The most straightforward modelling of scattering behaviour comes in the form of the Bragg formulation, which forms a special case of the more general Laue diffraction model. Bragg scattering occurs when the scattering vector $\Delta\vec{K}$ coincides with the reciprocal lattice vector of the structure $\vec{G}_{hkl}$, that is to say $\Delta\vec{K} = \vec{G}_{hkl}$. When this condition is met, constructive interference from the diffracted occurs with the planes of atoms acting as a specular reflector for the incident beam with a strong, observable reflection. This can be more readily understood as a geometric construction considering the paths of the incident beam as shown in fig. 2.8 which allows the formulation of Bragg’s law, which is given in the form:

$$2d_{hkl}\sin\theta = n\lambda$$

(2.43)

where $d_{hkl}$ denotes the distance between parallel planes of the crystal structure.
(the ‘d-spacing’) of the plane with Miller indices $hkl$ relating to the reciprocal lattice vector $\mathbf{G}_{hkl}$, $\theta$ is half the diffracted angle, and $n$ is the order of the diffraction. Whilst the Bragg formulation accurately describes the observed diffraction effect, an equivalent but more general and robust formulation exists in the form of the Laue formulation.

In the Laue formulation, instead of considering the crystal as a series of mirror-like layers of atoms, we must instead consider the lattice to be made of periodically arranged identical atoms resting on lattice sites with translation vector $\mathbf{T}$. When struck by radiation, instead of only scattering as if a specular mirror, each atom can reradiate in all directions; however, due to interference effects, scattering can only be observed when constructive interference occurs. This is shown through the use of Fourier optics, considering the incident monochromatic wave with frequency $f$ traversing the crystal structure. Considering the incident and scattered waves in the form of the wave equation;

$$f_i(t, \mathbf{x}) = A_i \cos\left(\omega_i t - \mathbf{k}_i \cdot \mathbf{x} + \varphi_i\right)$$

$$f_f(t, \mathbf{x}) = A_f \cos\left(\omega_f t - \mathbf{k}_f \cdot \mathbf{x} + \varphi_f\right)$$

where $t$ corresponds to the time, $\mathbf{x}$ is the position vector of the wave in Cartesian space and $\varphi$ corresponds to the initial phase of the wave. In the event that there are no atoms within the path of the beam continues on its path indefinitely; however, at the point at which the wave interacts with lattice structure at a point on the lattice vector $\mathbf{T}$ a scattering event occurs, and the phases of both the incident and scattered photons must coincide. This means at each point $\mathbf{x} = p\mathbf{a} + q\mathbf{b} + r\mathbf{c}$, where $p$, $q$ and $r$ are integers, the relationship

$$A_i \cos\left(\omega_i t - \mathbf{k}_i \cdot \mathbf{x} + \varphi_i\right) = A_f \cos\left(\omega_f t - \mathbf{k}_f \cdot \mathbf{x} + \varphi_f\right)$$

must hold. This means it must be true that,

$$\omega_i t - \mathbf{k}_i \cdot \mathbf{x} + \varphi_i = \omega_f t - \mathbf{k}_f \cdot \mathbf{x} + \varphi_f + 2\pi n$$

where $n$ is an integer. Since there is no change in angular frequency across the interaction we can rearrange to the form,

$$\Delta \mathbf{K} \cdot \mathbf{x} = (\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{x} = 2\pi n.$$
With this in mind, we are now able to prove that the Laue equations;

\[
\begin{align*}
\Delta \mathbf{K} \cdot \mathbf{a} &= 2\pi h \\
\Delta \mathbf{K} \cdot \mathbf{b} &= 2\pi k \\
\Delta \mathbf{K} \cdot \mathbf{c} &= 2\pi l,
\end{align*}
\]

are valid for all lattice points on the lattice vector \( \mathbf{x} \) with \( h \), \( k \) and \( l \) representing the Miller indices as previously described. By reducing \( \mathbf{x} \) to it’s component basis we get,

\[
\Delta \mathbf{K} \cdot \mathbf{x} = \Delta \mathbf{K} \cdot (p\mathbf{a} + q\mathbf{b} + r\mathbf{c}) = p(\Delta \mathbf{K} \cdot \mathbf{a}) + q(\Delta \mathbf{K} \cdot \mathbf{b}) + r(\Delta \mathbf{K} \cdot \mathbf{c}) = 2\pi n. \tag{2.50}
\]

which, to be a valid statement requires that \( \Delta \mathbf{K} \cdot \mathbf{a}, \Delta \mathbf{K} \cdot \mathbf{b} \) and \( \Delta \mathbf{K} \cdot \mathbf{c} \) all be multiples of \( 2\pi \) meaning that the Laue equations form a series of valid solutions and \( n \) must assume the form \( n = ph + qk + rl \).

The expected intensity of a scattering event is proportional to the square of the amplitude of the wave function of the scattered wave. However, with more than one scattering event, the observed intensities from each Bragg peak are equal to the sum of the contributions from all scattering events dependent upon their phase shift. This can be written in the form;

\[
I \simeq \left[ \sum_j A_j e^{i\phi_j} \right]^2. \tag{2.51}
\]

If, as previously, it is assumed that both the incident and scattered wavefronts can be treated as plane waves, we can apply the relationship outlined in the Laue formulation to this equation. Instead of the use of general position vector \( \mathbf{x} \) for crystallographic purposes, it is often more useful to think about positions in terms of the unit cell dimensions. We can instead use the fractional atomic positions \( \mathbf{r} \) of the lattice in the form \( \mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} \) to better reflect the periodicity of the structure. As both the reciprocal lattice \( \mathbf{G}_{hkl} \) and the scattering vector \( \Delta \mathbf{K} \) are equivalent we can construct the relationship for the structure factor, \( F(\mathbf{G}_{hkl}) \);

\[
F(\mathbf{G}_{hkl}) = \sum_j f_j(\mathbf{G}_{hkl}) e^{i\mathbf{G}_{hkl} \cdot \mathbf{r}_j} \tag{2.52}
\]

where \( f_j(\mathbf{G}_{hkl}) \) is the atomic structure factor (scattering power) and \( r_j \) is the atomic position of any given atom \( j \) in the crystal structure. As before, the scalar product \( \mathbf{G}_{hkl} \cdot \mathbf{r}_j \) can be expressed in the form \( \mathbf{G}_{hkl} \cdot \mathbf{r}_j = 2\pi(hx + ky + lz) \),
allowing the structure factor to be rewritten as;

\[ F(\mathbf{G}_{hkl}) = \sum_j f_j(\mathbf{G}_{hkl}) e^{2\pi i(hx + ky + lz)}. \]  

(2.53)

This equation for the structure factor is valid at absolute zero however, thermal motion in materials at temperatures above absolute zero causes atoms to deviate from their mean position at any instantaneous moment. This means that at a given instance there is some thermal disorder, with the atoms instead resting on the position \( \mathbf{G}_{hkl} + \mathbf{u}(t) \) where \( \mathbf{u}(t) \) is the displacement of the atom from its location on the reciprocal lattice at time \( t \). This causes an additional broadening and a reduction in intensity of the Bragg scattering angle, with this contribution to the structure factor known as the Debye-Waller or temperature factor. Mathematically this can be expressed as follows,

\[
F(\mathbf{G}_{hkl}) = \sum_j f_j(\mathbf{G}_{hkl}) e^{i\mathbf{G}_{hkl} \cdot \mathbf{r}_j} e^{i\mathbf{u}(t) \cdot \mathbf{r}_j}
\]

(2.54)

This can be averaged across time, removing the time dependence of the equation, allowing it to be expressed in the form,

\[
F(\mathbf{G}_{hkl}) = \sum_j f_j(\mathbf{G}_{hkl}) e^{i\mathbf{G}_{hkl} \cdot \mathbf{r}_j} \langle e^{i\mathbf{u}(t) \cdot \mathbf{r}_j} \rangle
\]

(2.55)

Where \( <> \) denotes the time averaging of that component of the equation. As this is in the same form as eq. (2.51), this allows the intensity of the Bragg peak to be re-expressed as;

\[
I(\mathbf{G}_{hkl}) \simeq |F(\mathbf{G}_{hkl})|^2
\]

(2.56)

which holds for an ideal system; however additional factors affect the intensity observed from scattering events, including structural factors; specimen factors such as the shape, grain size and overall size of the material; and factors from the instrumentation such as radiation polarisation, radiation flux, artefacts of beam shaping and the detector itself. This leaves the relationship for the integrated Bragg peak for a powder diffraction pattern to be expressed in the general form;

\[
I(\mathbf{G}_{hkl}) = N \Phi m_{hkl} |F(\mathbf{G}_{hkl})|^2 PLA
\]

(2.57)

where \( N \) is the number of unit cells within the sample, \( m \) a correction for
multiplicity (the case of powder diffraction referring to the number of equivalent reflections contributing to the powder ring which cannot be distinguished due to the random crystallite orientations), $\Phi$ is a term accounting for the flux during data collection, $P$ is a polarisation factor, $L$ is the Lorentz factor, and $A$ is the correction for attenuation and extinction when passing through the lattice. This is not an exhaustive list of correction terms but forms the basis contributions to the intensity of a Bragg peak.  

In the ideal infinite crystal, the collected diffraction intensities would be observable only at the angle of Bragg diffraction, creating a series of delta functions corresponding to each $hkl$ plane. In reality, however, collected diffraction data are best modelled as a Voigt profile as the shape of the peak varies from the delta function due to a number of different contributions. The Voigt function is a convolution of contributions from both the Gauss and Lorentz distributions. Due to limitations with reasonable analytical computation power and the complexity of the Voigt function and its derivatives, it is more beneficial to use the pseudo-Voigt profile for most practical uses. Instead of taking the convolution of the Gaussian and Lorentzian distributions, the pseudo-Voigt profile instead models the peak shape as a linear combination of both the Gaussian and Lorentzian distributions. This pseudo-Voigt profile is modelled in the form:

$$ V_p(x) = \eta \cdot L(x) + (1 - \eta) \cdot G(x) \tag{2.58} $$

$$ G(x) = e^{-\ln 2 \left( \frac{x-x_0}{w} \right)} $$

$$ L(x) = \frac{1}{1 + \frac{x-x_0}{w}^2} $$

where $\eta$ is a function of the Gaussian profile, Lorentzian profile and the FWHM with a value $0 < \eta < 1$ and $2w$ is the FWHM of the profile.

As previously mentioned, a number of different physical factors contribute to the peak shape. These can be broken down into three key areas: instrumentation, strain effects and size effects; however additional factors can contribute to the overall peak shape, such as thermal effects and atomic disorder within the periodic lattices such as dislocations and stacking faults. Typically with high-pressure XRD studies using synchrotron sources, as with this project, the broadening due to instrumental effects are negligible, so this will not be discussed here. However, due to the small sample volumes, there is a sizeable contribution due to the effects of sample size broadening. Naively, this effect can be explained by considering the Bragg formulation. With a powder sample, within the sample environment,
there are many small grains comprising of randomly oriented crystallites. When exposed to the incident photon source, each lattice has a chance to scatter in any direction. For an infinitely large lattice, all scattering events not at the Bragg angle will be cancelled out by the scattering of another lattice plane a multiple of $\pi$ out of phase. With a smaller crystal size, the probability of this scattering being eliminated by another lattice plane is greatly decreased, creating a ‘window’ of observed scattering events around the Bragg angle. Mathematically the effect of broadening on the peak shape allows for the crystallite size to be approximated from the observed peak width in through the use of the Scherrer equation,

$$S_c = \frac{K \lambda}{b_{hkl} \cos \theta_{hkl}},$$

(2.59)

where $S_c$ is the crystallite size (normally denoted as $L$), $K$ is the shape factor of the crystal (typically approximately 1), $b_{hkl}$ is the FWHM after corrections of other sources of broadening and $\theta_{hkl}$ is the Bragg angle of the plane.

If strain is present within the sample, the $d_{hkl}$ spacings will vary as neighbouring atomic layers vary in position relative to one another. This change in lattice spacing $\Delta d$ causes a shift in average peak position of $\Delta \theta$ which can be calculated as the derivative of the Bragg equation rearranged in terms of $d$.

$$dd = \frac{\partial d}{\partial \theta} d\theta + \frac{\partial d}{\partial \lambda} d\lambda$$

$$dd = \frac{n \lambda}{2 \sin \theta \sin \theta} d\theta + \frac{n \lambda}{2 \sin \theta} d\lambda$$

$$dd = \frac{d \theta}{\tan \theta} + \frac{d \lambda}{\lambda}$$

(2.60)

which given that the wavelength does not change the latter term can be set to zero, giving the peak broadening due to macroscopic strain as:

$$\Delta \theta = (2w)_{\text{strain}} = \frac{\Delta d}{\tan \theta}.$$

(2.61)

This variation in diffraction angle causes a wider range of acceptable diffractions to occur depending upon the number of atoms at each of the different spacings, causing an effective broadening of the peak position about the Bragg peak.
2.4.2 Powder XRD at High Pressure

As a diagnostic technique, XRD is of great importance within solid-state physics, particularly in extreme conditions studies. Incident x-rays strike the sample, scattering from interactions with electron clouds in line with Bragg’s law. This allows a non-destructive, indirect view of a material’s underlying crystal structure, properties that are essential when the sample environment is encased behind several millimetres of diamond. Due to its general importance and the relevance of this technique to the contents of this thesis, the details of this method will be discussed in the following section.

Data Collection

To collect x-ray diffraction patterns, it is necessary first to find a source of x-ray radiation. For this, two main techniques can be used. The more conventional and readily available technique is through the use of an x-ray tube. Within an x-ray tube, a large voltage is created between a filament and a positively charged anode plate; both are contained within a vacuum. The high temperatures reached in the filament causes the liberation of electrons which are then accelerated across the vacuum chamber before colliding with the plate. This interaction causes the excitation of electrons with the atoms of the plate and the creation of a hole within the inner electron shells which an electron from the outer shells relaxes, causing the emission of x-rays. The wavelengths of these x-rays emitted are characteristic of the anode plate used, with copper and tungsten being the most commonly used. Additionally, electrons which ‘miss’ the nucleus are instead slowed when passing the atom. This causes a change in the momentum of the electron and a loss of energy which is released in the form of photons, typically in the x-ray wavelengths, in a phenomenon known as Bremsstrahlung (literally: braking radiation) generation. The intensity of the emitted x-ray beam is proportional to the frequency electron beam striking a target which in tube sources requires an increase in temperature to increase flux. This means that there is an upper limit on flux based on the melting point of the electron source, which due to the very small sample area in DAC experiments, means that often very long collection times are required to obtain adequate statistics.

An alternate method of x-ray generation involves the use of synchrotron radiation sources. At its most basic level, a synchrotron source is comprised of a stream
of charged particles being accelerated around a curved path using magnetic fields. Consistent with the laws of conservation of energy and momentum, these changes in direction cause energy to be released from the charged particle as it interacts with the magnetic fields. As the path of the charged particles can be controlled by the use of the containing magnetic fields, it is possible to tune the wavelength of the emitted radiation to fit with the users’ requirements. In addition to the radiation emitted when travelling around the path of the accelerator facility, it is possible to encourage additional radiation releases at certain points within the radius with distinct characteristic emission features and polarisations through the use of wigglers and undulators. Both wigglers and undulators work using a similar method, with the beam of charged particles being passed through a series of magnets with alternating polarity. This alternating polarity causes a deflection of the beam, which oscillates about the mean beam path with x-rays being generated during the deflection process. As the beam path has a much sharper deflection than on bending magnets, it is possible to generate much smaller wavelength x-rays that are polarised perpendicular to the plane of oscillation. Whilst wigglers are tuned to generate a broad spectrum of incoherent x-rays, with undulators, the produced x-rays are coherent and are much narrower beams with much higher brilliance than the bending magnets and wigglers. This is ideal for angle dispersive XRD techniques as the smaller

**Figure 2.9** Example of a synchrotron XRD beamline configuration at beamline P02 at PETRAIII. This figure is reproduced from the work of Liermann et al.\[60\] ©2015 Liermann et al.[CC-BY-4.0].
range in wavelength means it is much easier to isolate a single wavelength using monochromators and the higher brilliance allows for much shorter collection times to be used. Data in this work was collected using several synchrotron sources at: GeoSoilEnviroCARS (GSECARS), Argonne National Laboratory, Chicago, USA; The European Synchrotron Radiation Facility (ESRF), Grenoble, France; PetraIII, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany; and the Super Photon ring-8 (SPring-8), Sayo Town, Japan.

Integration of XRD Patterns

After the collection has been carried out, the raw diffraction data exists in the form of a 2D image plate with varying intensities across the detectors individual pixel locations, which, in the case of powder diffraction, often appears as a series of concentric circles about a central point. Knowing the geometry of the detector plate relative to the incident beam and the focal point, it is possible to map the image to the 2θ values of the scattering. An example of the raw image plates and the integrated diffraction pattern before additional processing has been carried out can be seen in fig. 27. At this stage, it is also advisable to ‘mask’ the diffraction plate image, effectively removing areas from the diffraction image. Masking is typically done in DAC experiments to remove regions of shadow beyond the opening of the DAC seat and the bright single-crystal diffraction ‘spots’ associated with the diamond anvils themselves.

A series of calibration adjustments are carried out for the detector setup by collecting the diffraction pattern of a known calibrant material to perform this integration. A number of materials are viable for this, including Si, CeO₂ and LaB₆ as these materials have well-studied diffraction patterns with reliable pattern characteristics for calibration. The software then creates a mapping of the 2D detector plate as a function of 2θ from the central point of the Debye cone using the positioning of the diffraction rings of the calibrants on the detector plate combined with the diffraction setup parameters such as the incident wavelength, pixel size and the distances from the sample. Through the aid of computer software, these 2D image plates can then be integrated into a 1D series of 2θ vs intensity with the capability to break this integration down in arcs of azimuth if, as is needed in the case of poor powder or strain effects, certain regions need to be observed independently. In the case of these works DIOPTAS [61] was used for this purpose.
Structure Identification

After collecting diffraction patterns, it is possible to determine the structural information corresponding to the crystal structures within the sample environment. To achieve this, there are two main routes of investigation depending on whether the expected structures are known or unknown.

There are a number of ways in which determination of known structures can be determined, the simplest of which, from a users point of view, is through cross-referencing the diffraction patterns with a database of known diffraction patterns in the form of Powder Diffraction Files (PDF) of which a number of databases are available. This is particularly useful at ambient conditions, but this technique is much less useful for extreme conditions experiments due to the alterations in peak shapes and positions. An alternate method must be used within extreme conditions experiments for diffraction data when known structures are expected. One such method involves comparing the expected peak locations of the known structures with adjustments for the alterations in lattice parameters due to pressure accounted for. These changes in peak position are calculated through the application of EOS equations to the as outlined in section 2.2.1 to the structural information found in previous studies stored as either .CIF or .JCPDS files, which allows these previously determined structures to be compared to the unsolved diffraction patterns. Typically, these known structures will include pressure calibrants and gasket materials, which makes this a useful tool in simplifying diffraction patterns by allowing the assignment of Bragg peaks to non-sample material. In the case of these studies, this was done using the software package Dioptas [61] which allows the overlaying of peak positions and the integrated diffraction patterns without the need for fitting algorithms. Once the known peak positions have been identified or if the diffraction patterns cannot be attributed to known structures, it is necessary to use indexing techniques on the diffraction pattern to determine potential structures.

To index the diffraction patterns, first, it is necessary to identify the peaks attributable to unknown structures and attain the $2\theta$ values of these peaks. It is then possible to index these Bragg peaks to attain the Miller indices (hkl values) of each of the peaks. This process differs depending on whether the sample is single crystal or polycrystalline; however, as this work only involves polycrystalline samples, only the method pertaining to powder diffraction patterns will be discussed here. Due to the periodic nature of crystal structures, it is possible
To geometrically describe structures in accordance with the planes of atoms, with mathematical relationships being able to describe the spacing between lattice planes dependent upon the crystal symmetry family. The equations for the spacing between lattice planes combined with the Bragg scattering condition can be used to determine the miller indices of the diffraction peaks. The full details of the methods and the indexing relationships for the different symmetry groups are detailed in *International Tables for Crystallography: Volume H, Chapter 3.4* [62] and will not be reproduced here.

Whilst indexing can be done by hand for structures with high symmetry, such as cubic and hexagonal systems, this becomes substantially more difficult with lower symmetry systems. For these cases, it is often easier to use indexing software to speed up the process. There are a number of different indexing software available to be used for this purpose, with CONOGRAP [63] being used as the indexing software of choice throughout this work. In essence, indexing software takes the input of peak positions from diffraction patterns, sometimes as a manually input list of peak positions or by using peak detection algorithms. Then, typically using exhaustive searching methods, conducts trials of possible combinations of indices and lattice constants within a set parameter range using the assigned symmetry system rules. These calculated index peak positions are then checked back against the input positions using a figure of merit calculations across all peaks input to determine potential matches to the input data. This returns a weighting value as to the likelihood of fits being ‘good’ to guide the user on visual inspections of the indexing. Due to the lack of intelligent filtering within most indexing algorithms, an element of human input is then required to filter through the list of potential indexes to determine the most likely candidates systems for further analysis.

After indexing the diffraction patterns within the symmetry systems, the observed peaks can then be compared to the selection rules for the different symmetry groups within these systems to reduce the potential number of potential space groups, which may be valid solutions to the structure within the candidate systems. These selection rules can all be found in the *International Tables for Crystallography: Vol A* [64] and allow or forbid the presence of peaks with different Miller indices combinations. For example, in cubic structures for a BCC structure to be valid $h+k+l = 2n(even)$ for all be peaks and $h+k+l = 2n+1(odd)$ must not be true for any peaks observed. Some indexing software will also conduct these calculations across all potential point groups within each system showing the positions of the included peaks for each point group allowing visual elimination.
of some higher symmetry point groups at this stage based on the presence of ‘forbidden’ reflections. Whilst these methods may help minimise the number of potential structures to consider, as some space groups are directly related through second-order structural transitions or shared point group symmetry, it is not possible to distinguish between all structures by this means alone. This means that it is necessary to conduct quantitative analysis in the form of pattern fitting techniques.

**Structural Refinement Techniques**

To verify the validity of the indexing of crystallographic diffraction data, a quantitative method is required. Le Bail refinements form an important part of this process [65]. The Le Bail method comprises a two-step, cyclical process that allows for the refinement of peak shape, lattice parameters, and instrument zero error to approximate the raw data across the entire diffraction pattern. As the Le Bail method does not take into consideration the atomic occupations and the relative intensities of the differing Bragg peaks, as such, this means that each contributing peak is fitted with its own arbitrary intensity profile to minimise the residuals of the fitted profile. However, with a good quality fit to the data, it is possible with Le Bail refinement to extract the unit cell lattice parameters \(a, b, c, \alpha, \beta, \) and \(\gamma\) from the diffraction pattern. This outputted combined intensity profile composing of many individual peak profiles can then be used as the basis of further analysis techniques such as Rietveld analysis which with adequate sample quality allows for the determination of atomic positions from the diffraction pattern.

If adequate statistical data is available in the form of a well powder-averaged diffraction pattern with ‘smooth’ Debye-Scherrer rings it is possible to perform further profile refinement to determine the atomic structure factors and, from this, the atomic positions. One method with which this kind of analysis can be conducted is Rietveld refinement, pioneered in the 1960s by the group of Bert Loopstra, Bob von Laar and Hugo Rietveld at the Reactor Center Netherlands. This method and its history are explained in detail in *International Tables for Crystallography; Vol. H; Section 4.7* [66] however, a very brief summary will be presented here drawing from this source. This method developed on earlier work considering the peak widths and intensities of neutron diffraction and a technique allowing the resolution of overlapping peak intensities, an essential step
in structural solving allowing for fitting of the whole diffraction pattern. Rietveld later would go on to provide an open-source version of the code implementing this method written in the then widely used coding language FORTRAN allowing it to be adapted for use with XRD patterns. The provision of this code rightfully has earned the computational technique the name Rietveld Refinement.

Rietveld refinement comprises of the refinement of 4 main groups of parameters to make a full structure model. These are: structural parameters, including atom positions, occupations, thermal parameters, and displacement parameters; lattice constants; parameters associated with instrumental effects; and parameters specific to the samples being observed. Since the lattice constants can be determined, as was previously outlined, through the use of Le Bail fitting and the instrumental parameters are intrinsic to each different collection device and setup, this method is of interest to many crystallographers due to it allowing the determination of structural parameters. This is because it is the refinement of these structural parameters which allow diffraction data to be translated into a more human-readable form allowing models of the crystal structure to be created based on the atomic positions and occupation factors. A starting point for the determination of atomic positions can be approximated by consideration of the multiplicity, which can be approximately determined through a comparison of unit cell volume and the expected volume of a single unit of the sample material. This allows an estimate of the Z value to be calculated, which can then be used as a guide to determine the Wyckoff site occupations with a combination of sites of multiplicity values summing to the calculated Z value rounded to the nearest integer. For example, a simple elemental structure with Z=3 in the spacegroup \( P6_{3}/mmc \) may have atoms occupying the 1\( a \) and 2\( b \) Wyckoff sites or the 3\( c \) site. With a list of potential atomic positions gathered from the *International Tables for Crystallography: Vol A*. 

All crystallographic refinements contained within this thesis were conducted using JANA2006 which uses the least-squares fitting algorithm during its refinement process. Iteratively, the fitting software alters parameters as outlined by the user to conduct the least-squares fit to the diffraction data until either a fixed number of iterations or a stable minimum with alterations in refined parameters of less than 0.005 is reached over multiple consecutive iterations.

Some form of difference analysis can quantify the overall quality of the structural fits. In the case of XRD experiments, the methods typically used are the R-factor and the weighted R-factor; however, a number of other methods also exist for this
kind of analysis, including $\chi^2$ goodness of fit modelling \cite{68}. At its most basic, the profile R-factor compares the modelled structure to the collected diffraction data as a ratio of the entire collected pattern. This is calculated by the equation:

$$ R_p = \sum \frac{|F_{obs}| - |F_{calc}|}{\sum |F_{obs}|} $$

(2.62)

where $F_{obs}$ and $F_{calc}$ are the collected data points and modelled data points respectively. This method is however limited as it does not account for the intensities of the data points compared to the difference in fitted model. To combat this it also possible to the use the weighted R-factor ($wR_p$), given by the equation,

$$ R_p = \sqrt{\sum (w_i |F_{obs,i}| - |F_{calc,i}|)^2 \sum (w_i F_{obs,i})^2} $$

(2.63)

where $w_i$ is the weighting factor equal to $F_{obs,i}^{-1}$. The work of B. Toby \cite{69} discusses the limitations of these discrepancy values however this is beyond the scope of this work so will not be discussed in detail here.

\subsection*{2.5 Raman Spectroscopy}

Unlike x-ray diffraction, Raman spectroscopy is an optical analysis technique that relies on the inelastic scattering of incident photons from the target sample. When a photon hits a polarisable molecule, one of two things can occur beyond the possibility of elastic scattering as are depicted in fig. 2.10. Suppose the molecule is in the ground vibrational state. In that case, the incident photon elevates the molecule into an elevated virtual energy state before scattering, leaving the molecule in an elevated vibrational state. This reduces the energy of the scattered photon, in a phenomenon referred to as Stokes Raman scattering. The reduction of energy can be used to establish the energy of the vibrational mode. The second type of Raman scattering, anti-Stokes Raman scattering, occurs when the molecule is already in a non-ground state vibrational state. In this case, the incident photon causes the molecule to relax into the ground state, scattering the photon with an increased energy state, with the increase in energy being equivalent to the energy of the vibrational state of the molecule. These phenomena allow the use of optical systems to observe the bonding structure within materials and allows a so-called ‘fingerprint’ to be created, which can be later used to identify a molecule by comparing the spectra to databases of know
materials. This is particularly useful in the case of gas loading hydrogen within the DAC as the hydrogen $v_1$ vibrational mode can be readily observed using Raman spectroscopy and it’s presence within the spectra indicates a successful gas loading has occurred.

One major use outside of identifying structures is the measurement of pressure within the DAC and other pressure environments. This is often done using the fluorescence behaviour of ruby crystals. As a technique, this was pioneered by Piermarini et al.\cite{23,70} before being refined into an accurate pressure measurement model by others\cite{24}. This method uses the relative shift in the ruby R$_2$ fluorescence line as pressure increases, which has been widely studied and is the pressure standard up to 100 GPa as was discussed in section 2.2.2. Beyond these pressures, other pressure calibration techniques need to be used as the fluorescence intensity drops, and the peak broadens to an unusable level. In some optical studies where the use of x-ray techniques of pressure measurement are not possible either due to the extreme stress of the DAC or the confines of the sample space, through the use of Raman spectroscopy, the diamond T$_{2g}$ vibrational mode can be used as a pressure gauge. This vibrational mode mode has been studied up to pressures of 410 GPa and has been calibrated to an acceptable error to this pressure\cite{27,28}.
Figure 2.10  Visualisation of changes in energy levels of electrons during commonly occurring scattering effects.
Chapter 3

Studies of High-Temperature Elemental Germanium at High-Pressure

3.1 A Brief History of Germanium

Germanium (Ge) was discovered in 1886 by Clemens Winker as an elemental component of the mineral agyrodite (Ag₈GeS₆) [71], a mineral structurally isomorphous with the Sn bearing mineral (Ag₈SnS₆). Initially, studies concluded that germanium was a poor metal and over the next 40 years, little advancement was made in the understanding of the material properties of germanium beyond investigations into the isotope abundancies [72]. In the early 1940s, due to a need to improve rectifier circuits in crystal radios, a number of material trials were being conducted amongst a number of semiconducting materials. Due to its relatively low melting temperature compared to that of Si, it was considered that it might be possible to attain high purity combined with its relativity high stability to oxidation, making it useful for potential applications during the infancy of the semiconductor age [73]. A significant issue at the time was occurring in early RADAR receiver systems with crystal rectifier circuits frequently ‘burning out’ under moderate operating temperatures. It was quickly realised that germanium was an ideal candidate material for this function.

As a semiconductor with a bandgap of approximately 0.7 eV, Ge was able to
operate with some consistency as a point contact transistor. Early Ge transistors were, however, rife with issues limiting their operation. Under a moderate load, temperatures would rise beyond those of the intrinsic semiconducting regime alongside issues with the designs of early transistors, which were mechanically unstable. These issues would not be overcome until single crystal fabrication techniques were improved greatly in the early 1950s, allowing better control of crystal purity which in turn allowed the mechanical instabilities to be removed from the systems by the introduction of Shockley’s p-n-p and n-p-n-type transistor junctions created through developments of dopant control techniques. In the late 1950s, these techniques had been refined to the point that they were now capable of being used on silicon (Si) and as such, the days of mass use of germanium in the semiconductor industry were numbered. [74]

With surge in interest in the field of nuclear physics in the early 1960s, within which there was a great need to fabricate radiation spectrometers with high energy resolutions, potential uses were again considered for Ge. It was found early on that these high energy resolution devices could be made using mixtures of Ge and alkali earth metals. For example in early experiments GeLi detectors were fabricated and with impressive resolution being attained of just 0.45% for a 1.333 MeV gamma emission [74, 75]. These Ge based detectors fell in great favour with the Nuclear physics community of the day for a plethora of technical reasons. The detectors had significantly higher atomic numbers than a Si counterpart would do, and a with an atomic number of 32, Ge based detector devices offer good stopping power for gamma range emission. This, coupled with the electron and hole mobility and lifetimes, made GeLi detectors ideal for this work. This was, however, limited by the devices tendency to lose resolution when warmed to room temperatures [74].

3.2 Previous Studies of Germanium Under Pressure

Due to the relative abundance of the collective group-XIV elements on Earth, with Si being estimated to make up around 7.4% [76] of Earth’s composition, high pressure and high temperatures studies of these elements are of great geological significance. This has motivated a number of studies into carbon, Si and Ge under pressure. It is widely known that C exhibits two main solid-state
phases: C-graphite and the metastable C-diamond. Conversely, Si and Ge both exhibit a rich polymorphism both on compression and decompression at ambient temperatures with a number of the metastable decompression phases, which can be recovered to ambient pressure, having further metastable phases which can be reached with heating pathways [77–81]. It is interesting to note that, as with the previously mentioned similarities in material and electronic properties between Ge and Si, there are also observable parallels in the room temperature phase evolutions of Ge and Si.

Under ambient conditions, both Ge and Si conventionally exist in the C-diamond structure (Fd\(\bar{3}m\)) with these phases being referred to as Ge-I [82] and Si-I [83] respectively. Both of these structures are characterised with the main atomic occupation located in the 8a Wyckoff site with positional coordinates (0,0,0) with unit cell dimensions of a=5.658 Å and a=5.431 Å respectively compared to the unit cell of diamond with a=3.567 Å at 0 GPa. At 10.6 GPa, Ge-I undergoes a sluggish transition into Ge-II, with this transition being marked by a distortion into the tetragonal \(\beta\)-Sn type structure (I4\(_1\)/amd) [78, 84]. This distortion occurs due to the stretching of the [100] and [010] planes and compression of the [001] plane leading to a shift in atom position from the 8a site of Ge-I to the 4a site of Ge-II equivalent transition is seen in Si at 11.7 GPa [85] with the same dynamics as those seen in Ge, with the transition having an overall volume decrease of 23.7%.

Interestingly, Ge does not follow the same structural transition in reverse on decompression but instead transforms to several metastable allotropes. These phases are highly dependent on the rate of pressure release: fast compression from \(\beta\)-Sn Ge-II, results in the formation of a BC8 structure (Ia\(\bar{3}d\)), which gradually changes to a hexagonal diamond (Ge-hd) structure (P6\(_3\)/mmc) at ambient pressure [86, 87]. Alternatively, slow decompression from Ge-II, leads to the formation of Ge-III, a metastable tetragonal structure (P4\(_3\)2\(_1\)2) with 12 atoms per unit cell [77–81].

Ge-II does not exhibit further structural transitions on compression until 75 GPa where it begins a second-order transition into the orthorhombic Imma type structure [88], Ge-IV. At the lower pressure side of the transition, when \(a = b\) and the Ge atoms occupy the 4e Wyckoff site in the positions \((0, \frac{1}{2}, \frac{1}{8})\) or \((0, \frac{1}{2}, \frac{1}{4})\) the Imma and I4\(_1\)/amd structures are equivalent. With pressure, this distortion then gradually shifts the atomic positions and the general unit cell until the system approaches the point at which \(b/c = \sqrt{3}\) and the atoms occupy the positions
(0, \frac{1}{4}, \frac{1}{4}) and (0, \frac{1}{4}, \frac{1}{2}) at which point the Imma phase is structurally equivalent to that seen in Ge-V with a \( P6/mmm \) structure with atoms occupying the 1a Wyckoff site. This transition into Ge-V is complete at around 85 GPa [89, 90]. An equivalent transiting is observed in Si, with the Ge-IV equivalent structure, Si-XI, completing its transition at 13.2 GPa [82, 91].

The simple hexagonal phase Ge-V is stable at pressures up to 100 GPa at which point the unit cell undergoes a complex transformation in which the hexagonal layers reconfigure in an anti-symmetric manner [92] to form a \( Cmca \) structure, Ge-VI [93]. A structurally identical transition occurs in Si at pressures of 38 GPa leading to the onset of the \( Cmca \) phase Si-VI phase from the hexagonal Si-V [94]. Ge-VI has been observed to exhibit a wide range of stability being observable at pressures up to 170 GPa at which point there is a transition into the hexagonal phase Ge-VII which exhibits a \( P6_3/mmc \) structure with atoms resting on the 8d and 8f Wyckoff sites [95]. This is again analogous to the Si-VII structure observed at 42 GPa [82] and is observed to be stable up to pressures of 76 GPa [96]. It is clear that the structural evolution of the Ge-(IV-V-VI-VII) phase sequence is analogous to the Si-(XI-V-VI-VII), and molecular dynamics simulations have determined that the mechanisms of the transformation are likely the same in both systems [92]. A complete summary of these structures and their atomic occupations can be found for reference in Table 3.1.

Previous high-temperature studies have mapped out the \( P-T \) phase Ge-I/Ge-II boundary conditions and determined melting temperatures up to pressures of 37 GPa [84, 97]. It is observed that melting temperatures in Ge-I reduce with pressure, meeting a Ge-I/Ge-II/liquid triple point at \(~8.7\) GPa and \(~833\) K [84]. At higher pressures, the melting temperatures begin to increase with pressure reaching \(~1500\) K by 35 GPa. This previous phase diagram can be seen in fig. 3.1. Similar melting behaviour is observed in Si, with melting temperatures decreasing for the C-diamond Si-I phase and increasing in \( \beta \)-Sn, Si-II [98]. Despite the rich polymorphism exhibited below 100 GPa at room temperature, neither system has previously been shown to exhibit exclusively high-temperature phases.

### 3.3 Experimental Details

A number of samples were prepared in symmetric diamond anvil cells (DACs) using wide opening seats suitable for x-ray diffraction (XRD) experiments.
Diamonds of 50–150 µm culet size were indented into Re gaskets with holes being prepared to approximately 50-75% of the culet size. These samples were prepared in two main ways. In early experiments, in an attempt to synthesise hydrides of germanium, germanium chips were placed centrally within the gasket hole, and a number of samples were gas loaded with research-grade hydrogen gas (99.9995%, BOC) to 200 kPa. For these samples, diamonds of 50–150 µm culet size were indented into Re gaskets with holes prepared to approximately 75% of the culet size. Several small chips of Ge (99.999%, sim -100 mesh, Alfa-Aesar) with size <10 µm were loaded onto the non-gasket side diamond culet before the samples were gas loaded to 0.2 GPa as outlined in chapter 3.

As a control experiment to determine the source of the observations in the earlier experiments, samples were also prepared with MgO to stand in place of hydrogen. These samples were prepared first by loading a small quantity of MgO (Alfa-Aesar, Nanopowder, 99+%) into the gasket hole then adding a small chip of Ge powder (99.999%, sim -100 mesh, Alfa-Aesar) to the hole before covering with more MgO and closing the cell. In all of these samples, the cell was taken to approximately 5 GPa to confirm that there was no bridging of the Ge between the
Table 3.1 A summary of known room temperature phases of Si and Ge. * denotes formation on gradual decompression and presence of shear from Ge-II and Si-II and † denotes formation on rapid decompression, ‡ denotes that the structure forms from the bc8 structure at room temperature in Ge and 573 K in Si.

<table>
<thead>
<tr>
<th>Structure type</th>
<th>Ge phase</th>
<th>Transition pressure (GPa)</th>
<th>Si phase</th>
<th>Transition pressure (GPa)</th>
<th>Wyckoff site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fd3m</td>
<td>Ge-I [82]</td>
<td>10.6</td>
<td>Si-I [83]</td>
<td>11.7</td>
<td>8a</td>
</tr>
<tr>
<td>I41/amd</td>
<td>Ge-II [78, 84]</td>
<td>9*</td>
<td>Si-II [83]</td>
<td></td>
<td>4a</td>
</tr>
<tr>
<td>P4212</td>
<td>Ge-III [81, 99]</td>
<td>10.6</td>
<td>Si-ST12</td>
<td>11.7</td>
<td>4a, 8b</td>
</tr>
<tr>
<td>R3</td>
<td>Ge-r8 [99]</td>
<td>7†</td>
<td>Si-r8 [100]</td>
<td>10*</td>
<td>4f</td>
</tr>
<tr>
<td>P63/mmc</td>
<td>Ge-hd [99]</td>
<td>0‡</td>
<td>Si-hd [100]</td>
<td>0‡</td>
<td>4f</td>
</tr>
<tr>
<td>Ia3d</td>
<td>Ge-be8 [99]</td>
<td>6(573 K)†</td>
<td>Si-III [100]</td>
<td>13.2</td>
<td>4e</td>
</tr>
<tr>
<td>I41/amd</td>
<td>Ge-IV [88]</td>
<td>75</td>
<td>Si-XI [89, 90]</td>
<td>15.4</td>
<td>4f</td>
</tr>
<tr>
<td>P6/mmm</td>
<td>Ge-V [93]</td>
<td>85</td>
<td>Si-V [94]</td>
<td>38</td>
<td>8d, 8f</td>
</tr>
<tr>
<td>Cmca</td>
<td>Ge-VI [93]</td>
<td>100</td>
<td>Si-VI [94]</td>
<td>42</td>
<td>2c</td>
</tr>
<tr>
<td>P63/mmc</td>
<td>Ge-VII [95]</td>
<td>170</td>
<td>Si-VII [82]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.4 Results and Discussion

Experiments were carried out at a range of PT conditions between 40 GPa and 110 GPa in which a number of different structural transitions were observed,
Figure 3.2  X-ray diffraction patterns showing room temperature compression of elemental Ge in a H₂ environment. It can be seen that there is clear evidence that under room temperature compression, elemental Ge matches that expected from previous literature as summarised in Table 3.1.
including the previously observed Ge-II/IV transition above room temperature and diffraction evidence of a novel high-temperature phase of Ge which will be further detailed later in this chapter. Cold compression was also conducted at room temperature to verify that the samples conformed with the expected phase evolution of elemental Ge previously outlined in section 3.2. Diffraction patterns demonstrating this structural evolution at room temperature can be seen in fig. 3.2.

3.4.1 High-Temperature Ge-II/Ge-IV Transition

As is summarised in Table 3.1 at room temperature and pressures of around 74 GPa, Ge-II undergoes a sluggish distortion into the orthorhombic Ge-IV phase. As is often the case in elemental systems, structural transitions occur at different temperatures at different pressures. From the previous works of Prakapenka et al. we are aware that no evidence of the Ge-II/IV transition is observed at pressures up to 40 GPa. With this in mind, laser heating of Ge-II was conducted at pressures above 40 GPa up to its room temperature transition pressure at 74 GPa. Upon heating at pressures between 56 GPa and 74 GPa, as can be seen in fig. 3.3, an apparent broadening of the Ge-II 200 peak caused by the growth of the Ge-IV 200 peak accompanied by the appearance of a triplet at around $2\theta = 8.7^\circ$, approximately $d = 2.2\,\text{Å}$, comprised of the Ge-IV 020, 100 and 010 peaks can be seen in addition to the structural peaks associated with the Ge-II structure. Le Bail fits of these high-temperature data sets can be attained when incorporating the structures of Ge-II and Ge-IV with typical R factors of less than 5% indicating that this transition is consistent with that observed with increasing pressure at room temperature. Experimental data shows that the onset of the transition is characterised by a decrease in the intensity of the contributions from Ge-II and a corresponding increase in the intensities of contributions from Ge-IV with increasing temperature up to the expected transition point. This is consistent with what is expected due to the temperature profile created by laser heating (as discussed in section 2.3.3) and the second-order nature of the transition. As the peak temperature of the heated region exceeds the transition temperature, more of the surrounding sample area within the x-ray beam diameter also passes through the transition and due to the second-order nature of the transition, there is a gradual change into the Ge-IV structure as opposed to the sudden discontinuous volume change associated with a first-order transition. However, it should be noted that beyond the transition temperature,
Figure 3.3 Example of XRD patterns from a heating run conducted at 56 GPa with elemental Ge in MgO pressure transmitting medium. From these diffraction patterns, it is clear that at 1560(110) K there is a broadening in the Ge-II peak at around 8.3° caused by the appearance of the Ge-IV 200 peak before the appearance of the characteristic triplet at around 8.8° from the Ge-IV Imma structure at 1850(130) GPa. Alongside evidence of the transition is there is an apparent pressure increase over the transition temperature of around 4 GPa, calculated from MgO, which is observed in all experimental runs in which the Ge-II/Ge-IV transition is present.

62
some evidence can be seen of the broadened Ge-II 200 peak remaining within
the pattern. These remaining contributions from Ge-II can be attributed to
the thermal gradient across the surface of the sample and with sample depth, a
phenomenon commonly seen in laser heating experiments. This phenomenon is
discussed in greater detail in section 2.3.3.

With the onset of the Ge-II to Ge-IV transition being characterised by the growth
of the Ge-IV 200 peak, which appears as a broadening of the Ge-II 200 peak, along
with the growth of a strong triplet at 8.8° from the Ge-IV structure, these
were used as markers within the diffraction data. At 56 GPa and 61 GPa this
transition was observed to occur at temperatures within which visible emission
is observable with the transition being seen at 1550(110) K at 56 GPa and
970(130) K at 61 GPa as is shown in Figure 3.3. Evidence of this transition
was also observed at 71 GPa with the introduction of the heating laser to the
sample; however, the characteristic features of Ge-IV at this pressure can be seen
within the diffraction patterns before the onset of visible thermal coupling of the
sample. Due to the limitations of the wavelength range over which the blackbody
emission spectra were calculated and sensitivity limitations on the detector plate,
it is was not possible to attain accurate temperature measurements for these
transition conditions, but it is possible to apply a conservative upper estimate of
the temperature to be around 800 K due to a lack of observable thermal emission.
With a number of observed transition pressure and temperature conditions, it is
possible to fit a phase boundary between Ge-II and Ge-IV extending from the
known room temperature transition pressure up to the extended Ge-II melt line
as shown in Figure 3.17.

Using the temperatures at which the onset of the transition is observed, it
is possible to estimate the Clapeyron slope of the boundary between the two
phases. By confining the phase transition using the collected data of these
experiments, the expected room temperature transition pressure of 74(3) GPa and
extrapolation of the melt line generated by Prakapenka et al. an estimate for
the Ge-II/IV/liquid triple point at 53(3) GPa and 1650(100) K can be generated.
Using the confines of the melt line generated by these data points along with
the extrapolated melt boundary and room temperature Ge-II/IV transition at
74(3) GPa and 300(5) K a value of $dP/dT$ of $-0.014(3)$ GPa K$^{-1}$ can be obtained
for the phase II/IV boundary. This bears remarkable similarity in appearance to
that observed within Si with the equivalent transition from Si-II to Si-IX which
is experimentally observed to have a phase boundary between 1050 K at 12 GPa.
to 300 K at 13.2 GPa giving a value for $dP/dT$ of $-0.0016$ GPa K$^{-1}$.

### 3.4.2 Transition at High-Temperature Into the Novel Phase Ge-VIII

When laser heating Ge at pressures above 64 GPa an unprecedented change in the diffraction pattern can be observed at temperatures above 1600 K. At pressures below 74 GPa there is a lack of clarity within the diffraction patterns at lower temperatures due to the presence of both Ge-II and Ge-IV within the diffraction patterns as a result of thermal gradients as discussed in chapter 2.3.3. This presents some difficulty in identifying the characteristics of the contributions to the patterns of the novel structure. The origin of the novel peaks in the diffraction patterns is, however, greatly clarified when laser heating at increased pressure, due to the lack of Ge-II in the diffraction patterns above the room temperature transition pressure to Ge-IV of 74 GPa, with the reduction in complexity of the diffraction patterns allowing much easier identification of the novel peaks.

At 76 GPa, changes in the diffraction pattern can be seen occurring at temperatures above 1500 K, with these changes being characterised by the growth of a doublet at around 9.24° as can be seen in Figure 3.4. The growth of these new peaks, combined with a drop in intensity of the peaks attributed to the Ge-IV structure, is indicative of a structural transition occurring under these conditions. Due to repeated quenching between heating runs, the sample appears to become more thermally annealed with the room-temperature diffraction patterns of Ge-IV become more ‘spotty’ between successive heating runs. This indicates that the crystallites are growing in size and that the powder averaging of the Ge-IV within the sample chamber is becoming less complete. When comparing these Ge-IV peaks to the exclusively high-temperature peaks, there is a marked difference in the texture of the Debye-Scherrer rings, with the high-temperature phase exhibiting significantly better powder averaging on the diffraction image plate, as can be seen in fig. 3.5. This further gives credence to the idea that these diffraction peaks are attributable to a different crystal structure than that of Ge-IV. After heating a sample, when quenched to room temperature, all evidence of the novel high-temperature peaks disappears from the diffraction image plates with only the presence of the room temperature phase visible as shown in fig. 3.6. This is indicative of a fully reversible transition between the novel material and the room temperature phase alongside a reduced likelihood of the material occurring
Figure 3.4  High-pressure high-temperature X-ray diffraction patterns ($\lambda = 0.3344\AA$) at 76 GPa showing the IV-VIII transition.
Figure 3.5  
a) 2D image plates, $\lambda = 0.3344\text{Å}$ measured with a Pilatus detector with a $2s$ acquisition time at room temperature (left) and $1757(50)\text{ K}$ (right) at $76\text{ GPa}$. The blue lines indicate contributions to the diffraction image plate from Ge-VIII along with their corresponding Bragg peak indices. The existence of ‘spotty’ features in the diffraction pattern at high temperature from Ge-IV can still be seen along with strong Debye-Scherrer rings from MgO in both low and high-temperature images.  
b) This figure shows the ball and stick model of the determined atomic structure associated with the Ge-VIII phase at $76\text{ GPa}$ and $1750\text{ K}$.
Figure 3.6  Diffraction patterns at 76 GPa demonstrating the reversibility of the Ge-IV/VIII transition with temperature. The two room-temperature diffraction patterns are from immediately before (bottom) and after (top) laser heating (middle) in which it is clear that there are no contributions to the patterns from the novel phase Ge-VIII. MgO was used as the pressure transmitting medium.
due to a reaction within the sample chamber.

To confirm the novelty of the newly grown peaks, the diffraction patterns were compared to the expected patterns of the known phases of Ge as outlined in table 3.1. None of these known phases of Ge could be successfully indexed to the patterns beyond those peaks attributable to Ge-IV, which remain beyond the conditions of the onset of the transition. After eliminating the known Ge structures and the contributions to the pattern attributable to Ge-IV and when relevant MgO, the remaining unidentified peaks were then indexed (see section 2.4.2 for more details on indexing) using the crystallographic software CONOGRAP [63]. This software indexes the input peaks and compares them to the structural selection rules to determine a number of possible crystal structures that could explain the diffraction pattern.

These indexing runs suggested the possibility of a number of different possible space groups with a series of tetragonal space groups being listed as the most likely candidate structure and with a potential simple hexagonal structure also being offered as a candidate by the indexing software. Le Bail fits of the indexed structures with the highest figure of merit values were conducted on the high-temperature diffraction patterns to identify any possible matches to the collected data. Of those trialled, a body-centred tetragonal (bct) structure was found to provide the best quality fit. From these Le Bail fits and by comparing the observed peaks to the expected missing reflections for each point group in the bct family, it was possible to reduce the candidate structures to a list of 8 potential space groups, all of which are indistinguishable with only the use of Le Bail fits. These were the space groups 79, 82, 87, 97, 107, 119, 121 and 139.

To determine which of these structures was the most viable potential structure, these structures were compared to those calculated by Professor Chris Pickard, and Dr Miguel Matinez-Canles using Ab Initio Random Structure Searching (AIRSS) [101] calculations across a range of pressures. Of those results returned from the structure searches at 70 GPa only one of the candidate structures (space group 139, $I4/mmm$) was observed to be energetically favourable across the experimental pressure range, with simulations providing similar lattice parameters to those observed experimentally. Analysis of systematic absences within the collected diffraction patterns indicated an absence of glide and screw symmetry elements offers further agreement between the structure observed and the simulated structure at 80 GPa. As such, it was decided that $I4/mmm$ was an excellent candidate structure. Due to the high-quality powder data required to
attain meaningful Rietveld analysis, only diffraction patterns with good powder averaging such as those shown in fig. 3.5 in the novel phase were used and any image plates collected with poor powder averaging were fitted only using Le Bail profiling methods to attain cell volumes.

The unit cell volume of the indexed novel Ge structure, henceforth referred to as Ge-VIII, was compared to that of Ge-IV immediately before the transition onset to ascertain the potential $Z$ number of the structure. To establish accurate lattice parameters for this comparison, Le Bail fits of the diffraction patterns of the novel phase were conducted alongside inclusions of the contributions from the expected MgO and Ge-IV diffraction patterns. With lattice parameters of $a = 2.978(5)$ Å, $c = 2.732(3)$ Å for Ge-VIII at 76 GPa and 1757(130) K and Ge-IV having lattice parameters of $a = 4.577(4)$ Å, $b = 4.376(3)$ Å and $c = 2.473(15)$ Å at 76 GPa at approximately equivalent temperatures. This gives a volume of $48.44(4)$ Å$^3$ for the Ge-VIII unit cell compared to the volume per atom of $24.22(2)$ Å$^3$/atom for Ge-IV it is clear that a $Z$ value of 2 for the structure is required to bring the magnitude of the volume per atom to within a reasonable change throughout the transition. With a value of $Z = 2$ the volume per atom of Ge-VIII is approximately consistent with the volume of Ge-IV at these conditions of $24.76(3)$ Å$^3$/atom, indicating a potential displacive transition. To fulfill a value of $Z=2$ for the Ge-VIII structure, there are two possible atomic occupation sites for the Ge atoms, the 2a and 2b Wyckoff positions. With powder diffraction data, these two occupation sites are indistinguishable from one another as the 2b site is simply a translation of the 2a site position’s by a factor of $0.5c$ along the z axis of the unit cell. With this in mind, in the interest of simplicity the 2a Wyckoff site will be considered as the assumed unit cell for the remainder of this discussion. By comparing the collected diffraction profile to a simulated ideal powder pattern, as can be seen in fig. 3.7 there is a distinct similarity between the intensity profile of the collected data and the ideal powder with atoms occupying the 2a Wyckoff site (0,0,0).

Rietveld analysis of the highest quality diffraction patterns was conducted based on these results, which provided a good fit to the pattern intensity ratios, but due to the proximity of the MgO 202 peak to the Ge-VIII 200 peak combined with evidence of imperfect powder in the diffraction plate which likely contributes to the appearance of preferred orientation like discrepancies in intensity, this fit is not high enough quality to confirm the occupation of the 2a Wyckoff site conclusively. However, in the interest of completeness, the results of these Rietveld analyses are presented here. From these trials, with the Ge atoms resting on the origin
Figure 3.7  (Top) Le Bail refinement of Ge-VIII at 76 GPa and 1757(130) K with lattice parameters of $a = 2.978(5)$ Å, $c = 2.732(3)$ Å and a single atomic position for Ge resting on the origin. The wavelength used was 0.3344 Å with residuals shown as a continuous black line and the fit to the Ge-VIII phase shown as a continuous red line, and the experimentally observed diffraction pattern as black crosses. Experimental peaks observed from untransformed Ge-IV and MgO incorporated in the full pattern fit with Ge-IV having lattice parameters of $a = 4.577(4)$ Å, $b = 4.376(3)$ Å and $c = 2.4731(15)$ Å. (Bottom) In blue shows the expected peak intensities of the Ge-VIII structure with atomic occupations on the 2a Wyckoff site. As can be seen, whilst not a perfect match, there is visual similarity within the peak ratios.
Figure 3.8  
a) Rietveld refinement of Ge-VIII at 76 GPa and 1757(130) K with lattice parameters of \( a = 2.980(5) \text{ Å}, \ c = 2.718(13) \text{ Å} \) and a single atomic position for Ge resting on the origin. b) shows a Rietveld refinement of the HT phase Ge-VIII at 76 GPa and 2000(200) K in MgO with lattice parameters of \( a = 2.978(5) \text{ Å}, \ c = 2.731(3) \text{ Å} \). In a and b, the wavelength used was 0.3344 Å. 

Residuals are shown as a continuous black line, with the fit to the Ge-VIII phase shown as a continuous red line and experimentally observed diffraction pattern as black crosses. Experimental peaks observed from untransformed Ge-IV and MgO are not included in the Rietveld refinement. Untransformed Ge-IV and MgO are marked with red and blue asterisks, respectively. c) shows a Rietveld refinement of the HT phase Ge-VIII at 68 GPa and 1600(300) K in hydrogen with lattice parameters of \( a = 3.021(12) \text{ Å}, \ c = 2.849(19) \text{ Å} \). The wavelength used is 0.4066 Å. No evidence was seen of a reaction between the Ge and hydrogen under these conditions again, contributions from Ge-IV were not included in the fitted pattern. The peaks marked with the red asterisk correspond to those associated with ReH. In all of the figures, a March-Dollase model was used to account for preferred orientation on the (100) plane with the final fits having a \( wR_p \) of 3.21%, 0.66% and 0.63% and a \( wR_{obs} \) of 10.81%, 2.98% and 2.14% in figure a), b) and c) respectively.
in the 2a Wyckoff site, the structure provided the highest quality match to the collected diffraction data with a $R_p$ of 1.38% and $wR_{obs}$ of 10.59% at 76 GPa as can be seen in Figure 3.8a.

In order to better understand the stability regime of the novel high-temperature phase Ge-VIII a number of theoretical simulations were conducted by Dr Miguel Martinez-Canales. These calculations were carried out using density functional theory (DFT) with the Perdew-Burke-Ernezhof (PBE) functional and ultrasoft pseudopotentials as implemented in CASTEP. From these calculations, a comparison of the relative enthalpies can be made for the structures across a wide pressure range. The results of these calculations can be seen in fig. 3.10 and fig. 3.9. From these calculations we can see that Ge-VIII becomes energetically competitive, with an enthalpy difference of $<10$ meV when compared to room temperature structures at pressures above 72 GPa. Due to the limitations on the calculations caused by the second-order nature of the phase transitions throughout the Ge system, a P-T phase diagram using the quasiharmonic approximation was not carried out. Instead, a number of phonon calculations were carried out to assess the dynamics of the system. These were performed using QUANTUM-ESPRESSO using DFPT. Molecular dynamics calculations were also carried out on the Ge-IV structure to investigate its stability with the temperature at 80 GPa. Phonon dispersions calculated show that the Ge-VIII phase is competitive over the Ge-IV and Ge-V structures at high temperatures as can be seen in fig. 3.11. These ab initio molecular dynamics calculations were carried out using CASTEP 18.1 using the QC5 pseudopotential a 300 eV cut off, and a 2x2x2 k-point grid with a 0.3 eV smearing width. From these MD calculations, it is evident that Ge-IV should become unstable to melting at temperatures of around 1500K, consistent with the temperatures at which the onset of Ge-VIII can be observed experimentally, as can be seen in Figure 3.10. Symmetry analysis, initially conducted by Dr Jack Binns using the ISODISPLACED software [102, 103], indicates a direct displacive transition is possible between the high-temperature parent Ge-VIII and low-temperature daughter Ge-IV phases. This transformation occurs via a mode with $N_2$ symmetry involving antiparallel displacements of Ge atoms which is consistent with the theoretically calculated dynamics within Ge-IV. The trajectories of these MD calculations (shown in Figure 3.12) show that there is an antiparallel displacement within the Ge-IV structure occurring with increasing temperature. Full details of these calculations and the methods used can be found in the published article as found in appendix B.1 [1] and its supplementary material [104].
Figure 3.9 (top) Relative enthalpies of the room temperature phases of Ge and the novel high temperature phase from 40 GPa to 140 GPa relative to Ge-VI with the inset showing a zoomed view of the pressure range from 70 GPa to 80 GPa, the region over which much of the Ge-IV/VIII transition is experimentally observed.
Figure 3.10  Mean square displacement (MSD) (black line) and temperature (cyan dots) of the 80 GPa MD run of Ge-IV at 80 GPa. The continuous blue line represents the 200-step temperature running average. Clear fluctuations in the MSD appear 2 ps after increasing the temperature to 1500 K. The structure finally melts after switching to an NPT ensemble at 10 ps. The inset shows the atomic trajectory of NVT Ge-IV at 750 K (cyan) and 1500 K after the MSD fluctuations (magenta). Spheres depict the initial positions. Arrows are a guide to the eye, labelling some of the antiparallel displacement of planes resulting from the phase transition.

Figure 3.11  Phonon dispersions for various structures of Ge at 80 GPa: P6/mmm (left), Cmca (middle) and I4/mmm (right). The lower maximum and higher relative weight of the peak below 100 cm$^{-1}$ in I4/mmm indicate a competitive free energy at high temperatures.
Figure 3.12  Trajectories of Ge-IV at 80 GPa on the NVT ensemble. Purple spheres show the initial positions of the Ge atoms, and the green dots show the trajectories at 750 K. The silver dots show the trajectories after the MSD fluctuations are added. Arrows have been added to the figure showing the antiparallel displacement of the planes.
Figure 3.13  Diffraction patterns of Ge sample laser heated at 110 GPa with MgO pressure transmitting medium. From these diffraction patterns it can be observed that there is no evidence of Ge-VIII with increasing temperature up to temperatures of 2080(150) K. The unindexed peak at 8.5° is assumed to be from MgGeO₃.
This transition is observed experimentally in a number of heating runs at different pressures between 56 GPa and 85 GPa. Interestingly, however, this transition is only observed occurring from the \textit{Imma} phase of Ge, and under the conditions explored throughout these experiments, no evidence was seen for the existence of the Ge-VIII transition occurring from Ge-II or Ge-V upon heating. This, along with the evidence provided by the theoretical calculations, implies that there is a second-order transition between Ge-IV and Ge-VIII, with this being further compounded by the crystal group relations between the \textit{Imma} and \textit{I}$_4$/\textit{mmm} structures. The behaviour of the lattice parameters with temperature at 77 GPa has been included in fig. \ref{fig:A.2} for the interest of the reader but no clear conclusion on the dynamics of the transition have been drawn from this. Further heatings were conducted at pressures above 90 GPa in phases Ge-V and Ge-VI with no evidence of structural changes occurring up to 1700 K and 3200 K respectively (see Figure 3.13).

### 3.4.3 Extension to the High-Pressure Melt Line of Elemental Ge

When observing diffraction patterns, it is possible to see evidence of diffuse liquid scattering created by a reduction in long-range ordering as melting occurs which are often visible in the diffraction plates as ‘halo’. This ‘halo’ can, however be very difficult to observe if the molten material either has a low Z value and subsequently a low scattering intensity or when the melting is not complete due to the relative low intensity of liquid diffraction peaks compared to those of the Bragg peaks associated with powder diffraction with high-temperature gradients within them. In germanium samples, the latter of the two limitations provides the major contribution to the difficulties of determining the presence of melting within the DAC. Whilst melting may be occurring at the location of the peak measured temperature, due to the temperature profiles created by laser heating (see section 2.3.3), areas towards the edge of the heated region or deeper into the sample may not be fully molten. This means that whilst there may be a decrease in the intensity of the diffraction peaks associated with the solid phases, there is likely to be some residual crystal structure contributions within the diffraction patterns. Through the subtraction of a room temperature reference pattern from the sample, it is possible to minimise the intensity of the solid-state diffraction peaks within the sample environment \cite{97}. This allows the
Figure 3.14  Selected raw diffraction patterns of Ge in MgO pressure medium collected for 2s at (left) 44 GPa; (centre) 60 GPa; (right) 68 GPa. The insets correspond to the zoomed in regions of the diffraction patterns with the region of interest associated with the diffuse liquid scattering. Unexplained peaks correspond to reaction products between MgO and Ge, as a chemical reaction has been observed for some heating series when hot spots had been generated.
Figure 3.15  Diffraction patterns of germanium in MgO pressure transmitting medium while increasing temperature at: (left) 44 GPa; (middle) 60 GPa and (right) 68 GPa. Diffraction patterns shown have been background subtracted by the fitted room temperature Legendre background polynomial. Asterisks show peaks attributed to MgGeO₃ and the blue area shows the smoothed difference between the room temperature and high-temperature background. The bottom pattern shows the diffuse scattering from the melts obtained from subtracting the room temperature diffraction pattern to the high-temperature background.
Figure 3.16 2D images collected with the Pilatus CCD detector for 2 s of: a) Crystalline Ge-II at 44 GPa at room temperature (left); molten Ge and partially crystalline Ge-II at 44 GPa at 1600 K (right). b) Crystalline Ge-II at 60 GPa at room temperature (left); molten and partially crystalline Ge-IV at 68 GPa and temperatures of 2030 K (right) c) Crystalline Ge-II at 68 GPa at room temperature (left); molten and partially crystalline Ge-IV at 68 GPa and temperatures of 2750 K (right). The strong powder lines passing through the image plates correspond to the MgO pressure transmitting medium.
diffuse liquid peaks to be more easily observed as the difference between the low and high-temperature patterns manifesting as a broad peak in the background of the data set as the profile to attain a qualitative analysis of the presence of melting. A minor limitation of this technique, however, arises from the thermal shift of the diffraction patterns, which means that whilst the average intensity of the crystal peaks will be considerably lower with the onset of melting, a smaller negative and positive peak will form around the original peak position. If this occurs in the region of d-spacing at which the broad diffraction peak occurs, it can make the observation of the melting difficult. To overcome this, it is possible to directly subtract the differences between the background functions fitted to the diffraction patterns as the overall background of the system should be consistent if the sample environment has not been changed. This means that any changes within the background can be attributed to the onset of melting within the sample environment.

Throughout the experiments, potential evidence of melting was observed at three key pressures, 44 GPa, 60 GPa and 68 GPa. At these three pressures, a change in the background profile of the diffraction patterns compared to that seen at room temperature can be observed at high temperatures as shown in fig. 3.14. To establish whether the data had an additional broad peak present, the higher temperature data sets background subtracted using the background profile of the room temperature reference data set. In the event that a change in the ‘flatness’ of the data was observed, the difference between the two background profiles was calculated, as can be seen in fig. 3.15. The presence of these factors was taken as evidence of the onset of partial melting within the sample environment.

At 44(3) GPa the presence of an additional broad feature in the background profile of the collected data can be observed with the onset of this feature being visible at temperatures of 1600(120) K. Evidence of this feature is not observed in diffraction patterns below 1500(150) K, and as such, this can be used to offer a lower bound on the potential melting temperature at 44 GPa of 1550(100) K. This is consistent with the extrapolated temperatures of the Ge-II melt line provided by Prakapenka et al. This evidence of melting is also visible in the diffraction patterns at temperatures above 1900 K at 60(3) GPa and at temperatures above 2700 K at 68(3) GPa with no evidence of melting visible below these temperatures. These temperatures indicate an increase in the steepness of the melting temperatures from across the Ge-II/liquid.
3.4.4 Updating the Phase Diagram of Elemental Ge

With the previously mentioned observations in mind, it is possible to offer forth extensions to the P-T phase diagram of germanium to pressures of 110 GPa as can be seen in fig. 3.17 with the uncertainties shown in fig. A.1. Key additions to the phase diagram are the Ge-II/IV/liquid triple point, the Ge-II/IV phase boundary, the Ge-IV/VIII phase boundary and a possible extension to the Ge melt line up to 70 GPa. By extrapolation of the Ge-II line to meet the Ge-II/IV transition boundary determined from our experimental data sets as previously mentioned, it is possible to generate the position of the Ge-II/IV/liquid triple point to be at 53(3) GPa and 1650(100) K. Using the presence of Ge-VIII in heating runs as an indication of the lower bounds for the Ge-IV/VIII it is possible to add the Ge-IV/VIII phase boundary. Due to the lack of evidence of Ge-VIII or melting in samples at 61(3) GPa and 1900(100) K, it can be assumed that the Ge-IV/VIII phase boundary must decrease in temperature with increasing pressure. When attempting to continue the melt boundary, there appears to be an increase in the slope of the melt line required to fit these observations giving a Ge-IV/VIII/liquid triple point of 61(3) GPa and 1980(50) K. With evidence of solid Ge-VIII visible and no evidence of melting observed in samples at pressures of 70(3) GPa and temperatures of 2350(120) K, a sharp increase in the melt curve must be present beyond the Ge-IV/VIII/liquid triple point. The lack of observation of Ge-IV at low temperatures above 90 GPa is indicative that the Ge-IV/V is likely to be near vertical in this region; however, to accurately constrain the Ge-IV/V and Ge-V/VIII phase boundaries, further experimentation would need to be conducted.

As is shown in the revised phase diagram, there is a sharp increase in the melt as a function of pressure. This behaviour has also been observed in Sn [105], which rises steeply as a function of pressure with a decrease in slope. Within the experiments, we see no evidence of a decrease in slope to at least 80 GPa due to the presence of crystalline material. Whilst melting was not observed at 110 GPa evidence of crystalline material is observed up to 3200 K.

Due to the distinct similarities between Ge and Si mentioned earlier in this chapter, it is possible that these extensions to the high-temperature phases diagram of Ge will have implications for the P-T phase diagram of silicon. If the high-temperature phase Ge-VII has a structurally equivalent phase that can be observed in Si, the P-T range over which it may be observed will be
Figure 3.17 Proposed extensions to the Ge P-T phase diagram, phase boundaries added in collaboration with Dr Ross Howie. For clarity, due to the density of the points, the error bars have been omitted from the figure. The full figure with error bars can be found in fig. A.1. Filled data points represent the data previously collected and presented in the work of Prakapenka et al.[97], unfilled data points are those presented in this chapter.
considerably more narrow and may explain why previous experiments into the melting behaviour of Si have not observed this transition. If this is the case, there may be large implications for the understanding of the behaviour of Si in the earth’s interior as the pressure and temperature range in which this transition may occur are similar to those observed in the upper mantle.

3.5 Conclusions

In conclusion, a novel phase of Ge, Ge-VIII, has been identified and characterised. Ge-VIII can be observed to be between 56 GPa and 88 GPa at temperatures exceeding 1500 K with no metastability upon quench to room temperature. Through structural indexing and Rietveld structure analysis, Ge-VIII was confirmed to exist in a $I4/mmm$ structure with atoms occupying the 2a Wyckoff site. DFT calculations show that this structure is energetically competitive at high temperatures across the experimentally observed region of the transition. Molecular dynamics simulations were also conducted on the Ge-IV phase, which showed an instability to melt at 1500K, the approximate temperature of the transition onset, and showed evidence of an antiparallel displacement of lattice planes within Ge-IV with increasing temperature. This antiparallel displacement is consistent with that expected for the required change in symmetry for the second-order transition between Ge-IV and Ge-VIII.
Chapter 4

Mixed group-XIV and Hydrogen Systems

4.1 Literature Overview and Motivation

One of the most pressing issues is the demand for sustainable and environmentally friendly energy sources, with the use of hydrogen fuel cells being of great interest in the industrial sector [106]. There are current functional designs for hydrogen fuel cells; however, a significant issue within the development process is the safe storage of hydrogen in large enough quantities for useful operation [107]. Due to the reactivity and high risk of explosions associated with the storage and transport of pure liquid and gaseous hydrogen and the difficulty associated with handling the massive quantities needed for such an application, a large amount of research is being undertaken into potential solid hydrogen storage materials. One group of materials of interest in this area is the metal hydrides, which are readily observed as having complex structures and often readily allow the diffusion of hydrogen within the crystal lattice, with several materials having been put forward as candidates as is proposed which are summarised by Abe et al. [106]. At current, some of the more favourable candidates include Li [108], Mg [6], Ti [109] amongst a plethora of metal alloys (summarised in [106, 110]), however at current these materials are observed to not readily re-release hydrogen under industrially viable conditions. Due to the hydrogen density of metal hydrides, it is postulated that these materials may be able to be used as a method of studying pure hydrogen at high pressures [10, 111] through the use of chemical precompression. It is also
predicted that a large number of these metal hydrides will be superconducting at high pressure with $T_c$ much higher than most conventional superconductors [9, 10, 112].

One such hydrogen-rich material which exhibits interesting properties with hydrogenation is sulfur. Hydrogen sulfide ($\text{H}_2\text{S}$) has been widely studied up to pressures of 250 GPa; however, it remains quite controversial in its proposed properties. When considering the analogous structure of water at the molecular level, it could be assumed that the properties would be similar on bulk; however, this is very much not the case. Under ambient pressure, hydrogen sulfide has been shown to crystallise into three different molecular solids dependent upon the temperature, referred to as phases I-III [113, 114]. Upon pressurisation, three other phases are seen with pressures below 100 GPa; these are phases IV, V and VI. Phase IV is a polymeric structure occurring at pressures of around 14.6 GPa with a spiral-like structure of the sulfur atoms passing down the c plane and H-S hydrogen bonding occurring between adjacent spirals. This phase is non-conducting and, due to the inter-chain S-S bonding, has a visible yellow hue [115]. Phase V occurs at 36 GPa and is another non-conducting phase of hydrogen sulfide, with an observed black colour [116]. The predicted structure of this phase is similar to that predicted for phase IV; however, the length of the H-S bond length in the material is predicted to be much more inconsistent, creating localised $\text{H}_3\text{S}^+$ and $\text{HS}^-$ species exist dynamically in simulations [117]. Phase V, observed to occur at pressures above 46 GPa [118] is the point at which there is molecular dissociation within the solid structure, transforming the material into an ionic solid. Simulations have, however, shown this not to be the case as the decomposition of $\text{H}_2\text{S}$ into $\text{H}_2$ and $\text{S}$ is not thermodynamically likely [119].

At 96 GPa it is observed that there is a sudden change in the reflectivity of the hydrogen sulfide, indicating a transition into a metallic state [118]. This metallic state is of great surprise as this is very different to the behaviour of its structural congener $\text{H}_2\text{O}$ under high pressure, which is predicted to decompose in the terapascal pressure region before metallisation occurs [120]. Beyond this metallisation pressure, simulations show the onset of superconducting properties, which according to the works of Li et al. [119] have a $T_c$ which linearly increases with pressure. These simulated phases are thought to have a $T_c$ of 80K at 160 GPa however this disagrees with observed superconducting phases with $T_c$ of 200K at 150 GPa [121].

It was proposed through the mixing of $\text{H}_2\text{S}$ with molecular $\text{H}_2$ a new compound
H$_3$S will form with at around 3.5 GPa \cite{122}. This mixture has been simulated to pressures of 150 GPa, with these simulations indicating the material should have a $Cccm$ structure \cite{123}. However, this phase is expected to be more challenging to form, which may be the reason for the P-T path dependence of several experiments \cite{121}. Through comparisons of simulations, it was proposed that below 120 GPa the main product of the different pathways is this $Cccm$ phase. However, at higher pressures, there is a phase change into R3m or $Im\bar{3}m$ H$_3$S, which may be the superconducting structures with a $T_c$ of 200K at 150 GPa \cite{124}. This transition is, however, observed to be slow at low temperatures \cite{123}. A more recent study by Loubeyre et al. \cite{125} shows that if created as a pure H$_3$S sample, the $Cccm$ phase is stable up to pressures of from 100–160 GPa, which is in substantial agreement with the work of Duan et al. \cite{124} and Goncharov et al. \cite{123} and the predicted phase change to a metallic bcc structure, as predicted by DFT \cite{117}, has yet to be observed. Further studies by Pace et al. \cite{32} confirm the presence of the structures previously observed in (H$_2$S)$_2$H$_2$ samples. Additionally, through the use of Raman spectroscopy, a region with distinct lattice modes is observed, coined phase II’. Observation of the transition from phase III to the non-molecular H$_3$S was also observed with a transition pressure of 127 GPa at 80 K. However, due to the difficulties in observing hydrogen locations using XRD techniques, it is unknown if this structure matches that of the simulated superconducting structure.

Similarly, a group of molecules that are of interest within the metal hydrides are the group-XIV hydrides. This is particularly true for the congeners of methane such as silane (SiH$_4$), stannane (SnH$_4$), germane (GeH$_4$) and plumbane (PbH$_4$) due to the wide variety of potential to stabilise composite materials. They also often have uses in the semiconductor industry within epitaxial growth methods due to the thermal decomposition of the materials forming part of the layer forming reactions. The group-XIV hydrides have been simulated in a variety of pressure conditions, with these studies offering predictions of potentially metallic and superconducting phases at much lower pressures than that required to obtain metallic hydrogen \cite{10}. These simulations predict the formation of an alloy of the group-XIV metals and hydrogen to form environments analogous to those expected of metallic hydrogen, allowing the study of metallic hydrogen at much lower pressures than is predicted for elemental hydrogen through the means of chemical precompression \cite{10}.

One of these, silane, has been widely studied \cite{126,131} and evidence has been
presented to suggest the material to be a metallic superconductor at <17K and pressures of over 167 GPa. An experimentally obtained potentially metallic phase, which can be seen in Raman spectra occurring at 113 GPa, has been shown through x-ray diffraction to have a P6₃ structure [126] which is likely to relax into a stable Pcbm structure at 220 GPa [130]. However, these findings should be viewed critically as further studies provide evidence that this metallic structure may, in fact, be that of PtH created by a reaction between hydrogen and the electrode material [131] which may also be responsible for the observed superconductivity at this pressure. The occurrence of this reaction is particularly likely as the works of Strobel et al. report no evidence of the hexagonal metallic state of SiH₄ below 150 GPa [132] and attribute the metallic behaviour below 60 GPa to the presence of decompressed elemental silicon in the BC8 and R8 structures as summarised in table 3.1. These findings by Strobel et al. are consistent with the work of Hanfland et al. [131] which shows evidence of the decomposition of silane at pressures between around 60 GPa and 96 GPa.

At around 90 GPa it is widely reported that there is a darkening in the silane [126, 131, 132] attributed to the decomposition into atomic form before recombining into an I₄₁/a polymeric structure consistent with the structure formed through the pressurisation of hydrogen and silicon in this pressure region [126, 131]. It has been predicted that it is the most favourable phase up to 196 GPa which may transition into a superconducting phase above 300 GPa. This superconducting phase is predicted to have a T_c of 32K based on molecular simulations at higher pressures; however, it is predicted that this critical temperature will reach 107K at 600 GPa when the material enters a C2/m structure [133].

Much like silane, the other group-XIV methane congeners are predicted to undergo elemental decomposition under pressure. This reformation is predicted to occur at similar pressures to those seen in silane, with these pressures being up to 96 GPa for stannane [134], 136 GPa for plumbane [135] and 190 GPa for germane [136]. Similar structural evolutions are then expected to occur within the group, with several superconducting phases being predicted at high pressures with predicted T_c's of around 100K within experimentally obtainable pressures [137]. However, at the time of writing, little experimental work has been published to verify these predictions.

Interestingly, several of the group-XIV hydrides are predicted to be more stable in XH₂(H₂)₂ derived structures at high pressure which have been observed to occur in silane-hydrogen systems [127, 138] and germane-hydrogen systems [139].
These phases, based on simulations, appear to have higher $T_c$ superconducting phase than in the conventional methane congeners. This is consistent with the behaviour observed in H$_2$S, which, as previously discussed, with the addition of H$_2$ molecules becoming H$_3$S like in its molecular ratios, drastically increases its superconducting $T_c$ due to the composition change from H$_2$S 80K for to 200K for H$_3$S at 150 GPa [121, 132].

Plumbane is a complicated member of the group-XIV methane congeners to study due to its instability and rapid reaction at ambient conditions. These complications mean that thus far, predominantly theoretical studies have been undertaken into it, but these studies have yielded some exciting results [135]. The simulations by Zaleski et al. predict the existence of two high-pressure phases with interesting structures. The first, phase VII, consists of a distorted 3D hexagonal lattice of lead molecules in which 1D-like channels of (H$_2$)$_2$ quartets occurring at pressures of 250 GPa. The second phase, phase VIII, comprises of alternating intercalated layers of lead and hydrogen atoms, with the hydrogen layers having a graphite-like structure. These single layers may allow the material to glide freely, creating a liquid-like phase at pressures of around 400 GPa; whilst, the lack of apparent energy bandgap under density of state analysis implies that it is likely to be a nearly free electron metal at this pressure [135].

4.2 Attempted Fabrication of Hydrides of Germanium

Early experiments, the results of which are outlined in more detail in chapter 3 were conducted in an attempt to form hydrides of germanium, namely germane, from elemental germanium and hydrogen as was summarised as potentially possible in the work of Zhang et al. [136]. Previous experiments had been carried out by the group of Strobel et al. [139] loading germane (GeH$_4$) in an excess of hydrogen to synthesise higher hydrides of germanium at pressures much lower than the 136 GPa outlined in the paper of Zhang et al. [136]. However, experiments carried out in the works of this thesis were not able to replicate these findings from the elemental components at any pressure, with pressures trialled exceeding 110 GPa. Low-pressure experiments at around 30 GPa showed evidence of splitting in the hydrogen $v_1$ vibrational mode (referred to from this point as the hydrogen vibron) at around 4200 cm$^{-1}$ however, XRD studies show
no change in the crystal structure of germanium when these changes are present, so it is unlikely to be the formation of a hydride of germanium. Serendipitously, however, during the process of conducting these experiments, observations of structural changes within the system were observed at pressures around 70 GPa and at temperatures exceeding 1500 K which did not quench to room temperature. Initially, it was considered that these structural changes could be associated with the formation of hydrides within the sample environment, but further experimentation with different pressure transmitting mediums confirmed that this was, in fact, the formation of a novel phase of germanium Ge-VIII. The full findings of these studies are explained in detail in chapter 3.

4.3 Attempted Fabrication of Hydrides of Lead

As discussed earlier in this chapter, hydrogen-rich materials are of great interest in the field of extreme condition science. It is postulated that due to the effect of ‘chemical pre-compression’, many hydrogen-rich materials are expected to undergo transformations into metallic, superconducting phases at pressures much lower than those expected of pure elemental hydrogen [10]. A number of simulations of hydrogen-rich materials have yielded yet further predictions of such materials having high $T_c$ superconducting behaviours, several of which have been confirmed experimentally. More recently, high-hydride phases of lanthanum were shown experimentally to be superconducting of 215 K at 150 GPa [33] and 260 K at 188 GPa [9]. In Ashcroft’s [10] suggestion of superconductivity in hydrogen-rich alloys, a significant focus was put on the group-XIV hydrides as examples of suitable candidates. Since then, many studies have been carried out on the group-XIV hydrides offering numerous predictions agreeing with Ashcroft’s suggestions of the suitability of these materials as good candidates to exhibit these properties.

Within the group-XIV hydrogen compounds, a number of experiments have been undertaken. One such experiment was with germane (GeH$_4$), has been the subject of limited low-pressure Raman studies in hydrogen-rich environments up to 40 GPa by Strobel et al. [139]. In this study, it was found that at around 27 GPa the GeH$_4$+H$_2$ underwent decomposition into elemental germanium and hydrogen. These findings are consistent with the behaviour seen in silane, which also undergoes similar behaviour at 65 GPa [131] and then reforms at 90 GPa into a polymeric silicon hydride. This reformation is predicted to occur in the other group-XIV hydrides at pressures of 96 GPa, 132 GPa and 196 GPa for Sn-H$_2$.
Pb-H$_2$ [134] and Ge-H$_2$ [136] systems respectively, well within the limits of DACs.

Of the group-XIV hydrides, plumbane remains one of the most difficult to synthesise with the methods used to synthesise GeH$_4$ and SnH$_4$ failing (as summarised by Zaleski et al. [135], original german manuscripts [141-144]). Some experimental techniques have been capable of synthesising plumbane; however, it was found to be very unstable with samples decomposing after 10s [145]. The rest of this chapter will focus on attempts by the author to synthesise hydrides of Pb at high pressure using DAC techniques.

4.3.1 Experimental Details

Due to the instability of PbH$_4$, it was impossible to load a precursor to synthesise high hydrides. As such, high purity Pb (99% -200 mesh) was loaded into diamond anvil cells (DACs) with a pressure calibrant appropriate to the style of experiment (Ruby for most samples, with Au balls being used in some XRD collections). All of these samples were subsequently gas loaded with research-grade (99.9999%) H$_2$ to 0.2 GPa. Rhenium gaskets were used in all experiments for the sample chamber, except for one sample in which a W gasket was used to eliminate the presence of RhH from the sample environment. The initial sample size for the experiments ranged from 60-200 $\mu$m. Diamonds with culet sizes between 50 $\mu$m and 300 $\mu$m were used for the majority of experiments, with smaller diamonds being used for the higher pressure XRD collections. A single set of 400 $\mu$m diameter culet diamonds was used for a very low-pressure heating experiment with Raman in which pressures did not exceed 15 GPa.

Initial Raman experiments were carried out on a custom-built micro-focused Raman system with an argon ion excitation source emitting at 514.5 nm with the pressure being determined using a ruby pressure calibrant [24]. These samples were increased in pressure up to around 25 GPa to check the suitability of the samples for high-pressure laser heating and to ensure that no bridging was present within the sample chamber. Samples were then laser-heated before pressure was increased above 50 GPa and laser-heated again.

Further x-ray diffraction experiments were carried out on ID15b at the European Synchrotron Radiation Facility. The samples for this experiment were prepared with a 500 nm layer of alumina on either side of the sample to protect the diamond
during laser-heating. This sample was then increased in pressure to around 87 GPa before laser-heating the sample to temperatures above 1200 K with one sample then being increased stepwise in pressure to 135 GPa and another being decreasing the pressure to verify the region of formation of the observed changes in diffraction pattern. The samples were then decreased in pressure stepwise until diamond failure.

4.4 Results

After laser-heating at pressures of 88 GPa, a visible change in the diffraction pattern was observed in XRD collection at the synchrotron source. Upon decompression, to 54 GPa this change was observed to be stable with no decomposition of the novel peaks. Post experiment analysis of the structural data indicated that a $P1$ structure indexed to the array of peaks. A $P1$ structure is presented in the theoretical studies by Cheng et al.\textsuperscript{[140]}; however, after attempting a Le Bail fit of the indexed structure, this structure is found not to match with the experimental data. These factors heavily implied that the resultant products after laser heating were a mixture of multiple phases or distinct materials. It was, however, notable that at this point, these structures could not be resolved without further experimentation as the change in scattering angle was not sufficient to resolve the different structures across the pressure range observed.

Raman spectra were collected from the laser-heated sample areas, and several new Raman active bands were seen that were not present in the elemental mixture before heating. The first of these bands appear at around 50 cm\(^{-1}\) (as seen in Figure 4.1), which is may be attributable to small quantities of PbO within the sample environment \textsuperscript{[146]} or an unidentified lattice vibration. Due to the larger region of the spectra cut by the notch filter at the ESRF facility, this band was only observed in the follow-up Raman experiments. The band was, however, observed after laser heating in multiple different samples.

Another new band was visible in the Raman spectra after laser heating in both the synchrotron and in-house Raman experiment appearing as a visible splitting in the hydrogen vibron. This splitting is particularly notable in figure 4.2 (right), which was collected from the main laser-heated area in the in-house Raman experiment. A distinct splitting is visible in the hydrogen vibron in these
Figure 4.1 Low frequency Raman shifts with increasing pressure after laser heating. Due to a drop in intensity with pressure the spectra shown the collected spectra at 42 GPa and 50 GPa have been increased in scale by a factor of 3. The peak at around 50 cm\(^{-1}\) may be attributable to thin layers of PbO on the sample material [146].
Figure 4.2 (right) Raman shift of the hydrogen vibron and the mid-frequency modes in position 1 with increasing pressure after laser heating. The splitting in the hydrogen vibron is also seen in position 2 of the sample at a much lower intensity. The mid-frequency (left) region appears to comprise of contributions from a number of modes in two main bands separated by around 100 cm\(^{-1}\).
spectra, which grows with increasing pressure. This up-shifted hydrogen vibron is indicative of a new, higher energy, H$_2$ environment; likely caused by some interstitial hydrogen molecules trapped in a higher energy environment similar to that seen in NaH$_7$ \cite{147} or a higher energy covalent bond. This splitting is also visible in the sample region from the in-house heating experiment further from the centre of the main heated area; however, the intensity of this splitting appears to grow in with pressure indicating the possibility of another phase forming and breaking down into this structure. This is further implied by the appearance of another peak which has a rapid increase in Raman shift with pressure visible only in the second position (Figure 4.4).

Additional Raman bands were seen between 3000 cm$^{-1}$ and 3500 cm$^{-1}$ with the intensity of these bands being around ten times lower than the splitting seen in the hydrogen vibron. These peaks were seen in both regions of the sample, but the intensity at position 2 was a factor of two lower. In addition to this, the peak positions at positions 1 (figure 4.2) and 2 (figure 4.4) appear to vary by around 50 cm$^{-1}$. These bands were fitted to a collection of Lorentzian curves, and the position of the peaks was plotted as a function of pressure (Figure 4.5). The lower intensity at position 2 may explain the reduced number of peaks as the shape of the additional peaks cannot be distinguished from the contributions of the background to the overall peak shape. These peaks seem to separate into two main bands, which are visible at both measured positions, separated by approximately 100 cm$^{-1}$, a phenomenon which is also seen in NaH$_7$ \cite{147} which is typical of a H$_3^-$ environment.

The frequencies of all of the peaks from the in-house heating experiment were plotted as a function of pressure to allow comparisons with the peak positions of the Raman data collected at ESRF. As can be seen in Figure 4.5 the Raman peak positions overlap with those seen in the in-house heating experiment at around 50 GPa and above these pressures, the peaks appear to follow the curve beyond these pressures. This overlap implies that the product is most likely the same as that seen in the low-pressure Raman experiments and that the material formed at around 20 GPa is stable up to around 90 GPa. This is in contrast to the predictions of Cheng et al.\cite{140} which state that under these conditions, decomposition into elemental Pb and H$_2$ should be energetically favourable.

Further diffraction data were collected at PETRA III at DESY with laser heating of Pb in H$_2$ being carried out at 54 GPa at which time the same splitting in the hydrogen vibron and the appearance of the same structural peaks as the
Figure 4.3  Raman shift of the mid frequency modes and hydrogen vibron in the laser heated region of the sample upon decompression at ESRF. The low signal to noise ratio makes it difficult to determine accurately the presence of the Raman mode at around $3300 \text{ cm}^{-1}$ but an indication of its presence can be seen.
Figure 4.4  Raman shift of the mid-frequency modes and hydrogen vibron in the laser-heated region (position 2) of the sample collected upon compression. An additional frequency band is visible in this sample region when comparing to position 1 fig. 4.3 at a higher frequency than that of the hydrogen vibron seen at position 1. The fitted frequency shifts agree with those seen in position 1 for both the hydrogen vibron and the observed splitting at the same pressure. The peaks seen around 4550 cm$^{-1}$ at 25 GPa can be attributed to ruby fluorescence visible in the sample.
Figure 4.5  Raman shift as a function of the pressure of the vibrational modes of the laser-heated regions of the sample around the 3000 – 3500 cm$^{-1}$ region (left) and around the hydrogen vibron (right). The data presented by grey triangles correspond to the Raman signal seen on in-house spectroscopy facilities at ESRF. All other data shown was collected in a high-resolution Raman system. The two positions refer to two regions with a distinct Raman fingerprint. The expected Raman signal of bulk hydrogen is shown by the dashed yellow line.
Figure 4.6 Diffraction patterns with increasing pressure of Pb in excess hydrogen. Peaks marked with a black asterisk are attributed to diffraction from outside of the sample chamber. In this sample heatings were conducted at 86 GPa and 120 GPa with the data collected at 120 GPa and 135 GPa being collected 24 hours after the preceding data sets. No notable changes within the XRD patterns were observed beyond the expected appearance of Pb(bcc) at around 104 GPa.
ESRF experiment was observed. This sample was then increased in pressure up to 135 GPa with no indication of the breakdown of the structure. However, with increasing pressure, the structure no longer resolved to match the same P1 structure indexed in the ESRF data, with the apparent appearance of two distinct structures being visible. Re-indexing the diffraction patterns, comparing the diffraction patterns to known structures of compounds likely to be in the sample environment, including W and Re compounds from the loading process and gasket material. Further analysis using Le Bail fitting indicated the presence of Re and ReH across the sample, including the central laser-heated areas alongside the presence of unreacted Pb as well as the onset of bcc Pb at 111 GPa as can be seen in fig. [L6] To confirm these results, a further experimental run on a new sample was conducted using W as a gasket material. In this cell, no notable changes to the diffraction patterns were observed after laser heating at a range of pressures up to 80 GPa. The lack of changes confirms that the changes in the diffraction patterns observed in previous experiments were likely due to reactions of the gasket material, with these products being found across the sample chamber. This indicates that either the samples were contaminated during the loading process or that some of the gasket material was relocated towards the centre of the cell during the process of laser heating. It seems likely that this is the case as, during low-pressure heating, there was a visible ‘jumping’ of the Pb powder around the sample chamber when observing the cell, which could easily have brought gasket material into the centre of the sample environment. The lack of structural changes observed within the sample environment with laser heating is consistent with the findings of Guigue and Loubeyre [148] in which they also observe no evidence of hydrogenation or structural transformation in Pb in H₂ rich sample chambers.

Studies conducted (but as of yet unpublished) by my colleague Dr Miraim Peña Alvarez also offer clarity on the origin of the developed Raman signals within the sample after laser heating occurred. In several experiments in which Au is used as a pressure marker in the presence of hydrogen, the development of Raman signals observed within the sample chamber is not dissimilar to those observed within these experiments. With these samples containing different materials but with the same Raman profiles with indistinguishable features, including a splitting in the hydrogen vibron and the appearance of a Raman band around 3200 cm⁻¹, it seemed likely that there was a reaction occurring between components which were present across all of those samples. Potential candidates across the sample in which the reaction was observed were C from the anvils, Re from the gasket,
Figure 4.7 XRD patterns of Pb in H₂ on decompression from 87 GPa to the point of diamond failure at 54.4 GPa. Tic marks show the indexed location of peaks attributable to the hcp-Pb phase. No notable structural changes were observed within Pb on decompression which is consistent with all other experimental data sets collected in this study. Unindexed peaks are assumed to be from the delaminated cell coating of Al₂O₃ as these peaks were not seen when in the absence of the coating when laser heating at similar pressures (see fig. 4.6).
and H₂ with the potential of W being present from contaminants during the loading process. Au and Ruby (Al₂O₃:Cr) were also present in many of the samples, with some of the samples in different combinations. Comparisons to the behaviour of the high-pressure Raman spectra of combinations of these materials showed a similarity to the high-pressure Raman of CH₄ as is described in the work of Proctor et al. indicating a high likelihood of the presence of methane within the sample environment. The presence of the splitting in the H₂ vibron offers evidence that there may be higher hydrated compounds of methane such as CH₄H₂ or (CH₄)₂H₂ as is outlined in the work of Somayazulu et al. Further investigations would, however, need to be conducted to determine if this is the case.

4.5 Conclusions

After laser heating Pb in H₂ at a variety of pressures, up to 120 GPa, no evidence of the formation of novel compounds was observed, and all structural observations observed within the sample chamber can be attributed to the formation of reactions between H₂ and the gasket materials as is in agreement with the predictions of Zaleski-Ejgierd et al. Interestingly, the likely formation of methane and its related hydrogenated compounds were observed within the sample chamber. This heavily indicates that there is a high probability of reactions occurring within the sample chamber between the H₂ and the anvil surface as these are the most likely source of the C and H required for this reaction to occur. Given that this was also observed in samples in a colleagues experiments, it should be considered that when conducting laser heating experiments within DACs using H₂ as a pressure medium or sample, there is a distinct risk of reaction with the anvil surface, which may create Raman features similar to those expected of other hydrides.

Whilst no changes were observed within the Pb and Ge hydrogen systems to indicate the formation of a hydride of either material, it is interesting to note that in the studies of silicon hydrogen systems by Hanfland et al. reaction occurred only after an extended period of around 1 year at room temperature. Based on the similarities of behaviour between Si and Ge is possible that by leaving samples of Pb and Ge in hydrogen at sufficient temperature that similar kinetically slow reaction will occur. Some cells containing Ge and H₂ were left loaded between beam-times but no changes were observed at 100 GPa after 1 year. It is possible
that this was below the need pressure to achieve a reaction at room temperature and that at pressure exceeding those predicted in the theoretical studies [133–135], with extended time, stable hydrides of other group-XIV elements may stably form.
Chapter 5

Investigations Into the Cobalt-Hydrogen System

5.1 Previous Studies Into Cobalt-Hydrogen Mixtures

The presence of hydrogen within crystalline material can create profound changes in the material properties. These changes can range from macroscopic structural failures caused by hydrogen embrittlement all the way down to fundamental changes in the electrical properties of the materials. This is particularly the case with metallic structures with sufficiently high densities of hydrogen, many of which are thought to be good candidates for high-temperature superconducting behaviour [10]. Experimentally this postulation has been shown to be reasonable with the experimental observation of high-temperature superconductivity in hydrides of the rare earth metal lanthanum [9, 151]. In these experimental studies, evidence of superconducting behaviour was shown at temperatures exceeding 250 K, at current the highest accepted temperature of observed superconducting behaviour.

Previous computation studies similar to those which predicted rare-earth superconducting candidates have focused on the potential superconducting behaviour of the transition metal hydrides [7, 152, 153]. As a result of the readily accessible outer s² electrons, many transition metals are observed to readily give up electrons to stabilise the H⁻ anion over H₂ molecules encouraging the formation of hydrides
at very modest pressures. This property of transition metals leads to their prevalence as a catalyst across many different chemical applications. As an intermediate step in many of these catalytic processes, typically involving organic materials, most transition metals form monohydrides at very modest pressures, a number of which have been the subject of structural studies at high pressures [154, 155]. Whilst many low hydrogen content transition metal hydrides are not expected to have exhibit superconductivity at temperatures exceeding those of their elemental metal, with higher hydrogen content many are expected to exhibit some superconducting behaviours [156, and references therein]. It is not the case however that no low hydrogen content hydrides are expected to exhibit superconducting behaviours with higher $T_c$ than their elemental constituents. For example, Pt is known to form two distinct hexagonal close packed (hcp) monohydride compounds at a moderate pressure of 27 GPa, PtH-I and PtH-II, which can be observed to coexist at pressures up to 42 GPa beyond which point only PtH-II is observable [7]. Surprisingly simulations of the electrical properties of PtH-II showed an increase in the $T_c$ to 12 K at 90 GPa, however, when anharmonicity is included within the calculations this $T_c$ drops below 1 K [7, 152, 157]. Recent experiments have shown that this superconducting behaviour occurs at temperatures of 7 K [158] at 30 GPa with a decrease in critical temperature occurring with increasing pressure. Whilst this is a lower $T_c$ than that which was predicted, it is still many orders of magnitude larger than the $T_c$ of Pt and, along with Pd is one of only two experimentally observed increases in $T_c$ of a monohydride over the elemental transition metal [109, 155, 159, 165]. These findings, however, have had a stark impact on the studies of high-pressure hydride systems as this discovery drew into question the suitability of Pt as an electrode material and pressure marker in hydrogen-rich systems and may be responsible for superconducting behaviour observed in some hydride systems such as that reported in silane (SiH$_4$) [126, 132] especially as the superconducting properties of many transition metal hydrides including Pt have not yet been explored in pressure regimes approaching 100 GPa. There is, however, no conclusive evidence yet to allow a complete conclusion to be drawn on this matter.

Beyond the formation of transition metal monohydrides at moderate pressures, many transition metals are observed to readily form higher polyhydrides in an excess of hydrogen. For example, Fe is observed to exhibit a number of polyhydride species with experimental evidence thus far having been observed for the existence of stoichiometries up to FeH$_5$ at 120 GPa, and a synthesis temperature above 1500 K with this structure exhibiting layers of hydrogen within
the Fe lattice \[166\]. This observed intercalated layer structure is similar to that described by Ashcroft \[10\] and may potentially mean that these materials behave like an analogue to atomic hydrogen with the hydrogen atoms stabilised through the ‘chemical precompression’ effect of the Fe atoms. Several theoretical studies have been carried out into the electrical properties of the Fe polyhydrides. However, there does not seem to be a consensus on the superconducting potential of the FeH\(_5\) structure. These studies present predictions of a \(T_c\) of between 46 and 51 K being calculated by two different studies \[167\] \[168\], however another study concluded that there would be no superconductivity within the structure \[169\]. Interestingly, however, this study did suggest that with very few additional \(d\) electrons it is possible to bring these structures into a regime that supports superconductivity for hydrogen densities greater than three atoms per formula unit. Whilst this is not possible through the direct modification of Fe, this could be achieved by using transition metals with additional \(d\)-block electron shell occupations. This means that Co, Ni and Cu are good potential candidates to fit in this regime.

## 5.2 Methods

DACs were prepared as described in chapter \[2.1.3\] with diamonds of culet size 100 \(\mu\)m and loaded with high purity cobalt powder (99.8\%, 1.6 \(\mu\)m particle size) from Alfa Aesar and gold or tungsten added to act as a pressure marker before being further loaded with research-grade hydrogen gas (99.9999\%, BOC) at 0.2 GPa. Successful loading of hydrogen was confirmed through the observation of the hydrogen vibron using Raman spectroscopy, and the overall samples were checked for oxidation of Co, both using the same custom-built micro-focused Raman system. For these samples, Re gaskets were used with an indented thickness of 9–18 \(\mu\)m to form the sample chamber. A final sample size of approximately 30 \(\mu\)m was created after sample compression when hydrogen was in the solid-state with samples being increased in pressure to 30 GPa and left for 7-14 days to allow the hydrogenation of Co to occur before diffraction experiments were conducted.
5.3 Results

5.3.1 Observations of the Previously Observed CoH and CoH$_2$ Structures and the Previously Predicted CoH$_3$ Structure

As was previously observed by M. Wang et al. \cite{12} at 4 GPa Co undergoes hydrogenation at room temperature to form CoH. As the samples in this experiment were precompressed to pressures beyond this transition pressure, this reaction was not observed directly, but through observation of the sample environment via x-ray diffraction (XRD) at 30 GPa the presence of the $Fm\bar{3}m$ CoH was observed with no evidence of unreacted Co within the sample environment. With stepwise compression, the formation of CoH$_2$ can be seen at pressures of around 60 GPa as is consistent with the work of M. Wang et al. \cite{12} alongside remaining CoH within the sample environment with both structures reaming prevalent within the diffraction patterns. With further stepwise compression of the CoH, CoH$_2$ mixture in an excess of hydrogen to pressures of 88 GPa no distinct structural changes were visible within the diffraction patterns. As such, the sample was laser heated to stimulate any potential further reaction in an attempt to form the predicted CoH$_3$ structures. After laser heating at 88 GPa all evidence of diffraction from the previously observed CoH and CoH$_2$ structures disappeared from the laser-heated area, and the presence of new diffraction peaks can be seen within the collected data as seen in fig. 5.1a. As there were several potential structures predicted to be stable for CoH$_x$ compounds within this pressure range \cite{170}, initial investigations looked into fitting these new peaks to these crystal structures. At pressures around 100 GPa, the work of L. Wang et al. \cite{170} predicts that the $I4/mmm$ phase of CoH$_2$ and the $Pm\bar{3}m$ phase of CoH$_3$ will be stable. Le Bail fits were carried out using both structures, and a good fit was established to the CoH$_3$ $Pm\bar{3}m$ structure with lattice parameters of 2.417 Å at 88 GPa. The volume of this structure was calculated and compared to those of Co and H$_2$ combined, confirming that the structure was likely to stoichiometrically CoH$_3$.

With a good quality Le Bail fit to the collected diffraction patterns and strong powder diffraction lines visible on the diffraction plates, as can be seen in fig. 5.1c, it was decided that the data was of adequate quality for meaningful Rietveld
analysis to be conducted. By comparing the volume of the structure fitted during the Le Bail fits of 14.119Å³ to that of CoH₂ per atom, we can determine that the structure should have a Z of 1 to maintain a similar volume per Co atom when accounting for the volume contribution of hydrogen within the structure [171], which is consistent with the predicted CoH₃ structure by L. Wang et al. [170]. Only two potential Wyckoff sites are valid to achieve this Z value, the 1a and 1b sites. Both the 1a and 1b Wyckoff sites are equivalent to one another with the 1b site having atoms displaced 0.5c from the 1a site. Atoms were trialled occupying the 1a Wyckoff site at (0,0,0) and, with a wR_p of 39% and a wR_obs of 2.9% this was determined to be a reasonable fit to the structure. The large wR_p of the fit is due in part to the contributions of ReH within the diffraction plate image, which were included within the model due to the lack of overlap of the peaks as can be observed in fig. 5.1. This is consistent with the structure predicted by L. Wang et al. and using the results of these calculations with the basis of the structure changed to incorporate the Co atoms resting on the origin, the H₂ atoms will occupy the vacant face centres of the unit cell in the 3c Wyckoff site. This is structurally isomorphic with the structure observed in FeH₃ at 87 GPa by Pepin et al. [172] and IrH₃ at 55 GPa by Scheler et al. [163].

With the structure characterised and peaks identified to determine the range of stability for the formed CoH₃ structure then investigated by varying the pressure of the sample. Across multiple samples, evidence of CoH₃ was observed with increasing pressure to at least 110 GPa and on decompression down to at pressures as low as 50 GPa with no evidence of decomposition into Co+H₂, CoH or CoH₂. Due to diamond failures, it was not possible to collect structural information on CoH₃ to pressures below 50 GPa however, theoretical calculations outlined below indicate that this phase may be sustained to much lower pressures. Correlating the volume vs pressure data for the CoH₃ structure using eosfit7 [173] a fit was attained to the third order Birch-Murnaghan equation of state [174]. The fit parameters calculated from the data set were $V_0 = 22.11(15) \text{ Å}^3/Z$, bulk modulus $K_0 = 30(2) \text{ GPa}$ and $K' = 10.2(7)$ with a weighted $\chi^2$ value of 1.01 indicating a good fit to the P-V data set. These equation of state (EOS) parameters, along with those of the other known hydrides of Co are summarised in table 5.1.
**Figure 5.1** (a) High pressure x-ray diffraction patterns ($\lambda = 0.2895 \, \text{Å}$) taken on compression of the fcc $Fm\bar{3}m$ CoH and CoH$_2$. Subsequent laser heating above 75 GPa leads to the synthesis of new cobalt hydride CoH$_3$ $Pm\bar{3}m$. CoH$_3$ diffraction patterns in compression are showing up to 110 GPa. b) Rietveld fit of CoH$_3$ structures, unfigted peaks belong to ReH and Re. The fit matches the structure with a $wR_p$ of 0.39 and a $wR_{obs}$ of 2.9. c) Figure showing the diffraction plates of the sample at 70 GPa before (1) and after (2) laser heating. Coloured lines are a guide to the eye to the most intense for the structures seen in each pattern with each phase being denoted by the corresponding colour; CoH (grey), CoH$_2$ (green), CoH$_3$ (blue). In all panels, tick marks indicate the reflections of CoH (grey), CoH$_2$ (green), CoH$_3$ (blue). Asterisks correspond to Re and ReH, whilst crosses correspond to W.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$V_0$ ($\text{Å}^3/Z$)</th>
<th>$K_0$ (GPa)</th>
<th>$K'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co (fcc)</td>
<td>170</td>
<td>10.87</td>
<td>224.6</td>
</tr>
<tr>
<td>Co (hcp)</td>
<td>170</td>
<td>10.23</td>
<td>278.2</td>
</tr>
<tr>
<td>CoH</td>
<td>[12]</td>
<td>13.08(13)</td>
<td>194(11)</td>
</tr>
<tr>
<td>CoH$_2$</td>
<td>[12]</td>
<td>17.1(11)</td>
<td>129(29)</td>
</tr>
<tr>
<td>CoH$_3$ (This study)</td>
<td>22.11(15)</td>
<td>30(2)</td>
<td>10.2(7)</td>
</tr>
</tbody>
</table>

**Table 5.1** EOS parameters for the various hydrides of Co and elemental Co.
5.3.2 Implications and Recent Theoretical Findings

Alongside these experimental studies, theoretical analysis of the observed CoH₃ structure was carried out by Drs Andreas Hermann and Bin Li. The findings of these studies will be briefly discussed in this section, with the full manuscript [2] (included in appendix B.2) containing a more detailed account of these aspects of the study. These studies used variable-composition structure searches to determine energetically stable CoₓHᵧ compounds up to 400 GPa. These calculations were done using the USPEX evolutionary crystal structure predictive method packages [175] and particle swarm optimisation methods implemented in the CALYPSO code [176]. Through enthalpy calculations across the most stable structures, a CoH₃ structure adopting the \( Pm\bar{3}m \) with Co atoms occupying the 1a Wyckoff position at \((0, 0, 0)\) and H atoms occupying the 3c position at \((0, \frac{1}{2}, \frac{1}{2})\) was observed to be on the convex hull for all pressures from 18 GPa to 400 GPa as can be seen in fig. 5.3. This structure is identical to that observed in both FeH₃ [172, 177] and IrH₃ [163]. The computationally calculated EOS using VASP of the \( Pm\bar{3}m \) structure, as seen in figure 5.2, are in good agreement with the experimentally observed results discussed earlier in this chapter. Whilst CoH₃ rests on the convex hull at pressures above 18 GPa, as can be seen in fig. 5.3, the CoH and CoH₂ structures exhibit much larger formation enthalpies across the investigated pressure range, which may explain why these structures can still be observed at high pressures and why using laser heating is necessary to overcome the formation enthalpy barrier to form CoH₃ and provide the energy needed to undergo the structural reconfiguration of the Co atoms.

A recent study by Hiel et al. [169] suggested that structural analogues of the \( Pm\bar{3}m \) FeH₃ with heavier transition metals taking the place of Fe within the materials would be good candidates to exhibit superconducting properties. DFT calculations performed alongside this experimental study have demonstrated that all three observed hydrides of Co exhibit metallicity across their stability ranges. With CoH₃, at low pressures, it can be observed from the electronic density of states (DOS) that a sizeable contribution of this metallicity arises due to contributions from the hydrogen orbitals close to the Fermi level, indicating a possibility of superconducting behaviour. These projected phonon density of states calculations for the CoH, CoH₂ and CoH₃ structures show no evidence of imaginary frequencies indicating dynamical stability across the observed pressure range.
Figure 5.2  a) Absolute volumes of the different stoichiometries of CoH\textsubscript{x} compounds per Co atom with pressure. Pluses represent data collected in the study by Wang et al.[12] and diamonds representing data collected in this study. Dotted lines show the expected volume of the elemental constituents, and the combined dash-dot line is the theoretically calculated EOS for each compound through DFT using ultrasoft potentials (calculated using QuantumESPRESSO code). For CoH\textsubscript{3} the light blue dashed-dotted line was calculated with VASP, using ‘hard’ PAW pseudopotentials and the optB88-vdW dispersion-corrected functional. The solid line representing a third-order Birch Murnahan fit to the experimental data set with the parameters as found in table 5.1. b) Stick and ball models of the Pm\textbar 3m CoH\textsubscript{3} and the Fm\textbar 3m structures of CoH and CoH\textsubscript{2}.
Figure 5.3  *Convex hull calculations showing the relative enthalpies of the various composition ratios of Co-H compounds at pressures up to 200 GPa.*
5.3.3 Investigation Into the Structures of the Unidentified Peaks When Using Au as a Pressure Marker

In addition to the peaks attributable to CoH$_3$, when heating the sample using Au as a pressure marker, a plethora of additional peaks were present in some areas of the sample chamber after heating. After confirming that these peaks were not attributable to previously observed CoH$_x$ structures or those of elemental Co, an investigation was carried out to establish the structure of these peaks. At 88 GPa when heating CoH$_2$ and CoH with Au as a pressure marker, as with no pressure marker, all evidence of the CoH and CoH$_2$ peaks disappears and a strong contribution from the previously discussed CoH$_3$ $Pm\bar{3}m$ structure are observed. There are also a number of peaks with distinctly different textures observed within the sample. By comparing the intensities of these peaks in different regions of the sample chamber, along with the relative shifts in peak position with pressure, it was possible to establish that there was likely 2-3 distinct structures present within the sample environment in addition to the contributions from reacted gasket material picked up in the diffraction patterns when rotating the sample chamber.

A series of broad powder peaks with good powder averaging can be observed in the diffraction plate images creating an apparent broad doublet at around 8° with an incident x-ray wavelength of $\lambda$ of 0.3344 Å. This doublet, as was observed across all prepared samples, with the intensity of the peaks being larger near the edges of the sample, can be attributed to a combination of Re and ReH, the presence of which is typical of experiments using H$_2$ and Re gaskets as there is known to be pressure-induced hydrogenation of Re which is amplified by the use of laser heating [178]. Observing the remaining peaks in the diffraction pattern and their behaviour with pressure, it is apparent that there are seemingly two additional structures present within the sample environment. Due to similarities in the ‘spottiness’ of the unidentified peaks, texture analysis alone does not adequately distinguish between the peaks belonging to the two structures. Initial indexing of the unidentified peaks was conducted using CONOGRAPH [63] with the assumption that all peaks could be associated with the same structure, which yielded likely candidates to be an orthorhombic C structure belonging to the $mmm$ point group which without full structural information is indistinguishable from the $Cmcm$ spacegroup. Whilst this structure yields a good fit to the data set at high pressure, as pressure decreases, several peaks begin to drift.
from this potential fit, demonstrating that this is not the valid solution to the structural information collected. By comparing nearby regions of the sample from the collected x-ray grid scans, several peaks were observed to vary in intensity relative to the rest of the pattern across different regions. With this a guide to the potential separation of the peak attributions, when indexing these peaks again using CONOGRAPH, two key point groups were observed as viable candidates to trial. By observing selection rules, these were determined to be structures belonging to the 4/mmm and the 6/mmm point groups. Trialling these structures using Le Bail fits, it was determined that with the least unobserved peaks, the structure was most likely to belong to the 4/mmm point group with a face centred setting. Through observation of the reflection conditions I4/mmm was selected as a likely candidate structure with a unit cell of $a = 3.148(6)\text{Å}$, $c = 3.865(5)\text{Å}$ at 90 GPa. Comparing the volume of this structure (38.3 Å$^3$) to those estimated from the EOS of hydrogen [171] and Co [170] at these pressures, a Z value of 2 can be attained for the structure yielding an estimated stoichiometry of CoH$_5$ for this I4/mmm structure.

The remaining unidentified peaks were then indexed using CONOGRAPH yielding only low symmetry space groups being returned by this process. *Ab initio* structural searches were conducted on potential Co-H structures with a Co:H ratio of 3:7 were calculated by Dr Andreas Hermann and of the returned structures which were determined to be potentially metastable, one structure with the space group $P1$ matched well with an indexed structure and was trialled with the experimental data using Le Bail fitting techniques. At pressures of 90 GPa this structure has lattice parameters of $a = 4.713(3)\text{Å}$, $b = 3.788(4)\text{Å}$, $c = 3.792(5)\text{Å}$, $\alpha = 110.7(2)^\circ$, $\beta = 88.84(13)^\circ$ and $\gamma = 97.8(2)^\circ$. This gives an overall volume of 62.69 Å$^3$ which when compared to the volumes of Co and H$_2$ at 90 GPa gives a likely stoichiometry of Co$_2$H$_7$ and a Z value of 2, which is in great agreement with the predicted structure. Upon visual inspection of the fit however, it appears that many of the major peaks can be attributed to Re and ReH so it is unlikely that this P1 structure is a valid solution leaving one unidentified material.

These novel structures can be observed within the sample environment at pressures up to 110 GPa and on decompression down to 50 GPa showing that the formed compounds have a very wide range of stability to decomposition. Interestingly, attempts to replicate the formation of these compounds proved unsuccessful. These potential higher hydride structures of Co have only been observed in samples containing Au as a pressure marker. This means that it is
Figure 5.4  Room temperature diffraction patterns on decompression of the ‘contaminated’ Co+H regions of the sample chamber. Within these regions, several distinct structures can be observed with two distinct. Potential structures discussed in this chapter are included (I4/mmm CoH$_5$ and Pm$\bar{3}$m CoH$_3$), along with the expected peak positions for the P1 structure of the Co$_3$H$_7$ simulation. As can be seen, there is potential for the CoH$_5$ structure to be valid, but due to the poor powder averaging and relatively low intensities of the peaks, it is not possible to fully solve these structures. By inspection of the peak positions, it seems unlikely that the P1 structure is valid as many of the major peaks can be attributed to Re and ReH.
possible that either the Au is reacting within the sample environment and that the observed structures are either a hybrid Au$_x$Co$_y$H$_z$ material or are a potential alloy of Au and Co.

To establish whether this is the case, further experiments would need to be conducted to attain much higher quality powder averaging across the sample environment to allow full Rietveld analysis to be conducted on the product alongside additional studies into high-pressure behaviour of Co-Au Bimetallic mixtures as current studies into these materials do not exceed 15 GPa [179]. Additionally, within the repeated experiments in which ‘clean’ samples of CoH$_3$ were observed, due to the variation in the sample environment, stable coupling of the heating laser did not occur for prolonged periods of time. As such, the temperatures reached were likely much lower than those in the initial experiments. This means that, whilst the energetically stable CoH$_3$ structure was observed, it is possible that the temperatures required to form the other observed structures with potentially higher hydrogen content were not achieved. As such, there is a possibility that the reason for the reduced coupling within the sample environment is that when Au is present within the sample environment, which is known to couple well with IR heating lasers, these particles act as a coupler providing the initial ‘hot-spot’ which overcomes the absorption barrier of the reacted sample allowing for sustained heating. With this in mind, further experiments could be trialled using alternate pressure markers that are known to couple well at pressures of around 90 GPa to see if the same compounds can be observed and eliminate the possibility of bimetallic Au containing materials from the candidates for these novel peaks.

5.4 Conclusions

The previously predicted CoH$_3$ compound was observed and found to have to be consistent with the predicted $Pm\bar{3}m$ structure predicted by Wang et al. [12]. This compound forms readily heating CoH and CoH$_2$ at pressures of around 90 GPa and is observed to be stable on compression up to 110 GPa and down to pressures below 50 GPa upon decompression, indicating an extremely wide range of pressure for stability. This newly observed structure is theoretically metastable down to pressures below 10 GPa with potential superconducting properties with $T_c$ of 14 K at pressures of 18 GPa with $T_c$ increasing with decreasing pressure. Additional reactant products were observed in samples using Au as a pressure marker,
but the structure solution is not clear without further experimental evidence with more established powder averaging. A tentative partial solution has been presented of an $I_4/mmm$ structure of CoH$_5$ which may be a starting point for future investigations but attempts to replicate this product within this study were unsuccessful.
Chapter 6

Conclusions

The aim of this thesis was to explore the behaviour of Group XIV materials and cobalt at extreme conditions in the presence of elemental hydrogen. The studies into Ge in particular yielded an interesting insight into the behaviour of elemental Ge which formed the basis of the key findings of this thesis. As this work was presented as a series of chapters covering the systems as discrete studies using a series of similar techniques this conclusion shall be continued in the same format.

6.1 Elemental Germanium

Previous studies into elemental germanium had covered the structural evolution on compression upto 190 GPa and on decompression from around 30 GPa with 10 distinct structures having been identified across a range of conditions. Additional studies had also been conducted at temperatures above room temperature with compression upto 30 GPa mapping out the phase boundaries between Ge-I and Ge-II alongside the melting conditions of both Ge-I and Ge-II up to this pressure. The presented work explores the high temperature, high pressure behaviour of elemental germanium in both hydrogen and MgO as a pressure transmitting medium. Whilst no reaction was observed between Ge and H₂ at temperatures exceeding 1500 K at pressures between 56 GPa and 88 GPa the presence of a novel structure was observed which was not able to be quenched to room temperature. Through the use of diffraction pattern analysis and with supporting computational structural searches this novel phase, Ge-VIII, was identified to
belong to the spacegroup $I4/mmm$ with atoms occupying the 2a Wyckoff site. Further computational analysis was carried out by Dr Miguel Martinez-Canales into the thermal stability of Ge-VIII finding that it is favourable over the room temperature phase Ge-IV. This study showed no evidence of this phase above 88 GPa. This is of great interest as it possible that due to the analogous structural behaviour in both Si and Ge that this phase may exist in a narrow band of temperature and pressure in an equivalent position within the Si phase diagram which is yet to have been observed experimentally. This may be a topic of interest to future studies due to is potential applications in the understanding of planetary interiors. Evidence was also observed of the Ge-II/Ge-IV transition occurring above ambient conditions allowing for the suggested phase boundary between the two phases.

Further work within this study saw the observation of melting within elemental germanium at a number of different pressures. Whilst insufficient evidence was collected to accurately map the melt behaviour of Ge-VIII suggested extensions to the melt line were presented based on the observed data points with more studies needing to be carried out to confirm these boundaries. Collected evidence of melt is however consistent with what would be expected from the extrapolation of the Ge-II melt line for melting observed below 50 GPa. Based on the evidence observed across all elements of this study extensions to the phase diagram of Ge were presented to pressures up to 110 GPa.

### 6.2 Group XIV and Hydrogen

Prior studies into the formation of group XIV elements and hydrogen mixtures have yielded a range of results. Initial studies into this group contained within this project focused on mixtures of Ge and H in attempts to replicate the studies of Strobel et al. [132] surrounding GeH$_4$/H$_2$ mixtures without the use of GeH$_4$ as a precursor. These studies showed no evidence of the formation of hydrides of Ge with laser heating up to pressures of 110 GPa. Structural changes were observed when laser heating at pressures of around 74 GPa with these later being confirmed to be assigned to the novel high temperature phase Ge-VIII which is discussed in detail in chapter 3.

Further to these experiments into elemental Ge and H$_2$ mixtures, experiments were conducted using the same methods to attempt to fabricate the elusive
hydrides of Pb at moderate pressures motivated by the predictions of Zaleski-
Ejgierd et al. [135]. As with Ge/H$_2$ mixtures, no evidence of the formation of
hydrides of Pb was observed throughout these experiments at pressures up to
120 GPa. This agrees with the experimental findings of Guigue and Loubeyre
[148] who also see no evidence of the formation of hydrides of Pb up to 140 GPa.

6.3 Cobalt and Hydrogen

Prior experimental studies into cobalt hydrogen mixtures had yielded evidence
of the formation of CoH and CoH$_2$ through the increasing of pressure within the
sample chamber [12]. Using a similar experimental configuration as the previous
experiments, evidence was presented confirming the results of the studies of Wang
et al. [12] and forming the starting point of further investigations. Samples
comprising of a mixture of CoH and CoH$_2$ were laser heated at pressure of
around 90 GPa after which evidence was observed of a further transformation
in the material. This novel material after analysis of the XRD data points in
confirmed to match with the predicted $Pm\bar{3}m$ structure of CoH$_3$ [170] and is
observed to be stable on compression to 110 GPa and on decompression down to
50 GPa. Theoretical studies conducted alongside these experiments offer evidence
that the newly observe structure may be metastable down to 10 GPa and under
these conditions may exhibit superconducting properties with a predicted $T_c$ of
14 K at pressures of 18 GPa. It is also expected that this $T_c$ will increase with
increasing pressure.

In experimental runs in which Au was used as a pressure marker, additional
reactant products were also observed. Tentatively, a partial solution to this
structure is presented $I_4/mmm$ structure of CoH$_5$ which may be a starting point
for future investigations. Attempts to replicate this formation with additional
experiments within this study were unsuccessful. A potential explanation for
these novel peaks is that the Au acts as a coupler in these samples allowing the
mixture to reach much higher temperatures than when heating the CoH and
CoH$_2$ mixtures independently in hydrogen, with these increased temperatures
offering the ability to overcome the energy potential to reach further metastable
stoichiometries. This is currently only a working hypothesis and further
experiments would be required to confirm this.
6.4 Future Works

This work presents findings of studies into germanium and the discovery of the novel phase Ge-VIII at exclusively high pressure. Due to the parallels observed within the phase diagram of silicon and germanium it may be of interest to explore the equivalent region phase space for Si to establish if this phase exists in Si also. If an analogous phase were to be observed within Si based on the previously established phase diagram of Si [98], the transition is likely to occur in a narrow band of temperature of around 1000 K between 12 GPa and 15 GPa as this is the region above the Si-XI phase. Whilst no evidence has been observed of the occurrence of this phase in previous studies of Si in similar conditions, no extensive mapping of the Si-XI/liquid boundary has been conducted so it is possible that due to uncertainties in measured temperatures these conditions were not reached. It would also be of interest to continue the high pressure high temperature studies of elemental Ge to explore the potential of potential of further high pressure high temperature phases occurring above 90 GPa alongside exploration of the melt behaviour of the Ge-IV and Ge-VIII phases in which melting was observed during this study.

As the studies into Ge and Pb mixtures containing hydrogen showed no evidence of hydride formation at pressures up to 110 GPa and 136 GPa respectively it would be of interest to continue exploring these systems at considerably higher pressures. With the formation pressures of the XH$_4$ and higher hydrides postulated by Ashcroft [10] being predicted to occur at pressures within this pressure range, studies could be conducted for both materials extending the formation region up to 250 GPa to offer the best chance of observing the material formations. If these compounds can be discovered, it may offer some interesting insight into the behaviour of elemental hydrogen at considerably higher pressures as it is postulated that the intercalated layers of hydrogen that may occur in these structures is likely analogous to the predicted structures of solid metallic hydrogen. Additionally, it is possible that, as with silicon and hydrogen mixtures as seen in the works of Hanfland et al. [131], the reaction may be very kinetically slow for the absorption of hydrogen into both Ge and Pb, with the reaction of hydrogen and silicon taking more than 1 year at room temperature. With this in mind, it may be beneficial as an avenue of investigation to leave several samples of Pb and Ge in a hydrogen environment at pressures beyond the predicted reformation range leaving them for an extended period of time.
As was discussed in the concluding remarks of chapter 5 the presence of an unexpected crystal structures was observed within the diffraction patterns, but this was only the case in experiments where gold was used as a pressure marker. It is for this reason that it would be of interest to conduct further studies, firstly attempting to replicate the reaction observed with the Co/H/Au mixtures to attempt to generate the compound again. I would also be of interest to see whether these structures can be observed with alternated metallic pressure markers to see if it is likely to be a further reaction related to the higher temperatures reached. Secondly, to accompany these studies it would be of interest to test the theory that it may be a the formation of a bimetallic alloy by conducting investigations into Co/Au alloys above the 15 GPa that studies have been conducted \cite{179} to see if these structures can be observed in those mixtures to offer some potential explanation of the mystery structures. From there, depending whether these studies offer answers to the unexplained structures, it may also be of interest to attempt to heat the CoH$_3$ to much higher temperatures whilst in an excess of hydrogen to see if further hydrogenation is possible.
Appendix A

Supplementary figures

Figure A.1 Proposed extensions to the Ge P-T phase diagram inclusive of error bars. Filled data points represent the data previously collected and presented in the work of Prakapenka et al. [97], unfilled data points are those presented chapter 3 of this work.
Figure A.2 A plot showing the lattice parameters of Ge-IV (triangles) and Ge-VIII (diamonds) with varying temperature at 77 GPa. Open symbols represent data points collected with the laser operating in continuous mode and filled symbols represent those with the laser operating in pulsed mode. It is reasonably likely that due to the thermal gradients within the sample and the presence of Ge-IV being observed long after the transition temperature, particularly when operating in pulsed mode, that the temperature in regions of Ge-IV is considerable lower than those of Ge-VIII at the heating spot.
Figure A.2 shows the lattice parameters of both Ge-IV and Ge-VIII across a range of temperatures at 77 GPa under both pulsed and continuous wave laser heating. In the continuous wave heating runs, the overall presence of Ge-IV within the diffraction pattern is much lower than that observed in the pulsed heating, likely due to the larger area of the sample expected to be close to the observed temperature. This reduced presence means that an insufficient quantity of peaks remained to gather a meaningful fit to the Imma structure in many of the diffraction patterns. At around 1700 K it appears that there may be an increase in b-Ge-IV similar to that observed in the pulsed heating at temperatures above 2400 K. As the temperature gradients are typically much steeper in pulse heated samples, it may be that this apparent increase is the same phenomenon occurring in both heating runs, with the observed Ge-IV, being picked up on the outer region of the x-ray beam, being at a considerably lower temperature than the Ge-VIII region of sample.

To see if the transition is continuous, the ratio of lattice parameters should be considered as convergence in these ratios is indicative of a potential continuous transition. In this data set, \(c/a\) ratios across the temperature range do not seem to converge, with Ge-VIII having an increasing \(c/a\) ratio of between 0.91 and 0.92 below 2400 K and Ge-IV having an increasing \(c/a\) ratio between 0.53 and 0.54 across the same range. The \(c/b\) ratio of Ge-IV also is observed to increase from 0.57 to 0.59 across this range. The closest to converging ratios that is observed in the experiment is in the Ge-IV \(b/a\) ratio with this decreasing from 0.94 to 0.93 before sharply increasing again above 2400 K. This means that insufficient evidence is observed to confirm that a continuous transition is occurring however, the behaviour of the Ge-IV \(b/a\) ratio may imply that there is a rotation of the unit cell basis across the transition.

With the pulsed heating runs, it can be observed that the b-Ge-IV appears to be expanding anisotropically to the other lattice directions above 2400 K, possibly converging on the dimensions of a-Ge-IV. Looking at the values of a-Ge-VIII at the lowest temperature that Ge-VIII is observed in these heating runs and comparing it to the value of a-Ge-IV at the highest temperature recorded for this experiment. These two values can be made equivalent at a ratio of Ge-IV:Ge-VIII of 11 : 17 both of which are acceptable values for the expansion of isomorphic subgroups of each of the respective structures. Further studies to explore the relationship between the temperature and lattice parameters would need to be conducted to draw any meaningful conclusions about the dynamics of this phase.
transition, as the uncertainties in temperature typically exceed 150 K. With the transition temperature being expected to be somewhere in the region of 1700 K in this pressure range, it may be possible to observe this transition with the use of internal resistive heating which may provide smaller gradients of temperature in the sample environment.

In addition to the isotropic expansion observed in Ge-IV above 2400 K, evidence of isotropic expansion is also observed in Ge-VIII across the same temperature range. This may indicate the approach to a further phase transition at these temperature conditions. Again, to confirm or disprove this hypothesis, further experiments would need to be conducted, with higher temperatures need to be attained than those seen in this study.
Appendix B

Publications
High-temperature phase transitions in dense germanium

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ABSTRACT
Through a series of high-pressure x-ray diffraction experiments combined with in situ laser heating, we explore the pressure–temperature phase diagram of germanium (Ge) at pressures up to 110 GPa and temperatures exceeding 3000 K. In the pressure range of 64–90 GPa, we observe orthorhombic Ge-IV transforming above 1500 K to a previously unobserved high-temperature phase, which we denote as Ge-VIII. This high-temperature phase is characterized by a tetragonal crystal structure, space group I4/mmm. Density functional theory simulations confirm that Ge-IV becomes unstable at high temperatures and that Ge-VIII is highly competitive and dynamically stable at these conditions. The existence of Ge-VIII has profound implications for the pressure–temperature phase diagram, with melting conditions increasing to much higher temperatures than previous extrapolations would imply.

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I. INTRODUCTION
The understanding of the group-XIV elements holds importance to both fundamental science and technological applications due to their relative abundance in the Earth and diverse electronic properties that they exhibit.1–10 The use of germanium (Ge), in particular, was crucial in the early developments of transistors, paving the way for the technology we use today.1 Although Ge has been supplanted by its lighter group-XIV member, silicon (Si), in many applications, it still holds some advantages due to its higher intrinsic electron mobility and enhanced quantum-confinement effects.1,11

Owing to their chemical similarity, Ge and Si are observed to undergo the same sequence of structural transitions during compression at room temperature.11–13 At ambient pressure and temperature, both Ge-I21 and Si-I21 exist in a semi-metallic diamond-type structure (Pñ3m). Upon compression above 7 GPa, Ge-I undergoes a sluggish transition to Ge-II (Fig. 1), manifested by a tetragonal distortion to the metallic β-Sn type structure (Iñ4/a)24,31 with transition being complete at 12 GPa. This phase exhibits a remarkable stability of 55 GPa range21 (Fig. 1), compared to the interval of only 2 GPa of Si-II.10 Above 75 GPa, Ge-II undergoes a displacive transition into the orthorhombic Ge-IV (Imma). Ge-IV is stable at 85 GPa,13 when it transforms to the hexagonal phase Ge-V (P63/mmm)15 (Fig. 1). The analogous Imma phase of silicon is Si-XI, which appears between 11.7 and 13.2 GPa21,24 before transitioning to the hexagonal Si-V above 13.2 GPa.12,21 Ge-V (P63/mmm) is stable only over a narrow pressure interval, transforming to Ge-VI (Cmca) at 100 GPa17 (Fig. 1), which is structurally equivalent to Si-VI, observed at 38 GPa.21 Ge-VI (Cmca) transitions into Ge-VII (P63/mmc) at 170 GPa,17 which is analogous to the Si-VII structure observed between 42 and 76 GPa.12 Table S1 summarizes the structural information on Ge and Si.

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Interestingly, Ge does not follow the same structural sequence as Si on decompression; instead, it transforms to new, metastable allotropes. These phases are highly dependent on the rate of pressure release: fast decompression from β-Sn Ge-II results in the formation of a BC8 structure (Ia3d), which gradually changes to a hexagonal diamond structure (P63/mmc) at ambient pressure. Alternatively, slow decompression from Ge-II leads to the formation of Ge-III, a metastable tetragonal structure (P43212). Previous high-temperature studies have mapped out the $P$–$T$ Ge I–II boundary and determined melting temperatures up to 37 GPa (see Fig. 1). The melting curve of Ge-I has a negative slope, which ends in the I–II–liquid triple point at ~8.7 GPa and ~833 K. Above this point, the melting temperature increases, reaching ~1500 K by 35 GPa (Fig. 1). Similar behavior is observed in Si, with melting temperatures decreasing for the C-diamond Si-I phase and then increasing in β-Sn Si-II. Despite this rich polymorphism, neither system has experimentally shown to exhibit high-temperature phases.

In this article, we combine high-pressure and high-temperature x-ray diffraction measurements and density functional theory (DFT) calculations to study the phase diagram of germanium in a wide pressure–temperature range. Using double-sided continuous-wave (CW) laser heating in diamond anvil cells, we explore the behavior of Ge up to 115 GPa and 3000 K. Above 65 GPa and 1700 K, we observe that Ge-IV transforms to a previously unknown phase, which we denote here as Ge-VIII. This novel phase is determined to adopt a tetragonal structure (space group I4/mmm) and is stable only at high temperatures, reversing to Ge-IV on quenching. This structure has been confirmed in several experimental runs using MgO and H$_2$ as pressure-transmitting media (PTM). Density functional theory simulations demonstrate that the room temperature Ge-IV is unstable above 1500 K and Ge-VIII is energetically highly competitive and dynamically stable at these conditions. We also explore the $P$–$T$ space that Ge-VIII covers within the phase diagram and the high-temperature stability of Ge-V and Ge-VI.

**II. METHODS**

**A. Experimental**

For these experiments, Boehler-Almax cut diamonds were chosen with 100 µm culets. These diamonds were then used to indent a rhodium gasket to a thickness of 25 µm, in which a 60 µm hole was drilled to act as the sample chamber.

High-purity Ge powder (99.999%, 100 mesh, Aldrich) was used. Ge chunks were initially precompressed into foils of ~8 µm thick and loaded into diamond anvil cells (DACs) with the pressure-transmitting medium.

As pressure-transmitting media, we use either MgO (Alfa Aesar, nanopowder, 99+%) or research grade hydrogen (99.9995%, BOC) loaded at 0.2 GPa, as indicated in each discussed run. MgO was used as a pressure medium, as an insulating layer to protect the diamonds during laser heating, and as a pressure marker. The pressure was determined by MgO diffraction patterns and/or diamond edge.

Powder XRD data were collected at the APS, on the GeoSoilEnviRO-CARS 131DD beamline, and at the 16-IDB High Pressure Collaborative Access Team (HPCAT). The diffraction patterns from monochromatic 0.3344 and 0.4066 Å wavelength x rays were collected on a Pilatus 1M image-plate detector/PI-MAX, Princeton Instruments, which were integrated using DIOPTAS into a 1D dataset. Collection times ranged between 2 and 5 s. These data were then indexed using CONOGRAP and refined with JANA2006.

To allow the investigation of high-temperature transitions in Ge, several experiments were conducted making use of flattop continuous-wave laser heating techniques within diamond anvil cells using an Yb fiber laser setup for stable dual sided heating. We conducted simultaneous in situ double-sided continuous-wave (CW) laser heating and x-ray diffraction experiments in diamond anvil cells. Laser heating results in highly localized heating of the sample both radially from the “hot spot” and in depth. As such, these large thermal gradients result in probing both crystalline and
molten samples simultaneously at high temperatures. The temperatures in all experimental runs are determined by taking the average of the black-body thermal emission from both sides of the sample; see Fig. S1 for an example of emission spectra. Thermal emission spectra were collected with a central wavelength of 700 nm with a collection time between 0.1 ms and 1 s depending on the intensity of the emitted light. The emission spectra were sampled between two and eight times per temperature step from both the up-stream and down-stream sides of the sample simultaneously. The collected emission spectra were fitted using a two-parameter gray body Planck distribution, corrected for the transmission function of the optical system. For each set of temperatures, the mean average is used as the average temperature of the sample. The uncertainties of these temperatures were determined from the standard error on the mean of the fitted temperatures. In the event of poor quality thermal emission from one side of the sample or an unreasonable thermal emission spectra due to “flashing” or a non-convergence of the fit on one side of the sample, the uncertainty of the temperature measurement was estimated to be 7% of the fitted temperature as this was determined to be a conservative estimate of the uncertainties associated with this fitting technique.

B. Computational details

The computational–theoretical analysis of Ge under pressure has been performed within the Density Functional Theory (DFT) framework. Calculations have been performed using CASTEP. We have performed structural searches using AIRSS at 10, 80, and 100 GPa. Searches at 10 GPa were performed with a 4c×5 pseudopotential. All searches used the Perdew–Burke–Ernzerhof (PBE) functional. At higher pressures, the pseudopotentials of choice included the 3d6 electrons as a core. Searches at 10, 80, and 100 GPa with AIRSS (with unit cells with up to 24 atoms) identified Ge-III (I4/m) and Ge-IV (Imma), Ge-V (P6/mm), and Ge-VI (Cmca) in addition to the new Ge-VIII (I4/mmm). Our searches identified all structures in Table S1, as well as the proposed I4/mmm structure and other competitive structures. Further computational details and the structures found can be accessed in the Edinburgh DataShare repository. Overall, we relaxed almost 5000 structures.

III. RESULTS AND DISCUSSION

A. Experimental evidence of Ge phase VIII

Upon compression at ambient temperatures, there is good agreement with the previously reported phase transition pressures. Figure 2(a) shows the XRD patterns of Ge-III (I4/m) observed in compression at room temperature and its transition to phase IV (Imma) between 70 and 80 GPa, and the following transition to phase V (P6/mm). When heating Ge-II between pressures of 56–61 GPa, as shown in Fig. 2(b), we observe changes in the diffraction pattern corresponding to a transition to the orthorhombic Ge-IV. At 56–61 GPa, the II/IV transition is observed between 1560(110) and 1850(130) K, accompanied by a pressure shift of ~2–4 GPa. The combined data constrains the II–IV phase boundary with a dP/dT of ~0.014(3) GPa/K. Experimental studies on Si show the equivalent transition (Si-II and Si-XI) also having a phase boundary with a negative slope between 1050 K at 12 GPa and 300 K at 13.2 GPa.

Upon laser heating Ge-IV at pressures above 64 GPa and 1600 K, we observe changes in the diffraction patterns. With the emergence of new diffraction peaks, there is a simultaneous reduction in the intensity of the Ge-IV peaks that indicate a transition to a novel phase, which we designate Ge-VIII (see Figs. 2 and 3). The transition is completely reversible and Ge-VIII reverts to Ge-IV upon cooling, see Fig. 3(b).

This new set of peaks [2D image plates in Fig. 4(a)] can be indexed to a tetragonal unit cell with lattice parameters of \(a = 2.978(5) \text{ Å} \) and \(c = 2.732(3) \text{ Å} \). Figure 4(c) and 4(e) show the Le Bail refinements in different experimental runs, using MgO and H2 as PTM, respectively. We observe the same transition in both cases, validating the evaluation of Ge-VIII. Due to the overlap of Ge-VIII and MgO (202) Bragg peaks, combined with poor crystallinity around the transition temperature, our analysis was limited to the Le Bail refinements in combination with first-principles calculations. As shown in Fig. 4(c), fitting an I4/mmm structure with lattice parameters \(a = 2.978(5) \text{ Å} \) and \(c = 2.732(3) \text{ Å} \) along with the expected contributions from Ge-IV and MgO provides a high-quality fit. These lattice parameters give a volume of 12.11(1) Å\(^3\) atom. Comparing this with Ge-IV lattice parameters of \(a = 4.577(4) \text{ Å} \).
\( b = 4.376(3) \, \text{Å}, \) and \( c = 2.4731(15) \, \text{Å} \) gives an atomic volume of 12.38(1) \( \text{Å}^3/\text{atom} \), which is approximately constant across the transition indicating a potential displacive transition and a \( Z \) value of 2. Using this value of \( Z = 2 \), two potential atomic positions (2a and 2b) are possible for space group \( 14/mmm \). By comparing the collected diffraction profiles to a simulated ideal powder pattern, shown in Figs. 4(c) and 4(d), there is a distinct similarity between the intensity profiles of the collected data and the ideal powder with atoms occupying the \( 2a \) Wyckoff site (0,0,0).

To our knowledge, Ge-VIII represents the first high-temperature phase to be discovered in the group-XIV elements at high-pressure, other than the diamond form of carbon. Interestingly, tin (Sn), directly below Ge in group-XIV, also exhibits a structural transition from \( I4_1/amd \) (Sn-I) to \( I4/mmm \) (Sn-III) at 9.2 GPa and 300 K.\(^{17,46}\) As group-XIV elements seem to follow a parallel phase template, it would be expected that the remaining elements of the group also adopt the \( I4/mmm \) at different and yet to be explored conditions. Isotropy subgroup distortion analysis\(^{11}\) indicates that a direct displacive transition is possible between the high-temperature parent Ge-VIII (\( I4/mmm \)) and low-temperature daughter Ge-IV phases (\( Imma \)). Consistent with a displacive transition, transformation occurs via a mode with \( N \) symmetry involving anti-parallel displacements of Ge atoms, suggesting a possible mechanism for this transition.

**B. Density functional theory and Ge phase VIII**

To further understand the stability regime of Ge-VIII, we have analyzed the Ge structural energy landscape using DFT with the
Perdew–Burke–Ernzerhof (PBE) functional\textsuperscript{[19]} and ultrasoft pseudopotentials\textsuperscript{[20]} as implemented in CASTEP\textsuperscript{[18,1]}.

Calculations are detailed in the supplementary material and the raw data, including the search setup, DFT enthalpies and phonons, and \textit{ab initio} molecular dynamics (MD) runs, are accessible from the Edinburgh DataShare repository.\textsuperscript{16}

The enthalpies of the most competitive structures have been computed to a higher degree of accuracy, with the C18 pseudopotential, and k-point spacing denser than 0.025 Å\textsuperscript{-1}. Figure 5(a) shows the evolution of the enthalpy difference of these structures with pressure indicating that all of these structures are extremely competitive between 60 and 90 GPa. This has been done with the PBE functional (475 eV cutoff) and the PBEsol functional (600 eV). The transition pressures are almost identical:

**PBE:**

\textit{Imma} 75.9 GPa \textit{P6/mmm} 76.2 GPa \textit{Cmca} 100.5 GPa \textit{I4/mmm},

**PBEsol:**

\textit{Imma} 68.7 GPa \textit{P6/mmm} 76.5 GPa \textit{Cmca}.

We considered obtaining a $P$–$T$ phase diagram using the quasiharmonic approximation. This is complicated due to the second-order nature of the phase transitions and their vicinity to the region of interest. The presence of soft phonons is likely to render the high-temperature region in which our interest is very unreliable. Instead, we performed a series of phonon calculations with QUANTUM–ESPRESSO.
using Density Functional Perturbation Theory (DFPT) to assess the dynamics of the system. Figures 5(b)–5(d) show the phonons of P6/mmm, Cmca – 8, and 14/mmm at 80 GPa.

The high-temperature stability of the Imma phase, which is the experimental one at 300 K between 75 and 85 GPa, and the new 14/mmm candidate was probed using ab initio molecular dynamics (AIMD). We chose a time step of 2 fs, which would sample the highest frequency phonon mode in Fig. 5(b) over 40 times per oscillation. The initial Imma configuration was a $\sqrt{2} \times \sqrt{2} \times 2$ supercell of the conventional cell, with 128 atoms. The initial 14/mmm configuration was a $2 \times 2 \times 2$ supercell of the conventional cell, also containing 128 atoms. Both supercells have similar volumes and lattice parameters at 80 GPa. MD simulations were ran in CASTEP 18.1, with the QC5 pseudopotential, a 300 eV cutoff, and a $2 \times 2 \times 2$ k-point grid with a 0.3 eV smearing width. In total, four distinct MD runs were performed.

In Run 1, Ge–Imma at 80 GPa was stabilized for 1 ps at 300 K using the NVT ensemble. The ensemble was then changed to NPT, and the cell was further stabilized for another 1.5 ps. The cell was then heated up to 1500 K. However, the system melted within 0.1 ps, being comparatively too fast to be represented.

In Run 2 (Fig. 6 left), Ge–Imma, at the average 300 K and 80 GPa lattice parameters, was stabilized on NVT at 750 K for 3.5 ps. The cell was then heated up to 1500 K, using a thermostat chain five times longer than in run 1. The system was kept on these conditions, using the NVT ensemble, for a further 6.5 ps. After 3 ps at 1500 K, there is a large jump in the mean square displacement (MSD). This is related to anti-parallel displacements in the atomic positions and a potential phase transition. This is shown in Fig. 6. To test if the new structure is stable, the cell was relaxed under the NPT ensemble. The system melted, however, within 1 ps.

In Run 3 (Fig. 6 middle), Ge–14/mmm at 80 GPa was stabilized at 750 K on the NVT ensemble for 2.75 ps. The temperature was then increased to 1500 K as in Run 2. The ensemble was changed to NPT at 10 ps. No phase transition was seen for 3.5 ps at 1500 K.

In Run 4 (Fig. 6 right), Ge–14/mmm at 65 GPa was stabilized at 300 K on the NPT ensemble for 1 ps. The temperature was then increased to 1000 K and run for 4 ps. The temperature was again increased to 1500 K for a further 3 ps. No substantial changes to the structure were seen during the simulation.

In summary, within DFT, Imma Ge–IV is not stable at 80 GPa and 1500 K; at these conditions, there must be a transition to 14/mmm Ge–VII before melting at higher temperatures.

C. Further extensions of the Ge phase diagram

At pressures above 86 GPa at ambient temperature, Ge–IV transforms to hexagonal Ge–V and Ge–VI at around 100 GPa, shown in Fig. 7. While heating phase V, we still see the transition to phase VIII above 1700 K [Fig. 7(a)], but heating phase VI at 110 GPa shows no indication of the transition to phase VIII [Fig. 7(b)]. These results suggest that both Ge–IV–V and Ge–VIII–V phase boundaries are near vertical. The combined data consequently imply the existence of a IV–V–VIII triple point at 1600 K and 86 GPa.

We also observe evidence of melting in some of our heating cycles: in addition to a decrease in the intensity of the corresponding Bragg peaks of the solid phase, there is an emergence of diffuse scattering from liquid Ge, which is shown in Fig. S2. By subtracting the background function of the room temperature pattern from the high-temperature pattern, the diffuse liquid scattering can be readily extracted. As shown in Figs. S2 and S3, at 44 GPa, we detect Ge–II melting above 1500 K (Fig. 1). At pressures of 60 GPa, we identify Ge–IV melt around 1900 K, slightly higher than what would be expected from extrapolations of the Ge–II melt line and implying an increase in the gradient above the II–IV–liquid triple point. Heating Ge–VIII at pressures of 68 GPa (Figs. S2 and S3), we see evidence of melting at 2700 K, suggesting another change in gradient after the IV–VIII–liquid triple point. In all further heating runs above 68 GPa, no evidence of melting was observed (Fig. 7), with Ge–VI remaining solid at 110 GPa and 2080 K. The melting line of Ge has been previously determined up to pressures of 37 GPa, and we extend it up to 68 GPa.

IV. CONCLUSIONS

The extended phase diagram of germanium based on our results is presented in Fig. 1. Our experiments show that the 14/mmm structure that we assign as Ge–VIII is reached through heating Imma Ge–IV. The former is only stable at high temperatures, reversing back to Ge–IV after temperature quenching. Contrary to Ge–IV, Ge–V and Ge–VI remain stable at high temperatures, confining Ge–VIII to a narrow range of $P$–$T$ space. To our knowledge, Ge–VIII represents the first high-temperature phase to be discovered in the group-XIV elements at high pressure, other than the diamond form of carbon. Similarities between the pressure and temperature phase transitions among the group XIV elements pose an interesting question as to whether an 14/mmm phase could also be observed in Si. Experimental studies on Si show the equivalent transition to Ge–II–IV, which would be Si–II. Si–XI also has a phase boundary with
a negative slope between 1050 K at 12 GPa and 300 K at 13.2 GPa. In Si, the pathway toward an equivalent Ge-VIII phase would require heating Si-XI, which exists in a very narrow pressure range between 13.2 and 15.4 GPa. It is possible that due to a very narrow window at which the phase could exist, the Si-Ia4/mmm configuration might have been overlooked. Nevertheless, the discovery of Ge-VIII suggests that further high-temperature dense phases could exist in the group-XIV elements.

**SUPPLEMENTARY MATERIAL**

The supplementary material contains a table with the phase boundaries of Si and Ge, some examples of our temperature measurements from black-body emission, and Ge XRD image plates and diffuse scattering during melting.

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**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon request. Molecular dynamics runs are available in the Edinburgh DataShare at https://datashare.is.ed.ac.uk/handle/10283/3195.

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The physical properties of a host metal can be profoundly altered by the presence of hydrogen. It has been predicted that metallic structures that host high density hydrogen could exhibit novel properties such as high-temperature superconductivity. The potentials of these materials are exemplified by the recent high-temperature superconductivity experimentally observed in rare-earth hydrides. Prior to these findings, superconductivity was also proposed to emerge in transition metal hydrides (TMH).

The transition metals are good electron donors, as they tend to donate their two external electrons, thus stabilizing the $H^-$ anion over molecular hydrogen. Under moderate pressures, almost all transition metals form monohydride compounds. Platinum, for example, is observed to form two hexagonal monohydride variants, Pth-I and Pth-II, at pressures above 27 GPa. Ab initio calculations initially predicted Pth-II to be a superconductor, with a critical temperature, $T_c$, below 17 K at 90 GPa; however, with the inclusion of anharmonic effects, the $T_c$ was substantially reduced to $<1$ K. Recent electrical measurements found that at 30 GPa, Pth-II has a $T_c$ of 7 K, which decreased on further compression. Through a combination of high pressure and/or high temperature, TMH with more unusual stoichiometries become energetically competitive. Iron exhibits several polyhydride species, of which FeH$_3$ (14/mmm), synthesized at 120 GPa and temperatures $>1500$ K, is the most hydrogen-rich and possesses a unique layered structure. Potential superconductivity in FeH$_3$ has been a subject of debate, with two theoretical works predicting remarkably high $T_c$ values ranging between 46 and 51 K and, conversely, another computational study finding no evidence of superconductivity. However, the latter study did suggest that trihydrides heavier than FeH$_3$, with a cubic $Pm\bar{3}m$ structural type, could facilitate superconductivity through the addition of d electrons to the hybrid 3d electron shell of the metal−hydrogen band.

Cobalt is a prime transition metal candidate to also exhibit a trihydride form, being positioned in the same group as iridium and period neighbor iron, both of which form cubic trihydrides. Indeed, a recent theoretical study predicted the formation of CoH$_3$ above 30 GPa sharing the same $Pm\bar{3}m$ structure as both FeH$_3$ and IrH$_3$. However, both these studies and a further computational work predict CoH$_3$ to have a $T_c$ below 1 K at pressures above 150 GPa. Experimentally, the synthesis of CoH$_3$ has remained elusive, with only the formation of face-centered cubic (fcc) CoH$_2$ above 4 GPa and the stepwise transition to CoH$_2$ above 45 GPa.

Here, we demonstrate the synthesis of cobalt trihydride in a laser-heated diamond-anvil cell through a series of synchrotron X-ray diffraction experiments. On compression, we observe formation of the known CoH and CoH$_2$, which we find to coexist at least 75 GPa. Laser heating CoH and CoH$_2$ in a hydrogen matrix at pressures above 75 GPa and 700 K leads to the complete transformation of the sample, identified by new diffraction peaks. We identify the new
compound as CoH$_3$ and find it to be isostructural to FeH$_3$, with Co atoms occupying the vertices of a primitive cubic unit cell and H atoms occupying the vacant face centers. Total energy and electron−phonon calculations reveal that CoH$_3$ remains energetically stable down to 18 GPa, at which pressure it exhibits superconductivity with a $T_c$ of 23 K.

After gas loading at 0.2 GPa, mixtures of Co and H$_2$ were compressed to 33 GPa. After 1 week at this pressure, X-ray diffraction patterns reveal the synthesis of both CoH and CoH$_2$ compounds, in agreement with previous work. CoH has space group symmetry $Fm\overline{3}m$, with unit-cell length $a = 3.4849(7)$ Å (at 60 GPa), while CoH$_2$ has unit cell length $a = 3.7533(8)$ Å (at 60 GPa) within the same group. Interestingly, CoH$_2$ is not isostructural to FeH$_2$, which adopts a tetragonal $I4/mmm$ structure, but instead adopts the same structure as RhH$_2$ at 14 GPa. We find that both CoH$_3$ and CoH$_2$ coexist

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Figure 1. (a) High-pressure X-ray diffraction patterns ($\lambda = 0.2895$ Å) taken on compression to 111 GPa. Laser heating at 88 GPa yields the synthesis of $Pm\overline{3}m$ cobalt trihydride. Asterisks correspond to Re and ReH, while crosses correspond to W. (b) Rietveld refinement fit of CoH$_3$ structures, unﬁtted peaks marked by * correspond to ReH and Re. Refinement parameters are $wR_p = 0.39$ and $wR_{exp} = 2.9$. (c) Diffraction plates of the sample at 88 GPa before (left) and after (right) laser heating. In all panels, tick marks indicate the reflections of CoH (gray), CoH$_2$ (green), and CoH$_3$ (blue).

Figure 2. (a) Volume per Co atom for Co−H compounds. Diamond and square symbols correspond to measurements from two experimental runs, while crosses represent data taken from Wang et al. Dashed dotted lines were calculated through DFT using ultrasoft pseudopotentials (QuantumESPRESSO code). For CoH$_3$, the light blue dashed−dotted line was calculated with VASP, using hard PAW pseudopotentials and the optB88-vdW dispersion-corrected functional. Dotted lines represent the EOS derived from the atomic volumes of Co and H. (b) Convex hull construction for CoH$_x$ compounds at a sequence of pressures. Empty (filled) symbols denote metastable (stable) phases. (c) Crystal structures of cobalt polyhydrides, CoH ($Fm\overline{3}m$), CoH$_2$ ($Fm\overline{3}m$) and CoH$_3$ ($Pm\overline{3}m$). Co atoms are represented by blue spheres, and H atoms are represented by pink spheres.
up to pressures of 88 GPa (see Figure 1a), with no indication of further hydrogenation. We also do not observe a transition on compression to tetragonal (I4/mmm) CoH₂, which was predicted to become energetically favorable above 42 GPa.27

The laser heating of metals in a high-pressure hydrogen environment has been a successful synthetic tool in yielding hydrogen-rich metal hydrides3,17,30,31 and was utilized here to explore the synthesis of cobalt polyhydride species. Samples of CoH/CoH₂ and H₂ were compressed to pressures of 75 and 88 GPa and held here for 24 and 12 h, respectively, displaying no time-induced transformation. These samples were then laser heated to approximately about 800 K (Figure S1 and see Experimental and Theoretical Methods in the Supporting Information for further details). Upon quenching of the sample, we see the disappearance of the diffraction lines attributed to CoH/CoH₂, which are supplanted by new diffraction peaks (see Figures 1a,c and S132). All of the new diffraction lines can be indexed with a simple cubic unit cell (Pm3m) with lattice parameter a = 2.4358(2) Å at 75 GPa. Rietveld refinements of this structure (Figure 1b) show Co atoms to be on the vertexes of the unit cell, with final agreement factors of wRp = 0.39 and a wRobs = 2.9. Samples were compressed up to 111 GPa, the highest pressure reached in this study, and subsequently decompressed down to 52 GPa by ramping and stopping at 40 GPa (below which the sample was lost because of anvil failure) to determine the equation of state (EOS) and evaluate the stability of the compound. The volume per Co atom as a function of pressure of CoH, CoH₂, and the synthesized product was fitted with third-order Birch–Murnaghan P−V EOS’s (see Figure 2a) with the fit parameters shown in Table S1. The experimentally determined EOS gives volumes greater than Co + 2H. The determined structure also matches that which was previously predicted for CoH₂,27 and is isostuctural to FeH₂.15

![Figure 3. Phonon dispersion curves and projected phonon density of states at 25 GPa for (a) CoH, (b) CoH₂, and (c) CoH₃. The phonon dispersions ω(q) for each phonon mode ν at momentum space point q are drawn as circles with radii proportional to the magnitude of the electron–phonon line widths γq.](https://example.com/fig3)

Through enthalpy calculations for the most stable structures, we find CoH₂ to adopt a Pm3m unit cell identical to FeH₂15,38 and IrH₉14 with the H atoms occupying the 3c site (0, 1/2, 1/2). This, together with the computationally determined EOS, is in good agreement with experiments. CoH₂ is on the convex hull above 18 GPa; however, experimentally we see only CoH and CoH₂ which we attribute to kinetics barriers. CoH and CoH₂ have the highest formation enthalpies, 0.602 and 0.596 eV per atom, respectively, at 100 GPa (see Figure 2) and also share the same fcc-Co sub lattice. Pure Co adopts a hcp phase at pressures below 105 GPa, above which it transforms to fcc-Co.29 So although fcc-Co is not the ground state at 33−55 GPa, it is likely there is a low energy barrier39 to form metastable fcc-Co, which can then be filled with hydrogen to form CoH and/or CoH₂. Experimentally, both compounds can be formed on compression alone, with laser heating accelerating the process.20

CoH₃, however, is very different, because it has a simple cubic Co sub lattice. Because it is not close-packed, a major rearrangement of the Co lattice is required to allow the formation of CoH₃. Neither low pressure and high temperature or long times at pressures below 50 GPa are sufficient to initiate the CoH₃ formation,20 requiring pressures above 75 GPa and laser heating to trigger the CoH₃ synthesis. In agreement with the convex hull calculations, and Gibbs’ phase rule, only CoH₃ is formed after the laser heating in an H₂ rich environment. Our DFT calculations also find an unreported structural transition in CoH₃ above 275 GPa to a tetragonal P4/mmm phase (Figure S4).

Recent theoretical work anticipated that transition metal trihydrides isostuctral to FeH₃ but with heavier elements, like Co, would be candidates to undergo superconducting transitions.26 Our DFT calculations of the electronic structure and electronic bands demonstrate metallic character of the three hydrides at all pressures throughout their stability ranges (see Figures 5S−S8). At the lowest pressure, the electronic density of states (DOS) of CoH₃ (see Figure S18) has important
contributions from hydrogen orbitals around the Fermi level, indicative that it could exhibit superconductivity.

In Figure 3 we show the calculated phonon dispersion curves and projected phonon density of states (PDOS) for the low-pressure phases of CoH, CoH₂, and CoH₃ at 25 GPa (see Figures S9—S12 for higher- and lower-pressure results). Phonon structures of all the hydrides depict no imaginary frequencies along the high-symmetry k path, which demonstrates their dynamical stability. For Fm₃m-CoH₃, as shown in Figure 3a, a phonon gap between 400 and 900 cm⁻¹ divides the spectrum into two regions: the low-frequency acoustic branches and high-frequency optical branches. The optical modes are associated with almost exclusive motion of H atoms, whereas the acoustic modes are associated with the concerted motions of both Co and H atoms. From Figure 3b, CoH₂ has a similar gapped phonon spectrum compared to CoH, but with higher optical frequency branches up to 1400 cm⁻¹ in the hydrogenic sublattice. In CoH₂, there is a big change in the phonon dispersion and PDOS. The phonon gap has shrunk, and the larger number of optical branches occupies a much wider frequency region. From CoH to CoH₂, the magnitude of the electron–phonon line-widths increases with the higher hydrogen content, which may lead to a higher zone-averaged electron–phonon coupling parameter (EPC) and superconducting critical temperature, T_c.

We estimate the EPC and T_c using the McMillan–Allen–Dynes formula⁴⁰-⁴²:

\[ T_c = \frac{\omega_{\text{ph}} \exp \left( \frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right)}{1.2} \]

where \( \omega_{\text{ph}} \) is the logarithmically averaged phonon frequency, and taking the Coulomb parameter as \( \mu^* = 0.1 \). The EPC \( \lambda \) and \( T_c \) are plotted in Figure 4 as a function of pressure. For CoH and CoH₂, the calculated \( \lambda \) values are below ~0.45 in the studied pressure range. Such weak EPC values result in \( T_c \) below 2 K. However, as seen in Figure 4, CoH₃ shows a different and remarkable trend with \( \lambda \) significantly increased with decreasing pressure, which in turn leads to a rapid \( T_c \) increase upon decompression, reaching a predicted maximum of 30 K at 11 GPa.

There are some quantitative differences between our results and those obtained in previous calculations.²⁷ For CoH₃ at 200 GPa we obtain \( \lambda = 0.35 \) and \( T_c = 2 \) K, while Wang et al.²⁷ obtain \( \lambda = 0.19 \) and \( T_c \approx 0 \) K. We have repeated our calculations with parameters very similar to those used by Wang et al. (see Figures S13—S23) and reproduce the EPC and \( T_c \) data (Figure S23, \( \lambda = 0.21 \) and \( T_c = 4 \) mK). We postulate that the choice of pseudopotential—norm-conserving (NC) in Wang et al.²⁷ and ultrasoft (US) here—is the source of the quantitative differences we see. The US pseudopotentials are better suited than the NC to describe the EOS of pure Co and H⁴³ but give very similar EOS results for CoH₃; both also agree with VASP calculations using the PAW method (see Figure S13 in the Supporting Information). The choice of pseudopotential has a larger effect on phonon properties than on electronic properties; Figure S14 in the Supporting Information compares them to VASP results. Nonetheless, using either approach, the EPC and \( T_c \) share the same trend upon compression, but on different absolute scales (see Figure S23); with the NC pseudopotentials, the \( T_c \) of CoH₃ is predicted to reach 15 K at 13 GPa. The US pseudopotentials give the same value if the screened Coulomb interaction \( \mu^* \) would be increased to 0.18. These quantitative uncertainties might be best resolved by using more sophisticated theoretical approaches such as directly solving the Eliashberg equation or the superconducting DFT method.⁴⁴,⁴⁵

The strong negative pressure dependence of \( T_c \) in CoH₃ at these low pressures can be explained by the hardening of the phonon frequencies leading to a weakening of EPC \( \lambda \). As shown in Figures 3 and S9—S12, when the pressure increases from 10 to 300 GPa, the maximal frequencies of optical phonon branches for CoH₃ harden from 1500 to 2400 cm⁻¹, while the DOS N(0) (see Figures S6—S8) and magnitude of electron–phonon line widths \( \gamma_{\text{q}} \) remain almost unchanged. A similar trend in \( T_c \) was experimentally observed in PTH-II, from 7 K at 30 GPa to 5 K at 40 GPa.¹²

In our experimental runs, diamond failure on decompression prevented us from studying the stability of CoH₃ at pressures lower than 52 GPa. At 52 GPa, we predict CoH₃ to have \( T_c \) of 8 K, which could increase to 30 K at 11 GPa. We speculate that because of the large stability range predicted for CoH₃ (Figure S1), that low temperature could maintain the stability of CoH₃ down to it is maximal \( T_c \) conditions, and such behavior should be explored in future studies.

The predicted superconducting character of CoH₃ proves that TMH₃ samples heavier than FeH₃ do facilitate more efficient electron–phonon coupling. We have demonstrated the formation of CoH₃ synthesized at 75 GPa and stable in decompression to at least 52 GPa. CoH₃ adopts a cubic \textit{Pm}₃\textit{m} structure which is very stable both in compression up to 111 GPa and in decompression down to 52 GPa. Our DFT results predict that this structure should be superconducting with a \( T_c \) which increased with decreasing pressure, reporting a maximum of 30 K at 11 GPa. These results give an indication that superconductivity could also be observed in metal hydrides at low-pressure conditions.
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c01807.

Experimental and theoretical methods; equation of state parameters, electronic and phonon band structures, and experimental and calculated unit-cell parameters (PDF).

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Notes
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146


B-M EOS
Birch-Murnaghan EOS The 3rd order Birch-Murnaghan EOS was formulated in 1947 by A.F. Birch [16] based on the early work of F.D. Murnaghan in 1944 [17] from the the previously derived Murnaghan EOS

BA
Boehler-Almax IIaC: A diamond cut comprising of a conical crown (facet on the table side) manufactured by Almax-easyLAB

DAC
diamond anvil cell

EOS
equation of state

FIB
focused ion beam

GG-type
A colloquial term to refer to the variety of symmetric cell used in this work. This type of comprises of two wide-angle opening, cylindrical diamond backing plates separated by four guiding pins which retain the sample alignment.

hydrogen vibron
The hydrogen vibron refers to the Raman active hydrogen $v_1$ vibrational stretching mode

IR
infra-red

PTM
pressure transmitting medium
Vinet EOS

The Vinet EOS, sometimes referred to as the Rose-Vinet EOS, is a modification of the Birch-Murnaghan EOS (B-M EOS) with a reduced stiffness in the solid modelling, typically giving a slightly lower pressure than that of the B-M EOS.

XRD

x-ray diffraction